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IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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VOLUME CVI.

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No. 2745.—JULY 5, 1912.

THE

QUANTITATIVE DETERMINATION OF YTTRIUM.

By C. F. WHITTEMORE and C. JAMES.

HAVING encountered difficulties in the determination of yttrium in the presence of sodium, the authors made a systematic study of the qualitative determination of yttrium in the presence of this and certain other elements.

A neutral solution of yttrium chloride was first prepared and carefully standardised by precipitation with oxalic acid. Then the yttrium in 25 cc. portions of this solution was precipitated with various reagents in the presence of other elements.

In the Presence of Sodium.

For the purpose of studying the separation from sodium, 10 cc. of a saturated solution of sodium sulphate were added to each 25 cc. sample of the standard yttrium chloride solution. Sodium hydroxide, the first reagent employed, gave the following results:—

No. of cc. of standard YCl_3 solution.	No. of cc. of saturated solution of Na_2SO_4 present.	Grms. Y_2O_3 found.
25	10	0·1642
25	10	0·1647
25	10	0·1640
25	10	0·1647
25	10	0·1638
25	10	0·1640
	Average	0·1642
	In standard	0·1575

Since these figures were considerably too high, 5 normal ammonium hydroxide was tried, but with equally unsatisfactory results.

Oxalic acid gave exceedingly high results due to the carrying down of sodium.

The next precipitants used were the ammonium salts of several organic compounds.

Ammonium anisate formed a precipitate which gave low results owing to its slight solubility.

Yttrium palmitate was investigated, but was found unsatisfactory and no determination was made.

Ammonium phthalate and ammonium fumarate formed no precipitates with yttrium chloride in dilute solution, probably on account of the formation of soluble double compounds.

Ammonium benzoate precipitated yttrium from the neutral solution at first, but the compound dissolved in an excess of the reagent.

The next reagent, ammonium sebacate, gave a perfectly quantitative separation, and the precipitated yttrium sebacate was found to be comparatively easy to filter off and wash. The average of several determinations showed a good agreement with the standard:—

No. of cc. of standard YCl_3 solution.	No. of cc. of saturated solution of Na_2SO_4 present.	Grms. Y_2O_3 found.
25	10	0·1582
25	10	0·1573
25	10	0·1581
25	10	0·1579
	Average	0·1578
	In standard	0·1575

In the Presence of Potassium.

Having eliminated the difficulty of the separation of yttrium from sodium, the separation from potassium was next taken under consideration. Ammonium hydroxide and ammonium sebacate were tried without success. Finally, a double precipitation as the sebacate proved satisfactory. The following data were obtained:—

Ammonium Hydroxide.

No. of cc. of standard YCl_8 solution.	No. of cc. of saturated solution of K_2SO_4 present.	Grms. Y_2O_3 found.
25	5	0·1629
25	5	0·1625
	Average	0·1627
	In standard	0·1575

Ammonium Sebacate.

25	5	0·1592
25	5	0·1599
25	5	0·1590
25	5	0·1596
	Average	0·1594
	In standard	0·1575

Ammonium Sebacate.—Double Precipitation.

25	5	0·1536
25	5	0·1542
	Average	0·1539
	In standard	0·1537

After finding a satisfactory separation from sodium and potassium it seemed advisable to study the separation from iron, aluminium, lithium, and magnesium. As the result of several trials it was found that yttrium could be quantitatively separated as the oxalate in the presence of ammonium chloride.

In the Presence of Iron.

Ten cc. of a 10 per cent ferric chloride solution were added to 25 cc. of the standard yttrium chloride solution, and the whole diluted to approximately 100 cc. After heating to boiling, the yttrium was precipitated by means of oxalic acid. This oxalate was first slightly reddish brown, but became white on standing. The ignited oxide, however, was slightly coloured. Other determinations were made in which the oxalate was precipitated from a cold solution with ammonium chloride present. In this case a white oxide was obtained. The average of these determinations agreed well with the standard :—

Average grms. Y_2O_3 in presence of $FeCl_3$, 0·1536 ; grms. Y_2O_3 in standard, 0·1537.

In the Presence of Aluminium.

In order to study the determination of yttrium in the presence of aluminium, 10 cc. of a 10 per cent aluminium chloride solution were added to the 25 cc. sample of the standard solution. Yttrium oxalate was precipitated from the cold solution in the presence of ammonium chloride. The result of this determination was also in close agreement with the standard :—

Average grms. Y_2O_3 in presence of $AlCl_3$, 0·1539 ; grms. Y_2O_3 in standard, 0·1537.

In the Presence of Lithium.

To the 25 cc. of the standard solution of yttrium chloride 10 cc. of a 10 per cent lithium chloride solution were added. Yttrium was precipitated as in the previous case, and with equally satisfactory results :—

Average grms. Y_2O_3 in presence of LiCl, 0·1536 ; grms. Y_2O_3 in standard, 0·1537.

In the Presence of Magnesium.

Yttrium oxalate was precipitated from 25 cc. samples of the standard yttrium chloride solution, to which 10 cc. of a 10 per cent magnesium chloride solution had been added. As in the preceding cases, there was a complete separation :—

Average grms. Y_2O_3 in presence of $MgCl_2$, 0·1537 ; grms. Y_2O_3 in standard, 0·1537.

Summary.

1. Ammonium sebacate affords a quantitative separation of yttrium from sodium.
2. A double precipitation with the same reagent gives a complete separation from potassium.
3. Oxalic acid, in the presence of ammonium chloride, effects a perfectly satisfactory separation from iron, aluminium, lithium, and magnesium.

Durham, New Hampshire.

New Colouring Matters Derived from Phenyloxyaniline.—Alph. Mailhe.—The direct nitration of phenyl oxide in an acetic medium gives the paramononitro compound, $C_6H_5O.C_6H_4.NO_2$. When it is reduced with iron and acetic acid the amine, $C_6H_5O.C_6H_4.NH_2$, is obtained, and from the amine azoic colouring matters can be prepared. The chlorhydrate can readily be diazotised, yielding $C_6H_5O.C_6H_4N=NCl$. This diazo-compound with aniline gives yellow needles of formula $C_6H_5O.C_6H_4N=NC_6H_4NH_2$, and with diphenylamine $C_6H_5O.C_6H_4N=NC_6H_4NHC_6H_5$, the alcoholic solution of which, when treated with strong acids, gives a violet colouration. Dimethylaniline and α- and β-naphthylamines also give colouring matters with the diazo derivative of phenyloxyaniline.—*Comptes Rendus*, cliv., No. 19.

DRINKING WATER AND HEALTH.*

By FRANK T. SHUTT, M.A., F.R.S.C., Dominion Chemist.

Of the many natural blessings we possess good health is easily first in importance, if for no other reason than that it enables us to enjoy life—to make the most of life—and to do our duty by ourselves, our families, and the State. Good health means something more than freedom from disease and pain ; it implies strength and activity, physical and mental, to do our work in the world, and to it at our best. It is, indeed, something to be prized and well guarded, for it is easier to maintain than to get back again once having lost it.

While still enjoying good health it is doubtful if we recognise the obligation—the religious obligation I might call it—to protect and preserve our health. To do so we must oftentimes be willing to forego temporary pleasure and enjoyment. Too many take little heed, until perhaps they come to middle life or later, of those things and conditions that contribute towards the conservation of health. Perhaps a better day is dawning. The fundamentals of hygiene are being taught in our schools, and the rising generation should know something of the laws of health. Hitherto, as a people, we have had to pick up here a little and there a little, oftentimes learning by bitter experience —and perhaps too late. Forewarned is in a large measure to be forearmed. At all events those who are to take our places will not be able to urge ignorance in matters relating to food, water, fresh air, and a great many other things all closely connected with the preservation of health.

But I would point out that a knowledge of these things, necessary as it is, will not in itself, be sufficient, there must be the desire to profit thereby, to put it into practice. And with all there must be the exercise of common sense, nothing can take its place. We shall find if we will only cultivate this gift it will help us along very satisfactorily many a time when science is apparently silent as to which path to choose, what action to take.

Our health, as we all must know, is largely dependent upon the character and amount of the food we eat and its freedom from adulteration, the purity of the water we drink, the freshness of the air we breathe, and the character of the exercise we take, or of the work we do. To-night we are to consider one of the more important of these factors—the water we use for drinking purposes.

The water we drink may become, does in part become, part and parcel of ourselves. The metabolism always going on within us and resulting in growth, in the repair of waste, in the production of energy, requires that every tissue of the body should possess water. Thus, the blood that bathes every tissue, and constitutes about one-twelfth of the body weight, is about 80 per cent water. Of the body weight about 60 per cent is water. The adult individual requires 5 to 6 pints of water, or its equivalent, daily. The consumption of certain foods, such as milk, which is 85 per cent water, of fruits and vegetables which have a high water-content, lessen the volume necessary to take as a beverage.

With this knowledge of the part played by water in the animal economy and its presence everywhere throughout the system, it is not difficult to understand how polluted foul water may affect health. We are all aware nowadays that certain diseases, zymotic diseases as they are termed, are caused by specific bacteria or germs. It may suffice to say these pathogenic bacteria having gained an entrance into the system, through the water we drink, the food we eat, or the air we breathe, may and often do cause disease within us. It is the function of the phagocytes, or white corpuscles of the blood, to combat with and destroy these germs, and in good health, when we have strong vitality, they perform their function well and keep us free from

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* A condensed account of a Lecture delivered before the Ottawa Field-Naturalists' Club, Ottawa, January 9th, 1912. From the *Ottawa Naturalist*, xxv., Nos. 11 and 12.

disease. But with a lowered vitality when the host of intruders is too great and strong to battle with, they may be beaten in the warfare, and we succumb. Among water-borne diseases the one we have to fear most is typhoid fever. The excretal discharges of its victims are loaded with its bacilli, and when such waste finds its way into a water supply the disease is disseminated, and an epidemic results. Herein lies the chief and great danger in using a supply polluted with sewage or execretal waste. It must, however, be added that water is not the only vehicle which conveys this disease; the ubiquitous house-fly, as we know, must now bear its share of the blame.

But there is another danger in impure water, though of this bacteriology takes no note. I refer to the presence of certain poisonous substances, the products of the decomposition of organic matter—either of animal or vegetable origin. There is good evidence that such polluted water may cause headache, nausea, indigestion, diarrhœa, lassitude, and generally lower the vital tone of the system. It is quite true that such toxic compounds have not been isolated, but I might answer that such is the case with many ptomaines, organic compounds occasionally occurring in our foods—and especially in those which have been stored. Such foods may be, and frequently are, consumed with fatal results. There is every reason to believe that certain waters, and more particularly stagnant waters in which there is decaying vegetable and animal matter, possess this poisonous property. Some of us may have experienced the nauseating effects of water from a pond or lake containing the products of decaying algæ. It is scarcely necessary to add that such water is unfit for consumption. Moving water is, as a rule, free from this class of impurity. This is a phase of the water question that has not received from sanitarians the attention it deserves, but I am convinced of its importance in judging of the merits of a water for a city or house supply.

So far we have learnt that what we have to fear in our water supplies is, first, the presence of disease germs, due to contamination with sewage, and secondly, those products of the decay of organic bodies from certain classes of matter, excretal or vegetable, and which exert a toxic action on the system. A third form of pollution met with is the waste waters of manufactories which are run into the water course without proper purification. These refuse waters may contain organic or inorganic substances detrimental to health. Fortunately in Canada this kind of pollution is not often found, but in the protection of our lakes and rivers legislation must take cognisance of it, and the laws preventing the discharge of such waste into possible sources of water supplies rigidly enforced.

In considering the *rôle* of rain and snow in Nature some two years ago, we learnt two facts of a fundamental character. The first was that the earth's moisture was in continual circulation. The ascension of water in the form of vapour, due to the heat of the sun, went on constantly, day and night, winter and summer, from earth and water surface alike. Ice and snow, as we saw, could be converted into vapour without visually passing through the liquid state. This vapour of water ascends until it reaches the higher and colder strata of the atmosphere where it is condensed to fall as rain, hail, or snow, according to the atmospheric conditions prevailing at the time of the precipitation. This process of evaporation and condensation —distillation, in fact—is from the point of view we are considering to-night one of the greatest importance, for it is primarily one of purification. The sun, then, is the agent above all others that renders it possible to obtain a wholesome supply of drinking water, for the water in being converted into vapour leaves behind all those substances—mineral and organic—which it held in solution, and descending gives us one of the purest forms of water found in Nature.

And, secondly, it was apparent that all our water supplies—lakes, streams, springs, and wells—were directly dependent upon the fall of rain and snow, and therefore there was a very close relationship between the annual precipitation of a district and the volume of water which might be available for a water supply.

There are two properties of water that must be referred to, if only briefly, in order that we may intelligently consider the various classes of water that are suitable and wholesome for domestic use—its solvent power and its carrying power. Water is known as the universal solvent. It is because of its ability to dissolve gases and solid substances, whether they be inorganic (mineral), or organic, and the constant exercise of this power that in Nature there is no such thing as pure water—that is, chemically speaking. Pure water, as formed in the laboratory, consists solely of oxygen and hydrogen. All natural waters, then, contain dissolved matter, some more, some less, and, speaking broadly, the nature of this matter—whether injurious or harmless to health and its amount, will be determined by the character of the rock or soil it passes over or passes through. Thus we have soft waters from the Laurentian districts because the gneisses and granites are not easily soluble and impart but little mineral matter to the water; and we have hard waters in limestone districts, because the water with the aid of the carbon dioxide it has taken from the atmosphere is capable of exerting a very considerable solvent effect upon such rocks and contains as a result more or less lime in solution. Next to the sun, the soil is Nature's greatest water purifier, for it can remove by oxidation and filtration impurities in solution and suspension, but if the soil is choked with filth then the water in passing through it will dissolve such, and be rendered foul.

The carrying power of water is secondary to its solvent power in this consideration of natural waters for drinking and household purposes. The descending rain, the storms, the spring freshets, and floods, wash the surface of the land, and carry much which they find there to the nearest stream or lake. Similarly, the banks and channels of streams are eroded—even rocks may be slowly worn away, and the detritus, the *débris*, borne in the turbid waters, perhaps hundreds of miles, to be deposited as their velocity is checked. In this way deltas of clay and silt, and fine sand mixed with organic particles are formed at the mouth of great rivers, and areas of vast size and of extreme fertility built up. Since turbid waters, those with clay and silt in suspension, are not desirable for supplies, they must be subjected to filtration. If such waters possess no organic filth, the filtered and now clean water will be quite satisfactory.

Waters as used by towns or for isolated households, as on the farm, may be classified as follows:—Rain-water, upland surface waters, ground waters or those of shallow wells, and deep-seated waters, as obtained by drilling or boring and among which many springs may be placed.

Rain-water.—This can be caught and used as such. As a drinking supply little need be said of this source. In Canada, where in most districts other and larger sources of supply are readily available, rain-water is seldom used, save for washing and laundering purposes, for which by reason of its extreme softness it is eminently suitable. Its quality or purity will depend on the condition of the atmosphere through which it falls; if in town we may expect it to contain soot and gases from which it would be comparatively free if falling in rural parts. Again, dirty roofs and eave troughs, storage tanks in which organic *débris* accumulate, all contribute towards making this supply foul and unfit for consumption—so that even a fairly pure rain-water that has been stored is difficult to find. However, if fresh and clean, it is not at all unwholesome, though not very palatable. If stored in vats or tanks these should be of cement, and frequently examined and cleaned. The water for use should be passed through an efficient filter, and boiling would be an additional safeguard, though the presence of disease germs would not naturally be expected.

Upland Surface Waters.—These constitute the waters of our lakes and streams, and are formed by the run-off om the lands, though to some extent, of course, these sources are fed by springs. By far the larger number of supplies of Canadian cities and towns are drawn from lakes and rivers, and hence the importance of immediate and efficient legislation that will protect these natural bodies of water from sewage and other pollution. The fact should be emphasised that these natural waters are, almost without exception, eminently suited without any preliminary treatment for drinking and domestic use. But as our population increases, and especially as cities and towns build up on the margins of lakes and the banks of streams, the necessity of adequate filtration becomes apparent. It will therefore be the part of wisdom from this on, not only to protect these waters from pollution as effectively as possible, but, also for those communities drawing upon them for their supply to establish filtration plants. Experience in other countries has shown that despite the most viligant protective measures such waters may at any time, through accident or otherwise, receive excretal waste, and become a source of danger, a menace to good health. It is now generally recognised by the highest authorities that filtration is imperative—a sine qua non—if the supply is at all seasons to be relied on as free from injurious bacterial life.

The nature of the country and the composition of the rocks of the catchment area will largely determine the character of these waters. Thus a limestone district gives rise to a hard water, a Laurentian area, with gneiss, granite, and similar rocks, results in a comparatively soft water. Again, the colour of these waters is largely determined by the presence or absence of swamps in the country from which they draw their supply. A coloured water, that is, one brown or yellowish brown, through the presence of dissolved peaty matter, though offending the æsthetic sense (for we all prefer a colourless water), may be perfectly wholesome, and especially so when such is from a large body of quickly flowing water, as, for instance, the Ottawa river. There are very few cases of illness or indisposition on record—if indeed any that can be definitely traced to the consumption of these peaty waters from large actively flowing waters, provided of course such have proven to be free from excretal pollution. These so-called peaty waters, and from sources such as I have described, have shown themselves almost universally to be perfectly satisfactory for city supplies, not only from their extreme softness (which means a considerable saving in soap and labour to the community), but from the hygienic standpoint. These waters keep well, for their dissolved peaty matter does not readily undergo further decay, is, in fact, remarkably stable. It is true that temporary indisposition frequently follows the use of these waters when one has been accustomed to a hard colourless water, but it is equally true that the reverse happens. Any change in the character of the water consumed may bring about a slight derangement, for the system becomes habituated to a certain water, and some persons are very susceptible, for a time, to any difference in its character. The case, however, with coloured waters from low-lying swampy shallow lakes and ponds is very different. Such bodies of water being more or less stagnant, produce an abundance of vegetable growth largely algal, which under favourable weather conditions may rapidly decompose, giving rise to offensive and nauseating products. If, as frequently happens in summer, these decay products accumulate, in other words get ahead of growth that can utilise them, the water becomes foul and unfit for consumption. The result of drinking such water usually shows itself in an attack of diarrhœa or nausea. From these considerations it would be obvious that colour is not in itself a quality or factor that can be used alone in deciding upon the suitability of a supply. Leaving out of consideration sewage pollution, we may have on the one hand a comparatively colourless water, but one in which algæ and other low forms of life are present in large numbers, and in which chemical analysis proves the presence of easily decomposable organic matter, and on the other hand a highly coloured peaty water from a large and quickly flowing river, and the former will be distinctly the inferior water, one that must be efficiently filtered and purified before it can be regarded as a wholesome potable supply.

Ground Water.—This is the rain and melted snow absorbed and retained by the soil and subsoil. It is the source that supplies the shallow domestic well so commonly used on the farm homestead and in the village. When the surroundings are perfectly satisfactory from the sanitary standpoint, these wells are frequently a source of excellent water, but when, as is usually the case, convenience to the house or farm buildings is alone considered in the location of the well, the water is seldom of first-class quality, and more often must be adjudged as quite unfit for consumption. On the larger number of farms we find these wells, usually between 10 and 25 feet in depth, sunk in the barnyard or under the stable or other outbuildings, or not very far from the privy (a most crude and unsanitary affair as a rule), or near the back door, out of which the household slops may be thrown, and near which the garbage heap with all sorts of refuse may be found. It is quite true that most soils, and more particularly those that are porous and well aërated (gravels and sands), possess filtering and purifying properties in a marked degree, but the soil surrounding wells located as we have described must in time become saturated with organic filth of a most objectionable character, and is then no longer able to purify, but rather serves to more seriously contaminate the water passing through it to the well, which under such conditions may be said to act as a cess pit.

Further, we frequently find these wells become the watery grave for rats, mice, frogs, and other small animals, the decomposing bodies of which render the water foul and unfit for use. Imperfect protection of the mouth of the well may allow the entrance of surface wash. Rotten crib work is another source of contamination. Other causes of pollution could be enumerated, but enough has been said to justify the conclusion that the ordinary farm well is at the best a poor supply, and should be abandoned for a safer, purer source. The examination in the laboratories of the experimental farms of hundreds of samples of such well waters have shown that few of these wells furnish a supply that can be considered wholesome, by far the larger number must be condemned as totally unfit for use. Considering the location of most farm wells it is not a matter of surprise that but a very small proportion of them yield water of sufficient purity to be classed as satisfactory. Many of these waters are colourless, bright, sparkling, clear, and cool, but these qualities are no criterion, and it is by no means uncommon to find waters possessing all these commendable properties and at the same time reeking with filth. Of course, if a well-water becomes turbid after a rain there is reason to reject it, for in this turbidity we have a sign that the soil is no longer able to do its work as a filter and purifier.

A precaution of very considerable value towards protecting the well-water from organic filth is to line the well to a depth of, say, 10 or 12 feet to a thickness of, say, 6 inches with concrete or puddled clay. This lining should project some 6 to 12 inches above the mouth of the well. This prevents the direct inflow of wash and of water from the surface soil in which the larger amount of putrescible organic matter is found, and ensures a certain amount of filtration through clean layers of soil.

Another safeguard is to keep an area of, say, 50 yards radius round the well free from manure and all deposition of filth (it should preferably be in sod), and this plan we would heartily recommend to those who are contemplating sinking a well for household use or for watering stock. If the ground surrounding the well is an undisturbed area and free from all excretal waste, it will perform its function as a natural filter and the water may be very good. Especially is this the case if the soil is sand or gravel, for such will not only remove suspended matter and germ life, but will also foster the destruction by oxidation of the organic matter held in solution. A clay subsoil is far inferior to sand in its purifying effect.

Deep Seated Waters.—These are waters that have percolated through the soil and permeable rock strata until arrested by an impervious stratum. They may appear on the surface as springs, but are more commonly obtained by deep wells, driven or bored, possibly through several overlying impervious strata to the water bearing rock. If there are no fissures in these overlying strata and there is no opportunity for water to flow downwards between piping and the sides of the boring, a good water will in all probability be obtained. While it cannot be taken for granted that a bored well will necessarily yield a good drinking water, it is the source of supply to be generally recommended for the isolated households. Examination has shown that they are capable of furnishing in the larger number of instances, and when proper precaution has been taken to exclude surface water, a supply of high organic purity and very low bacterial content. In certain districts we find these deep seated waters characterised by an excess of saline matter, rendering them unsuitable for domestic use; but when such is not the case the deep well undoubtedly constitutes a safer and better source of supply than the shallow, ground water well. With a pump actuated by a windmill, small gasoline or hot air engine, tanks can be filled in the farm buildings for the watering of the stock, and in the farm house to supply the bath room and kitchen. Such an arrangement would mean much, not only in the matter of convenience and the saving of labour, but in the still more important matter of securing a supply that would lead to better thrift in the stock and better health in the family.

Before bringing this Address to a close I must answer, though it may be briefly, one or two questions that have been handed me for reply.

1. Is a hard water injurious to health? The human system has a remarkable adaptability, and though certain authorities have considered that a hard water is inducive to the formation of calculi there is very little evidence to support the statement. Cities having even a very hard water supply do not show the prevalence of any disease that can be attributed to the water, and we may conclude that the lime compounds present do not work any injury to health. As already remarked sudden changes from one character of water to another, whether hard to soft or soft to hard, may cause disturbance in the system, but such will only be temporary. The system requires lime to build up its skeleton and for its other tissues, and it may take it from the water as well as from the food; there is nothing to prove that the lime taken in the water is not as readily assimilable as that in the food-stuffs we consume. Consensus of opinion points to a moderately hard spring water, in which all possibility of contamination is out of the question, as probably the best supply, but such is unfortunately very hard to find.

2. Is distilled water wholesome? The only argument that can be urged against its use for drinking is that it does not contain the necessary mineral elements for the building up of the tissues and for the replacement of the daily outgo of these elements. The answer is that in the ordinary normal diet there is such an abundance of the mineral salts that the absence of them in the drinking water need cause no alarm. There is much to be said in favour of distilled water, as it should be free from all forms of organic matter and disease germs.

3. What means can the householder take towards making a suspicious water harmless? Undoubtedly the best plan is to boil the water for from five to fifteen minutes. This is the most efficient safeguard that can be proposed for the individual. Household filters, though removing suspended matter, are seldom to be depended upon to deprive the water of germ life, and at the best require constant attention and cleansing to be kept even fairly efficient. The addition of hypochlorite of lime, now largely used in the purification of city supplies, is not readily applicable in the house, and cannot be regarded as equal to boiling for the destruction of germs. The boiled water may be rendered palatable and the "flat" taste removed by being allowed to cool in the open air.

And now, in conclusion, I must emphasise two points. The first is the insidious character of polluted water. The danger that lurks in water polluted with excretal products is not always apparent. This fact must not be lost sight of. There may be no outbreak of typhoid fever, but it may be generally undermining the health. In far too many cases the well goes unsuspected until the victim is stricken down. The moral is, ascertain the purity of the supply.

And the second point is that there is abundance almost everywhere of pure water. There is no better watered country in the world than Canada. We can unhesitatingly affirm that the normal waters of our lakes, streams, and springs, our ground waters and our deep seated sources, are of the purest. It becomes our duty as communities and individuals to preserve and protect them from pollution, and to see to it that the water we drink is as irreproachable in quality as that with which Nature has supplied us.

ON STRÜVERITE FROM THE FEDERATED MALAY STATES.

By T. CROOK, A.R.C.Sc. (Dublin), F.G S., and S. J. JOHNSTONE,
Scientific and Technical Department, Imperial Institute.

General Remarks.

The mineral dealt with in this paper was sent for examination to the Imperial Institute by Mr. J. B. Scrivenor, Government Geologist to the Federated Malay States. It occurs on the river Sebantun, about half a mile above Salak North village, Kuala Kangsar district, Perak. The ground on which it was obtained was held on a tin-mining lease, but had to be abandoned owing to the presence of the unknown mineral, which rendered mining unprofitable.

Mr. Scrivenor has ascertained that the locality is occupied by a small alluvial flat, that the mineral in question forms the bulk of the concentrate obtained from the alluvium, and that cassiterite, monazite, topaz, tourmaline, zircon, and iron pyrites also occur. The mineral was originally supplied to Mr. Scrivenor by Mr. R. L. Corbett, who stated that he had obtained it by magnetic separation with a Wetherill machine, using a current of from 70 to 75 volts and 10 to 14 ampères.

As received at the Imperial Institute the sample consisted of coarse angular grains, 4 or 5 millimetres in diameter. They appeared to consist entirely of a lustrous, black mineral. On looking over the specimen with a lens, however, some grains of a more brownish appearance could be picked out, and these proved to be cassiterite. Occasional particles of quartz were also observed to be intimately associated with the black, lustrous grains.

A preliminary analysis of the specimen indicated that titanium, tantalum, and iron were the essential ingredients. This composition, taken in conjunction with the physical characters of the mineral, led to the conclusion that we were dealing with a specimen of strüverite, as defined by Drs. Prior and Zambonini ("On Strüverite and its Relation to Ilmenorutile," *Mineralogical Magazine*, 1908, vol. xv., pp. 78-89). The analytical difficulties, however, made the satisfactory chemical proof of this a very tedious piece of work.

Physical Characters.

In the mass the mineral is black, and has a somewhat lustrous appearance. The specific gravity, determined on an amount weighing about 13 grms., which had been freed as far as possible from fragments of cassiterite, was found to be 5·30. The streak is not quite black, but has a somewhat greenish tint. This feature suggested the probability that the mineral was not likely to be quite opaque in microscopic splinters.

An optical examination of the fine crushings in this particular case gave interesting results. As far as can be judged from the appearance of the small particles obtained by fine crushing the mineral seems to be homogeneous. These particles are not opaque, and they show strong pleochroism. Examined with one nicol most of the thin flakes show a change from brownish-yellow to dull bluish-green on rotating the nicol. These flakes are birefringent, and compensate with a gypsum-plate when the fast vibration-trace of the plate lies along the maximum-absorption vibration-trace of the flake. Occasionally flakes are observed which show only the brownish-yellow colour on rotating the nicol, and these act isotropically. The optical behaviour thus suggests that the mineral is uniaxial, and on this assumption the pleochroism for the thinnest flakes may be defined thus: *o* = brownish-yellow, *e* = dull bluish-green. Thicker flakes show a change from brown to black, somewhat resembling that of brown tourmaline, but in the reverse sense, the ordinary ray being less absorbed.

In describing the physical characters of strüverite from Piedmont, Zambonini states that the mineral is opaque even in the thinnest flakes. His description of the mineral powder as "grey-black," however, may be taken as an indication that the mineral is not quite opaque. In a recently published paper by Hess and Wells ("An Occurrence of Strüverite," *Am. Journ. Sci.*, 1911, Ser. 4, vol. xxxi., pp. 432-442), Hess states that the strüverite of South Dakota is opaque, but he describes the powder as having a slightly greenish tinge, from which we may perhaps infer that a closer examination of microscopic flakes would reveal optical characters somewhat resembling those of the Perak specimen.

In this connection it is interesting to note that the Norwegian ilmenorutile shows a pleochroism closely resembling that of strüverite. Further, as one would expect, flakes of ilmenorutile are more transparent, so much so that flakes showing a good uniaxial figure of positive sign can be obtained without difficulty.

Numerous attempts were made to obtain a definite uniaxial figure with the Perak strüverite, but the results were inconclusive, owing to the less transparent nature of the flakes. The optical behaviour of strüverite, however, as outlined above, indicates clearly that it also is positive. (As indicated by compensation with a gypsum-plate, the maximum-absorption vibration-direction is that of the slow ray; and as indicated by the pleochroism it is also the vibration-direction of the extraordinary ray). In view of Prior's suggestion that ilmenorutile and strüverite are solid solutions of mossite and tapiolite respectively, in rutile, it is interesting to note that these minerals are both optically positive, and that the ordinary ray in each case is less absorbed than the extraordinary. In these respects they resemble rutile.

Chemical Analysis (S. J. J.).*

A preliminary analysis of the mineral showed that it is completely soluble in 5 per cent sulphuric acid after fusion with potassium hydrogen sulphate, and almost completely soluble in concentrated sulphuric acid after digesting for several days. Titanium, tantalum, and iron appeared to be the chief ingredients, but tin, niobium, and silica were also present. Calcium, magnesium, aluminium, chromium, uranium, tungsten, vanadium, zirconium, cerium and its allies, and thorium were proved to be absent.

By quantitative analysis the results given in Table I. were obtained.

The analysis was made as follows:—The mineral was finely ground and dissolved by heating for several days with hot concentrated sulphuric acid, allowing to cool, and pouring into a large bulk of water. There remained only a slight amount of insoluble residue, which consisted of stannic oxide and silica. A more rapid method of solution is to fuse the mineral with potassium hydrogen sulphate, and then to dissolve the melt in 5 per cent sulphuric acid containing a few drops of perhydrol.

TABLE I.

	Per cent.
TiO_2	45·74
Ta_2O_5	35·96
Nb_2O_5	6·90
FeO	8·27
MnO	trace
SnO_2	2·67
SiO_2	0·20
H_2O at 105° C.	0·08
H_2O above 105° C.	0·42
	100·24

The insoluble residue was reduced in hydrogen, and the tin and silica separated in the usual way.

The sulphuric acid solution was diluted, nearly neutralised with dilute ammonia, and acidulated with hydrochloric acid, and the tin precipitated by passing a current of hydrogen sulphide for some time. The precipitated stannic sulphide contained a small amount of titanium, from which it was freed by treatment with ammonium sulphide and re-precipitation with acid. The matter insoluble in ammonium sulphide was fused with potassium hydrogen sulphate and added to the hydrogen sulphide filtrate.

The stannic sulphide precipitate, together with that obtained from the insoluble residue, was oxidised with nitric acid, ignited, and weighed as stannic oxide. The quantities of stannic oxide found in two determinations by this method were 2·63 and 2·71 per cent. A check determination of the tin, made by fusing the mineral with potassium hydrogen sulphate, dissolving in 5 per cent sulphuric acid, adding a few grms. of tartaric acid, and passing hydrogen sulphide, gave 2·68 per cent of stannic oxide.

The filtrates from the hydrogen sulphide precipitation were nearly neutralised, a considerable excess of sodium thiosulphate added, and the whole boiled for about twenty minutes. The precipitate, which contained all the titanium, tantalum, and niobium, together with traces of iron, was freed from the latter impurity by dissolving in fused potassium hydrogen sulphate and re-precipitation as thiosulphate. The iron was obtained from the filtrates by boiling with excess of ammonia, filtering, and re-precipitating as acetate and finally as hydroxide. The iron was weighed as ferric oxide, the gravimetric determination being checked volumetrically by titration with potassium permanganate.

Several methods were tried for the separation of tantalic and niobic oxides from the titanium dioxide. Amongst these may be mentioned the following:—

(*a*) The fractional crystallisation of the acid potassium fluorides (Marignac method). This was found to be unsatisfactory, owing to the complicating influence of the titanium salt, which interferes with the separation of the tantalic and niobic salts.

(*b*) Fusion with potassium carbonate at a high temperature was also tried, but although the chief part of the tantalic and niobic oxides was soluble, varying amounts of titanium also passed into solution. The addition of potassium nitrate to the melt seemed to intensify rather than diminish this difficulty.

The following was found to be the most satisfactory method to adopt. The well-washed thiosulphate precipitate was ignited and ground with about its own weight of pure sugar-carbon, transferred to a small porcelain boat, and heated to a high temperature in a Jena-glass tube in a current of chlorine which had passed through carbon tetrachloride. The temperature of the tube, excluding the portion containing the boat, was maintained at about 70° C., and by this means the less volatile tantalum and niobium chlorides were condensed practically free from titanium. The titanium chloride passed over and was caught by a series of wash-bottles containing water; it was

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* My thanks are due to Mr. J. Shelton, A.I.C., Assistant in the Scientific and Technical Department of the Imperial Institute, for valuable assistance rendered in connection with the analysis of strüverite.—S. J. J.

found impossible to condense the titanium chloride quite completely by these wash-bottles. By repeating the distillation twice on the more volatile portion, almost complete separation of the tantalum and niobium from the titanium could be effected. The first distillation separated 93 per cent of the total tantalic and niobic oxides found. The trace of manganese present in the mineral remained in the boat. The chlorides of tantalum and niobium were removed from the tube with the aid of strong hydrochloric acid, precipitated as hydrates, washed, ignited, and weighed.

This method is essentially similar to that adopted by Wells in separating titanium from tantalum and niobium. The use of carbon tetrachloride alone, as suggested by Wells, was found to be less satisfactory than the method we adopted.

A qualitative test for niobium in the above precipitate by the Giles method indicated that this element was present in small quantity (W. B. Giles, Chemical News, 1907, vol. xcv., p. 37). An estimation of the niobium by the Metzger-Taylor method of reduction with zinc and titration with potassium permanganate gave 6·9 per cent of niobic oxide (F. J. Metzger and C. E. Taylor, *School of Mines Quarterly*, New York, 1909, vol. xxx., p. 323). The factor used was 1 cc. N/10 $KMnO_4$ = 0·00708 grm. Nb_2O_5. The tantalum and niobium of another portion of the mixed oxides, which had been separated from the titanium as above, were separated by the Marignac method. By this means the quantity of niobic oxide found was 7·2 per cent. This result is probably slightly in excess of the quantity actually present, owing to the temperature of the experiment being rather high.

The chlorides which had passed over into the wash-bottles (chiefly titanium chloride) were precipitated by thiosulphate, fused with potassium hydrogen sulphate, the melt dissolved in 5 per cent sulphuric acid, and the titanium and any tantalum and niobium present estimated gravimetrically as oxide. The titanium was estimated volumetrically by the following process:—An aliquot part of the sulphuric acid solution was reduced with zinc and then titrated against N/20 ferric alum solution in an atmosphere of carbon dioxide, using ammonium sulphocyanide as an indicator. The ferric alum solution had been previously standardised against pure titanium sulphate.

The results obtained by the two methods showed that the solution obtained in the wash-bottles contained a small percentage of tantalum and niobium, which varied in amount but did not exceed 2 per cent. In the analysis recorded this difference amounted to 0·98 per cent, and this quantity was divided proportionately between the niobic and tantalic oxides already found.

A direct estimation of the titanium was made by fusing a fresh portion of the mineral in potassium hydrogen sulphate, and, after removing the stannic oxide, estimating the titanium volumetrically by the process given above. An allowance was made for the niobium already found to be present. The titanium dioxide found in this way amounted to 45·74 per cent. The ferrous iron present was estimated by digesting the finely-ground mineral with 50 per cent sulphuric acid in a sealed tube at 200° C. for several weeks and titrating with standard potassium permanganate.

The Presence of Scandium in Strüverite.—Prof. A. Fowler, F.R.S., kindly undertook to examine the mineral spectroscopically, and found that it yielded the spectrum of scandium. This is of considerable interest, in view of the rarity of that element, and the fact that strüverite has some features in common with "wiikite." The latter was found by Sir William Crookes to contain more scandia (1·17 per cent) than any other mineral, and had tantalic oxide, titanium dioxide, ferrous oxide, and silica as its chief constituents (*Phil. Trans. Roy. Soc. London*, 1908, Ser. A, vol. ccix., p. 17). Since, however, no other mineral examined by him was found to contain as much as 0·01 per cent of scandium, there seemed to be little chance of finding this constituent in strüverite with the comparatively small amount of material available for analysis; and the chemical examination of the mineral for this purpose led only to the indication of a possible trace.

(Note.—A specimen of orthite has since been described as containing 0·8 to 1·0 per cent of scandia; see R. J. Meyer, "Ueber einen scandiumreichen Orthit aus Finnland und den Vorgang seiner Verwitterung," *Sitzungsber. Akad. Wiss. Berlin*, 1911, pp. 379—384. Still more recently a new mineral supposed to consist essentially of scandium silicate, and to contain about 37 per cent of scandia, has been described; see J. Schetelig, "Ueber Thortveitit, ein neues Mineral, *Centralblatt Min.*, 1911, pp. 721—726).

Conclusions.

The mineral strüverite, as defined by Prior and Zambonini (*loc. cit.*), has now been found in three widely separated localities, viz. (1) at Craveggia, in northern Piedmont, Italy; (2) in the Etta mine, Black Hills, South Dakota, U.S.A.; (3) Perak, Malay Peninsula, and it is rather remarkable, in view of the probable nature of the mineral, that the composition, as seen from the analyses given in Table II., should show such slight variations.

Table II.

	Piedmont (Prior).	South Dakota (Wells).	Perak (Johnstone).
TiO_2	41·20	47·8	45·74
Ta_2O_5	46·96 (*a*)	34·8	35·96
Nb_2O_5		6·2	6·90
FeO	11·38	7·3	8·27
MnO	trace	—	trace
CaO	0·51	—	—
MgO	0·17	—	—
SnO_2	—	1·3	2·67
SiO_2	—	2·0	0·20
H_2O	—	0·4	0·50
	100·22	99·8	100·24
Sp. gr.	5·59	5·25	5·30

(*a*) This percentage was divided equally between the niobic and tantalic oxides to accord with a rough indication that these two oxides were present in approximately equal amounts. It seems highly probable, however (see below), that there was a substantial preponderance of tantalic oxide.

There is apparently no reasonable alternative to the view suggested by Prior, that strüverite is a homogeneous isomorphous mixture, and that it is to be regarded as consisting essentially of a solid solution of tapiolite in rutile. On this assumption we may regard the ferrous oxide of the Perak specimen as combined with the niobic and tantalic oxides to form tapiolite, and treat the mineral as an isomorphous mixture of rutile and tapiolite with small admixtures of cassiterite, silica, and water. (The stannic oxide in the Perak specimen as analysed is present, in part at least, as free cassiterite, and the silica as quartz granules).

If now we calculate the separate volumes of these constituents, add these together and divide into the total mass, we get the value 5·33 for the density of the mineral as against the value 5·30 actually found. (Assuming the following specific gravities—rutile 4·2, tapiolite 7·35, cassiterite 7·0, quartz 2·65, water 1). Treating the analysis of the South Dakota specimen in the same way we get the value of 5·17 for the calculated density of the mineral as against the value 5·25 actually found. The approximation of the calculated to the observed values for the specific gravity may be regarded as sufficiently close, in such a mineral, to be consistent with the solid-solution view.

On the same assumption a consideration of the analysis of the Piedmont strüverite in relation to its specific gravity leads to an important conclusion. The Piedmont specimen, as the analysis shows, was much purer than those from South Dakota and Perak. The state of combination of the lime and magnesia is uncertain, but the amount is very small. Neglecting these and recalculating the analysis to 100 in terms of TiO_2 and $Fe(Ta,Nb)_2O_6$ we get:—

	Per cent.
TiO_2	41·39
$Fe(Ta,Nb)_2O_6$	58·61

If now we take the specific gravity of this as being approximately 5·6, and, assuming a specific gravity of 4·2 for the rutile, calculate what the specific gravity of the $Fe(Ta,Nb)_2O_6$ constituent should be, we get the value 7·3, which is approximately the specific gravity of a typical tapiolite, *i.e.*, one containing only a few per cent of niobic oxide. It appears, therefore, that the $Fe(Ta,Nb)_2O_6$ constituent of the Piedmont specimen must be tapiolite, and if so it follows that this specimen is really representative of typical strüverite.

In stating the results of his analysis, Prior made it quite clear that he had not adequate quantitative data for stating the exact relative percentages of niobic and tantalic oxides present. These considerations do not seem to have been taken into account by Hess and Wells, who (*loc. cit.*) have rather hastily concluded that the Piedmont specimen is not a typical strüverite. The evidence detailed above proves their conclusion to be incorrect, if we accept the view, to which they subscribe, that strüverite is an isomorphous mixture.—*Mineralogical Magazine*, May, 1912.

THE NATURE OF THE ELECTRIC DISCHARGE.

By Prof. NIPHER.

Former results of Prof. Nipher's work seem to point very strongly to the one-fluid theory. It would follow that the two waves which were shown to exist in the Wheatstone experiment were compression and rarefaction waves. The negative wave is in the nature of a supercharge which travels along on the outer surface of a thin outer film of the conductor. The positive wave is one in which a thin outer film of the wire is suddenly drained of the negative charge at the instant of passing of the wave. We had been led to suspect, as a result of recent experiments, that matter in this latter condition is explosive. The tests have been made on thin fuse wires sealed into long glass tubes through which the wire passes. The wires were sealed in by means of hard sealing-wax. A discharge from a battery of Leyden jars was passed through the wires. The disintegration of the wires is much greater at the positive end. The sealing-wax, wire, and glass tube, in almost every case, break down at that end. The lead is dispersed in a fine powder or dust.

Prof. Nipher remarked that he had just found in the London *Phil. Mag.*, 1815, xlvi., pp. 161 and 259, an account of the work of De Nelis and Singer, who passed a positive discharge through a lead wire of 0·01 inch diameter contained in an iron tube. The wall of the tube was usually about 0·14 inch in thickness. In one case the tube was 1 inch in external diameter, with a small bore admitting a steel needle with wax insulation, and terminating in the short lead wire resting on the bottom. The lead wire was surrounded by oil. Such tubes were burst by repeated explosions of the lead wire, which required to be replaced at each discharge. The discharge was from a battery of Leyden jars, having an area of from 75 to 100 square feet. The needle and part of the liquid were thrown out at each explosion. In some cases the liquid was thrown to a height of 40 feet. The experimenters do not seem to have used the negative discharge. They attributed the effects to the expansive power of the electric fluid.

What they were doing was to suddenly drain that lead wire of the negative fluid. The atoms of lead then repel each other. Some of the effect is, of course, a heat effect. The question arises, however, will the negative discharge produce a like or an equal effect? Is it not possible that such molecular repulsion is primarily concerned in the formation of disruptive channels in air, and resulting in spark discharges and lightning?—*Science*, N.S., xxxv., No. 905.

THE DIRECT DETERMINATION OF SMALL AMOUNTS OF PLATINUM IN ORES AND BULLION.*

By FREDERIC P. DEWEY.

By the old method of determining platinum in ores and bullion, the silver-alloy first obtained in the regular course of assay is parted in strong sulphuric acid and the residual metal weighed. This is re-alloyed with silver by a second cupellation and parted in nitric acid, the residual metal being again weighed. Any difference shown between the two weighings is assumed to be, and is called, platinum. Sometimes it is so, and if any considerable amount of platinum be present there will be a decided difference between the two weighings; but a slight difference is no real evidence whatever of the presence of platinum. On the other hand, the second weight may equal or possibly exceed the first, even when traces of platinum are present. Again, other members of the platinum group may go into solution in nitric acid more or less. If present these would be called platinum and escape detection. The method does not provide any direct tests whatever as to the presence or absence of platinum. It is often indecisive and sometimes gives erroneous results. It is, therefore, quite unsatisfactory.

Being called upon many times to determine platinum in a wide variety of materials, particularly when present in very small amounts, I have realised the disadvantages and defects of this old method.

In an article on the solubility of gold in nitric acid (*Journ. Am. Chem. Soc.*, 1910, xxxi., 323), I have briefly outlined a method of gathering a little gold out of a solution containing much silver, which furnishes the basis of an excellent method for the direct and absolute determination of small amounts of platinum, and has the added advantage that the metal weighed may be subjected to suitable tests to determine that it really is platinum, and to reveal the presence of other members of the platinum group.

In the regular course of assaying for the precious metals, gold is parted from silver by dissolving the silver in nitric acid. If platinum be present in small amounts only, it will readily go into solution in the nitric acid. If now a limited amount of hydrogen sulphide be added to the solution from parting, any platinum present will be precipitated as sulphide along with some silver sulphide. On filtering off the precipitate (which generally is sufficiently washed by the operations necessary to transfer it from the precipitating dish to the filter), the moist filter is transferred to a small porcelain crucible, dried at a low heat, and burned off by gentle ignition. This transforms the sulphide precipitate into a metallic sponge, which is wrapped in a small piece of thin lead-foil and cupelled. The resulting bead is then parted in strong sulphuric acid, when the platinum will be left as a dark residue, generally collected in spongy form, even when minute in quantity. This sponge, after re-boiling in fresh acid, if necessary, is suitably washed by decantation, annealed, and weighed.

Generally the final metal speaks for itself as being platinum, but if there should be any doubt it may be dissolved in a drop or two of aqua regia and gently evaporated. The solution obtained may be tested with potassium iodide, or a few small crystals of ammonium chloride may be added, when the characteristic precipitate will show itself. As a further test this may be filtered off and gently ignited to produce spongy platinum. If the amount of the final metal be considerable, the platinum may be determined by the double-chloride method. Any decided difference shown would indicate the presence of other members of the platinum group, for which direct test could then be made.

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* Presented at the New York meeting of the American Institute of Mining Engineers, February, 1912, and published in the *Bulletin of the American Institute of Mining Engineers*, April, 1912, Serial No. 64.

For precipitating the platinum and the necessary silver from the parting solution, a very dilute solution of hydrogen sulphide should be used. One part of a strong solution should be diluted to from 10 to 20 parts with water. If the solution of silver nitrate be strongly acid it should be largely diluted, or it may first be evaporated and then diluted. The very dilute hydrogen sulphide solution should be added very slowly to the silver nitrate solution with constant stirring. The solution is, of course, at once darkened, but there should be no immediate separation of a visible precipitate. The solution should be stirred occasionally, and in about two hours flocks of precipitate should appear. It may be filtered in from three to four hours, but it is a good plan to let it stand over night if possible.

The amount of hydrogen sulphide required depends, of course, upon the amount of platinum present. If this should be roughly known or suspected, the amount used should generally be enough to precipitate the platinum and from three to five times as much silver. On an entirely unknown ore I should at first use 1 cc. of strong hydrogen sulphide solution diluted to 15 cc., and reserve the filtrate from the sulphides for re-treatment, if necessary. On an unknown bullion I should use 2 cc. of strong solution diluted to 30 cc., partly because bullions are liable to carry much more platinum than any ordinary ore, and partly because the volume of the silver nitrate solution from parting the gold must necessarily be larger. If, however, it is known that minute amounts of platinum are present, it is still necessary to use sufficient hydrogen sulphide to give a silver bead large enough to handle comfortably. For this reason I seldom use less than the equivalent of 1 cc. of strong hydrogen sulphide solution.

It may happen that the final metal shows the yellow colour of gold, due to the fact that exceedingly fine float-gold passed over in decanting the solution of silver nitrate from the gold. In such a case the metal must be re-alloyed with silver and the treatment repeated. When the proportion of gold to silver in the metal being parted is so small that the gold separates in a very finely divided state, it will often save trouble to filter the silver-nitrate solution, to separate any float-gold, before adding the hydrogen sulphide.

This method has been used with the utmost satisfaction in determining very minute amounts of platinum in various silver products directly. Much of our silver coinage, for instance, will show a few tenths of a milligrm. of platinum in 100 grms. of coin. Recently I examined samples from two purchases of fine silver. Very large samples were dissolved in nitric acid. The acid in portions was poured upon the samples and allowed to act at a gentle heat until exhausted. Finally, a small amount of residual silver was removed from the solution and dissolved in a small amount of fresh acid, the solution being then united with the main solution, and the whole evaporated nearly to dryness. It was then diluted to about 250 cc. and 5 cc. of strong hydrogen sulphide solution diluted to 50 cc. was poured in with constant stirring.

This operation concentrated the gold and platinum of the silver into a small amount of sulphide precipitate. This precipitate was filtered off, roasted, and cupelled. The resulting bead was parted in nitric acid and the gold determined. The silver nitrate solution was treated with dilute hydrogen sulphide solution, equivalent to about 1 cc. of strong solution, and the platinum parted from the silver by strong sulphuric acid.

These two samples yielded the following results:—

No.	Silver taken. Grms.	Gold found. Mgrm.	Platinum found. Mgrm.
1..	122·32	0·28	0·67
2..	125·47	0·12	0·18

In case we have a material containing a considerable amount of platinum, the well-known fact that platinum alloyed with silver is not entirely soluble in nitric acid must be considered. In such a case the gold from the first parting in nitric acid must be alloyed with silver and parted in nitric acid a second, or even a third time, before proceeding to precipitate the platinum from the parting solutions with hydrogen sulphide.

It is also very satisfactory to use the general method of gathering gold in a precipitate of silver sulphide in determining minute quantities of gold in high-grade silver, such as that produced by electrolytic refining. It is comparatively easy to gather the gold from very large samples of silver, up to 100 grms. or more, into a decigrm. of silver, and then part by nitric acid as usual.

Probably this method of precipitating a noble metal in solution, or removing it from suspension in a liquid, by adding hydrogen sulphide in the presence of silver in the solution, could be used to advantage in determining gold in metallic copper and similar materials.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 20th, 1912.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Investigation into the Life-history of* Cladothrix dichotoma (*Cohn*). By David Ellis, D.Sc.

"*Relation between Secretory and Capillary Pressure. I.—The Salivary Secretion.*" By Leonard Hill, F.R.S., and Martin Flack.

"*Origin and Destiny of Cholesterol in the Animal Organism.* Part IX. *On the Cholesterol Content of the Tissues (other than Liver) of Rabbits under various Diets and during Inanition.*" By G. W. Ellis and J. A. Gardner.

"*Note on the Protozoa from Sick Soils, with some Account of the Life-cycle of a Monad Flagellate.*" By C. H. Martin, M.A.

"*Further Observations on the Variability of Streptococci in relation to certain Fermentation Tests, together with some Considerations bearing on its Possible Meaning.*" By E. W. Ainley Walker.

"*Chemical Action on Glucose of a Variety of* Bacillus coli communis (*Escherich*) *obtained by Cultivation in Presence of a Chloroacetate.*" (Preliminary Notice). By A. Harden, D.Sc., F.R.S., and W. J. Penfold.

The organism in question produces no gas when grown on glucose peptone water, aerobically, in a test-tube provided with a Durham gas tube; but when grown anaerobically in presence of chalk it yields an amount of hydrogen and carbon dioxide which is approximately 0·25—0·3 of that given by the normal organism. The amounts of alcohol and acetic acid are similarly diminished and that of lactic acid increased. The organism retains the power of decomposing formates.

It is probable that the normal organism decomposes glucose by the aid of at least three enzymes:—

1. $C_6H_{12}O_6 = 2C_3H_6O_3$;
2. $C_6H_{12}O_6 + H_2O = C_2H_4O_2 + C_2H_6O + H_2CO_2$;
3. $H_2CO_2 = H_2 + CO_2$.

The process of selection by means of chloroacetate leads to the survival of organisms containing relatively less of the enzyme conditioning reaction (2) than the normal organism.

It is hoped that the study of other organisms on similar lines may yield some information as to the nature of their characteristic fermentation processes.

"*Action of Enzymes on Hexosephosphate.*" By Victor J. Harding.

Lipase from castor-oil seeds and emulsin from almonds possess a slow hydrolytic action on the hexosephosphate obtained by fermenting sugars with yeast-juice in presence of phosphate. Autolysed ox pancreas has practically no action on hexosephosphate.

An extract of zymin hydrolyses hexosephosphate slowly. Autolysed yeast-juice possesses an enzyme which has a marked action on hexose phosphate, and which is precipitated in an active form by the addition of alcohol and ether.

"*Oxydases of* Cytisus Adami." By Prof. Frederick Keeble, Sc.D., University College, Reading, and Dr. E. Frankland Armstrong.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).
Ordinary Meeting, June 17th, 1912.

Mr. E. Grant Hooper in the Chair.

The following papers were read and discussed:—

"*Production and Polymerisation of Isoprene and its Homologues.*" By W. H. Perkin.

The results obtained by a group of English workers, of whom the author is one, are described in the paper.

The important early work of our fellow countrymen, the late Greville Williams and Tilden, and others, who observed that the polymerisation of isoprene under varying conditions results in the formation of a rubber-like body, is reviewed, and allusion is made to the experiments of Kondakow, Motiewsky, Thiele, Harries, Klages, and others on a variety of compounds containing the conjugated double linking $—C=C—C=C—$, which is usually connected with a tendency to polymerise. The observation of Dr. F. E. Matthews in September, 1910, that isoprene which had been left in contact with sodium since July of that year had turned into a solid mass of rubber, and the conclusion, based on further investigation, that sodium was a general polymerising agent, marked an important epoch in the history of the synthesis of rubber. Curiously, this observation was confirmed by the independent but later work of Carl Harries, who in publishing his discovery was unaware that he had been anticipated. The polymerising action of sodium is practically quantitative, and is not seriously affected by impurities. It will take place in the cold or in moderate heat, which is an advantage. This discovery renders the cheap production of rubber possible, if divinyl or erythrene, isoprene, di-isopropenyl, &c., or other similar compounds containing conjugated double linkings can be prepared cheaply. The great and fluctuating cost of turpentine are against its employment as a raw material. The only possible substances for rubber production at, say, 1s. per pound, seem to be wood, starch or sugar, petroleum, or coal. Starch was chosen, and the formation from it of cheap fusel oil was made possible by a discovery of Prof. Fernbach, of the Pasteur Institute, who after long work found a suitable fermentation process by which the higher alcohols can be produced at a low cost. It has since been found that acetone can be produced very cheaply by fermentation.

Specimens of Sir William Tilden's synthetic rubber and that produced by the new process were shown.

"*Oxidation of the Drying Oils.*" By J. N. Friend and W. J. Davison.

The authors have studied the changes in weight undergone by the following oils during oxidation consequent upon exposure to the air in thin films:—Raw and boiled linseed oils, Chinese wood oil, cotton-seed oil, poppy-seed oil, hemp-seed oil, soya bean oil, walnut oil, and rosin oil. It is shown that all these oils, save rosin oil, at first rapidly increase in weight to a maximum, after which they relatively slowly begin to lose in weight. Rosin oil is exceptional, exhibiting no setting power, but continuously losing weight, owing presumably to the escape of its more volatile constituents. Linseed oil sets to an elastic film when half the time has elapsed necessary to arrive at the maximum increase in weight. Hence, in giving two or more coats of paint to a surface, at least double the time required for each coat to set should elapse before the next coat is put on; otherwise the undercoat will continue to change in volume as it absorbs oxygen until the maximum point is reached, and will thus tend to tear away from and destroy the fresh coat above it. Whence once this interval has elapsed, however, further alteration in weight is so slow, relatively, that succeeding coats may be painted on at leisure.

The initial stages of the setting of raw linseed oil are accompanied by the absorption of water, the so-called "drying" being in reality a moistening. In very dry air raw linseed oil sets extremely slowly, and it is suggested that if both the oil and air were perfectly dry no oxidation would take place.

In the case of boiled oil, the presence of moisture apparently makes no difference to the rate of setting. In an atmosphere of hydrogen, both the partially oxidised and the oils that had completely set remained permanent, suffering no disintegration or alteration in weight.

"*A New Hand Photometer.*" By W. J. Dibdin.

A convenient portable instrument for the determination of the light emitted in any direction by a lamp or any other source of light is described. It is designed to embrace —(1) Maximum open scale readings; (2) convenience and accuracy in comparing lights of different colour; (3) reliability by reason of the facility with which its indications can be checked. The rays falling on a Leeson star disc as improved by the author, when the instrument is tilted at the desired angle at such a distance from the illuminant that they shall be normal to the disc, are measured against those emitted by an electric incandescent lamp, the illuminating power of which is varied by means of a rheostat so graduated as to give readings in foot candles.

The readings compare well with those of standard photometers.

NOTICES OF BOOKS.

Spectroscopy. By E. C. C. Baly, F.R.S. With 180 Illustrations. New Edition. London, New York, and Calcutta: Longmans, Green, and Co. 1912.

In the above new edition Prof. Baly has brought together a large amount of information in connection with the rapidly extending field of spectroscopic research. The size of the work has been increased in the present edition to some 700 pages, and the half-tone illustrations are good. The scope of the work runs upon very practical lines, owing possibly to the fact that the author was associated with Sir William Ramsay during the period occupied by the discovery and investigation of the inert gases of the atmosphere, and thus, having been in touch with the work of other spectroscopists, has been able to give minute details of devices and manipulations otherwise inaccessible to the average worker. In spite of the fact that many of the illustrations of apparatus and instruments are of a highly complex character, and bear the names of prominent instrument makers, we are glad to note that in many instances instructions and drawings are given for the construction of useful apparatus: a case in point is that of a simple form of spectrograph that looks capable of doing useful work. Although the book is chiefly occupied with the practice of spectroscopy, the theory and mathematics involved are thoroughly explained. The work can scarcely fail to become a handbook in any laboratory where spectroscopic research is carried out.

Water Analysis for Sanitary and Technical Purposes. By Herbert B. Stocks. London: Charles Griffin and Co., Ltd. 1912.

This handbook gives short directions for the analysis of samples of water for sanitary purposes, without going fully into the minutiæ of a complete examination. Biological methods of investigation are not included, and the description of microscopic work is far too short to be of any practical use; in fact it consists of not much more than a list of a few names of organisms which might be present, and gives no help towards the identification of them. The chemical examination is treated much more fully, and ordinary methods employed in it are described in enough detail for a straightforward analysis to be carried out by any one who had had some little practice in elementary quantitative work. Only thoroughly tested methods are described, and the directions as to quantities, the time necessary for the completion of the experiment, &c., are precise and clear. Some data relating to average results are given as a guide for estimating the quality of any particular water, and full directions for the preparation of all the reagents required are included.

Cast-iron in the Light of Recent Research. By W. H. Hatfield, B.Met., A.M.I.Mech.E. London: Charles Griffin and Co., Ltd. 1912.

Recent research on the properties and nature of cast-iron and malleable cast-iron is admirably described in this book. The author's own work occupies a good deal of space in it, but he has by no means neglected the investigations of other metallurgists, either English or foreign, and his attitude towards opinions which he does not share is very impartial and restrained. At the same time his criticisms are shrewd and incisive, and his suggested explanations of some results show great ingenuity and resource. He bases his study of the subject upon the equilibrium diagram of the iron-carbon system, which is discussed in detail after a short historical introduction. The influence of silicon, phosphorus, sulphur, manganese, and other elements upon the properties of cast-iron is critically discussed, and the effects of casting temperature, superheated steam, and shrinkage and contraction are the subjects of later chapters. The student will find some suggestions in the work for profitable research work, and the engineer and metallurgical chemist will be able to obtain from it a thorough knowledge of recent investigations of cast-iron.

A Text-book of Rand Metallurgical Practice. By the following authors: Ralph Stokes, Jas. E. Thomas, G. O. Smart, W. R. Dowling, H. A. White, E. H. Johnson, W. A. Caldecott, A. McA. Johnson, C. O. Schmitt. Volume I. London: Charles Griffin and Co., Ltd. 1912.

This book, each of the two volumes of which is complete in itself, has been produced by the collaboration of a number of metallurgists, works managers, &c., who are actually engaged in metallurgical work upon the Witwatersrand, and who, from the important positions they fill, may safely be regarded as writing authoritatively each upon his special subject. As a guide for other practical men working in similar conditions, and for students, this very definite and detailed account of metallurgical practice on the Rand will have considerable value, giving students especially an insight into actual working methods and the routine and difficulties of every day work. The book is mainly concerned with actual practice, and hence does not go into questions of research or yet unsolved problems. Each division of the subject—Sorting, Stamp Milling, Tube Milling, Treatment of Slime, Assaying, &c., is discussed in a separate chapter, and the bibliographies given are more than mere lists of works, often providing a short abstract of the papers or articles tabulated.

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique, et de Tecnologie." ("Annual Tables of Constants and Numerical Data Relating to Chemistry, Physics, and Technology"). Paris: Gauthier-Villars. Leipzig: Akademische Verlagsgesellschaft. London: J. and A. Churchill. Chicago: University of Chicago Press. 1912.

The tables in this book, which is published under the direction of an International Committee appointed by the Seventh Congress of Applied Chemistry, have been collected from more than 300 periodicals by a special staff of abstractors, and are printed in English, French, German, and Italian. The data given relate to chemistry, physics, and technology, and have been brought down to the end of the year 1910, it being the intention of the Committee to issue a new volume during the present year if possible. The arrangement of the book seems to be systematic and in every way convenient for reference, and the volume will be a useful addition to the library of the chemist and technologist.

The Measurement of High Temperatures. By G. K. Burgess and H. Le Chatelier. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

In 1898 Prof. Le Chatelier, who was one of the pioneers in the investigation of the measurement of high temperatures and the construction of pyrometers, delivered a course of lectures on the subject at the Collège de France. In this course he not only gave a full account of his thermo-electric and optical pyrometers, but also summarised all that was then known of pyrometry. These lectures were translated into English by Mr. G. K. Burgess of the Bureau of Standards at Washington, and the translation met with such a large demand that a second edition was soon called for. Since its appearance the theory and practice of pyrometry have very rapidly extended, and so many new instruments have been devised and new methods perfected that Mr. Burgess, in preparing a third edition, has been forced practically to re-write the book. It deals more with the principles of the measurement of high temperatures than with the various types of instrument employed for the purpose, although these are usually fairly fully described, and it is intended for the use of the student and the engineer rather than that of the investigator, who, however, will find that the very complete bibliography will give him all the information that he is likely to require as to original English and foreign publications, both books and periodicals.

Notions Fondamentales d'Analyse Qualitative. ("Fundamental Principles of Qualitative Analysis"). By V. Thomas and D. Gauthier. Paris: Gauthier-Villars. 1912.

This book is not intended for the use of candidates for examinations, but for those who wish to acquire a real knowledge of the principles of qualitative analysis and of the reactions of acids and bases. The authors have aimed specially at thoroughness, believing that in analysis a half-knowledge is very much worse than complete ignorance. Though writing for beginners they enter into the fullest details of the reactions they describe, and frequently give quite a considerable choice of methods of detection and confirmation, since they argue that success with a particular experiment depends very largely upon the personal factor as well as the skill of the experimenter. After discussions of the general operations of qualitative analysis, including some microscopic and spectroscopic work, the reactions of the individual bases are discussed in detail; the similar treatment of the acids follows, separations and systematic analysis being left for the last quarter of the book. The general style of the work suggests that the authors had in their minds the training of the research chemist, and for thoroughness and attention to detail the course that they suggest would appear to be admirable.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 20, May 13, 1912.

Action of Hydrogen Peroxide on Lactic Acid and Glucose.—Jean Effront.—By the action of hydrogen peroxide lactic acid is readily converted into acetic acid according to the equation—

$$CH_2.CH.OH.COOH + O_2 = CH_3COOH + H_2O + CO_2.$$

The theoretical yield is very nearly obtained. A small amount of alcohol is always formed. With glucose hydrogen peroxide gives formic, acetic, and oxalic acids and some alcohol.

Bulletin de la Société Chimique de France. Vol. xi.—xii., No. 8, 1912.

Knœvenagel's Method of Preparing Glutaric Acid.—H. Gault.—Knœvenagel's method of preparing glutaric acid consists in condensing two molecules of ethyl malonate with one molecule of formaldehyde in presence of small quantities of diethylamine or piperidine, and saponifying the methylene dimalonic ether formed. The yield of the latter, and therefore of the glutaric acid also, can be very considerably increased by using four molecules of ethyl malonate to one of formic aldehyde, and a yield of 81 to 82 per cent can thus be obtained.

Cyanhydrines, Benzoyl-amides of Aldehydes and the Corresponding Alcohols.—J. Aloy and Ch. Rabaut.—When benzoyl chloride acts on aldehyde phenols in presence of potassium cyanide, cyanhydrines are obtained containing two benzoyl groups, of which one is attached to the phenol function. Two molecules of chloride and two of cyanide have to be used to one of aldehyde. The corresponding benzoyl amide can sometimes be prepared by simply leaving the cyanhydrine in contact with fuming HCl at the temperature of the laboratory. In other cases it is better to heat in a sealed tube to 100°. The saponification of the benzoyl amides gives the corresponding acid alcohols and acid phenols.

Preparation of Crystallised Quinine.—J. Ville.—Anhydrous crystallised quinine can be easily and rapidly obtained by passing a current of air containing ammonia through a solution of hydrobromide of quinine heated on a water-bath. The quinine is thus precipitated in the form of white anhydrous crystalline lamellæ. When a solution of the hydrobromide is made alkaline with ammonia, and is allowed to evaporate after the addition of acetone, long silky needles of the hydrate containing three molecules of water separate. This hydrate is efflorescent, and loses some of its water of crystallisation at the ordinary temperature. Dehydration is rapid in a dry vacuum.

Action of Mercury and its Salts on Aluminium.—Paul Nicolardot.—When aluminium foil is left in a solution of mercuric chloride the water is decomposed by the aluminium, and if there is sufficient chloride the oxidation is complete. Alloys and impure aluminium (98 per cent) are not attacked, and it is thus possible to distinguish between a utensil made of pure aluminium and another made of a copper alloy. The fact that aluminium, when rendered oxidisable by mercury or its salts, attacks water, may be used to determine the alkaline or alkaline earth metals which may be present in the aluminium employed. After the action is over the alumina may be filtered off and the lime precipitated with ammonium oxalate, while the sodium is determined in the filtrate from the calcium oxalate.

Detection of Arsenic and Lead in Wines.—P. Carles and L. Barthe.—When the vines are treated with an excess of lead arsenate the wines obtained from them contain negligible traces of arsenic and lead; if the vines are treated with a normal amount of lead arsenate neither arsenic nor lead can be detected in the wines; in both cases the dregs contain quantities of arsenic and lead which are not negligible.

Reactions of Salicylic Acid.—E. Barral.—When 10 per cent sodium nitrite is added to a solution of a salicylate containing concentrated sulphuric acid an orange coloration, finally turning red, is obtained. If a solution of salicylic acid is heated with ammonium persulphate the liquid turns yellow and then brown, and gives a brown or black precipitate. On cooling the precipitate separates from a colourless or yellowish liquid. A blue coloration is obtained when Mandelin's reagent is added to a solution of salicylic acid.

Atti della Reale Accademia dei Lincei. Vol. xxi., No. 7, 1912.

Transformation Constant of Radium D.—Paolo Rossi.—From measurements of the activity of a specimen of mineral containing radium D and its derivatives, the author has found that the half period of transformation of radium D is approximately seventeen years.

Formation of Solid Solutions of Sodium Halogen Salts at High Temperatures.—M. Amadori.—The crystallisation of the system NaCl—NaBr has a minimum at 744°, *i.e.*, about 4° below the melting-point of NaBr, and that of the system NaBr—NaI a minimum at 645°, 17° below the melting-point of NaI, but for both potassium and sodium the systems chloride-bromide and bromide-iodide show complete solubility in the solid state. For the system chloride-iodide the solubility in the solid state is limited, and a eutectic-point occurs at a concentration of 49 molecules per cent of chloride for the potassium salt and 37 molecules per cent for the sodium salt. In both cases the eutectic temperature is a little lower than the solidification-point of the iodide.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 1st inst.; Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. J. S. Highfield and Mr. W. Judd were elected Members.

Ozonair Portable Apparatus.—We have received from Messrs. Ozonair, Ltd., 96, Victoria Street, Westminster, London, S.W., a copy of the new edition of their catalogue No. 1 "Ozonair Apparatus for General Purposes." This catalogue contains illustrations, prices, and other particulars of Ozonair portable generators for purifying the air in rooms of from 3000 to 12,000 cubic feet capacity, for connecting the supply circuits or to portable accumulators. These apparatus are made in a variety of patterns; for standing on the table (horizontal or vertical current of ozonised air), for fixing on the wall, with medical fittings, &c. They are of handsome and compact design, and the consumption varies from only 10 watts to 130 watts, so that in all cases, where intended for use on a supply circuit, they can be connected to any lampholder or plug. The makers claim that their Ozonair apparatus, as compared with other methods of producing ozone, are noiseless and generate pure ozone, free from the oxides of nitrogen. The catalogue also contains some very interesting information regarding the nature of ozone and the many public and industrial purposes to which Ozonair apparatus can be applied, such as ventilation, water and food sterilising, brewing, bleaching, deodorising, &c. That these are not hypothetical is proved by a list of important users, not only in Great Britain, but on the Continent and in other parts of the world, comprising public buildings, breweries, slaughter houses, cold storage, waterworks, laboratories, and so on. Messrs. Ozonair, Ltd., will be pleased to send a copy of the catalogue to all those who are interested in the subject.

THE CHEMICAL NEWS.

Vol. CVI., No. 2746.

SCANDIUM.

By R. J. MEYER and H. GOLDENBERG.

In earlier papers (R. J. Meyer, *Zeit. Anorg. Chem.*, 1908, lx., 134; R. J. Meyer and Herbert Winter, *Zeit. Anorg. Chem.*, 1910, lxvii., 398) it has been shown that scandium can be comparatively easily isolated from the wolframite ores from Zinnwald-Attenberg or from the Sadisberg copper mine. The method which has hitherto been employed for the preparation of the pure earth may be described in outline as follows:—

i. The hydrochloric acid solution of the wolframite oxides was precipitated whilst boiling with hydrofluosilicic acid.

ii. The fluorides thus precipitated were converted into sulphates by means of sulphuric acid, and the hydroxides were separated from the solutions by the addition of ammonia.

iii. The solution of the hydroxides in hydrochloric acid was treated with sulphuretted hydrogen and then precipitated with sodium thiosulphate.

iv. After the thiosulphate had been decomposed with hydrochloric acid, the solution was finally precipitated with oxalic acid.

By this series of processes all the substances accompanying scandium in wolframite, viz., lead, calcium, iron, manganese, as well as the other rare earths belonging chiefly to the yttrium earths, are removed, and *only thorium* accompanies scandium through all the stages of the purification. The complete separation of thorium and scandium presents very special difficulties, owing to the remarkable similarity of their chemical properties, which is by no means to be expected in view of the great distance between them in the periodic table. But after many unsuccessful attempts Dr. Speter found a method of separating them, depending upon the insolubility of the scandium sodium carbonate, of composition $Sc_2Na_8(CO_3)_7 6H_2O$, which separates from boiling soda solution. When subjected to spectroscopic examination, the scandium oxide thus obtained is found to be quite free from thorium, and this is in agreement with the fact that the distinct radio-activity of the impure products is no longer electrometrically measurable in the preparations which have been purified in the form of the sodium double carbonate. Moreover, the thorough examination of the spectra did not reveal the presence of any other impurities. This was all the more remarkable because atomic weight determinations always gave values which approximated to 45, while Nilson, the discoverer of scandium, had obtained the value 44·1 in four very concondant determinations. A further purification was then attempted by the fractionation of scandium acetyl-acetonate, but the atomic weight remained unchanged. However, it did not seem advisable to take the value 45 as final, until it had been found that it undoubtedly remained constant after the application of further methods of purification.

Meanwhile, R. J. Meyer and M. Speter (*Chem. Ztg.*, 1910, No. 35; R. J. Meyer, *Zeit. Anorg. Chem.*, 1911, lxxi., 65) had found that iodic acid is an excellent reagent for separating thorium from mixtures with other earths. The method depends upon the precipitation of thorium iodate from strong nitric acid solution by means of a large excess of potassium iodate. Based upon this a quantitative determination of thorium in presence of other earths could be worked out. When the experience thus obtained was applied to the separation of thorium from scandium oxide containing thorium, the result was different from that obtained in earlier experiments with other methods. The details of the method will be given fully elsewhere, and here it will be described in outline only:—By means of an excess of potassium iodate, thorium iodate is precipitated from a nitric acid solution as a flocculent amorphous precipitate. But in presence of a large excess of scandium it is appreciably soluble in scandium iodate, and hence the thorium can be separated quantitatively only if the addition of a large excess of potassium iodate has reduced the solubility to such an extent that some of the scandium iodate is simultaneously precipitated. When the liquid containing the precipitates has stood for some time, it is found that the amorphous thorium iodate is mixed with distinctly crystalline scandium iodate. The complete separation of the thorium cannot be ensured unless this method of procedure is adopted. Different specimens of scandium oxide, which had previously been freed from other impurities as described above, were separated from thorium by this method. Determinations of the atomic weight gave the following result:—

	I.	II.	III.
Sulphate	1·5924	2·4207	2·6394
Oxide	0·5766	0·8765	0·9565
Atomic weight ..	44·11	44·11	44·20

Thus by strongly treating the scandium containing thorium with iodic acid the atomic weight was reduced to the value given by Nilson, 44·1. If the alteration from the value previously obtained, viz., 45, to a value one unit lower is caused only by the elimination of the last trace of thorium, this must show that 0·5 per cent of ThO_2 in scandium oxide cannot be directly detected either chemically or physically. As a matter of fact, as Prof. Eberhard, of the Astrophysical Observatory in Potsdam, has had the kindness to prove, the arc spectrum of the oxide of atomic weight 45 is in every respect identical with that of the oxide of atomic weight 44, purified by means of iodic acid. On the other hand, the thorium in the precipitate obtained in the iodate separation can of course be detected in the usual way. These precipitates consist of thorium and scandium; no unknown lines can be detected in the spectrum, so that in any case these experiments give no warrant for the suggestion previously made that scandium of atomic weight 45 might contain an unknown element. Thus spectrographic and electrometric methods have proved not sensitive enough to detect 0·5 per cent of thorium oxide. (The sensitiveness of the spectrographic method of detecting thorium is impaired by the fact that only lines of feeble intensity appear in the spectrum; it is the same with cerium). On the other hand, it is interesting to notice that the magnetic method, the great sensitiveness of which in its application to the analysis of the rare earths has already been pointed out by Urbain, does not fail (Urbain and Jantsch, *Comptes Rendus*, 1908, cxlvii., 1286; Urbain, *Comptes Rendus*, 1910, cl., 913; 1911, clii., 141). Prof. Urbain, of Paris, was kind enough to determine the magnetic susceptibility of two preparations of scandium oxide, the first of which, of atomic weight 45, had been purified by sodium carbonate, and the second, of atomic weight 44, by iodic acid. The actual determinations were carried out by Mademoiselle Feytis, whose valuable work in this region is well known, and to whom we offer our hearty thanks. The coefficients of magnetisation, x, referred to unit weight are as follows:—

Atomic weight:	45	44
$x \cdot 10^6$	$+0·04$	$-0·12$

Thus the impure product of atomic weight 45 is very feebly paramagnetic, while the purer product, of atomic weight 44, is diamagnetic. This fact is of general interest. Mainly owing to the work of du Bois and his pupils, and of St. Meyer, it is known that the group of the rare earths from cerium to ytterbium is strongly paramagnetic, reaching a maximum, as Urbain has proved, in dysprosium. In contrast to this group, the individual members of which cannot be allocated in the Periodic Table owing to the r extraordinarily close resemblance, so that they appear to form a cluster in the eighth series consisting of a swarm of elements between lanthanum and tantalum, the elements lanthanum and yttrium and also, as we now know, scandium, are diamagnetic. These three elements, which undoubtedly occur as homologues in the third group of the periodic system, and which in many respects differ from most of the rare earths, also differ from them in their magnetic behaviour. This is specially important in the case of scandium because in many ways it completely repudiates the character of the rare earths.

Thus if iodic acid provides a means of completely separating thorium from scandium, this method is suitable only for the working up of small quantities. For, apart from the fact that it necessitates the use of a great deal of potassium iodate and that the regeneration of the scandium from the liquid containing iodic acid is very troublesome, the yields are also unsatisfactory, as some of the scandium has to be precipitated with the thorium. We therefore endeavoured to find a method which would enable us to purify larger quantities of scandium quickly and without much loss of material. Guidance in our experiments was provided by the knowledge that the more negative earths — and both thorium and scandium are included among these—are relatively most easily separated from one another when they are present in the form of the most complex compounds possible, because in such the chemical properties are individual in a higher degree than in salts of simple ions. This point of view has not been sufficiently taken into account in the many attempts to split up the involved group of yttrium earths into its components. At all events it proved very useful in our case.

It is already known that the precipitation of the hydroxides of the rare earths with ammonia is prevented by the addition of a sufficient quantity of tartaric acid or ammonium tartrate; in this respect they behave like the other trivalent elements. There is a difference between the members of the cerium earths and those of the yttrium earths, for the latter are separated in the form of difficultly soluble ammonium double tartrates, while the corresponding complexes of the former are soluble. There is no mention in literature of this very simple fact. (It has occurred to us to use this difference in behaviour for separating the cerium and yttrium earths, and also to try to base separations in the group of yttrium earths on the same difference. The results of the experiments which are now in course of progression will be announced later). Now while scandium exactly resembles the yttrium earths in its behaviour towards ammonium tartrate and ammonia, with thorium no precipitation occurs with ammonia in the ammonium tartrate solution even on boiling, either because the tartrate complex formed is easily dissolved or because, in consequence of the more negative nature of thorium, it can completely resist the action of hydroxyl ions; for it is not improbable that the difficultly soluble precipitates of the yttrium earths are to be regarded as the products of a partial hydrolysis of tartrate complexes richer in tartaric acid. This fundamental difference in the solubility and stability of the tartrate complexes may very easily be applied in the separation of scandium from thorium.

The neutral solution of scandium to be freed from thorium is slowly dropped into a concentrated solution of neutral ammonium tartrate, which is meanwhile mechanically stirred, and the clear solution thus obtained is precipitated with ammonia while boiling. The scandium then separates as scandium ammonium tartrate, while the thorium remains in solution. The precipitate is washed with a dilute solution of ammonium tartrate. Synthetic preliminary experiments with small quantities of the two earths showed that by this method the thorium could be removed without causing any considerable loss of scandium.

This process was successfully applied to the preparation in the pure state of 100 grms. of scandium oxide. An atomic weight determination carried out with the oxide obtained from the ammonium double tartrate gave the following result :—

Sulphate, 1·5207; oxide, 0·5495; atomic weight, 43·90.

On the ground of this result we may say that we have here a method for the preparation of pure scandium which is perfectly satisfactory from the point of view of simplicity and economy. For we are now able to prepare the earth in a pure state by a series of easily performed and almost quantitative analytical operations. The atomic weight determinations certainly exhibit differences that are so great that the results cannot be accepted as final, and the question of the exact atomic weight will have to be subjected to a special study. This seems the more necessary because at present we can bring forward no definite proof that 44 is actually the true atomic weight of scandium. The question cannot be finally settled till the constancy of the value during the fractionation of a larger quantity of the earth has been tested.

Wissenschaftl-Chemisches Laboratorium.

THE HEAT TEST FOR CHINESE WOOD OIL.

By FRANK BROWNE, F.I.C., Government Analyst, Hong Kong.

The quality of this oil is determined to a large extent, particularly in the United States, by its behaviour to heat. The oil has the well known characteristic property of forming a jelly when raised to 250° C. for a few minutes. Different observers employ usually different temperatures, so that results are not easily comparable. It seemed very desirable, in view of the large and increasing export of this article, to so arrange a heat test which could be repeated by both buyer and seller in any part of the world. In working out a satisfactory method it was essential to bear in mind that as far as possible samples must be heated in an identical manner in order to obtain concordant results. In the apparatus employed for these experiments attention was given to a number of details, which will be seen from the following description :—

Test-tubes for containing the oil were 16 cm. by 15 mm., with a mark near the bottom to indicate 5 cc., and closed by a cork so perforated that a glass rod 3 mm. in diameter could move freely.

Bath.—This was a copper beaker, height 12 cm., internal diameter 6 cm., filled with cotton-seed oil to a height of 7·5 cm.

Thermometer.—The length was 30 cm. The graduations were from +100° to 400° C., and were verified by comparison with a standard instrument. In the experiments the thermometer was placed so as to be 1·5 cm. from the bottom of the bath. In ascertaining the temperatures of the bath, due attention was given to the cool column of the mercury, so that corrected temperatures are recorded.

Method of Procedure.—When the bath temperature is 293° C. (560° F.) and very slowly rising at this point, the tube containing 5 cc. of the oil to be tested is fixed in so that the bottom of the tube is level with the lowest part of the bulb of the thermometer. The time is noted, and the source of heat is removed for about forty-five seconds and then re-applied. Before two minutes have elapsed the temperature of the bath will have fallen to 282° C. (540° F.), at which point it should be kept as steady as possible. When the wood oil has been in the bath about nine minutes, the glass rod is raised at intervals of half a minute, and when the rod is firmly set the time is again noted. As setting or jellying takes place within a few seconds of fluidity a good end determination is afforded. The specimen is at once removed, the bath is again heated to 293° C., and the experiment is repeated with another portion of the sample. There is no difficulty in obtaining results which do not differ by more than half-a-minute. No stirrer is used in the bath. A screen round the bath enables the temperature to be more easily reached. When the cotton-seed oil has become tarry and viscid, it should be renewed, otherwise heating may be irregular. The jelly may be removed by half filling the tubes with strong sulphuric acid and placing in a warm place for a few hours.

Table I. shows this heat test on seven samples from different consignments. Each testing was in duplicate.

Table I.

(Showing the number of minutes required for wood oil to set when heated).

No. of sample...	1.	2.	3.	4.	5.	6.	7.
Expt. 1.. ..	12	12½	11	13	12	12	11
Expt. 2.. ..	12½	12½	11	13	12½	12	11

A series of experiments was then instituted to see the effect of adulterants on the period of setting. Sample No. 1 was mixed with 10 per cent by volume of bean, ground nut, mineral, and cotton-seed oil respectively, and samples Nos. 3 and 7 with bean and mineral oil respectively. Table II. shows that each adulterant behaved in practically the same way in prolonging the heat test.

Table II.

(Showing the number of minutes required for wood oil containing 10 per cent of adulterant to set).

	+10 per cent.			
	Bean oil.	Ground nut oil.	Mineral oil.	Cotton-seed oil.
Sample No. 1.				
Expt. 1	15	14½	14½	15
Expt. 2	15	15	14½	15
Sample No. 3.				
Expt. 1	13½	—	13	—
Expt. 2	13½	—	13½	—
Sample No. 7.				
Expt. 1	13	—	13	—
Expt. 2	13	—	13½	—

The heat tests of wood oil containing 20 per cent by volume of adulterant were then determined. The results are shown in Table III.

Table III.

(Showing the number of minutes required for wood oil oontaining 20 per cent of adulterant to set).

	+20 per cent.		
	Bean oil.	Mineral oil.	Cotton-seed oil.
Sample No. 1.			
Expt. 1	18½	18½	18½
Expt. 2	19	18½	19
Sample No. 3.			
Expt. 1	17	17	not tested
Expt. 2	17	17	
Sample No. 7.			
Expt. 1	16½	16½	not tested
Expt. 2	16½	16½	

The results show that a heat test carefully applied is of considerable help in ascertaining quality. If the time required does not exceed twelve and a-half minutes the oil is in all probability genuine. For heat tests of thirteen minutes further examination is desirable. A useful test in such cases is that with chloroform and iodine (*Analyst*, xxxiii., 43). In Table IV. will be seen the times required for this test. Adulterated oils jelly more slowly. Thus oil No. 1 mixed with 10 per cent of bean oil required 105 seconds, and when mixed with 20 per cent of the same adulterant no setting took place for more than five minutes. For the chloroform and iodine test 1 grm. of oil in a small dish was dissolved in 5 cc. of chloroform, 5 cc. of a saturated clear solution of iodine in the same liquid added, and the mixture was stirred till a jelly was formed. For comparison experiments the same iodine solution, free from suspended iodine, must be used.

Table IV. gives the constants of the wood oils examined, from which it will be seen that they were genuine.

The iodine numbers were obtained with Wijs solution, to which when decolorised had been added enough of the original solution of iodine in acetic acid to restore the iodine colour, and thus to give a slight excess of iodine. When used under identical conditions this has given concordant results. Of the oil 0·10 to 0·11 grm. was dissolved in 10 cc. of carbon tetrachloride, and after the addition of 25 cc. of Wijs solution, absorption was allowed to go on for three hours. The quantity of oil recommended to be taken must not be exceeded or the results will be too low. The temperature was not above 26° C. during absorption for the iodine numbers recorded in the table. The figure for oils Nos. 1, 3, and 7, obtained with Hubl solution, was the same for the three, namely, 169.

Table IV.

No. of sample.	Sp. gr. at 15·5° C.	Saponification number.	Iodine number.	Iodine and Chloroform test, seconds.
1.	0·9405	191	173	40
2.	0·9412	192	174	40
3.	0·9402	194	173	45
4.	0·9408	191	174	55
5.	0·9405	191	173	45
6.	0·9406	191	174	40
7.	0·9431	193	173	40

(For Heat Test, see Table I.).

THE SEPARATION OF THE RARE EARTHS.

By C. JAMES.

Since writing a scheme for the separation of rare earths in 1908, many new methods have been introduced and others modified. Furthermore, since communications asking for reprints still arrive, the author has considered it advisable to bring the methods of separation up to date.

The operations herein dealt with concern only the rare earth elements, La, Ce, Pr, Nd, Sm, Eu, Gd, Tr, Dy, Ho, Er, Tm, Yb, Lu, and Ct, together with Yt and Sc, it being considered that other metals, such as thorium, zirconium, &c., have been removed if found occurring in the oxalate precipitate. A description of the working up of rare earth minerals will be found included in a paper on thulium (*Journ. Amer. Chem. Soc.*, xxxiii., 1332, and Chemical News, civ., 73).

There are four different methods for attacking the crude oxalates, which depend upon the composition of the latter:—(*a*) If the mixture is chiefly composed of lanthanum, much cerium, praseodymium, neodymium, samarium, europium, and gadolinium, it should be converted into the neutral nitrates and boiled with potassium bromate and marble, as required for the separation of cerium. (*b*) If only a little cerium is present; the oxides should be converted into double magnesium nitrates, which are then fractionated, the cerium being separated from the fractions where it is found to occur. (*c*) Should the mixture be composed of gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, celtium, yttrium, and scandium it is best to commence with the fractional crystallisation of the bromates. (*d*) When the cerium and yttrium metals occur together one must commence with the sodium sulphate treatment.

Separation of Yt and Ce Group.

The solution in the form of the chloride or sulphate is stirred with sodium sulphate crystals until the praseodymium and neodymium bands disappear. Sodium sulphate is better than potassium sulphate when used with care. The solubilities of the yttrium earth sulphates increase with the addition of sodium sulphate until the latter reaches a certain concentration, after which the former rapidly decrease. When all the cerium group double sulphates (1) are precipitated, they are filtered off and washed with sodium sulphate solution. The filtrate is acidified, and the rare earths thrown out by means of oxalic acid (2).

Separation of Ce.

The double sodium sulphates (Precipitate 1) are boiled with strong sodium hydroxide until thoroughly decomposed. The mass is diluted, filtered, and washed with boiling water until free from sulphates. The hydroxides are dissolved in nitric acid, the solution made nearly neutral, heated to boiling, and potassium bromate added (James and Pratt, *Journ. Amer. Chem. Soc.*, xxxiii., 1326, and Chemical News, civ., 61). When the red fumes of bromine make their appearance, a few lumps of marble are added to keep the liquid nearly neutral. (Recent experiments show that powdered marble added very gradually can be used with great advantage when working upon the large scale). The whole is then boiled until some of the filtered liquid fails to give the hydrogen peroxide test for cerium. The marble, if in the lump condition, is removed, and the precipitate of basic ceric salts is allowed to settle as much as possible, after which it is filtered off and washed with water acidified with nitric acid (Precipitate 3). The filtrate can either be precipitated in the cold by oxalic acid or else heated to boiling, and the hydroxides separated by means of an excess of sodium hydroxide. The hydroxides or oxalates form Precipitate 4. In case oxalic acid is used to throw out the rare earths, it is advisable not to use too much potassium bromate in the early part of the operation, as otherwise much oxalic acid is used up by the oxidation, and quantities of bromine are liberated. When large quantities of cerium are present, the boiling should be continued until only a little remains in solution; under these conditions the cerium basic salt, after washing with acidified water, is obtained in a very pure state. The small amount of cerium remaining in solution can then be removed by continuing the boiling as described above.

If necessary the cerium can be purified by repeating the process, or as follows:—The precipitate is dissolved in concentrated nitric acid by the aid of a *very little* alcohol. The orange-red liquid obtained in this manner is diluted and boiled with lump marble. The solution must not be allowed to become alkaline by boiling too long. The portion remaining in solution is then treated with potassium bromate, &c. The basic salts may be further purified by dissolving in hydrochloric acid, adding a slight excess of sulphuric acid and heating. The crystalline cerium sulphate is separated and washed with alcohol. The sulphate is then rendered anhydrous, made into a cold saturated solution, and the pure hydrated sulphate thrown down by heating.

Separation of La Group.

The cerium free earths (4) if in the state of oxalates are ignited to oxides. For roughly separating these earths upon the large scale the crystallisation of the double magnesium nitrates is employed. These compounds crystallise more readily than the double ammonium nitrates. The magnesium double salts (Demarçay, *Comptes Rendus*, cxxx., 1019), $2R'''(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$, are prepared by dissolving the rare earth oxides in a known amount of nitric acid. An equal amount of nitric acid is then neutralised by magnesium oxide, after which the two solutions are mixed and evaporated until, upon blowing on the surface, small crystals form. Water is sprayed over the surface, and the whole allowed to crystallise for about twenty-four hours. The mother liquor is then poured off and evaporated further, while the crystals are heated with water until dissolved, the correct amount to use being soon learnt by experience. Both fractions are again allowed to crystallise for a like period, the concentration being such that half of the solid separates upon cooling. In the subsequent fractionations the more soluble moves in one direction and the less soluble in the opposite. After the crystallisation of the second series is complete, the liquid from the most soluble portion is poured off and evaporated, while the liquid from Fraction I. is used as the solvent for the crystals forming Fraction II., water being added or evaporated as may be necessary. The least soluble portion, Fraction I., is again dissolved by heating with water. The above is repeated many times. When the fractions at either end become too small to work they should miss one series of operations and then be added to the next lot.

After a few series of crystallisations the least soluble portion becomes very light coloured, later growing nearly colourless, and finally takes a faint green tinge. When the fractions at this end no longer show the characteristic absorption bands of neodymium, they should be placed aside and mixed together according to the amount of praseodymium contained therein; in other words, fractions of the same colour are united.

The most soluble portion changes very rapidly. It soon takes a yellow colour and shows a samarium spectrum, together with the bands of dysprosium, holmium, and erbium. Sometimes at this point the liquid refuses to crystallise, or else a precipitate may form. If either of these things happens, it is best to dilute with water and precipitate with oxalic acid in order to separate the impurities that have accumulated and interfere with the crystallisation. The insoluble oxalates are converted back to the double magnesium nitrates in the same manner as already described. The neodymium bands finally become very weak in the mother liquors from the most soluble fractions. These are then set aside for the preparation of samarium, europium, and gadolinium. When the samarium has been separated the more soluble portion of the remaining fractions rapidly turns to a beautiful amethyst, and when this occurs it is separated from the rest as crude neodymium. After the process has been continued for some time longer it will be found that the material has been split up into four groups, according to the order of their solubilities. Commencing with the least soluble we have:—

5. Lanthanum and praseodymium magnesium nitrates.
6. Praseodymium and neodymium magnesium nitrates.
7. Crude neodymium magnesium nitrate.
8. Samarium, europium, and gadolinium magnesium nitrates, together with the simple nitrates of terbium, dysprosium, holmium, yttrium, &c.

Separation of La.

Lanthanum and praseodymium are best separated from each other according to the method of Auer von Welsbach (*Monatsh. Chem.*, vi., 477), which consists of the fractional crystallisation of the double ammonium nitrates of the type, $M'''(NO_3)_3 \cdot 2(NH_4NO_3) + 4H_2O$. These compounds are crystallised from water containing nitric acid to the extent of one-tenth the weight of the dissolved solid. The double salts are obtained by dissolving the oxides in the required amount of nitric acid, and for every three parts of acid required for the oxides two additional parts are neutralised by ammonium hydroxide. The resulting solutions are mixed, filtered, if necessary, and evaporated until small crystals form on blowing over the surface of the liquid. A little water is then sprayed over the hot solution and the whole set aside to crystallise. The time required for large amounts is about twenty-four hours. The process of fractionation is then carried out similarly to the double magnesium nitrates. The lanthanum is rapidly obtained in a colourless condition. A saturated solution gives no praseodymium absorption spectrum, even when very thick layers are used. The lanthanum ammonium salt encloses only a small amount of mother liquor, while the double magnesium compound carries large quantities. Both cerium and praseodymium pass into the more soluble fractions (10).

The lanthanum may be further purified by dissolving in water and precipitating by means of oxalic acid. This oxalate is treated with a slight excess of sulphuric acid, and the whole gently ignited until nearly all the free acid has been driven off. The sulphate is powdered and dissolved in water at about 1° with rapid stirring until the liquid becomes saturated, after which it is filtered, placed in a water-bath, and gradually raised to about 32°. The solution rapidly becomes solid owing to the separation of hydrated lanthanum sulphate. It is filtered upon a Buchner funnel and washed with hot water. The small quantity that remains in solution is then thrown out by means of oxalic acid. The crystallised sulphate may be again converted into the anhydrous state by heating, and the solution precipitated by heating again. This lanthanum material (9) should give a fine white oxide.

Though the crystallisation of such compounds as the metanitrobenzene sulphonates and bromates may give satisfactory results, the old method of Auer von Welsbach is the best all-round procedure.

Separation of Pr.

Praseodymium can be obtained from two sources:—(*a*) From the more soluble lanthanum fractions (10); (*b*) from the mixed praseodymium and neodymium double magnesium nitrates (6). These are treated separately. Praseodymium containing lanthanum is purified by continuing the fractional crystallisation of the double ammonium nitrates. The process is continued until no more lanthanum ammonium nitrate separates from the less soluble portions of the series. In this method the praseodymium accumulates in the most soluble portions. By fractionating the bromates the order is reversed, since lanthanum bromate is very much more soluble. At a temperature of 30° the latter compound crystallises with great difficulty.

In the second case, where praseodymium and neodymium occur together, it is best to convert the double magnesium nitrates into the corresponding manganese compounds, $2[M'''(NO_3)_3].3[Mn(NO_3)_2]+24H_2O$. In order to do this the magnesium double salts are dissolved in water, the solution acidified, and the rare earths thrown down by oxalic acid. These oxalates are washed, dried, and ignited to the oxides. The oxides are dissolved in a known amount of nitric acid. An equal amount of nitric acid is then neutralised by manganese carbonate. Any peroxide remaining undissolved can be brought into solution by the addition of a few drops of dilute oxalic acid solution to the hot double nitrates. The manganese double salts are crystallised from nitric acid having a specific gravity of 1·3. This fractionation is carried on until the spectrum of neodymium disappears. A very concentrated solution of the nitrate should give no trace of the bands of the latter element even when observed through a thick layer.

The double nitrate (ammonium or manganese) is dissolved in water and precipitated with oxalic acid. This oxalate is free from all rare earth metals, with perhaps the exception of traces of cerium. There are several methods for removing this element, such as:—

(*a*) Boiling the almost neutral nitrate solution with potassium bromate and marble. Instead of marble a little precipitated calcium carbonate may be added occasionally as long as there is any effervescence.

(*b*) Potassium permanganate and sodium carbonate. Since praseodymium is thrown down also to a slight extent the precipitates require working up again.

Praseodymium oxalate is found at 11.

Separation of Nd.

The crude double magnesium neodymium nitrate forming (7) is the starting-point for the preparation of pure neodymium salts. The mother liquors, together with the most soluble crystals from the double manganese fractionation, can also be used. Moreover, this last double salt can be used for the purification of neodymium with results equal if not surpassing those of the magnesium salts. In the case of the double magnesium nitrates water is used as the solvent, which makes the process cheaper and more convenient to handle than nitric acid.

After more series of crystallisations have been carried out the liquid assumes a beautiful bluish lilac colour, which is better seen when some of the liquid is diluted somewhat. The absorption bands in the blue stand out clearly. An excellent test of the purity of neodymium is found by observing the colour of the oxide, which is blue when pure.

By crystallising the bromates, the order of the solubilities is reversed; neodymium becomes the least soluble, while praseodymium passes into the mother liquors.

Pure neodymium material is found at 12.

Separation of Sm and Eu.

Fraction 8 contains not only samarium and europium, but large quantities of gadolinium, yttrium, dysprosium, and erbium earths. The double magnesium salts are crystallised from 30 per cent nitric acid (*Journ. Amer. Chem. Soc.*, xxxiii., 1363; CHEMICAL NEWS, civ., 163). The fractions rapidly change in their appearances, the least soluble showing the yellow tint due to samarium, while the most soluble portions begin to crystallise badly owing to the quantities of yttrium earths present. At this point it is best to commence the addition of the isomorphous bismuth magnesium nitrate, which, as Urbain (*Comptes Rendus*, cxxxviii., 84) has pointed out, places itself between samarium and europium. When working upon the large scale the bismuth salt is crystallised through the mother liquors in portions of 1 kgrm. at a time. This rapidly removes all europium from the yttrium earth nitrates. After crystallising many times, the mother liquor, which shows a strong spectrum of dysprosium, holmium, and erbium, is placed aside. The series is then allowed to expand to twenty or more fractions. Samarium is removed from the least soluble end, after a very large number of crystallisations, when it is considered certain that all europium has passed further along the series. As soon as the gadolinium fractions next to the samarium show a fine sharp absorption band in the blue—due to europium—nitric acid of about 50 per cent is used as the solvent. By this time most of the samarium has been removed in a pure condition (13), and nearly all the yttrium, dysprosium, and erbium earths, together with quantities of gadolinium from the opposite end. Since the fractions now take up only a comparatively small space, it is best to transfer all to large casseroles, which can be covered with watch-glasses and so prevent a considerable amount of inconvenience and deliquescence. As the work proceeds the europium band is observed to become stronger in the fractions between samarium and gadolinium. Later, the two bands in the green make their appearance. The fractions become smaller and smaller, since all mother liquors, beyond one or two that give no europium spectrum, have been removed. Only traces of samarium should be left by this time. Finally the samarium bands disappear, and the remaining fractions consist almost entirely of bismuth magnesium nitrate. The fractions containing no gadolinium are mixed, diluted, and all bismuth thrown out by means of hydrogen sulphide. The clear filtrate is next treated with oxalic acid, and the europium oxalate separated upon a Buchner funnel, washed, and dried (14).

All the more soluble portions, consisting of gadolinium, together with varying amounts of yttrium, &c., form 15.

Separation of Gd.

The earths from fraction 15 are converted into oxalates. These are ignited to oxides and dissolved in nitric acid. The simple nitrates are then fractionated from strong nitric acid (Demarçay, *Comptes Rendus*, cxxii., 728). Gadolinium and terbium collect in the first crystals; dysprosium, holmium, and yttrium come next; while yttrium, erbium, &c., accumulate in the mother liquors. These mother liquors are precipitated with oxalic acid, and the insoluble oxalates added to fraction 2. The intermediate nitrates, consisting of dysprosium, holmium, and yttrium, form lot 17.

The least soluble nitrates, comprising gadolinium and terbium (16), cannot be purified by the continued crystallisation of the double magnesium nitrates, since the oxide remains of a yellow colour, even after many thousand operations. The crystallisation of the simple nitrates effects a separation but slowly. Apparently the best method for obtaining a white gadolinia is that of the double nickel nitrate of the type $2Gd(NO_3)_3.3N:(NO_3)_2+24H_2O$ (Urbain, *Comptes Rendus*, cxl., No. 9). This salt is crystallised from nitric acid of specific gravity 1·3. Terbium collects in the more easily soluble crystals (24). The position of gadolinium is found at 18.

(To be continued)

TOXICITY OF METHYL ALCOHOL.*

By THOMAS TYRER, F.I.C., F.C.S.

In a recent issue of the *Chemist and Druggist* reference was made to preparations made with methyl alcohol in Germany. It should be clearly understood that such preparations, toilet or otherwise, pay duty as alcohol (ethyl) on entry here. One has wondered why methyl alcohol was freer in Germany than here. On the purer qualities of high strength duty is imposed here, and methyl alcohol for research purposes (scarcely any other existing here) is more expensive than ethyl alcohol of equal strength and purity, and subject to the same restrictions as to duty and use. Opinions differ as to the toxicity of methyl alcohol, and in the United States, Columbia spirit (as methyl alcohol of all grades is called) opinions are different in various localities. In Protectionist States its toxicity is regarded with complaisance. Generally, however, now that ethyl alcohol is under practically similar conditions to those existing in Great Britain, methyl alcohol is regarded with increasing disfavour. In official quarters its toxicity was doubted until comparatively recently, but it is said that the late chief of the Government laboratory has now definitely stated that methyl alcohol is toxic. If so, and there is considerable evidence to support that view, the ordinary methylated spirit has a protection in this respect other than ascribed to the presence of the bodies which constitute its suitability as a denaturant of alcohol for industrial use under official sanction. *The Oil and Colour Trades Journal*, in its issue of July 8th, 1911, in an excerpt from a letter from M. Barbet, probably the highest living authority on fractional distillation (industrially), to Mr. J. G. McIntosh (a voluminous writer on alcohol), unhesitatingly declares methyl alcohol to be toxic. Barbet cites the catastrophe in a German locality, and observes that the introduction of methyl into liqueurs, &c., is a fraud from every point of view, as it is not a fermentation product. Mr. McIntosh observes, in concluding Barbet's excerpt, that on the basis of toxicity there is no excuse for the present excise duty on methyl alcohol. It is within my knowledge and experience that the authorities will not permit even now the sufficient purification of wood naphthas for the production of formaldehyde at a reasonable cost, unless under the strictest supervision. I have seen the only works in Great Britain producing formaldehyde, and have examined the conditions which seriously handicap progress, not to say expansion. Surely, if methyl alcohol is toxic, the restrictions and control can, and ought to be, less exacting. But so long as the department regards methyl alcohol from the "dutiable" point of view, progress is stayed. Of course, complete freedom, with instances of use immorally in existence, cannot be expected, but liberal concessions are absolutely needful for industrial development. A friend of mine has made the bold experiment of taking up to nearly 20 cc. of methyl alcohol, with resulting sensations that severely warned him to stop. Friends on the Continent have stated that workmen who have been under the impression that the alcohol they were using was simply another type of potable alcohol have fallen helpless on the floor, and become delirious in a short time on doses about equal to 25 cc. They have no doubt that if the doses had been 100 cc. paralysis and death would ultimately have ensued. Whenever cases of this kind arose, the stomach pump was immediately employed to minimise the effects of quantity taken. In the "United States Dispensatory of 1907," p. 1569, under "Methyl alcohol," is a most interesting article comparing it with ethyl alcohol therapeutically, which writes emphatically on methyl alcohol in any form the word "Dangerous." It is remarked: "It has very properly fallen into complete desuetude in medicine, and under no circumstances should it be used by pharmacists as a menstruum." Much more could be adduced against the use of methyl alcohol in any form for internal use—or, for that matter, personal external use either; but enough—methyl alcohol *is* a "poison." Technical, excise, and fiscal questions may stand over for another communication.

[The scores of deaths recently in Berlin and Japan from methyl alcohol liquors is surely evidence enough that it is a poison, and in a different class from ethyl alcohol. As to the importation of methyl alcohol preparations into this country, we quote from our issue of September 1st, 1906, p. 367:—"Certain medicinal and toilet articles are now being imported from and largely sold in this country which are free from ethylic alcohol, but are made with methylic alcohol. They pay no spirit duty, because the ingredients dissolved in the methylic alcohol are considered by the Customs authorities to make the alcohol impotable. This appears to be a rational interpretation of Section 133 of the Spirits Act, 1880, and powers to deal with purified methylic alcohol obtained since." Mr. Tyrer now says that duty is charged on these; if so the Revenue authorities are putting a different interpretation upon the law, and it would be interesting to know why.—Editor, *Chemist and Druggist.*]

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* From the *Chemist and Druggist*, May 25th, 1912.

THE FRUIT OF *DIERVILLA FLORIDA*.

By LOWELL E. DAWSON.

The fruit of *Diervilla Florida*, bush honeysuckle, was gathered the first part of July, 1911, at the home of Senator W. C. Stuckslager, of Lisbon, Iowa. It is a cultivated shrub of China and Japan, and attains a height of 5 to 8 feet. The berries seemed fully ripe when gathered, and were beautiful dark red in colour, resembling ripe currants, between a half centimetre and a centimetre in diameter. They are somewhat flattened at each end. The taste is very bitter and produces nausea when a small quantity are eaten. Two berries grow on one stem. They are quite juicy, and the yield is abundant. There were 265 grms. of the dried fruit available. The average weight of each was 0·0802.

The Sugars.

Two hundred grms. of the fruit were taken for the sugar extraction. They were placed in a litre flask, fitted with an inverted condenser, and treated with successive portions of alcohol for sixteen days. The alcoholic extraction was removed each day, and a fresh portion applied. The alcohol was distilled off, leaving a dark thick syrup. The first extraction was a decidedly dark brownish red, with an odour of scorched sorghum. The second extraction was more red in colour, and the scorched sorghum odour almost disappeared. The extractions became a lighter red each day, and on the tenth day the colour became yellow. A sweet odour was noticeable. The extractions reacted acid to litmus-paper.

A test with Fehling's solution at the end of sixteen days showed that the sugars were almost extracted, and distilled water was substituted for alcohol. The berries under the alcohol treatment remained hard and firm, but on the addition of water they became soft and mushy. The alcoholic extract at the end of sixteen days was a very light yellow, while the first water extractions were black

The water extractions became lighter each day, until the last one, at the end of twelve days, was a beautiful amber colour. Fehling's solution now showed that all the sugars were removed. The solution reacted acid to litmus.

The percentage of the sugars was determined by Fehling's solution of such a strength that 10 cc. corresponded to 0·05 grm. sugar. The determination was made by taking 1 cm. of the extract and evaporating to dryness in the case of the alcoholic extract, then diluting with 50 cc. of distilled water in a small beaker. This was heated to boiling, and treated with the Fehling's solution. To ascertain when the end-point was reached an indicator was used. The indicator is made by mixing 10 grms. of glacial acetic acid 1 grm. of potassium ferrocyanide (*Journ. Industr. and Eng. Chem.*, April, 1911, p. 256). To use the indicator:—When approximately sufficient Fehling's solution has been added to the sugar solution, take a folded filter-paper and place a drop of the mixture (sugar and Fehling's solution) on one side. The filtrate passes through free from copper oxide to the under side of the paper. The filtrate is touched with a drop of the indicator. If a red precipitate forms there is an excess of Fehling's solution. If no precipitate is visible, it indicates that the reduction is not complete. This is a delicate and satisfactory test. There were found to be 76·09 grms. of sugar, equivalent to 38·04 per cent. The water and alcoholic extractions were determined separately.

Portions of the two different sugar extractions were mixed together and evaporated to dryness. The residue gave a strong odour. It was tough and sticky. The taste was strong and bitter, like the original fruit.

This residue was purified by heating it for several hours with alcohol and purified bone-black on the water-bath. After filtering and evaporating to dryness the residue was hard like toffy, and dark brown in colour. With portions of 0·01 grm. of the purified sugar, 0·04 grm. phenylhydrazine hydrochloride, and 0·03 grm. sodium acetate, the test showed the presence of fructose.

The residue of the fruit after the sugar extraction was dried and weighed. The loss of weight was 77·4 per cent. They were now black in colour, shrivelled, and hard.

The Ash.

Five different 2 grm. portions were ashed in a platinum dish. From the first portion silica, iron, alumina, calcium, and magnesium were determined; from the second, the sodium and potassium by a modification of the J. Lawrence Smith method; from the third, the sulphates; from the fourth, the phosphates; from the fifth, the manganese by colorimetry. Chromium was not present. The analysis showed more potassium than sodium, and the flame test of the original berry pointed in the same direction. The results of the analysis are as follows:—

	Per cent of the ash.
SiO_2	0·00
Al_2O_3	10·15
Fe_2O_3	2·96
CaO	14·81
MgO	8·88
K_2O	31·70
Na_2O	5·69
SO_3	11·59
P_2O_5	11·76
MnO	0·13
Chromium	0·00
Total	97·67

The amount of CO_2 was not determined. The ash is 3½ per cent of the original fruit.

The Oils.

The dried berries from the sugar extraction, weighing 39·9 grms., were finely powdered with mortar and pestle, and used for the oil extraction. The powder was placed in a 500 cc. flask, tightly fitted with an inverted condenser, and treated with ether. Thirty-eight days were required to extract the oil. The ether was removed from the oil by distillation. The oil at first showed a slight yellowish green coloration, but as more and more was accumulated it became reddish brown in colour. After all the oil was extracted it was treated with ether and bone-black in a flask fitted with an inverted condenser for eighteen hours. The oil and ether were now filtered, and the ether evaporated off. This required about two days, as the last traces of ether seemed difficult to remove. The finished oil was a clear deep red when held before the light, and had a penetrating rancid odour. Its specific gravity was 0·9488. Two saponifications were made by Koetstorfer's method, resulting as follows:—

No.	Amount taken (grms.)	Approximate time (days).	Saponification equivalent.
1.	1·5756	3	318·6
2.	1·6924	3	319·2

The oil is difficult to saponify, and requires long concontinued heating.

According to Allen's "Commercial Organic Analysis," this would seem to belong to the castor oil group and to the Japanese and Chinese wood oil, whose saponification equivalent is given as from 266 to 360. The oil in question has the characteristic disagreeable odour of castor oil.

The products of the first saponification were separated. The soapy solution after saponification was diluted with distilled water, and a quantity of ether added, which dissolved the unsaponified portion and admixtures. This was separated from the liquid, evaporated to constant weight, and found to weigh 1·3650 grms. This would not seem to be a satisfactory result. The residue was dissolved in hot alcohol, filtered, and allowed to evaporate spontaneously. No crystals were formed, but a substance resembling paraffin with an odour suggesting phenol.

After separating the ethereal layer, the remaining liquid was acidified with dilute sulphuric acid and slightly heated. Whereupon the fatty acids liberated by saponification collected on the top of the liquid. The amount was almost inappreciable, and nothing was done with them.

An attempt was next made to obtain the weight of the soluble fatty acids. The acidified liquid was separated from the insoluble fatty acids, and exactly neutralised with normal caustic soda, using phenolphthalein as an indicator. Two-thirds of this was now distilled, and the distillate evaporated to dryness and constant weight, which was 0·0278 grm. The number of cubic centimetres of normal caustic soda was multiplied by 0·022, and the product subtracted from the constant weight, 0·0278 grm. This gave the weight of the soluble fatty acids as 0·0223 grm.

Each fruit bears four flattened stones which undoubtedly contain the oil. In all, 7·5 grms. of oil was obtained from the original 200 grms. of fruit, or 3·75 per cent.

The Proteins.

Some of the dried berries were crushed and boiled in distilled water for a short time. While heating an odour came off resembling very much that of postum. The solution reacted acid to litmus. A small amount of the solution was heated with dilute nitric acid. This produced a straw-yellow colour, which became an orange-red when made alkaline. This showed the presence of albumen. A portion of the fruit was heated alone in a dry test-tube. The fumes reacted acid to litmus.

The nitrogen was determined by a modification of the Kjeldahl method. 3·0153 grms. of the fruit were boiled in a round bottom 4-ounce flask with 50 cc. concentrated sulphuric acid for several days until the liquid became perfectly colourless. The solution was removed to a casserole, and diluted with distilled water to 250 cc. Then caustic potash was added to alkalinity. After cooling thoroughly the solution was filtered, and two-thirds of it distilled into a beaker containing 25 cc. of normal hydrochloric acid then titrated with normal caustic soda solution. We obtained 2·86 per cent of nitrogen.

The acid tests were made from the sugar extraction. We found both tartaric and citric acids.

The Alkaloid.

We took about 30 cc. of the alcoholic sugar solution, rendered it strongly alkaline with ammonia, added 50 cc. chloroform, and shook the solution well in a stoppered cylinder. The chloroform solution is separated, returned to the cylinder, about 80 cc. dilute sulphuric acid added, and again well shaken. The alkaloid now passes from the chloroform into the sulphuric acid, which changes to a coffee-brown colour. The acid and chloroform were now separated. When the chloroform evaporated spontaneously, a few crystals remained, which were colourless, flat, and rectangular. This would point to narceine, a basic associate of morphine. The coffee-brown colour of the sulphuric acid solution also points in the same direction. Some of this acid solution was placed in a porcelain dish and heated. A beautiful violet-red coloration appeared as soon as the liquid was sufficiently concentrated. This is a delicate and characteristic test for narceine (Plugge, *Journ. Am. Chem. Soc.*, iii.).

An effort was made to precipitate the alkaloid from the acid solution. We employed picric acid as the best reagent available. A 1 per cent cold solution of picric acid was added to the acid solution, and an abundant light yellow precipitate was produced. This was filtered, and the precipitate was found to be soluble in acetic acid. The test would indicate the possibility of conine, atropine, narceine, and veratrine. Further tests were made for the first two and the last, but nothing satisfactory was obtained.

Another test for narceine was as follows:—A freshly made mixture of ferric chloride and potassium ferricyanide, free from ferrocyanide, in aqueous solutions, has a yellowish brown colour; but in presence of this acid solution it turns blue or green owing to the production of Prussian blue.

Attempts to re-crystallise the precipitate from alcohol and water proved unavailing, because of the presence of picric acid.

There seems to be sufficient evidence that narceine is present, but we were not able to determine the amount. It is an expensive substance, and it might exist in the fruit in paying quantities. Its formula is $C_{23}H_{29}N_2O_6$. Possibly this is the constituent of the fruit that produces the nausea before mentioned.

Our thanks are due to Dr. A. Knight for his timely suggestions.

Cornell College, June 15, 1912.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 27th, 1912.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Electrical Vibrations on a Thin Anchor Ring.*" By Lord Rayleigh, O.M., F.R.S.

"*Molecular Statistics of some Chemical Actions.*" By Prof. The Hon. R. J. Strutt, F.R.S.

1. Where ozone acts on a silver oxide surface, every collision results in the destruction of the ozone molecule concerned.
2. An active nitrogen molecule must, on the average, collide 500 times with an oxidised copper surface before it is destroyed.
3. Two molecules of ozone at 100° C. must, on the average, collide 6×10^{11} times before the right sort of collision occurs for chemical union.

"*Experiments with Rotating Films.*" By C. V. Boys, F.R.S.

An apparatus is described whereby a film may be rotated in its own plane, and in which air at atmospheric pressure above and below the film is rotated also at the same speed. Twenty experiments are described which refer mainly to the ring and spiral patterns of colour that may be produced to the development of black films and patterns, and to the instability of the margin of the black. In this connection the definite phenomenon of "line tension" is described and shown to be probably a special case of surface tension. The isolation of areas of the thinner double black film is described, and for this the instrument is specially suitable.

The limits of variation of surface tension of a soap film are referred to. Experiments with rings of fibre or hair and with bubbles in the film, whether rotating or not, are described, and the means that they provide for weighing a film of any colour are indicated. The action of vapours on coloured and on black films is described.

"*Morphological Studies of Benzene Derivatives. III. Para-dibromo-benzene-sulphonates (Isomorphous) of the 'Rare Earth' Elements—a Means of Determining the Directions of Valency in Tervalent Elements,*" By Prof. H. E. Armstrong, F.R.S., and E. H. Rodd.

Para-dibromo-benzene-sulphonates of lanthanum, neodymium, praseodymium, cerium, gadolinium, and samarium are described. The first four crystallise with either 18 or 9 molecular proportions of water, the salts with the latter proportion being very closely isomorphous. The gadolinium salts contain either 7 or 12 and the samarium salt 18 molecular proportions of water. When interpreted in the light of the Barlow-Pope theory the crystallographic data justify the conclusion that, in the case of the salts containing $9/OH_2$, the crystal structure is derived from that of benzene by opening out the latter symmetrically in a plane along the three axes perpendicular to the trigonal axis in the crystal, so making room for the insertion of the three sulphonic groups, together with the metal and the water of crystallisation. The metal appears to occupy the central position. It is highly probable, therefore, that the valencies of the metal are directed symmetrically in a plane.

"*Intensity of Natural Selection in Man.*" By Karl Pearson, F.R.S.

"*Optical Rotatory Dispersion.* Part I. *The Natural and Magnetic Rotatory Dispersion in Quartz of Light in the Visible Region of the Spectrum.*" By Thomas Martin Lowry.

Measurements have been made of the optical rotation in quartz of light of the following twenty-four wave-lengths:—

Li 6708. Na 5896, 5890. Il 5351.
Hg 5790, 5769, 5461, 4359.
Cd 6438, 5086, 4800, 4678.
Ag 5472, 5466, 5209.
Zn 6364, 4811, 4722, 4680.
Cu 5782, 5700, 5219, 5154, 5105.

The material used included two columns of quartz of length 226·3670 and 226·3654 mm., built up in optical contact from cylinders cut from a massive crystal of lævo-quartz, entirely free from optical flaws, and a column of 181·4382 mm. of dextro-quartz selected with some difficulty from a crystal containing local faults. The lævo-cylinders produced a rotation of 25·5371° per mm. for light of wave-length 5460·97; the dextro-cylinders gave a lower value, 25·5361°/mm. The observational errors in the readings of rotatory dispersion amounted on the average to about six parts per million.

The rotations in degrees per mm. agreed satisfactorily with those calculated from the formula—

$$a = \frac{11{\cdot}6064}{\lambda - \lambda_1^2} + \frac{13{\cdot}42}{\lambda - \lambda_2^2} - \frac{4{\cdot}3685}{\lambda^2}$$

where $\lambda_1^2 = 0{\cdot}010627$, $\lambda_2^2 = 78{\cdot}22$, the deviations being less than 0·001°/mm. for ten wave-lengths, and less than

0·0025°/mm. for all but two of the twenty-four wave-lengths.

Measurements made with light of six different wave-lengths showed that Wiedemann's law of the proportionality of the natural and magnetic rotations holds good accurately in the case of quartz, but no such agreement has been discovered in a series of thirty optically-active liquids.

Two new methods are described for detecting optical faults in specimens of quartz that have passed the tests usually applied by opticians.

"*Apparent Change in Mass during Chemical Reaction.*" By J. J. Manley.

"*Diurnal Variations of the Electric Waves Occurring in Nature, and on the Propagation of Electric Waves round the Bend of the Earth.*" By W. H. Eccles, D.Sc.

The natural electric wave train radiating from a lightning discharge produces, it is well known, a disturbance in apparatus for the reception of wireless telegraph messages. Normally these disturbances form a steady stream of faint or loud clicks in the receiving telephones. The rate at which they are received at a station varies from hour to hour during the twenty-four hours, and also with the season, but as a general rule the disturbances—or "strays" as they are often called—heard at night are stronger and more frequent than those heard in the day. The change from day to night and from night to day conditions is very noticeable at sunrise and sunset. It is chiefly this transition period that is investigated in the present communication. It is found that very frequently there is not the gradual transition that might be expected, but instead a passage through a sharply marked minimum, amounting sometimes to a discontinuity.

In order to explain the phenomena the author develops a hypothesis, which is based on a proposition established in the paper. The proposition is to the effect that the velocity of electric waves through ionised air increases with increasing ionisation. Now it is probable that the ionisation produced by solar radiation increases, within limits, with increase of the height in the atmosphere. Hence it follows that a system of waves with vertical wave fronts must suffer a forward tilting of the wave fronts as it traverses the heterogeneous medium, and the rays will follow curved trajectories, having their concavity downwards. This alone explains many of the hitherto unexplained phenomena of wireless telegraphy, but to explain the stray minima found at sunset or sunrise it is necessary to suppose that the process of ionisation of the atmosphere at sunrise and the process of deionisation at sunset produce a turbulence of the medium that leads to difficulty of propagation. It is shown in the paper that the existence of this turbulence is corroborated by observations on telegraphic waves coming from great distances.

"*Report on the Total Solar Eclipse of April 28th, 1911.*" By Rev. A. L. Cortie, S.J.

"*Experimental Investigation of the Influence of the Condenser on the Working of a Ruhmkorff Coil, together with a Practical Outcome thereof.*" By W. Hamilton Wilson.

"*Studies on the Reductase of Liver and Kidney.*" (Part I.). By Prof. D. Fraser Harris and Dr. H. J. M. Creighton.

"*Borohydrates.*" (Part I.). By Prof. Morris W. Travers, D.Sc., F.R.S., and Ramu Chandra Ray, M.A.

i. When the product of the action of heat on a mixture of anhydrous boric acid and magnesium is treated with water a yellow solution is obtained, the properties of which have been investigated. The yellow colour appears to be due to colloidal boron. The solution, when treated with acid effervesces, evolving hydrogen gas, and precipitates the heavy metals, including lead, from solutions of their salts.

ii. The properties of the solution appear to be due to the presence of borohydrates, compounds of boron, hydrogen, and oxygen, the compositions of which have been deduced from the results of quantitative experiments.

iii. It appears that the boride Mg_3B_2 is not the sole product of the action of heat upon mixtures of boric acid and magnesium. Other borides of magnesium, and also compounds of boron, oxygen, and magnesium, are also produced. These have been partially investigated.

"*Specific Conductivity of Solutions of Oxyhæmoglobin.*" By Prof. G. N. Stewart.

"*Existing Limits of Uniformity in Producing Optical Glass.*" By J. W. Gifford.

"*A Petrified Williamsonia from Scotland.*" By Prof. A. C. Seward, F.R.S.

"*On Negative After-Images and Successive Contrast with Pure Spectral Colours.*" By A. W. Porter, F.R.S., and F. W. Edridge Green, M.D., F.R.C.S.

A definite portion of the retina was fatigued by steadily gazing at an isolated region included between two definite wave-lengths in the Edridge green colour perception spectrometer. After the fatiguing light had been viewed for a period of about twenty seconds, the eye was turned to a screen on which a spectrum was situated, so that the after-image formed a band running right across the spectrum on the screen and occupying its centre. Experiments were also made with the spectrum replaced by monochromatic bands, and on the appearance of the sodium flame after fatigue to various colours.

The first point which was evident was the very great importance of the intensity of the light which was used, especially in relation to the reacting light.

1. Very little effect was produced, except when the intensity of the reacting light was the same or less than that of the fatiguing light.

2. The effect was chiefly noticed on the less luminous portions of the spectrum; for instance, after fatigue for yellow there was very little effect in the yellow, but considerable effect in the violet.

3. The after-image is not surrounded by the primary colour.

4. The effect of fatiguing the eye with a monochromatic region produces a uniform grey band across this region, when both fatiguing and reacting lights are of the same intensity.

5. The after-image does not change colour on fading.

6. Violet was the most affected after fatigue for red.

7. An after-image is seen in the absence of all external light.

8. Except after fatigue by a very bright light, as, for instance, direct arc through coloured glass, yellow does not change to green after fatigue to red, or to red after fatigue to green.

The same is found with the sodium flame, though the after-image was strongly marked on each side of it.

9. The after-image, even in the absence of all external light, is always darker than the surrounding visual field.

10. The complementary to the exciting light is never strengthened in the spectrum on the screen by the after-image.

These facts cannot be explained on either the Hering or Young-Helmholtz theories. The explanation on the Edridge-Green theory of colour-vision is the same as that given for other facts of simultaneous contrast (*Proc. Roy. Soc.*, B, 1912, lxxxiv., 546).

"*Relation between Capillary Pressure and Secretion. II. The Secretion of the Aqueous and the Intra-ocular Pressure.*" By Leonard Hill, F.R.S., and M. Flack.

"*Some Conditions Influencing Nitrogen Fixation by Aerobic Organisms.*" By Prof. W. B. Bottomley.

"*Effects of Stimulation and Extirpation of the Semicircular Canals of the Ear and their Relation to the Motor System.*" By J. G. Wilson and F. H. Pike.

"*Absorption and Reflection of Homogeneous Particles.*" By W. Wilson, B.A.

"*Effect of an Obstacle on a Train of Electric Waves.*" By Prof. H. M. Macdonald, F.R.S.

"*Optical Investigation of Crystallised Nitrogen, Argon, Methane, and some of the Simpler Organic Compounds of Low Melting-points.*" By Walter Wahl, Ph.D.

A quartz glass vessel, holding a very thin layer (0·05 mm.) of substance between polished quartz glass plates, has been constructed. In this vessel N, A, CH_4, &c., have been crystallised and investigated crystal-optically:—

1. Nitrogen crystallises in the regular system.
2. Argon is regular.
3. Methane is regular.
4. Ethylether is rhombic. Ethylalcohol, acetone, methylalcohol, and carbon-bisulphide are monoclinic or triclinic. Methylalcohol occurs in two polymorphic forms, changing reversibly into each other.

"*Colour Blindness and the Trichromatic Theory. Part IV. Incomplete Colour Blindness.*" By Sir W. de W. Abney, K.C.B., F.R.S.

In this communication the author shows how a simple test is capable of giving a quantitative measure of the degree of colour blindness which a colour-blind person possesses. By matching a single colour of the spectrum with the colour of the light coming from such a solution as of chromate of potash the degree of colour blindness can be immediately determined. Further, he gives a method by which any displacement of the green or red sensation curves can be measured with great accuracy.

"*Multiplication of Successions of Fourier Constants.*" By Prof. W. H. Young, F.R.S.

"*Diffusion of Ions into Gases at Low Pressure.*" By C. E. Haselfoot.

"*Effect of a Magnetic Force on the Motion of Negative Ions in a Gas.*" By Prof. J. S. Townsend, F.R.S., and H. T. Tizard.

INTERNATIONAL INSTITUTE OF AGRICULTURE.

The *Bulletin of Agricultural Statistics* for June has just been issued by the International Institute of Agriculture in Rome.

The *Bulletin* contains tables showing the area under wheat, rye, barley, oats, maize, and rice, and the estimated production in a few countries for the first four of these crops.

The weather was not, in general, very favourable for the crops during May, on account of the heavy rains and late frosts. The production of wheat is estimated in Spain at 31,943,600 quintals, *i.e.*, 79 per cent of last year's production; in the United States it is estimated at 98,794,080 quintals, or 84·3 per cent of last year's outturn (winter wheat only); and in India at 90,709,772 quintals, or 97·7 per cent.

The Statistical Service of the Institute, which was lately extended to include flax and cocoons, has, with the present issue of the *Bulletin*, been still further enlarged, and now also embraces tobacco and sugar-cane. Tables are given showing the latest official information available with reference to these two crops, and also in regard to vineyards and sugar-beet.

A table concerning the sericultural campaign of 1912 gives the estimated production of cocoons as smaller than that of last year in Spain (1,175,000 kgrms. as against 1,250,000 kgrms. in 1911), and in Japan (92,206,000 kgrms. as against 96,711,885). A poor crop is also predicted in Bulgaria and Italy, though more satisfactory accounts have been received from Austria and France.

The general condition of the sugar beet and tobacco crops, and of the vines, is given as good; the vines are flowering, for the greater part, under favourable conditions.

Somewhat unsatisfactory accounts have been received from Egypt, Japan, Tunis, and the United States with regard to the cotton crop. In the latter country the condition on May 25th is given as 78·9 per cent of a normal condition, as compared with 87·8 per cent at the same date last year.

The notices published with reference to the preparations for autumn sowings in Chile and Australia, state that unfavourable conditions for field work prevail, and that the work is less advanced than usual at this date.

Final returns of area and production of the various crops in 1911 are given for Servia and Japan, as well as the final returns of area cultivated in British India for the same year.

The *Bulletin* closes with the results of the live stock census in Luxemburg in 1910.

NOTICES OF BOOKS.

Louis Olivier. Printed by Louis Marethen, Paris. 1911.

It was a happy idea to invite the many friends of the late Louis Olivier to honour him by writing a scientific book, and no better method of perpetuating his memory could have been chosen. This book, of which only a limited number of copies will be issued, is composed of articles which cover a very wide range of subjects. The funeral oration which was pronounced by Dr. J. P. Langlois is reproduced, and a biography written by M. C. E. Guillaume is also included. No branch of natural knowledge is left unrepresented in the collection of papers. Prof. Ostwald contributes an article on the Organisation of Science, in which he recommends a scheme for organising and controlling scientific literature, especially that relating to chemistry. Prof. Guye writes on a somewhat similar subject, confining his remarks, however, to the organising of research work, especially in laboratories devoted to physical chemistry, and giving the results of his experience in the laboratory of the University of Geneva. Astronomical science is represented by a short paper on the Evolution of Astronomy by Prof. G. Bigourdain, in which the author puts forward the view that the origin of the study of the science was the need felt by man for having some means of dividing time accurately. The reform of the Calendar is discussed in a paper by Prof. Pierre Duhem, and M. Henri Dehérain writes on the exploration of Ethiopia and the Emperor Menelik. The scientific spirit in business and the relations of science and industry are discussed in two papers, and some articles on more specialised subjects are included, such as alcoholysis and the oxidases.

L'Acide Formique ou Méthanoïque. ("Formic or Methanoic Acid"). By André Dubosc. Paris: Dunod and Pinat. 1912.

The author of this monograph claims that he is the first to bring together from its very scattered sources all the work that has been done on formic acid, and to write a monograph in which its preparation and properties are considered from the technical as well as from the purely scientific point of view. He has had many opportunities of studying its applications in the industries, and the monograph is well up-to-date in all matters of detail. In Part I. the occurrence of formic acid in the three natural kingdoms, the history of its investigation, and its constitution and structure are discussed. Then full accounts of all methods of preparation are given, including reliable information as to their yields. The physical, chemical, and thermochemical properties are treated in the second part, while the last section of the book is devoted to the consideration of the derivatives of formic acid and of various methods which have been suggested for its detection and quantitative estimation.

CORRESPONDENCE.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

To the Editor of the Chemical News.

Sir,—I am told that many chemists are hesitating about attending the Eighth International Congress of Applied Chemistry (New York, September, 1912) because of the supposed enormous expense. If I am correctly informed, statements have appeared in print indicating £130 as the minimum cost per person. Being familiar from personal experience with all the modes of crossing the Atlantic, and being concerned also in the arrangements made for the entertainment of the members of the Congress, I ask the hospitality of your columns for the purpose of correcting so utterly false an impression. The minimum expense for comfortable accommodation may be estimated as follows:—

1. From Liverpool, August 21st, by American Line s.s. *Dominion*, only one class of cabin passengers to Philadelphia, thence rail to New York, inclusive fare £10.
2. From Glasgow, August 23rd, Allan Line s.s. *Numidian* (only one class of cabin passengers) to Boston, thence rail to New York, inclusive fare £9.
3. From Glasgow, August 24th, Anchor Line s.s. *California* to New York, first cabin fare £14.

The first two of these routes afford an opportunity to see Philadelphia and Boston, without additional expense.

Columbia University has offered to members and their families the free use of rooms in the Residence Halls, which will be available from August 31st to September 13th. Until the end of July rooms will be assigned, in order of application, to guests from abroad exclusively. Application should be made to the Secretary of the Congress, Dr. B. C. Hesse, 25, Broad Street, New York. The expenses in New York are limited, therefore, to the membership fee (£1), the cost of excursions and entertainment (£2), meals, which will be furnished at very low rates, and incidental expenses (say, £5). The necessary expenses per person are therefore:—

	II.	III.
Steamship fare, going	£9	£14
,, returning	9	14
,, gratuities, &c...	2	2
Congress	3	3
Meals and incidentals in New York	5	5
	£28	£38

The inaugural meeting of the Congress in Washington for those who desire to attend it, and to see the magnificent scientific institutions in that city, will involve railway fare to Washington and back and two nights in that city, total £5.

Following the meetings of the Congress there will be two excursions, described as the "short trip" and the "long trip" respectively. These will afford visitors an unrivalled opportunity to see the sights and the chemical industries of the country. The "short trip," lasting eleven days, includes Philadelphia, Pittsburg, Niagara Falls, Detroit, Chicago, Cleveland, and Boston (2513 miles). The fare (£16 12s.) includes meals in transit and sleeping accommodation (excepting for two nights in Chicago). On account of the large amount of hospitality which will undoubtedly be offered by local chemists at the places visited, the total expense of this trip will probably be less than £20. The "long trip," lasting thirty-six days, extends to the Pacific Ocean, and the fare, including sleeping accommodation (except at Chicago, San Francisco, and Los Angeles), will be £84. Members desiring to join one or other of these excursions should notify Dr. Geo. D. Rosengarten, P.O.Box 1625, Philadelphia, Pa., before July 15th.

From these statements it will be seen that it is possible to attend the whole of the meetings of the Congress, and visit a selection of the innumerable chemical industries in New York and its neighbourhood, which will be open for inspection during the meeting, and to see Washington, and to do all this in comfort for a moderate sum. Chemists, particularly the younger men, and the teachers of the science, are not accustomed to extremes of luxury at home, and need not deny themselves this opportunity merely because they cannot afford "regal suites" on the ocean.

I shall be very glad to reply to inquiries, which may be sent to me at the address below.—I am, &c.,

Alexander Smith,
Professor of Chemistry in Columbia University and Member of the Executive Committee of the Congress.

34, St. Albans Road, Edinburgh,
July 3, 1912.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

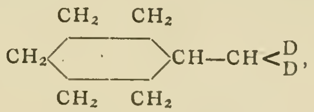
Note.—All degrees of temperaturs are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 21, May 20, 1912.

Preparation and Heat of Formation of Magnesium Nitride.—Camille Matignon.—Magnesium nitride can be prepared by heating finely divided magnesium in a nickel or magnesium crucible in a current of perfectly pure dry ammonia, obtained from liquid ammonia which has been kept for some time in contact with fused soda. The heat of formation of the nitride from its elements is 119·7 cal., and thus the affinity of nitrogen for magnesium is greater than that of lead for oxygen; it would be comparable with that of iron for oxygen, if magnesium and iron had not very different volatilities.

Method of Formation of Acroleïn.—Œchsner de Coninck.—Sodium formate was submitted to dry distillation, and the gases evolved passed through an alcoholic solution of ammonia. When absolute ether was added to the alcoholic ammonia a yellow amorphous precipitate was formed. This exhibited all the properties of acroleïn ammonia, and thus the dry distillation of sodium formate leads to the formation of acroleïn.

Hexahydrogenated Malachite Green.—P. Lemoult.—The leucobase—



$$CH_2\left\langle\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}\right\rangle CH-CH<\begin{matrix}D\\D\end{matrix},$$

where $D = C_6H_4N(CH_3)_2$, is not oxidised by lead dioxide, but chloranil readily oxidises it, giving not hexa-hydrogenated malachite green but ordinary malachite green. Thus the oxidation must take place in two stages:—(i.) The removal of the six supplementary atoms of the cyclohexyl nucleus with regeneration of the phenyl nucleus; (ii.) the regular oxidation of the leucobase of triphenyl methane thus formed. This is an example of a single dye being obtained from two different leucobases, and of a dye which on reduction does not give the leucobase from which it has been obtained by oxidation.

Condensation of Primary Sodium Alcoholates with Secondary Alcohols.—Marcel Guerbet.—The sodium salt of isoamyl alcohol condenses with isopropyl alcohol when they are heated together in a sealed tube. The product is methylisohexylcarbinol, $CH_3-CHOH-(CH_2)_3-CH=(CH_3)_2$. When oxidised with chromic mixture this acid yields an acetone of formula $C_8H_{16}O$, which is identical with isoamylacetone. Similarly propylic and caprylic alcohols condense to give 3-propyl-2-octanol, from which the corresponding acetone is obtained by oxidation.

Berichte der Deutschen Chemischen Gesellschaft,
Vol. xlv., No. 8, 1912.

Salts of Tetrasulphamino-platinous Acid.—Ludwig Ramberg and Sten Kallenberg.—When sulphaminic acid acts on platinous hydrate a colourless solution is obtained, from which crystals of the ammonium salt of tetrasulphamino-platinous acid separate out. The salt, which is only slightly soluble in cold water, has the formula $(H_4N)_2Pt(SO_3NH_2)_4.6H_2O$. From a hot saturated solution small needles separate, which are probably a lower hydrate. The potassium salt of the acid can be obtained by the double decomposition of *cis-* or *trans-*potassium dichloro-disulphamino-platinite with silver aminosulphate. Its formula is $K_2Pt(SO_3NH_2)_4.2H_2O$; it is not isomorphous with the ammonium salt.

Red Phosphorus.—Alfred Stock, Hans Schrader, and Erich Stamm.—Ordinary commercial red phosphorus is not a single substance, and its physical and chemical properties depend on the temperature at which it was made from colourless phosphorus. It is the visible part of the spectrum adjacent to the ultra-violet which converts colourless into red phosphorus. The influence of the temperature on the transposition is comparatively small. The temperature of ignition of red phosphorus in air is apparently very much higher than that generally stated. At 380° it begins to fume and become luminous, and as this is also the temperature at which it begins to give fumes of colourless phosphorus obviously it is these latter which catch fire in air, and not the red phosphorus itself. When heated vapour of colourless phosphorus is cooled it is found that the product contains more red phosphorus the higher the temperature to which it has been heated, but the duration of heating has no influence on the amount of red phosphorus. The hot vapour must be cooled as quickly as possible. Colourless and red phosphorus are chemically different from one another, and the difference is not due to polymorphism.

Bulletin de la Société Chimique de France.
Vol. xi.—xii., No. 9, 1912.

Union of Iodine and Oxygen.—Marcel Guichard.—The direct union of iodine and oxygen would be exothermic $I_2(gas) + O_5(gas) = I_2O_5(solid) + 61$ cal. (Berthelot) or 45 cal. (Thomsen), and by the application of Matignon's rule it may be shown that at 173° the equilibrium tension in the system I, O, I_2O_5 would reach 1 atmosphere. The reversible union of iodine and oxygen can be realisable over only a small temperature interval, if at all, and the author has found experimentally that the conditions of reversibility are very difficult to attain.

Preparation of Anhydrous Bromides.—M. Barre.—When sulphur is added to bromine it dissolves, and a dark red liquid containing S_2Br_2 is formed. It is partially decomposed when heated at the ordinary pressure. Its action on metallic oxides provides a very convenient method of preparing anhydrous bromides, especially when the bromide formed does not fuse at the temperature of the experiment or when it is volatile. The method is less general than the corresponding method of preparing chlorides, for in some cases, *e.g.*, with thoria, it yields the oxybromide.

Preparation of Double Hyposulphite of Bismuth and Sodium.—Jean A. Sanchez.—To prepare in a crystalline state the double hyposulphite of bismuth and sodium basic bismuth nitrate is heated with concentrated acetic acid, and a solution of sodium hyposulphite is added. Then aniline is added, and finally alcohol, whereupon a yellow crystalline precipitate separates. This is the double hyposulphite of bismuth and sodium, Carnot's reagent. It is very soluble in acidulated alcohol, while the potassium salt is only slightly soluble.

Reactions of Sulphosalicylic Acid.—E. Barral.—Bromine water gives a precipitate with salicylic acid, but none with sulphosalicylic acid. Mandelin's reagent gives an indigo coloration with sulphosalicylic acid and a green coloration with salicylic acid. Denigès' reaction for salicylic acid, with methylglyoxal, is negative with chemically pure sulphosalicylic acid. Millon's reagent gives a pink coloration with a trace of sulphosalicylic acid and an orange red coloration with salicylic acid. The action of heat on a mixture of sulphosalicylic acid, methyl alcohol, and sulphuric acid, produces an aromatic smell very different from that of methyl salicylate. When a solution of sulphosalicylic is boiled with a little ammonium persulphate a black or brown precipitate is formed, and disappears when the boiling is continued and more persulphate is added. Neutral acetate of lead gives no precipitate with solutions of sulphosalicylic acid or neutral sulphosalicylates. The addition of ammonia causes partial precipitation.

Action of Quinone and Sulphonic Quinone on Divided Silver in Presence of Alkaline Haloid Salts.—A. Seyewetz.—Quinone reacts with silver in presence of alkaline bromides to give an oxybromide of silver of formula $Ag_5Br_7 + Ag_2O$. It can be crystallised from ammonia in the form of transparent colourless crystals, which turn brown in the light. The sodium salt of sulphonic quinone in the same conditions gives silver bromide and not the oxybromide. If the potassium bromide is replaced by the chloride the action is much slower, and no oxychloride is formed, and quinone and sulphoquinone in presence of potassium iodide transform divided silver into its iodide.

Atti della Reale Accademia dei Lincei.
Vol. xxi., No. 8, 1912.

System Sb_2S_3—SnS. — N. Parravano and P. de Cesaris.—The authors have studied the thermic behaviour of mixtures of antimony sulphide and stannous sulphide in different proportions and find that in all probability the compound formed is $Sb_2S_3.SnS$ or $Sn(SbS_2)_2$.

MISCELLANEOUS.

Award.—The Franklin Institute of Philadelphia, Pa., has awarded the Edward Longstreth Medal of Merit and diploma to Dr. Charles Baskerville, Professor of Chemistry and Director of the Laboratory at the College of the City of New York, for his investigations on the chemistry of anæsthetics (ethyl ether, chloroform, nitrous oxide, and oxygen).

Change of Address.—Samuel Deacon and Co., the well known firm of advertisement agents and contractors, established at Snow Hill over a century ago, and who have occupied No. 154, Leadenhall Street for the last fifty-seven years, have removed to No. 7, Leadenhall Street, nearly opposite. We understand their premises have been acquired by a large Insurance Company for reconstruction.

Isomeric Thujylalcohols and Thujene. — L. Tschugaeff and W. Fomin.—Ordinary raw thujyl alcohol contains at least two stereo-isomers. One of them has already been described by Paolini; it is liquid and dextrorotatory, while the other is solid and lævoratory. By means of the xanthogen reaction from the former a lævo terpene can be obtained, α-thujene, while the second liberates an essentially different dextro-compound, β-thujene.—*Berichte*, xlv., No. 7.

THE CHEMICAL NEWS.

Vol. CVI., No. 2747.

THE
ALKALINE WATERS OF THE LONDON BASIN.*

By JOHN C. THRESH, M.D., D.Sc.,
Medical Officer of Health to the Essex County Council.

It is now over twenty years since I first became acquainted with the somewhat curious character of the waters derived from the Chalk and Thanet sand in various parts of Essex, and during the last twelve years I have been making a somewhat detailed analysis of all deep-well waters concerning the source of which I could obtain any reliable information. In 1901 I published a report on "The Water Supply of the County of Essex, and included therein a map showing that to the east of a curved line passing from Dedham in the north to Barking in the south the waters derived from the chalk (save at the Purfleet outcrop) were "soft" and contained more or less salt and sodium carbonate, whereas on the west of this line the waters had the ordinary character of chalk waters, that is, they contained very little salt and were free from sodium carbonate, but contained a considerable quantity of chalk in solution and were therefore "hard." I also pointed out that in many localities the beds between the base of the London clay and the top of the chalk yielded waters containing an excessive amount of lime and magnesium salts, chiefly sulphates.

In the map above referred to the dotted line is said to suggest a probable fault in the chalk. In some cases the marked difference in the character of the water derived from wells not more than, perhaps, 1 mile apart, seems to indicate the presence of a fault, but there is no other evidence in support of this suggestion, and my further investigations lead me to conclude that it is not necessary to assume the presence of a fault to account for the facts observed.

All the observed results admit of another explanation. So long as the water in the chalk contains carbonic acid it continues to dissolve the chalk and open out the fissures. When all the acid has been used up in dissolving the calcium carbonate it no longer possesses the power of opening out the fissures, and as the chalk becomes more compressed by the superincumbent mass of sand and clay it becomes so dense as almost to be impervious. Beyond this point therefore the water cannot travel in the chalk, and it comes up through the fissured chalk into the sands above and then becomes exposed to their softening action. The compact chalk acts very much like a fault would do assuming a solid impervious stratum abutting upon a pervious one.

I do not purpose dwelling so much upon the geological aspect of the question as upon the varying character of the waters derived from the chalk and Thanet sands in different parts of the London basin, but more especially in Essex, and of offering an explanation for the variations in character.

The nature and progress of this change is well exemplified by the analyses of waters taken from various wells sunk into the chalk at Eton, Datchet, Shepherd's Bush, the Strand and Lambeth, London (Table I.).

Well (No. 1) is on the outcrop of the chalk. The well (No. 2) at Datchet is nearer the chalk outcrop than well No. 3, and the latter therefore has a greater covering of London Tertiaries. Wells No. 4 and 5 are bored through a considerable thickness of London clay. At Lambeth we are approaching the chalk outcrop in Kent and Surrey.

Table I.—*Chalk.*

	1.	2.	3	4.	5.	6.
	Eton.	Datchet.		Shepherd's Bush.	London.	
					Strand.	Lambeth.
Ca carbonate	21·8	16·3	14·7	5·0	3·0	12·75
,, sulphate	6·4	—	—	—	—	—
,, chloride	—	—	—	—	—	—
Mg carbonate	—	3·6	3·1	3·5	2·1	7·85
,, sulphate	—	—	—	—	-	—
,, chloride	2·3	—	—	—	—	—
Na carbonate	—	3·4	5·6	21·6	12·8	6·9
,, sulphate	—	7·6	7·6	24·1	18·1	11·1
,, chloride	1·1	5·8	5·6	22·6	18·2	14·4
,, nitrate	3·5	1·3	1·2	—	—	—
Silica, &c.	1·4	1·4	1·9	0·6	1·2	1·0
Total ..	36·5	39·4	39·7	77·4	55·4	54·0
Hardness..	30°	22°	18°	8°	5°	20°

Notes.

1. The decrease in the calcium carbonate up to London and its increase towards Kent.
2. The appearance of sodium carbonate and its increase towards London and decrease towards the Southern outcrop.
3. The disappearance of calcium sulphate in the waters under the London clay.
4. The appearance of sodium sulphate in the waters from under the London clay.
5. The increase and decrease in the amount of sodium chloride.
6. The whole series showing a marked change in the character of the chalk water as the distance from the outcrop of the chalk increases.

Table II. of analyses includes typical samples of water taken in Essex along a line almost north and south from the bare chalk at Foxearth through Halstead, Bocking, Braintree, Witham, Chelmsford, and Billericay to Grays, where the chalk again outcrops. (The analysis of Grays water will be found on Table VII., No. 6). Note again the amount of calcium and magnesium salts in the chalk waters at and near the outcrop, the diminution of this amount as the chalk gets deeper and the corresponding increase in the carbonate and sulphate of sodium, together with the increase in the amount of common salt.

Table II.

	Foxearth.	Halstead.	Bocking.	Braintree.	Witham.	Billericay.
Ca carbonate	31·0	25·3	21·9	5·3	2·8	1·8
,, sulphate	—	—	—	—	—	—
,, chloride	—	—	—	—	—	—
Mg carbonate	—	2·3	4·4	5·5	1·2	2·8
,, sulphate	6·6	2·9	—	—	—	—
,, chloride	1·6	0·2	—	—	—	—
Na carbonate	—	—	3·1	19·8	26·7	26·3
,, sulphate	—	—	9·0	11·8	10·8	9·4
,, chloride	4·5	14·0	28·0	67·2	78·3	36·5
,, nitrate	0·2	0·4	0·2	0·2	0·2	0·2
Silica, &c.	2·0	0·9	1·0	0·2	0·5	1·0
Total ..	45·9	46·0	67·6	110·0	120·5	78·0
Hardness ..	40°	32°	26°	11°	5°	5°

The table shows, however, that whilst the carbonates and sulphates of sodium increase approximately in proportion to the decrease in the corresponding salts of magnesium and calcium, the amount of common salt seems to bear no relation to any of the other constituents. This is better brought out in Table III., which refers to a localised area which has recently had to be studied somewhat fully, viz., the Tendring Hundred, Mersea Island, and the Tollesbury districts. I have analyses of waters from about fifty deep wells in this area, and the salt varies from 23 parts to 180 parts (or probably more) per 100,000,

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* A Paper read before the Essex Field Club, March 30, 1912.

and it will be noted that some of the waters containing least salt are derived from wells near tidal estuaries, whilst many of the waters containing much salt are miles inland. The analyses of certain of the waters, however, indicate that tidal water is gaining access. This is well marked in the analysis of the Manningtree waters, No. 2 on Table III. The Geological Survey refers to wells at Ramsey, Pewit Island, Frinton, and other places which yielded brackish water and were apparently abandoned. Dr. Cook, Medical Officer of Health for the Tendring district, informs me that at Walton a well was bored and the water found to become more salt as the depth increased, the figures being:—

At 100 ft.	Salt per 100,000 parts of water	257 parts.
At 200 ft.	,, ,,	258 ,,
At 300 ft.	,, ,,	293 ,,
At 360 ft.	,, ,,	308 ,,

A well sunk at Clacton gave me the results No. 3 on Table III. The yield of water was trifling, and upon continuous pumping the water became so brackish that it was abandoned. It will be noted that the water which rose naturally in the bore was comparatively soft and contained sodium carbonate and no more salt than the deep well-waters of Mid-Essex. I am sorry that I did not obtain a sample of the water after continuous pumping, but the engineer informed me that it was so salt that no analysis was necessary to show that it was too brackish for domestic use.

TABLE III.

	1.	2.	3.	4.	5.	6.
	10 per cent sea-water.	Chalk. Manningtree	Chalk. Clacton.	Layer Marney.		Mersea.
				568 feet.	900 feet.	
Ca carbonate	0·8	23·5	5·3	1·4	6·3	5·5
,, sulphate	13·3	—	—	—	—	—
,, chloride	—	—	—	—	—	—
Mg carbonate	—	6·5	4·2	0·4	3·8	5·2
,, sulphate	21·9	7·2	—	—	—	—
,, chloride	36·7	1·8	—	—	—	—
Na carbonate	—	—	22·0	39·1	29·2	32·5
,, sulphate	—	—	16·1	12·7	12·4	22·9
,, chloride	267·6	22·9	61·7	66·3	144·3	136·8
,, nitrate	—	0·2	2·6	0·6	—	—
Silica, &c.	—	2·7	2·6	1·5	—	0·6
Total ..	357·0	64·8	114·5	122·0	196·0	203·5
Hardness	abt. 100°	45°	11°	2°	11°	12°

There is no doubt that in this area the water varies in character at different depths. The salt in the Walton water shows this, as does also the analyses of waters taken from borings recently made at Layer Marney, Nos. 4 and 5 on Table III. The yield at 568 feet was very limited, under 200 gallons per hour, and the boring was continued to 900 feet and blasts of dynamite used, but the yield of water was not materially increased and the proportion of salt increased to such an extent that the water was useless.

Layer Marney is so far from the sea that it appears difficult to ascribe this increase in the amount of salt to any direct influx of sea-water, but my impression is that sea-water or tidal water is gaining access to the chalk in the Thorpe-le-Soken area and at and near the chalk outcrop in the Stour Valley. The proof that these saline waters are derived from an admixture of sea-water and chalk water is, I think, proved by the analyses of mixtures of chalk water and sea-water after passing through a filtering medium which can remove the calcium and magnesium salts more or less completely, substituting sodium and potassium in their place. The mere proximity to the sea does not enable anyone to say whether a water will be salt or not, as a well near the coast may or may not contain an excessive amount of salt. For example, compare typical waters from Brightlingsea with those from Mersea Island and Tollesbury.

I have made several experiments with mixtures of sea-water and chalk water to show the effect of the softening process which I shall describe presently, and Table IV. is designed to show how the various waters in the London Basin can be imitated by mixing chalk water with sea-water and then submitting them to this peculiar treatment.

TABLE IV.—*Sea-water and Chalk Water.*

	Untreated.	Treated.	Untreated.	Treated.	Untreated.	Treated.
Ca carbonate	12·7	2·0	25·2	1·0	24·3	3·8
,, sulphate	29·0	—	—	—	—	—
,, chloride	1·0	—	—	—	—	—
Mg carbonate	—	1·7	2·5	0·5	3·4	0·4
,, sulphate	—	—	12·3	—	8·9	—
,, chloride	10·3	—	6·6	—	—	—
Na carbonate	—	9·0	—	31·8	—	29·2
,, sulphate	—	30·3	—	16·3	—	15·6
,, chloride	103·5	118·8	113·1	126·2	72·0	73·0
,, nitrate	—	—	—	—	—	—
Silica, &c.	—	3·2	1·0	2·2	—	2·0
Total ..	156·5	165·0	161·0	178·0	111·0	124·0
Hardness	40°	4·0	40°	1½°	33°	5°

Varying proportions of chalk water and sea-water were mixed, a portion reserved for analysis, and the remainder filtered through Thanet sand of varying thickness and of varying activity so as to remove a portion or nearly the whole of the calcium and magnesium salts. It will be observed that the lime and magnesium salts have been more or less completely removed and that the resulting filtrates are exactly of the type of the waters in the Tendring area as exemplified by the Tollesbury sample.

It would be difficult to regulate the rapidity of filtration or to vary the thickness of the filtering medium so as to remove exactly the right proportion of the salts of calcium and magnesium, but as we know that these can be removed to any desired extent the effect of the filtration can be easily calculated.

TABLE V.—*Halstead Chalk Water + 2 per cent Sea-water.*

	1.	2.	3.	4.	5.
	Untreated.	Treated.	Compare with Braintree.	Treated.	Compare with Witham
Ca carbonate	27·3	5·3	5·3	2·8	2·8
,, sulphate	1·8	—	—	—	—
,, chloride	—	—	—	—	—
Mg carbonate	—	5·5	5·5	1·4	1·2
,, sulphate	8·0	—	—	—	—
,, chloride	9·8	—	—	—	—
Na carbonate	—	16·7	19·8	25·2	26·7
,, sulphate	—	11·4	11·9	11·4	10·8
,, chloride	63·3	75·2	67·2	75·2	78·3
,, nitrate	0·3	0·3	0·2	0·2	0·3
Silica, &c.	1·0	1·1	1·2	1·3	0·4
Total ..	111·5	115·5	111·1	117·5	120·5
Hardness ..		12°	12°	5°	5°

Table V. shows how a mixture of 2 per cent of sea-water with 98 per cent of chalk water from Halstead would be altered by filtration through different thicknesses of sand.

Braintree is about half way between Halstead and Witham. Assume that the water in the chalk at Halstead becomes mixed with 2 per cent of sea-water on its way to Braintree and at the same time is traversing the Thanet sands and becoming softened. Then the result at one stage would be the water (2) which, as will be seen, bears the closest possible resemblance to the Braintree water (3). Travelling onwards towards Witham the water would become still softer, more of the calcium and magnesium salts being removed, and at some point a water having the composition of No. 4 would result, and this it will be noted bears the closest resemblance to the Witham water No. 5.

Towards Chelmsford the water would become still softer, which is actually the case, but as the water in the Chelmsford area contains a little less salt, we have to suppose that dilution with a less saline water is taking place, probably from the neighbourhood of Saffron Walden. By varying the source of the chalk water and the proportion of sea-water, I think every water from the chalk and Thanet sands in the County of Essex and under London could be imitated.

Assuming that the salinity is due to sea-water, then the bromides which exist in sea-water should be capable of detection in the saline waters. This proved to be the case, but when it came to the question of estimating the amount great difficulties were encountered, and have not yet been entirely surmounted. I give the following figures with some reluctance, but I think they can be depended upon for the purposes of comparison.

TABLE VI.

Chlorine and Bromine in Sea-water and Essex Deep Chalk Waters.

	Chlorine in 100,000 parts of water.	Ratio of Bromine to Chlorine.
Sea-water, Clacton	1885	1 to 274
Sea-water, Blackwater Estuary (*a*)	1850	1 to 328
Sea-water, Blackwater Estuary ..	1850	1 to 378
Tollesbury deep-well water	75	1 to 225
Chelmsford deep-well water (*a*) ..	35	1 to 250
Chelmsford deep-well water ..	35	1 to 322
Maldon deep-well water	50	1 to 442
Tillingham deep-well water.. ..	76	1 to 317
Barking deep-well water	324	1 to 312

(*a*) Two separate determinations of each water showing variation in results due to difficulties in analysis.

The proportion of bromides to chlorides is therefore much the same as in sea-water, whether the saline water contains as much salt as the Barking water, or little salt like the Chelmsford water.

The Barking water was especially selected, because there is no manner of doubt that tidal water is entering the chalk here. From Grays to London tidal water is getting into the chalk at divers places, and frequently in such quantities as to render the water derived therefrom useless for manufacturing or domestic purposes. A further proof is the effect of pumping. The lower the water is reduced the more and more closely does the water pumped resemble the tidal water of the Thames in composition.

Moreover, cases are recorded of the rise and fall of the water levels under tidal influence, as, for example, Thames Haven, where I am informed that the water in the bored well rises and falls with the tide, and this is confirmed by the note in connection with this well in Whitaker's "Geology of London." Evidently in this locality there is some connection between the chalk and the river.

TABLE VII.—*Chalk Waters.*

	1.	2.	3.	4.	5.	6.
					Grays (chalk well).	
	Barking town.	Barking creek. Well at.	Barking creek, Well at.	Thames. Grays. River.	Heavy pumping.	No pumping.
Ca carbonate	5·3	28·2	29·8	16·3	25·0	17·1
,, sulphate	—	2·5	—	71·4	28·4	4·8
,, chloride	—	—	—	—	—	—
Mg carbonate	1·4	—	—	—	—	—
,, sulphate	—	7·4	13·1	129·5	8·8	1·6
,, chloride	—	18·6	9·9	154·8	24·6	1·7
Na carbonate	14·9	—	—	—	—	—
,, sulphate	9·9	—	—	—	—	—
,, chloride	7·0	112·5	75·9	1411·6	140·4	2·6
,, nitrate	—	—	—	—	—	—
Silica, &c.	0·5	0·8	1·3	70·4	15·8	4·2
Total ..	39·0	170·0	130·0	1854·0	243·0	32·0
Hardness..	7°	55°	50°	330°	78°	24°

The Barking waters are very interesting (Table VII.). Away from the river (1) they resemble the chalk water of the Lee Valley partially altered by filtration through Thanet sand, but near the river they consist of a mixture of this chalk derived water and river water. Nos. 4 to 6 show the effect of the Thames water on the Grays wells when heavily pumped.

TABLE VIII.—*London Chalk Waters.*

	E.C.	Caledonian Road.	Clement's Inn.	King's Cross.	Charing Cross.	Millwall.
Ca carbonate	4·4	4·0	4·4	3·4	4·0	27·6
,, sulphate	—	—	—	—	—	21·5
,, chloride	—	—	—	—	—	46·8
Mg carbonate	3·5	2·8	2·3	1·9	2·5	—
,, sulphate	—	—	—	—	—	—
,, chloride	—	—	—	—	—	15·2
Na carbonate	18·0	19·1	21·4	21·8	18·4	—
,, sulphate	20·1	20·0	23·2	21·9	24·8	—
,, chloride	16·0	16·7	23·6	17·9	30·3	182·7
,, nitrate	0·3	0·6	0·2	0·3	0·3	0·2
Silica, &c.	1·0	0·4	0·4	0·5	1·2	0·2
Total ..	63·0	63·6	75·5	67·7	81·5	293·8
Hardness..	9°	7°	8°	6°	7°	100°

Table VIII. shows the saline constituents of typical waters derived from deep wells in London. It will be observed that most of them are of the alkaline type, but that the proportions of the constituents vary. Nearly all indicate the admixture of a very small amount of sea-water with the chalk water prior to it having undergone the softening process. Others derived from the chalk near the river show the presence of unchanged tidal water, as at Millwall.

TABLE IX.—*Various Sources.*

	Chalk. Herne Bay.	Hastings Beds. Kent, Stye Place.	Barton Beds. Cowes.	Challow, Berkshire, beneath Gault and K.clay.		Swindon. Middle oolite.
Ca carbonate	3·4	0·4	14·7	6·2	0·3	31·3
,, sulphate	—	—	—	—	—	—
,, chloride	—	—	—	—	—	—
Mg carbonate	3·5	0·2	3·7	2·6	0·2	3·5
,, sulphate	—	—	—	—	—	—
,, chloride	—	—	—	—	—	—
Na carbonate	23·0	65·2	1·4	41·4	73·9	14·0
,, sulphate	41·7	—	5·6	8·6	—	48·3
,, chloride	36·3	24·9	3·3	47·0	68·8	11·2
,, nitrate	0·2	0·3	0·4	0·4	0·4	0·5
K chloride	5·6	—	—	5·6	8·4	14·4 (K_2SO_4)
Silica, &c.	0·3	2·0	0·4	2·7	2·0	4·3
Total ..	114·0	93·0	29·2	114·5	154·0	127·5
Hardness	8°	1°	19°	10°	1°	35°

Table IX. shows that so far away as Herne Bay the lower London tertiaries yield an alkaline water containing much sodium carbonate and sulphate, and other analyses on this Table and on Tables X. and XI. show that similar waters are obtainable from the most diverse geological formations. The examples given include waters from the Hastings sands, Barton sands, upper and middle oolite, Ashdown sands, upper greensand, porphyrite and calciferous sandstone, new red sandstone, millstone grit, coal measures, Lincolnshire limestone, and Table XI. gives two examples of similar waters from Denmark and Damaraland. In fact, these alkaline waters appear to occur in all parts of the world.

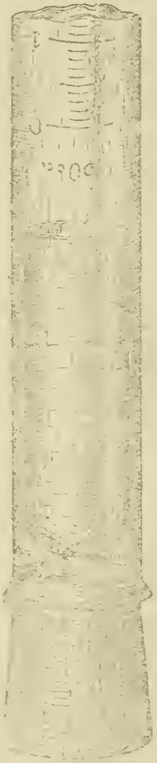
(To be continued)

SIMPLE GAS ANALYSIS WITH A BURETTE.

By G. FOWLES, B.Sc., F.C.S.

A method employed at the Latymer Upper School by which simple gas analysis can be carried out with ordinary burettes by a class of junior boys, has proved so successful that some account of it may be of interest to teachers of chemistry.

A little tube, about 1½ inches long, of bore just smaller than that of a burette, is drawn out at one end; or, better, one end is closed and sealed on to a small length (½ inch) of glass rod, so that it can be fixed into a one-holed cork, which fits the end of the burette. This little arrangement, called by us the burette cup, is charged with the required absorbing material, which can then be readily introduced into the burette without fear of any gas entering or escaping.



Suppose that breath is to be analysed. The volume of the burette between the tap and the last graduation must first be found; this affords an interesting exercise. The burette is then filled with water and inverted over a trough of water. Breath is sent in by means of a bent glass tube (care being taken to collect only the last portions expelled from the lungs), and its volume noted. A piece of stick caustic potash is now placed in the cup, any remaining space filled with water, and the charged cup placed in its position in the burette. If the caustic potash is so thick that it will not go into the cup, it is held by tongs in water for a few seconds, whereby its size is quickly reduced. Having absorbed the carbon dioxide by rocking for a few minutes, the burette—which has been warmed by the chemical action and the handling—is cooled in a stream of water. The cup is removed, replaced by a bung, and reopened in a gas-jar or big cylinder full of water, so that the levels can be adjusted. The volume of carbon dioxide being thus obtained, the cup is next charged with a piece of caustic potash and crystals of pyrogallol. For this purpose the ordinary crystals are preferable to the sublimed product. The oxygen is now absorbed, the cooling and levelling processes being repeated.

By this means a class of junior boys of an average age of fourteen and a-half in a practical lesson of one and a-half hours' duration can find the percentage of oxygen and carbon dioxide in breath, and write notes of their work.

We have also used this method to find the percentage of oxygen in the air, and to analyse the gas boiled out of tap-water. In the latter case the product from several workers is collected and analysed. The method should also be applicable to other cases, *e.g.*, the absorption of nitric oxide.

Of course, a graduated tube closed at one end would in some respects be better than a burette, although the tap of a burette is not without its advantages. However, this would mean special apparatus, whereas the procedures mentioned above can be performed with ordinary laboratory stock. The burette cups for a class of boys can easily be made in less than an hour.

The sketch was kindly drawn for me by A. V. Gale, to whom I tender my thanks.

Latymer Upper School, Hammersmith, W.

THE SEPARATION OF THE RARE EARTHS.

By C. JAMES.

(Concluded from p. 18).

Separation of Crude Yt Earths.

Fraction 2, consisting of dysprosium, holmium, erbium, thulium, ytterbium, lutecium, celtium, and small amounts of gadolinium and terbium, together with yttrium and scandium, is converted into the anhydrous sulphate by treating the oxalates with a slight excess of sulphuric acid, and heating until all fumes of sulphuric acid cease to be evolved. The ignited sulphates are dissolved in cold water. The fairly strong solution is then gradually added to barium bromate, covered with a layer of water, and heated upon the steam-bath (James, *Journ. Amer. Chem. Soc.*, xxx., 182; Chemical News, xcvii., 61). The mass is well stirred until decomposition is complete, *i.e.*, when some of the clear liquid gives no precipitate with barium bromate solution after diluting and boiling. It is necessary to dilute and boil, owing to the fact that a strong solution of the rare earth bromates causes a precipitate of barium bromate itself. The whole is next filtered, and the barium sulphate well washed with hot water. If the barium bromate is not in a very fine state of division a large amount remains unattacked. The clear filtrate is evaporated until a drop removed upon the end of a glass rod nearly solidifies when stirred upon a watch-glass. A little water is then sprayed upon the surface and the dish placed aside to crystallise. The mother liquor and the crystals are fractionally crystallised. The absorption spectrum soon shows that a rapid change is taking place. Samarium and gadolinium rapidly separate in the least soluble crystals (19) together with terbium. The next fractions are coloured yellow, and contain dysprosium, holmium, and yttrium, with very small quantities of terbium (20). The bromate that follows consists almost entirely of yttrium, contaminated with very small quantities of dysprosium, holmium, and erbium. Further along the series the bands of dysprosium and holmium disappear, and the only impurity found is erbium (21). Practically the whole of the erbium is contained in the portions more soluble than yttrium (22). The erbium absorption is extremely intense, and the solutions possess a beautiful rose-red colour. The mother liquors (23) are nearly colourless, or possess only a very faint pink tint. The absorption spectrum shows only a trace of erbium, together with a strong spectrum of thulium. This fraction consists almost entirely of ytterbium, lutecium, and celtium.

Scandium occurs only in traces in the minerals usually worked up. Probably nearly all is lost during the oxalate precipitations, due to the fact that scandium oxalate is not entirely insoluble in water. The solubility is increased rapidly by free acid. During the fractional crystallisation of salts, scandium tends to collect in the mother liquors. However, if the solutions become basic it is likely to be found in the fractions further down the series. In the case of the bromates the solutions gradually become basic owing to a slight decomposition. When this is the case the mother liquors are free from scandium, while the erbium fractions contain small quantities. If dysprosium and holmium fractions are carefully examined it will, in all probability, be found there as well. The various methods for the purification of scandium will be given towards the end of this paper.

The bromates forming (19) are converted into the simple nitrates, and fractionated from strong nitric acid similarly to the more soluble earths derived from the samarium-europium process. However, in this case the least soluble goes to 24 and the more soluble to 17.

Separation of Tr.

Practically all the terbium concentrates in 24. In addition to this element there are also present gadolinium and dysprosium. Three methods have been used to separate this mixture:—

(a) Crystallisation of the simple nitrates.

(b) Fractional precipitation by ammonium hydroxide.

(c) Crystallisation of the ethyl sulphates.

When the simple nitrates are used it is best to add a quantity of bismuth nitrate, which is isomorphous with the rare earth nitrates, and, as Urbain has shown, comes between gadolinium and dysprosium along with terbium. By fractionally crystallising the nitrates from nitric acid for a few thousand times, it is found that bismuth nitrate accumulates in the middle fractions accompanied by terbium. Gadolinium is removed in the least soluble (26) portions, while dysprosium is removed in the mother liquors (27). The middle fractions are diluted and saturated with hydrogen sulphide. The bismuth sulphide is filtered off, and the filtrate precipitated by means of oxalic acid. The terbium oxide obtained by igniting the oxalate (25) forms a black powder, which in solution gives a characteristic absorption spectrum.

Fractional precipitation with very dilute ammonium hydroxide gradually concentrates terbium in the fractions slightly more basic than dysprosium.

When working with the ethyl sulphates, terbium places itself between gadolinium and dysprosium.

Separation of Dy.

So far the only really satisfactory method for the separation of pure dysprosium material is the crystallisation of the ethyl sulphates, as proposed by Urbain. Fractions 17, 20, and 27 carry nearly all the dysprosium present in the original material. There are two methods by which the ethyl sulphates may be prepared:—

(a) Action of the rare earth sulphate in solution upon barium ethyl sulphate in a similar condition.

(b) By mixing alcoholic solutions of the rare earth chlorides and sodium ethyl sulphate.

When the writer endeavoured to prepare the ethyl sulphates by using the barium salt, the precipitates obtained often required days to filter. They were very difficult to wash, and, in addition, the barium sulphate thrown down entrained quantities of the rare dysprosium and holmium sulphates. It can readily be seen from this that the preparation of large quantities of material takes a very long time, and, in addition, there is a loss of valuable material. These difficulties are all removed when we employ alcoholic solutions of the rare earth chlorides and sodium ethyl sulphate both hot and concentrated.

The fractions rich in dysprosium are precipitated with oxalic acid, the resulting oxalates filtered off and ignited to oxides. These oxides are then dissolved in hydrochloric acid. Small portions of oxides are then added until the solution becomes very slightly basic, after which the solution is evaporated to such a consistency that it would solidify upon cooling. When it has cooled down considerably, but while still liquid, it is poured into a quantity of 95 per cent alcohol. This last operation requires considerable care if the mass is very hot. Because the salt is somewhat basic the alcoholic solution is very turbid. This solution is now cleared by gradually adding concentrated hydrochloric acid drop by drop. Sodium ethyl sulphate in alcohol, very hot and strong, is poured in and the whole well stirred. After heating for a while upon the water-bath the crystalline precipitate of sodium chloride is filtered off, washed with hot alcohol, and the filtrate set aside to crystallise. The mother liquor is poured off and the crystals well drained. The liquid and crystals are systematically fractionated for a very long time. The small quantity of terbium separates in the first few fractions, together with some dysprosium (28). Pure dysprosium (29) comes next, and these fractions are followed by dysprosium and holmium. The most soluble portions are found to contain holmium and yttrium (30).

Separation of Ho.

Holmium has never been obtained in a very pure form. Small quantities may be freed from dysprosium, but then again the fractions so obtained are very rich in yttrium and carry a little erbium. The fusion of the nitrates is as yet the best method for separating yttrium from holmium. However, this method calls for more material than is usually obtained. Probably two or three years may elapse before this element is obtained in the form of a pure compound. Fraction 30 must be converted into the nitrate and fractionated as described under yttrium. This should eventually give a pure basic holmium nitrate (31), while yttrium, nitrate, and some holmium nitrate (32) will remain as the more stable portion.

Separation of Yt.

The best sources for yttrium are found in fractions 21 and 35, *i.e.*, if the latter has been obtained.

Many methods have been described for the purification of yttrium, such as:—

The Chromate Method.—The decomposition of the nitrate by fusion. The action of magnesium oxide upon a concentrated boiling solution of the nitrate, &c. The chromate method is very useful if terbium is present as an impurity. However, under usual conditions, when bromates or ethyl sulphates have been used, it is absent. Muthmann and Bohms' chromate method, one of the best, is as follows:—

The oxides are dissolved in chromic acid solution; 40 grms. R_2O_3 are contained in each litre. The liquid is then treated with potassium chromate solution until it becomes cloudy. It is placed in a retort, heated to boiling, and rapidly stirred with a current of steam. Another tube passing through the cork carries a stopcock, by means of which the potassium chromate solution can be added and controlled. Six fractions are usually taken. Fractions I. and II. are obtained by employing 10 per cent potassium chromate solution. To get the remaining fractions, potassium chromate of 5 per cent strength is used. By regulating the burner underneath the retort the volume can be kept constant. This method is excellent when one is working upon the small scale. The writer finds that a neutral earth nitrate solution, to which potassium dichromate has been added, works as well as the chromate solution.

When there are large quantities of yttrium material to be purified, the old method of fusing the nitrates is undoubtedly the best. If terbium is present as an impurity a pure white yttrium oxide cannot be obtained. In order to carry out this method the oxides are dissolved in nitric acid, the solution evaporated, and the nitrates fused until a portion has decomposed. When working on a large scale porcelain dishes are used, while casseroles are found very convenient for smaller amounts. During the decomposition the evolution of red fumes is allowed to proceed until the surface assumes a glazed appearance. This point is easily ascertained by experience. The decomposition should never be allowed to advance so that the mass becomes of a thick creamy nature. The best method for obtaining a solution of the melt is to pour the fused mass into a sufficient quantity of cold water. Great care, however, is required, and stirring usually aids the operation very much. A large amount of cold water must be avoided, since it is desired that the solution should be concentrated after about five minutes boiling. As the fused nitrate is gradually added to the water the temperature rapidly rises, and the whole suddenly begins to boil violently. When the dish, which contained the melted salt, has cooled sufficiently a little water is added, and the whole heated until the glassy mass has disintegrated, after which it is added to the main bulk. The latter is then boiled for five minutes and set aside to cool.

Under the best conditions the entire mass goes into solution; especially is this true of the yttrium end of the series. Upon cooling it will be found that the basic nitrate separates in a crystalline form. At the opposite end, the least basic portion of the fractions, there always remains an insoluble basic nitrate, unless the decomposition is stopped at an earlier stage, *i.e.*, when there is a copious evolution of red fumes.

In case a precipitate remains it is highly important that it be well agitated by thoroughly boiling. After cooling the precipitate (Fraction B) is filtered off, re-dissolved in nitric acid, and again fused. The filtrate (Fraction A) is also boiled down and fused. This second series gives two filtrates and two precipitates. The filtrate from Fraction B is mixed with the precipitate from Fraction A, with the result that the second series contains three fractions, &c.

Pure yttrium nitrate, which is eventually obtained, forms lot 33, while the less basic portion forms 34.

Separation of Er.

Fractions 34 and 22 contain practically the whole of the erbium found in the original mineral. It contains a considerable amount of yttrium, with perhaps traces of scandium, thulium, and holmium. Yttrium is best separated by fractionally decomposing the nitrate by fusion. Since erbium nitrate decomposes easily, the temperature is not raised quite so high as in the case of nearly pure yttrium. The least basic portion obtained after a large number of series consists of erbium basic nitrate (36). The yttrium concentrates in more basic fractions, which, when united, form 35. The best method for removing scandium is to crystallise the nitrates from nitric acid (fairly strong). Holmium and thulium are separated, if still found contaminating the material, by converting back to the bromate and employing fractional crystallisation from water. This last method also causes yttrium to pass into the less soluble crystals.

According to work carried out by the author, erbium is not nearly so common as many are led to believe. During concentration the material rapidly becomes less, the erbium solutions become more rose-coloured, and the absorption spectrum appears very intense.

Separation of Tm.

For the preparation of pure thulium material, the most soluble fractions obtained during the original bromate crystallisations are used. These contain thulium, ytterbium, lutecium, and celtium, with traces of erbium. The solution is nearly colourless. It shows the absorption bands of thulium and mere traces of those of erbium. Usually, however, the greater portion consists of the ytterbium metals. The fractionation of the bromates is carried on in a room which has a temperature of about 60° F. Higher temperatures are inconvenient, owing to the formation of very concentrated solutions. Casseroles form the best containers, and the concentration should be such that the greater portion separates in the solid condition upon cooling. From the fact that supersaturated solutions tend to form with extreme ease, the crystallisation must necessarily be started by a tiny crystal.

During the first few series erbium rapidly separates in the least soluble portion, after which the other fractions become coloured greenish. As soon as the mother liquors fail to give any thulium absorption bands, when examined in a saturated solution of about 10 cm., they are placed aside for the preparation of ytterbium, &c. Thulium is found to collect in the fractions between erbium and ytterbium. The solutions become coloured a faint bluish-green, and show a very intense absorption spectrum consisting of three bands. If very great care is taken dilute alcohol can be used as solvent for a short time, best towards the end of the work. However, it soon shows signs of being attacked by the bromate.

Thulium is very rare, and in order to obtain a few grms. of the oxide in a pure condition one must commence with large quantities of suitable mineral.

Yb, Lu, and Ct.

Ytterbium, lutecium, and celtium are contained in the mother liquors from the purification of thulium (38). They can be fractionated by means of the bromates, if the solution be not allowed to become basic. One must deal with large amounts owing to their great solubilities. Urbain recommends the use of the nitrates from nitric acid.

Celtium is said to occur in gadolinite, from the crude earths of which it can be separated by repeatedly crystallising the simple nitrates from nitric acid. It separates in the mother liquor, being more soluble than lutecium.

Scandium.

Scandium occurs in few minerals to any extent, such as Wiikite, from Lake Ladoga, Finland (Crookes, *Proc. Roy. Soc.*, lxxx., A, 516), also in orthite from the same locality (R. J. Meyer, *Sitzungsber. K. Akad. Wiss*,, Berlin, 1911, 379), also in residues from the working up of certain tungsten minerals. This element is easily detected by means of its spectrum, as Crookes has pointed out, and when found to occur in any fractions or in minerals in quantity can be separated by methods of R. J. Meyer. (*a*) The hydrochloric acid solution is precipitated with sodium silicofluoride (*Zeit. Anorg. Chem.*, lxvii., 398); (*b*) scandium can also be separated by sodium thiosulphate. Meyer says the separation is almost quantitative; no trace of scandium remains in the filtrate. The precipitate contains thorium (if present) and only very small amounts of the yttrium earths, which can be removed by repeated precipitation with thiosulphate. This method is better than the sodium silicofluoride.

(*c*) Separation of thorium and scandium by means of sodium carbonate. The concentrated chloride solution is poured into a solution of sodium carbonate containing 20 per cent of anhydrous carbonate. One litre of sodium carbonate solution is used for every 10 grms. of scandium oxide. The scandium dissolves entirely on stirring and warming. It is then boiled rapidly for half-an-hour, when the double carbonate is precipitated as a powder. The volume of the solution should be kept constant during the boiling. After the crystalline powder has settled the liquid is poured off, and the precipitate washed by boiling with 20 per cent sodium carbonate solution for fifteen minutes—this is repeated three times. The double carbonate is dissolved in 2 litres of cold water; four hours and constant stirring are required for this purpose. The liquid is then filtered, acidified with hydrochloric acid, and the hydroxide thrown down by ammonium hydroxide while boiling. The scandium hydroxide is filtered off, well washed with boiling water until free from alkali. If necessary the operation is performed again. Finally the chloride solution is precipitated with oxalic acid.

Durham, New Hampshire,
March 18th, 1912.

VITAL EFFECTS OF RADIUM AND OTHER RAYS.[*]

By Sir JAMES MACKENZIE DAVIDSON, M.B., C.M.

In the year 1902 it was my privilege to deliver a discourse in this place on "X-rays and the Localisation of Foreign Bodies." On this occasion we shall consider the influence of these rays on living tissues, and pass in review, so far as time permits, the effect of various forms of radiation upon living matter generally.

Heat Rays.—If we are to adopt the chronological order in which these radiations were discovered and applied, we shall have to consider in the first place the effects of light and radiant heat. It is common knowledge that exposure to heat rays will produce changes in living cells, and, if sufficiently intense, will lead to their destruction. In the same manner light also will cause changes in living tissue. In the case of light and heat rays there is no conveyance of material from the source to the object affected. All

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[*] A Discourse delivered before the Royal Institution, February 2, 1912.

that occur are wave-motions, set up in the ether of space, or, as it is sometimes called, the "luminiferous ether." One of our greatest statesmen, the late Marquis of Salisbury, who had such a profound knowledge of science, described the ether which fills all space as "the nominative of the verb 'to undulate'." It is the cardinal fact that ether undulates and that waves are produced within it. Isaac Newton thought that light consisted of corpuscles shot out from the sun into space at an enormous velocity, but now it is known that light is produced by waves in the ether, although it may be mentioned in this connection that as we proceed to deal with radium we shall find that corpuscular projections proceeding nearly up to the velocity of light really do exist.

Some of the waves which are produced in the ether, impinging upon the living tissues, produce effects in a marked degree. Others do not seem to have any effect upon them at all. The rays which affect living tissues include heat waves, some of the light waves, X-rays, and some of the rays of radium. On the other hand, the long waves produced in space-telegraphy—the so-called wireless telegraphy—have no such appreciable effect. A powerful and constant magnetic field is apparently without influence upon living cells, although Prof. Silvanus Thomson has shown that if this magnetic field is made rapidly alternating, physiological effects will be produced. By placing the head between the coils through which powerful alternating currents are passing, the observer will experience a flickering sensation of light. The sensation of taste may also be stimulated in the same manner. Prof. Thompson suggests that these effects are due to eddy currents set up in the nerves, and this seems highly probable.

Light Rays.—We may forego any further reference to heat rays, and proceed at once to consider which of the rays of light have most effect upon living matter. When a narrow beam of white light is split up into its primary rays, a spectrum such as can be seen on the screen is produced. In nature we are familiar with this phenomenon in the shape of the rainbow. If, now, a strip of bromide paper is stretched along the screen so as to receive the length of the spectrum, the action of the light will take place upon its surface and can be revealed by development in the ordinary way. On this exposed paper being brushed over with developer, the affected parts will be found gradually to darken, and it will be observed that the darkening takes place more especially under the blue and violet rays, and even beyond the violet end of the visible spectrum.

[Strip of bromide paper across spectrum, develop and fix, to show monochrome equivalent].

These have been called the chemical rays, and it is precisely these rays which are most readily absorbed in their passage through matter. The difference between the absorption of the various rays may be observed in the case of the sun revealed through a fog. Yellowish at first, the sun becomes red as the fog increases in density, the reason being, that the red waves alone are able to get through the fog-bank, while the violet and the shorter wave-lengths generally are scattered.

[Glass cells before lantern, filled with hypo solution, with hydrochloric added, to show the absorption of the blue and violet rays].

It is the shorter waves, at the violet end of the spectrum, which have vital effects upon the tissues. They are the cause of sunburn—a fact, which is well observed in the higher reaches of the Alps, where the atmosphere, being comparatively free from suspended matter, the blue, violet, and ultra-violet rays get through so richly that, without any special sensation of heat, severe effects are produced upon the skin. If the ground be covered with snow, the rays are reflected, and a more intense action results. It is interesting, further, to remember that the blue and violet colour is the last to be seen at the close of the day; that when a person has his sight temporarily impaired by overindulgence in tobacco he loses in the centre of his field of vision the perception of red and green but rarely that of violet; and that, in cases of blindness coming on gradually from wasting of the optic nerve, blue or violet is the last colour to go. Many years ago Sir James Dewar, in conjunction with Prof. McKendrick, demonstrated that when light fell upon the retina of the eye an electrical current was generated in the optic nerve.

Finsen Light Treatment.—For a long period advantage was taken of the physiological effect of sunlight in the treatment of certain diseases, but Finsen, of Copenhagen, was the first to make a systematic study of the curative properties of light. The obvious drawback to this method of treatment is that sunlight is not always available. It is evident that if we were to depend upon sunlight in London for the treatment of certain diseases, cures would indeed be tardy. Finsen, therefore, adopted the method of using powerful artificial lights, and in this manner he soon discovered that the most effective rays were those of the violet and ultra-violet. He used the electric arc for the purpose, and, as ultra-violet light is intercepted by glass, he employed quartz lenses. The readiness with which these active rays were absorbed rendered them only useful in superficial diseases, and it was found that even blood intercepted them to so great an extent that treatment could be made more effective by introducting compression, whereby the blood was forced out of the area upon which the light fell. Finsen's results were very brilliant. More recently, a quartz mercury-vapour lamp has superseded the arc for the production of active violet light in large quantities. Its action upon living cells is very powerful, and it is most destructive, even after short exposures, to all forms of bacteria. But its ready absorption confines its influence to the production of surface effects, and it fails to reach deeply. The effects of light upon plant life are well known, but the limited time does not permit us to deal with the subject. A familiar instance is that of a plant grown in the dark, which is deprived of its colouring matter.

X-rays.—We pass now to the consideration of the Röntgen or X-rays. It was in 1895 that Prof. Röntgen's discovery that a Crookes tube emitted rays, which would pass through opaque substances as readily as light passes through glass, created immediate and world-wide interest. The fact that these rays could pass through our bodies and reveal the shadow of our bones so absorbed the interest of the early workers in this field as to mask for a time the terrible effects upon our living cells which followed over-exposure. The precise nature of the X-rays has not yet been ascertained. It is highly probable, as the late Sir Gabriel Stokes suggested, that they are impulsive in ether of extremely short wave-length. As they travel in straight lines from their point of origin into space, and are not affected in their course by a magnet, and can be neither diffracted nor refracted, their wave-length cannot be determined.

X-ray Burns.—The burning effect of X-rays upon the skin was in a certain sense discovered accidentally. The early tubes used for the production of X-rays were rather imperfect, and therefore very long exposures had to be given in order to obtain radiographs. In this way many severe burns were produced upon unfortunate patients. The operators themselves also began to suffer; and in this country we were all shocked by the untimely death of Dr. Blacker, of St. Thomas's Hospital, who was a most enthusiastic pioneer in X-ray investigation, and whose death was directly due to the destructive effect of X-rays upon the tissues. It was a sad instance of a young and promising life being cut short by this new, and, as it has ultimately proved, beneficial agent, before we had learned to guard against its dangers.

It is worthy of note that most, if not all, X-ray burns produced in operators began in the uncovered parts of their skin, such as the hands and face. A good deal of doubt still exists as to whether the primary X-rays alone are responsible for these manifestations. Having suffered from chronic X-ray burn in my hands, especially in my right hand, it seemed to me rather remarkable that the area of trouble at the back of the hand should end sharply at a line corresponding to the usual position of the coat cuff, for cloth is quite transparent to the X-rays; and the adjacent parts of the skin beneath the sleeve were, in my own case, equally exposed with the uncovered hand itself.

Secondary Rays.—Many views have been brought forward to explain the causation of some X-ray burns, without any very definite results, and it appears probable that the secondary or indirect rays given off from the surface of the glass may be, if not in some cases the primary factors, certainly largely contributory to these superficial skin burns.

The existence of these secondary and less penetrating rays can be very readily demonstrated by exciting a Crookes tube in the ordinary way, and suspending opposite the point from which the primary rays emerge a mass of lead, through which no primary or direct X-rays could possibly penetrate. Naturally, a shadow of this lead is cast by the X-rays coming from a fine point in the anode, and which we may at present call the primary rays; but within this eclipsed area we get shadows caused by other rays, and when these are traced they can be shown to be produced on the glass of the tube, which fluoresces green. These rays are much more richly produced in what is called a high or hard tube. I demonstrated them in my lecture here on April 25th, 1902.

Mr. Campbell Swinton alludes to the existence of these rays in a paper on "The Source of the Röntgen Rays in Focus Tubes," published in 1898. He describes them as secondary rays from the green fluorescing glass of the X-ray tube, and has taken pin-hole photographs of them.

As a further confirmation of the possibly vital effect of these rays upon the skin, I may mention that Freund found that a tube so high as to give no fluorescence on the screen caused the hair to fall out, and also that with a tube having the electric current passed in the reverse direction, so as to produce only very weak primary X-rays, similar results were obtained. It would be interesting to construct a tube so as to employ, for therapeutic purposes, these secondary rays alone.

I have made comparative measurements of these rays by means of the fall of the gold-leaf electroscope. The simple instrument called an electroscope, which is merely a strip of gold leaf or aluminium leaf attached to a support, is discharged by the action of X-rays, which makes the air a temporary conductor, and it is a most convenient method to measure the degree of conductivity produced, the time taken by the gold-leaf to fall through a given distance being taken in each case. Measured by the fall of the electroscope leaf, I found that with a "high tube" giving very penetrative X-rays, if the action of the primary rays were taken as 1, the action of the secondary rays would be $\frac{1}{2}$, and that with a low tube, or a tube giving X-rays of a low order of penetrability, if the primary rays were again taken as 1, the secondary rays would be $\frac{1}{7}$.

Prof. Silvanus Thompson several years ago showed that the cathode stream, after impinging upon the target and thus giving rise to the primary X-rays, was reflected and impinged upon the glass walls of the tube, causing a green fluorescence. He called these reflected cathode rays para-cathodic. Whether they produce X-rays upon this second impact or not does not appear to have been proved, but as Barkla and Sadler and others have demonstrated that X-rays outside the tube, impinging upon solid matter, give rise to secondary rays, it seems certain that X rays, in passing through the walls of the tube in which they are generated, must give rise to secondary X-rays, and it may well be the case that the green fluorescing glass of an X-ray tube emits two sets of X-rays—one, as we have mentioned, produced by the primary X-rays in their impact on passing through it, and the other possibly by reflected cathodal rays. Be that as it may—and this is a matter for the physicist—I feel sure that their physiological action upon the skin must be considerable, especially as they are much more readily absorbed than the primary X-rays. In illustration of this, I can show you a photograph which has been produced by them. As far as I am aware, the physiological importance of these rays seems to have been entirely overlooked, and I am sure they present a field worthy of immediate investigation.

[Secondary rays from glass of tube shown by fluorescent screen, the primary rays having been cut off by a mass of lead. Diagram 1, showing production of secondary rays from tube. Diagram 2, showing how these rays may produce photographs. Pinhole photographs; photographs of different layers of tinfoil by means of the primary and secondary rays. Show *electroscope*, and describe by means of which a comparison of the primary and secondary rays has been made].

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Joint Meetings with the Optical Convention, June 21st, 1912.

The President, on behalf of the Physical Society, welcomed the opportunity the present meeting afforded of co-operation with the Optical Convention.

A Demonstration of Apparatus for the Teaching of Optics was given by Dr. G. F. C. Searle and discussed by Prof. S. P. Thompson.

A paper on "*Diffraction Patterns*" was read by Mr. J. W. Gordon, and discussed by Prof. S. P. Thompson and Mr. C. P. Butler.

A paper on "*The Shape of Scales required for Reflecting Instruments with Concave Mirrors*" was read by Mr. E. H. Rayner, and discussed by Messrs. Chalmers, Milne, and Trotter.

A paper on "*The Visibility of Distant Lights*" was read by Messrs. C. C. Patterson and B. P. Dudding, and discussed by Prof. S. P. Thompson and Messrs. Chalmers, Clay, Mees, Milne, Rayner, Rosenhain, and Trotter.

A paper on "*Some Points in the Use and Design of Refractometers*" was read by Dr. T. M. Lowry, and discussed by the President and Messrs. Chalmers, Mees, Rosenhain, and Von Rohr.

A paper on "*Some Recent Advances in the Measurement of Light and Illumination*" was read by Messrs. J. S. Dow and V. H. Mackinney, and discussed by the President, Prof. S. P. Thompson, and Messrs. Chalmers, Paterson, Trotter, and Whipple.

Some Models Illustrating Geometrical Optics were exhibited by Prof. S. P. Thompson and discussed by Messrs. Beck, Blakesley, Chalmers, Davis, T. Smith, Von Rohr, and Wilmott.

A paper "*On the Measurement of Colour*" was read by Mr. A. C. Jolley and Mr. Bull, and discussed by Prof. S. P. Thompson and Messrs. Edridge Green, Trotter, and Twyman.

The paper by Dr. J. A. Harper on "*Optical Pyrometry*" was postponed to a later meeting.

Ordinary Meeting, June 28th, 1912.

Mr. A. Campbell, Vice-President in the Chair.

A paper on "*Hysteresis Loss as Affected by Previous Magnetic History*," by Prof. Ernest Wilson and Messrs. B. C. Clayton and A. E. Power, was read by Prof. Wilson.

This paper is concerned with hysteresis loss in iron at atmospheric and liquid air temperatures under three different conditions:—(1) After the iron has been carefully demagnetised; (2) after it has been subjected to a large force (previous history) of about 26 C.G.S. units; and (3) whilst it is under the influence of an external constant magnetising force after demagnetisation. One object is to discover (*a*) how the dissipation of energy varies in the above three cases when the maximum magnetic induction B is the same in each; (*b*) how it varies in cases (2) and (3) when not only the maximum magnetic induction is the same, but the value of the reversal force H is the same in each. This matter should concern any molecular theory of magnetism.

It is shown both at atmospheric and liquid air temperatures that the loss for a given value of the magnetic induction B is greater in case (2) than in either (1) or (3), and that the loss in case (3) is greater than in case (1). Moreover, the loss at liquid air temperature is for corresponding cases greater than at atmospheric temperature. For given values of the magnetic induction where the reversal force H and the temperature is the same for each, the loss in case (2) is greater than in case (3), and the percentage difference between the losses rises to a maximum of about 20, when H has a value of about 0·5 C.G.S. units in stalloy. This percentage difference has about the same maximum at about the same value of reversal force H at atmospheric and liquid air temperatures.

As regards the importance of the subject to engineers, it may be mentioned that the watts dissipated by magnetic hysteresis may be increased by as much as 45 per cent, and the magnetising force by 85 per cent on the values these quantities need only have when previous history effects have been wiped out. It would seem, therefore, that after severe short-circuits it might pay to demagnetise the cores of transformers, static-balancers, &c.

Discussion.

Prof. C. H. Lees asked if the effect due to the previous history would not disappear after the alternating current had been applied for a little time.

Mr. G. L. Addenbrooke asked how Prof. Wilson distinguished between hysteresis and eddy current losses.

Mr. C. W. S. Crawley pointed out that the curve of percentage increase in energy loss showed a minimum for low values of H in the case of stalloy, as well as the maximum, and asked if the effect was a real one.

Mr. A. Campbell remarked that it is now being found that it is almost as important that the iron should be demagnetised before applying an alternating current to it as a direct one.

Prof. E. Wilson, in reply to Prof. Lees, stated that although the alternating current had been applied to the specimen for an hour or more during the tests, it would not wipe out the effect of a previous history field that was stronger than itself. In order to demagnetise the specimen by an alternating current, the current must be large enough to produce a magnetisation greater than the previous history effect it was desired to wipe out, and must then be gradually reduced to zero. The ballistic method had been employed which would take no account of eddy currents. He thought the minimum shown by stalloy at low values of H was a real one, though the accurate measurements were very difficult to obtain at those low values. Lohys also showed the same minimum.

A paper on "*Dielectric Hysteresis at Low Frequencies*" was read by Prof. W. M. Thornton.

The paper is an attempt to determine from dielectric hysteresis loops the nature of the change of polarisation which gives rise to the absorption of energy. Current and voltage wave-forms in large condensers were oscillographically recorded at a frequency of 36 a second. Certain substances, like glass or gutta-percha, are found to show a marked triple frequency harmonic in the current wave out of phase with the fundamental. Most of these have a low power factor; others, like presspahn, show little distortion, but have a high power factor. The loops for the former have straight parallel sides, and a true hysteresis retardation as the voltage begins to fall; the latter have lens-shaped loops corresponding to a purely viscous retardation. Every variety of transition is observed between these extreme types.

The cause of the former would appear to be interattraction between the induced molecular charges, which reaches a maximum when these are greatest—*i.e.*, at the highest voltage; that of the latter is a resistance to their movement through the substance during the establishment of the usual polarisation, the retardation reaching a maximum when the rate of change of the voltage is greatest—*i.e.*, in passing through zero.

The dielectric constants of substances with lenticular loops are more affected by change of frequency than the straight-sided type, that of presspahn changing from 4·3 at 78 to 6·3 at 15 per second. Ebonite and paraffined paper, on the contrary, change by less than 1 per cent during the same range. For the same substances change of voltage gradient, short of breakdown voltage, has little or no influence on dielectric constant at this frequency. Power factor appears to increase with frequency within the range determined.

Discussion.

Prof. E. Wilson asked what degree of accuracy the author had reached. The accuracy of results obtained with an oscillograph were marred by the thickness of the lines.

Prof. C. H. Lees asked if the different loops could not be accounted for by assuming the dielectric to be made up of two parts, in one part of which the polarisation was proportional to the electric field and independent of the time, and in the other part in which it rose with the time to its final value following an exponential law.

Mr. G. L. Addenbrooke thought there were two effects here, one depending on the periodicity, and the other an absorption effect.

Mr. D. Owen asked if Prof. Thornton had ascertained there was no C_2R loss or leakage current in the condensers.

Mr. A. Campbell thought the different classes of hysteresis loops obtained were interesting. The fact that the author had dealt with dielectrics in practical use increased the importance of his paper.

Prof. W. M. Thornton, in reply, stated that he thought the accuracy of the oscillograms he had obtained was sufficient for the purpose. In reply to Prof. Lees he did not think the loops could be accounted for without assuming more than one exponential term. Leakage current was tested for by applying a continuous-current pressure of 480 volts. In no case was any measurable current observed except with presspahn, which showed a current of $3{\cdot}5 + 10^{-6}$ ampères.

A paper on "*The Efficiency of Generation of High-frequency Oscillations by Means of an Induction Coil and Ordinary Spark-gap.*" by Prof. G. W. O. Howe and Mr. J. D. Peattie, was read by Prof. G. W. O. Howe.

The apparatus used was similar to that employed in small radio-telegraph stations. A 10 inch induction coil, operated from cells through a mercury interrupter, supplied power to an oscillatory circuit containing a spark-gap between spherical electrodes. Coupled to this circuit was another oscillatory circuit representing the aerial, and containing a variable resistance which constituted the high-frequency load. The input, output, and efficiency were determined for various degrees of coupling, various aerial decrements, different lengths of spark-gap, and with various primary voltages, the object being to determine the effect of these various factors on the working of a small radio-telegraph station.

A second part of the paper dealt with some oscillographic records of the primary and secondary currents of the induction coil. These showed many points of interest, and explained several peculiarities in the working of the coil, especially the variation of input with spark length. This was shown to be due to the particular phase at the moment of "make" of the remnant current in the primary induced in it by the oscillations in the secondary produced by the last spark; this depended on the time which had elapsed since the last spark.

A paper on "*The Resistance to the Flow of Water along a Capillary Soda-glass Tube at Low Rates of Shear*," by Dr. A. Griffiths and Miss C. H. Knowles, was read by Dr. Griffiths.

In 1905 Prof. W. Duff concluded that the viscosity of water at low rates of shear increases when the water is allowed to stand in a capillary glass tube. He employed Poisenille's method. Later, L. E. Gurney, by a method involving the use of a rotating cylinder, found that there is no increase in the viscosity of water which has stood in contact with powdered glass for a week.

The authors, working at Birkbeck College, in the City of London, find that almost invisible fungoid growths develop in ordinary distilled water in glass tubes, and they suggest that organic growths were probably the cause of Duff's results. They detect no increase in the viscosity of water that has stood for days in a glass tube when the water is sterilised by the addition of a trace of copper nitrate. Their apparatus is a modification of Duff's, and consists of a calibrated capillary tube 130 cm. long of ⅓ mm. bore, joining two cylindrical tanks of ⅓ metre diameter. The difference of head is about 1 mm. The flow is measured by means of a coloured column, consisting of a feeble aqueous solution of uranine.

A paper, entitled "*The Self-demagnetisation of Steel*," by Messrs. S. W. J. Smith and J. Guild, was read by the Secretary.

The constituents, iron and iron carbide, are easily traceable in annealed steel, owing to the differences between their magnetic properties. The ferro-magnetic transition point of the carbide is about 500° C. lower than that of the iron. The carbide is also magnetically harder at ordinary temperatures, and possesses greater coercive force, although, like iron, it is magnetically very soft at temperatures near the transition point. In consequence of these facts, the effect of heat upon the residual magnetism of an annealed steel rod is peculiar and, at first sight, mysterious. As the temperature rises the residual magnetism falls continuously until it becomes zero in the neighbourhood of 200° C. It then changes sign and reaches a maximum negative value at about 220° C. Beyond this the negative magnetisation decreases slowly, and finally becomes imperceptible between 700° C. and 800° C. If the rod is cooled from 800° C. it remains without perceptible polarity as the temperature falls; but if the heating is interrupted before the whole of the residual magnetism is destroyed the behaviour on cooling is quite different. Thus, to quote one case, the rod was heated until, at 600° C., the residual intensity of magnetisation was about $-0{\cdot}5$. On cooling the intensity increased to a maximum negative value of about $-1{\cdot}6$ at about 245° C. Then the magnetisation began to fall, reached zero at about 210° C., became positive, and, finally, was about $+15{\cdot}5$ at the air temperature.

An explanation of these and other results which were described is given in the paper, in which it is shown that the residual magnetism of short annealed steel rods is determined by the retentivity of the carbide, and that the residual polarity of the iron is negative. The iron may thus be said to contribute less than nothing to the residual magnetism of the rods.

The paper was discussed by Profs. Mather and Howe and Mr. Campbell, to whom the Secretary replied.

FARADAY SOCIETY.

Annual General Meeting, July 2nd, 1912.

Prof. A. W. Porter, F.R.S., in the Chair.

The minutes of the Annual General Meeting, 1911, were read and approved.

The Chairman moved the adoption of the Report of the Council, and the Statement of Accounts and Balance Sheet for the year ending December 31, 1911, as printed in the June number of the *Proceedings*.

An abstract of the Report appears below.

The motion was carried unanimously.

Mr. J. W. Hinchley suggested that it might be desirable to decrease the subscription to the Society from £2 to, say, one or one-and-a-half guineas, as this might be the means of considerably increasing the membership and through that the usefulness of the Society. The matter was referred to the new Council for their consideration.

The following Officers and Council were elected to serve for the ensuing year.

President—Dr. R. T. Glazebrook, C.B., F.R.S.

Vice-Presidents—G. T. Beilby, F.R.S.; Prof. K. Birkeland; Sir Robert Hadfield, F.R.S.; F. W. Harbord; Prof. Bertram Hopkinson, F.R.S.; Alexander Siemens; Prof. James Walker, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—R. Belfield, M.I.E.E.; Dr. H. Borns; W. R. Bousfield, K.C.; Dr. J. A. Harker, F.R.S.; Prof. A. K. Huntington; Dr. R. S Hutton; Dr. T. M. Lowry; Dr. R. Seligman; Dr. G. Senter; Maurice Solomon.

On the motion of Dr. R. Seligman, seconded by Dr. W. C. McC. Lewis, Mr. Leon Gaster and Mr. J. W. Hinchley were re-elected Honorary Auditors, and a cordial vote of thanks was accorded them for their past services to the Society.

The Chairman then proposed a vote of thanks to the Institution of Electrical Engineers for granting the Society the use of their Lecture Theatre for the Ordinary Meetings. The motion was carried with acclamation.

On the motion of the Chairman, a vote of thanks was passed to the retiring Officers and Members of Council. This concluded the business of the meeting.

Abstract of the Eighth Annual Report of the Council of the Faraday Society.

Eight Meetings were held during 1911, at which twenty-six papers were read.

On May 2nd, Mr. A. Scott-Hansen, who is intimately connected with some of the great Norwegian water-power schemes, came over from Christiania to read a paper describing these plants and their application to electrochemical industry. Arising out of this meeting the Council has endeavoured to arrange a visit to Norway this summer to inspect some of the installations described by Mr. Scott-Hansen, but up to the present the response on the part of members has been so meagre that the visit, it is feared, may have to be postponed. Unfortunately it has not been found possible to obtain permission to visit some of the most interesting of the electrochemical works, which perhaps would have formed the greatest attraction to members of the Faraday Society.

The practice of holding a General Discussion was continued in 1911, the subject chosen having been "High Temperature Work." The Discussion was opened by Dr. Arthur Day, Director of the Geophysical Laboratory, Carnegie Institute, Washington, and on the afternoon preceding the meeting Dr. Day and a party of members and their friends visited the National Physical Laboratory, by the kind invitation of the Director, and inspected the high-temperature equipment described in some of the papers contributed to the Discussion.

On June 13th the Society was honoured with a visit by Prof. Ernst Cohen, of Utrecht, who delivered a lecture on "Allotropic Forms of Metals," while advantage was taken of Dr. Edward G. Acheson's visit to Europe in the autumn, when, by invitation of the Council, he addressed the Society on his work in connection with electric furnace products.

The visits of these distinguished friends from abroad to lecture before the Society were made the occasion of several pleasant social gatherings, all the more successful on account of their informal character, the lecturers being invited to meet the members of the Society and to dine with them prior to the meetings.

The two meetings held on October 3rd and 17th, devoted to the discussion of a group of papers dealing with the different types of electric furnaces in use for the manufacture of iron and steel, are worthy of special note. At the meeting held on December 6th a group of papers on Thermostats was presented, and a small collection of these instruments and appliances used in connection therewith was arranged for the occasion.

On several occasions the Council has invited members of kindred Societies to attend meetings likely to be of special interest to them. These invitations have been much appreciated, and have tended not only to promote friendly relations between the Faraday Society and other scientific bodies, but likewise to popularise the work of the Society and bring it before the notice of a wider public than would be possible if meetings were always confined strictly to its own members.

Ordinary Meeting, July 2nd, 1912.

Prof. A. W. Porter, F.R.S., in the Chair.

Dr. W. C. McC. Lewis and Mr. A. P. Roshdestwensky read a paper entitled "*Electrocapillary Pulsation of a Mercury Meniscus.*"

The measurements were carried out in a very narrow capillary tube in which a mercury column came into contact with aqueous solutions of mercury cyanide. The apparatus for measuring the variation of the interfacial tension with e.m.f. applied was similar to that of Lippmann, the pressures which had to be applied in order to bring the meniscus back to the zero point, giving thereby a measure of the interfacial tension, being read by means of a calibrated double-limbed burette. To see if the apparatus was working satisfactorily, a series of measurements was made with the mercury in contact with sulphuric acid solution, a similar type of curve to that of Lippmann being obtained. This normal behaviour was not found, however, in some of the mercury cyanide solutions examined. The solutions examined were $Hg(CN)_2$ saturated, N/10, N/100, N/1000 respectively, and in addition each of the latter three solutions in presence of N/10 KCN.

The first point noticed was the difficulty of reproducing readings. The pulsation of the meniscus was observed first in the solutions of N/10 $Hg(CN)_2$. It made its appearance when the applied e.m.f. was raised to 1 volt (the meniscus being the cathode) and the amplitude of the pulsation increased as the applied e.m.f. increased. The pulsation itself when e.m.f. $= 1\cdot5$ volt consists of three stages—first a slow fall of the meniscus (indicating a decrease in the interfacial tension), which lasted for about 30 secs., this being followed by a rapid fall and quick return to zero, which occupied about 5 secs.

Besides the application of a minimum e.m.f., it was found that the diameter of the capillary was a determining factor. With a very narrow tube ($< 0\cdot02$ mm.) no pulsation was observed. Further, the nature of the solution has likewise to be taken into acconnt. Pulsation was observed with saturated mercuric cyanide and with the decinormal solution. It was not observed under the conditions so far employed with any of the other solutions. It seems likely, therefore, that a minimum concentration of mercury ion is essential.

A paper was communicated by Mr. G. E. Bairsto, M.Sc., B.Eng., on "*The Variation of the Conductivity of Aluminium Anode-films with Temperature.*"

An investigation into the variation of the conductivity of Al anode-films with temperature, and the influence of the chief factors in the formation of these films upon this variation.

1. The law of the temperature variation of conductivity is given by $i = A\epsilon^{a\theta}$, the curves obtained by plotting log to θ being straight lines over the whole range of temperature from ordinary temperatures to the boiling-point of the electrolyte.

2. The value of the exponent a is independent of the voltage of formation, the time of formation, the concentration of the electrolyte, and the cation present in the electrolyte, and depends only on the anion (provided the test is made at the voltage of formation), whereas A varies widely with these variables.

3. $AmHCO_3$ is an exception to the general law. At 55° its a abruptly changes, but this behaviour is explained by the decomposition of the film and by the OH ions playing most part in the conduction.

4. For a given formation voltage a decreases with the voltage of the test, but when a certain current density (which is the same for all voltages of test) is reached, the conductivity increases much more rapidly than that given by $A\epsilon^{a\theta}$, in such a fashion that for temperatures above about 60° the current-volt curves have a maximum at a voltage below that of formation.

5. For voltages up to about one-half of the voltage of formation the resistance of an Al anode-film is practically constant, but rapidly falls off as the voltage reaches that of formation.

6. a is a definite function of the equivalent weight of the anion in solution; one increases with the other. It furnishes a method of determining the latter quantity.

7. The cooling-down curves lie above the heating-up curves, but a ultimately becomes practically the same for both.

NOTICES OF BOOKS.

A Manual of Practical Biochemistry. By H. Leighton Kesteven, D.Sc. Sydney: Angus and Robertson, Ltd. 1912.

This book had its origin in sets of typewritten papers giving directions to the laboratory assistants for preparing for the lectures on Physiology and Biochemistry delivered at the Technical College, Sydney. These condensed directions were found very useful by the students of the classes, and they were therefore revised and amplified and published in the form of a practical manual of biochemistry. The author had in his mind more particularly the needs of students to whom the demonstrator could not devote very much time in the laboratory, and he described very fully both the objects of the experiments and the details for carrying them out. The first section deals with the tests for elements present in organic substances generally and in the tissues; here a good deal of the work is reminiscent of the obsolete test-tubing methods, but possibly this is almost unavoidable, since many of the students using the book will have no previous knowledge of chemistry whatever, and hence their early work in such a subject as biochemistry can hardly fail to be somewhat mechanical. Some theoretical discussion is given in Section II. on the carbohydrates, for it is realised that otherwise the practical work would be quite unintelligible. In Sections III. and IV. the fats and proteins are treated, and the fifth and sixth sections explain the application of tests and methods previously described to the case of foods and the secretions of the animal body. Although the standard set is not very high the book will no doubt be useful to students preparing for elementary examinations in physiology.

Dogs, Dirt, and Disease. By J. Lawrence-Hamilton, M.R.C.S.

These leaflets give some data relating to the spreading of infection by dogs, and point out in somewhat unmeasured terms the danger they be to health, and the part they play in the dissemination of tuberculosis. The leaflets are partly reprinted from papers read at the Brighton and

Sussex Medico-Chirurgical Society, and the author hopes that by circulating them he will educate public opinion as to the insanitary nuisance caused by dogs, and that then pressure will be brought to bear upon the Local Government Board, who will be induced to see that the scavenging and cleansing of public thoroughfares are more thoroughly carried out.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperaturs are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 22, May 28, 1912.

Preparation of Phenylcyclohexane and of Dicyclohexyl. Direct Hydrogenation of Diphenyl.—Paul Sabatier and M. Murat. — On applying to diphenyl $C_6H_5.C_6H_5$, the general method of hydrogenation over nickel, Eykman obtained only phenylcyclohexane, $C_6H_5.C_6H_{11}$, only one radicle being hydrogenated. To explain this singular result the authors have first prepared directly phenylcylohexane and dicyclohexyl. Phenylcyclohexanol is readily transformed into phenylcyclohexene, which can be hydrogenated over nickel to give phenylcyclohexane. Cyclohexylcyclohexanol is dehydrated when it is heated with anhydrous zinc chloride, and is totally transformed into cyclohexylcyclohexene, which yields dicyclohexyl when hydrogenated over nickel. When diphenyl vapour mixed with excess of hydrogen is passed over reduced nickel at a temperature of about 180° a colourless liquid is obtained which does not contain an appreciable amount of dicyclohexyl, but if this liquid is subjected to a fresh hydrogenation with a large excess of hydrogen, dicyclohexyl is formed.

Selenide Cells.—H. Pélabon. — Some metals, like silver, lead, copper, &c., unite with selenium to give compounds which at a sufficiently high temperature dissolve in an excess of liquid selenium. When the proportion of selenium exceeds a certain limit the liquid separates into two layers; the upper layer consists of pure selenium, while the lower contains the two elements in proportions which point to the existence of a compound. The author has investigated the composition of the mixtures by determining the electromotive force of the various cells. With silver the compound Ag_2Se is obtained, and with lead PbSe. In the case of copper the compound Cu_2Se gives solid solutions with the excess of selenium, and tin yields two compounds, SnSe and $SnSe_2$.

Action of Ultra-violet Rays on Starch. — Jean Bielecki and René Wurmser.—Pure starch in aqueous solution when exposed to the ultra-violet rays undergoes decomposition and oxidation with production of dextrines, reducing sugars, pentoses, formic aldehyde, and substances with acid functions.

Bulletin de la Société Chimique de France. Vol. xi.—xii., No. 10, 1912.

Compounds of Iron and Zinc.—E. Vigouroux, F. Ducelliez, and A. Bourbon.—The authors have made a detailed study of the alloys of iron and zinc, using the method of electromotive forces. They have thus proved the existence of the compounds $FeZn_7$ and $FeZn_3$ which Vegesack also discovered by thermic analysis. They also find that compounds Fe_3Zn and Fe_5Zn probably exist. By the action of cold acetic acid they have isolated from the alloys the compound $FeZn_7$ in the form of small non-magnetic crystals.

Action of Concentrated Sulphuric Acid on some Aromatic Nitramines.—Frédéric Reverdin and Franz Liebl.—When concentrated sulphuric acid acts on the nitramines obtained from the methyl derivatives of *o*- and *p*-phenetidine the corresponding nitrosamines are obtained, but the yields are much smaller than with the anisidines, the phenetidine derivatives being more easily oxidised. On solution in sulphuric acid more or less intense colorations are observed, and thus in many cases the presence of small quantities of nitramine may be detected in an impure nitrosamine.

No. 11, 1912.

Uranium Oxalate.—W. Œchsner de Coninck and A. Raynaud.—Re-crystallised uranium oxalate contains 3 molecules of water. The water is removed by heating for four hours to 100°. When the dry salt is ignited in a closed crucible a black residue of pure uranous oxide is left. Dry uranous oxalate takes up 3 molecules of water from the air if it is exposed to a very damp atmosphere. If uranium oxalate is ignited very rapidly, or if air is allowed to enter the crucible during the operation, some uranic anhydride is formed owing to the partial oxidation of the UO_2.

Syntheses by means of Mixed Organo-derivatives of Zinc. α-Alkoxy-alkylacetic Acids.—E. E. Blaise and L. Picard.—The authors hoped that the condensation of diethoxyacetyl chloride with mixed organo-derivatives of zinc would lead to the formation of a diethylacetal of an α-ketone aldehyde. But as a matter of fact the action of thionyl chloride on diethoxyacetic acid yields not the chloride of diethoxyacetyl, but an isomer essentially different from it. This isomer is ethyl chloroethoxyacetate. The chlorine in it is very mobile, and with the organometallic derivatives of zinc it gives α-ethoxy-acids in the form of ether salts. This reaction is interesting from a theoretical point of view because it entails the fixation of the group $—CHOH—CO_2H$ on any radicle.

Binary Mixtures containing Camphor.—M. Jouniaux. —If one of the following compounds is added to pure camphor: — Naphthalene, α-mono-nitronaphthalene, β-naphthylamine, pyrogallol, benzoic acid, the first crystals which are deposited on cooling the liquid mixture consist of pure camphor, provided that the proportion of compound added does not exceed 30 molecules per cent of the total mixture. If even a very small amount of a definite compound is added to pure camphor the temperature at which solidification begins is very decidedly lowered. It has long been known that from a pharmaceutical point of view camphor is incompatible with phenolic derivatives, *e.g.*, mono- and polyphenols. The mixtures formed are liquid at the ordinary temperature of the laboratory, the lowering of the solidification point exceeding 150°. This property of camphor is not peculiar to the phenol group. Thus camphor is a good solvent for cryoscopic work.

Atti della Reale Accademia dei Lincei. Vol. xxi., No. 9, 1912.

Analogy of Copper and Silver.—G. A. Barbieri.— The author has isolated in the solid state a salt of divalent silver, the persulphate of silver and pyridine, $AgS_2O_8.4Py$. A similar copper compound, $CuS_2O_8.4Py$, exists, and a series of different coloured (orange, yellow, green) solid solutions of the two compounds may be obtained. Thus the two substances are isomorphous. All the mixed crystals are stable in the solid state.

Synthesis of Tetramethyl-pyrrol.—G. Plancher and T. Zambonini.—When trimethylacetyl-pyrrol is treated with sodium dissolved in absolute methyl alcohol crystals of tetramethyl-pyrrol are obtained. The compound is rapidly decomposed when heated in air or water. In its original state it does not give Ehrlich's reaction with dimethylamino-parabenzaldehyde, but does after being boiled with water. Thus it is probably hydrolysed by water, yielding γ-diketone or γ-ketoaldehyde.

THE CHEMICAL NEWS.

VOL. CVI., No. 2748.

IS HELIUM FUNDAMENTALLY AN ELEMENT OF ELECTRO-POSITIVE MAKE-UP?

By F. H. LORING.

THE perfect inertness of the argon gases has been explained by assuming that negative electrons are firmly held to the atom, and that there are no free bonds of affinity.

However this may be, the position of helium in a series comprising the strongly basic or alkaline elements of Group I., as given below, suggests that helium is in some way fundamentally of electro-positive make-up.

It will be seen that the regularity in the *differences* apparently justifies the inclusion of helium in the strongly electro-positive group.

Elements.	At. wts.	Differences.
Hydrogen	1	
		3
Helium	4	
		3
Lithium	7	
		16
Sodium	23	
		16
Potassium	39	
		46½
Rubidium	85½	
		47¼
Cæsium	132¾	

It must also be remembered that argon, potassium, and calcium are so nearly alike in atomic weight as to suggest some intimate connection between them.

Whatever these numerical relations signify, there seems to be a strong indication that the inactive gases are, in some way, more related to the elements of Groups I. and II. than to any other groups, and the great physical and chemical difference is perhaps to be sought in the influence of the electrons, which are bound up with the atom. It may, however, be said that the elements of Group VII. claim some recognition in the matter of relationship. A method of extrapolation given in the *Physikalische Zeitschrift* (xii., 107) as a purely artificial device for deducing the atomic weights of the higher members of the inactive series brings together elements of Groups II. and VII., and may, after all, foreshadow some fundamental truth awaiting elucidation. It will be remembered that Masson (CHEMICAL NEWS, lxxiii., 283) adduced good reasons for placing hydrogen at the head of Group VII.

The following statement is a further argument in support of the idea that helium is fundamentally electro-positive in make-up.

One must grant that, chemically and physically, there is a big step between the alkali metals and the elements of the argon type. Therefore, the latter are to be considered as a distinctive group comprising about 8 elements. If there are more, then they may possibly be associated members or components of those of great magnitude, such as the emanations; or, leaving the emanations out of consideration, there are probably 8 *stable* elements of the inactive type.

The elements forming Group VIII. are also distinctive, and in all there are 9. Copper, silver, and gold form the end-row members of a rather distinctive grouping,* numbering, when complete, 20 or 21 elements.

The next and last grouping is a characteristic one, in which the alkali metals are the corresponding end-row members, which, when complete, should probably comprise only 43 elements, including hydrogen, since the rare earth elements, as pointed out some years ago by Brauner, form quite a distinct group. The lower part of the table of this grouping after Brauner would be conveniently shown thus:—

					⟼(Pr, Nd, &c. = 13)		
(5th Series)*	Cs	Ba	La	Ce ǁ	Ta	W	—
(6th Series)	—	Ra	—	Th	—	U	—

We, therefore, have the numbers, 8, 9, 13, 20, and 43, answering to well recognised groupings, *falling in the order of their average chemical activities.*

These numbers (N) may be expressed closely by the equation—

$$35\left(1-\sqrt{\frac{a-n^2}{a}}\right)+\frac{a}{2}=N;$$

in which n assumes the successive values:—0, 1, 2, 3, and 4; and $a=16$.

This series gives differences:—1 (= H), 4 (= He), 7 (= Li), and 23 (= Na), the sum being 35 (= a constant in the above formula, which, of necessity, is the sum of the differences). From this series it is natural to suspect that helium might possess latent properties analogous to the other elements which appear to identify themselves with this scheme. However, the sequence may be accidental. Very unstable radio-active elements or products have not been counted.

Apart from the question of helium being electro-positive in make-up, the above groupings strengthen the view expressed in different quarters by several chemists that some of the older tables contained too many gaps.

The term electro-positive may be interpreted in a general sense, namely, as signifying some similarity to such elements as hydrogen, lithium, sodium, &c. In the case of helium, the principal characteristics necessary for a proper identification in this respect appear to lie dormant. It is as if the electrons completely neutralised the electro-positiveness of the element, if such a term may be used.

In considering the division of the groups as here indicated, it should be remembered that the periodic tables of Mendeléeff and others involve the bringing together, or separating, of a few elements which are respectively dissimilar or allied, as if some disturbing factor prevented a perfect continuity of type. For example, manganese is not altogether in fitting sequence to chlorine or fluorine in Group VII. If an opinion may be ventured, it seems better to give preference to the most regular and natural order of arrangement by atomic weight, and seek rather for the cause of the irregularity than to attempt to make an arrangement that is somewhat artificial from this point of view. The special arrangements are, nevertheless, of practical use, but they should not be adhered to too closely when attempting to trace out new fundamental causes; at least, both views should be considered.

The process of radio-active disintegration supports the idea that the elements were laid down in a consecutive order by Wright, but implications of this kind are by no means certain; the elements may have been evolved in groups, as indicated above, by some cyclic process, the return phases sometimes laying down elements that fall in between those previously laid down. It is as if certain materials were exhausted during each cycle or phase, and only upon the reformation or reappearance of such materials could the repeating process proceed or become productive, the character of the cycle as a whole being determined by the quantity of material available each time. This is but a suggestion, thrown out to open up fresh lines of thought in connection with the numerical relations given, and is at best obviously only a crude guess.

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* The term "grouping," in itself an inadequate term, here and elsewhere connotes a collection of groups (in contradistinction to the term group"), being thus understood from the context where it so admits.

* Owing to the assignment of the more noble metals (Cu, Ag, Au, &c.) to a separate group, the serial numbers are altered.

VITAL EFFECTS OF RADIUM AND OTHER RAYS.*

By Sir JAMES MACKENZIE DAVIDSON, M.B., C.M.

(Continued from p. 32).

Protection.—Many years ago I made an experiment in which a Crookes tube was completely buried in a large quantity of red lead contained in a box, and when this was excited in a dark room the fluorescent screen showed that no X-rays at all were able to penetrate. Then a small opening was made by scooping away the red lead until the primary rays got through, together with only a very few of the secondary rays from the small area of glass opposite the orifice. This was the most effective means of screening everybody from the rays except the individual under observation, but it was highly inconvenient, the apparatus being difficult to handle, especially when a fresh tube had to be embedded. Therefore a box was constructed, lined with a mixture of red and white lead, and a small hole was cut in it for the emission of the rays. Some such method is now fairly generally adopted, and is most important for the protection of the workers.

When a fluorescent screen is used for examining patients it should be lined with thick lead-glass. This allows the shadows of the screen to be perfectly observed, while at the same time protecting the faces of the observers from the injurious effects due to the X-rays. Since these precautions have been taken the disasters to workers have been minimised, and should be entirely abolished. The opacity to the X-rays of any material is in proportion to its atomic weight. Therefore any material impregnated with a compound having heavy atomic weight would act as an effective protection.

Pastilles.—Great difficulty was experienced at first in the use of X-rays owing to the variability of the tube. No reliable means existed of knowing what dose—to borrow a term from medicine—was being given. At present we have several fairly reliable methods which have led to more precise results without bringing about the unfortunate injuries previously occurring. The method most in general use is that of the Sabouraud pastille, which consists of barium platino-cyanide in compressed form—the same material as that which is employed in the making of the fluorescent screen.

The pastille changes gradually in tint from a pale yellow to a deep orange, according to the amount of X-radiation it receives. It is arranged in a definite position, and by careful experiment sufficient data have been forthcoming to enable any desired biological result to be obtained with approximate precision. The great advantage of this method is that it can be used at the very time that the X-rays are being applied to the patient, so that whatever variations may take place in the output of the tube all of them are recorded, so to speak, by the tint produced in the pastille. With these safeguards the X-rays, applied for medical purposes, may now be said to be entirely free from all risk to the patient.

Penetrability.—Unlike the violet and ultra-violet rays, the X-rays penetrate deeply—can, in fact, pass right through the body easily—but they vary in penetrability according to the condition of the Crookes tube. The tube may be in a condition which is called "soft" or "low," so that the rays produced will cast a shadow of the hand without showing the bones at all, or it may be "hard" or "high," so that the rays, passing easily through, make the bones look quite pale on the fluorescent screen; and there are all intermediate stages.

I have already said that the opacity of a substance to the X-rays is in proportion to the atomic weight of that particular substance. Recently Dr. Lindemann has made a glass of light atomic weight which, when put in the tube as a window, allows many rays of very low penetration, which in ordinary tubes are prevented from escaping beyond the glass, to pass through. Already very valuable therapeutic results have been obtained by the use of these tubes.

[Show Lindemann tube.]

X-ray Effects on Cells.—The most striking and general vital effect of the X-rays is to be witnessed upon young and growing cells. Guinea-pigs a day or two old are killed with great rapidity, and before any visible effects of radiation, in the shape of burning, make their appearance. The adult animal, on the other hand, shows a greater capacity for resistance. In a recent communication to the Royal Society, J. F. Gaskell, who has studied the action of the X-rays on the developing chick, stated that he had found this action to be confined to a lowering of the mitotic (or cell-multiplying power) of the growing tissues. If this diminution were not too great complete recovery occurred, and the chicks were hatched out at the usual time, but if it fell below a certain degree all further development was arrested. On the same principle of attacking young and growing cells, the X-rays injure the hair follicles and bring about the fall of the hair—a convenient method of epilation now employed with signal success in the treatment of ringworm in children. Prolonged exposure to the rays will produce total baldness. The sweat glands can also be destroyed in the same manner. The action of X-rays upon the blood is limited chiefly to the white blood corpuscles, the red blood corpuscles being very resistant. The central nervous system also, fortunately, has great resisting capacity.

Latent Period.—When the skin is exposed to the X-rays no immediate visible effect is produced. But if the duration of exposure has been sufficiently prolonged to bring about what is called a reaction, the period intervening between the time of application and the appearance of the reaction in the skin will be found generally to vary between a couple of days and about three weeks. The duration of this "latent period" depends upon the amount of the dose. The stronger the dose the shorter the latent period. There is no doubt that the X-rays produce certain changes or injuries to living cells, which remain hidden until the absorption of the abnormal products due to these changes causes redness and inflammation to become evident. At first it was thought that these effects were confined to the skin, but it soon became apparent, on researches by Haenisch and others, that some of the deep organs were more susceptible to the action of X-rays than the skin itself. The most sensitive of all the tissues are the lymphoid tissues generally, especially the spleen, which shrinks and becomes strongly pigmented under their attack.

Plant Growth.—In considering the effect of X-rays upon the lower forms of life, we have first to note their influence upon plant growth. Wetterer, the German radiologist, relates an interesting experiment in this connection. He has taken collections of sunflower seeds and applied X-ray doses of varying strengths. The seeds which had received very small doses, equal to or slightly above a dose which would produce an inflammation of the skin, sprouted in about the same time as seeds which had been untouched by the rays. In seeds which had received heavier doses the sprouting took place much later, and the plant showed clear symptoms of degeneration. Seeds which had received still stronger doses gave no sign of growth whatever. The effect of X-rays upon bacteria, however, seems to be very feeble, if, indeed, it exist definitely at all. And this is in marked contrast to the bactericidal action of ultraviolet light previously mentioned.

Skin Diseases.—It is evident that an agent having such vital effects as those described—and there are many other effects which could be demonstrated if time permitted—will find a wide field of application in the treatment of disease. In many skin diseases it is of signal service. In certain diseased conditions of the spleen also its action is very marked. In malignant tumours, while it may be of service in arresting the rapidity of the growth, it cannot be

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* A Discourse delivered before the Royal Institution, February 2, 912.

looked upon as a method of cure, although, after the removal of such growths by operation, the application of the rays to the involved area may assist in destroying any of the malignant cells which the surgeon's knife has missed, and preventing re-development. And as the technique of the X-rays is being improved, the field of their utility in therapeutics is being gradually extended.

Radium.—We may now proceed to consider the action of radium and other radio-active substances. It is necessary before approaching the question of the vital effect of these rays to review briefly their physical properties. Immediately after the discovery of the X-rays, in 1895, Henri Becquerel proceeded to investigate the possibility of fluorescent substances giving out invisible rays similar to those of Röntgen. Very fortunately, as it turned out, he selected uranium for his purpose. Wrapping a photographic plate in black paper, so that it was completely shielded from all light, he placed upon it a salt of uranium, his idea being that the fluorescence induced by the light in the uranium compound might give rise to invisible rays like those from a Crookes tube. He found that the photographic plate was, indeed, blackened underneath the salt, but that such an effect was produced equally well without the uranium being exposed to light. In short, it became evident that the property of emitting these invisible rays was a property inherent in the uranium element itself. Further investigation proved that these rays from uranium, like the X-rays, had the power of discharging electrified bodies.

Radio-activity.—This discovery of Becquerel was really the discovery of that which we now know as radio-activity. The term "radio-active," as applied to elements which spontaneously emit invisible rays that possess the power of passing through opaque substances, has now come into the general vocabulary. The rays of radio-active substances also have the power of discharging electrified bodies, of acting on a photographic plate, and of making certain substances fluoresce. They cause air and other gases to become temporarily conductors of electricity, and, finally, they generate heat spontaneously.

[Show pitchblende.]

Becquerel's discovery was also the starting-point for the investigations of the Curies, which resulted in the separation by chemical processes of the various active substances in a large quantity of residues of the mineral pitchblende. This mineral was found to be more radio-active than the uranium it contained. Madame Curie, after separating a substance which she called *polonium*, succeeded ultimately in isolating the substance which is now known as radium, and which proved to be two million times more radio-active than a corresponding amount of uranium. Radium, chemically considered, is an ordinary element, very similar to barium or calcium, and producing similar salts. The sulphate, chloride, and now more generally the bromide of radium, are the salts used. Metallic radium has been isolated by Madame Curie.

[Show calcium which resembles radium.]

The Radium Atom.—Up to the time of the discovery of radium the atom had been looked upon as indivisible. Rutherford and Soddy found that radium was disintegrating, and Sir William Ramsay, with Mr. Soddy, investigating this disintegration of radium, proved that helium was one of its products. This discovery may be looked upon as the first actual proof of the transmutation of elements. Chemists had long been familiar with the energy evolved by the rearrangement of molecules, such, for example, as in the explosion of dynamite, but the enormous energy evolved by the disintegrating atom was found to be almost incredible. There is, however, this marked difference, that while we have control over the molecular combinations, we have no control whatever over the disintegration of the atom, which is a purely spontaneous action. This disintegration proceeds at the highest temperatures exactly in the same way as has been proved to be the case in the lowest temperatures. The beautiful researches of Sir J. J. Thomson have helped us to realise that an atom consists of a large number of corpuscles. Soddy has stated that the amount of heat evolved by any quantity of radium every hour is just about as much as is required to raise an amount of water equal in weight to the radium from the freezing-point to the boiling-point. The quantity of radium obtainable is so small, being only one part in five millions of the best pitchblende, that it has never been experimented with as a drug in the ordinary sense to any extent, and its biological properties in this respect are consequently unknown.

It is the radiant energy evolved by the disintegration of the radium atom which is of value to us in medicine. The average life of radium is 2500 years, so that anyone who buys radium can have no personal anxiety about its lasting qualities. So far as we are concerned this evening we have to consider the three rays, called Alpha, Beta, and Gamma rays, which radium gives off.

In the process of flying to pieces, or disintegration, the radium atom first gives off an atom of helium at a velocity of about twenty thousand miles per second. This is called the *alpha* ray, which is beautifully demonstrated by a little instrument devised by Sir William Crookes and called the spinthariscope.

[Show spinthariscope.]

The remainder of the atom evolves as a gas or "emanation." The emanation in its turn decomposes, losing half its energy in about four days, and finally gives rise to an active deposit of rapid change. In its turn also this deposit gives off alpha, beta, and gamma rays, and these are the three kinds of rays, together with the emanation, which are of importance in the consideration of the vital effects of radium. It is very probable that the ultimate product of this disintegration is lead.

Alpha Rays.—The alpha ray, as already mentioned, consists of an atom of helium travelling with a comparatively small velocity. It has a very feeble power of penetration, being stopped by 2 or 3 cm. of air, while a sheet of paper will suffice to prevent it from issuing. The action of the alpha rays on living cells is uncertain. From some experiments with the "active deposit" from thorium, I think that the action of these rays upon the skin must be very slight.

Beta Rays.—The beta rays consist of what are called corpuscles, being extremely minute material particles about one thousand times smaller than the alpha ray, travelling at varying velocities from half that of light, or less, almost up to the velocity of light itself, which is 186,000 miles per second. They carry a negative charge of electricity, and their power of penetration varies with their velocity, but all of them are stopped by lead 1 cm. in thickness.

Gamma Rays.—The gamma rays, which are almost certainly a wave disturbance in the ether, are similar in that and in other respects to the X-rays, but they are of much greater penetrability, passing easily through 1 cm. of lead. No Crookes tube, even with the highest vacuum, could give rays as penetrative as the gamma rays produced spontaneously by radium.

[Show sparkler burning.]

Emitting as it does these three kinds of rays, radium will affect a photographic plate, cause a diamond to shine in the dark, give a sensation of light to the human eye, and make barium platino-cyanide and willemite fluoresce. It has definite biological effects, and it will also discharge an electroscope. I have already described the electroscope, which enables us to measure the strength of a particular specimen by comparing the rate of fall of the leaf with the similar action in the case of some standard quantity.

[Show radium tube containing 20 mgrms. of pure radium bromide; show also radium lent by Mr. Francis Fox. Slide showing magnetic deviation of alpha and beta rays. Slide: Different penetrability of α, β, γ rays. Slides: (1) The "A" slide, showing the feeble penetrability of the alpha rays, and the absence of effect on a photographic plate when a piece of paper was interposed. (2) Slide showing the darkening of a plate exposed to gamma rays through a lead box 1 cm. in thickness. Effect of radium on platinocyanide screen and willemite. Discharge of electroscope under radium rays.]

(To be continued)

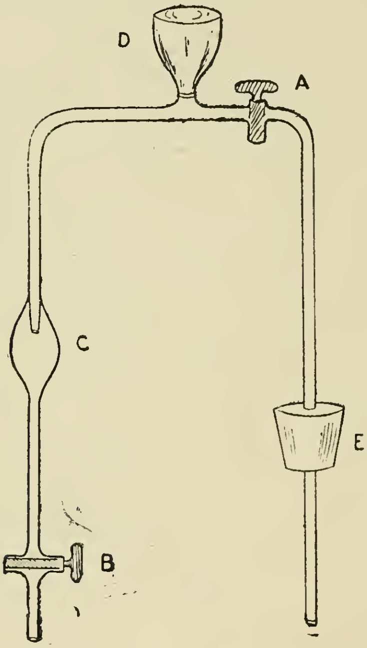
AN IMPROVED SYPHON.

By W. R. FORBES, B.Sc.

THE ordinary pipette is not very suitable for removing a quantity of supernatant liquid, especially if it is corrosive or poisonous.

The following apparatus much facilitates such operations, and is modified from a form described by Jacobson and Dinsmore (*Journ. Amer. Chem. Soc.*, 1910).

The apparatus is constructed of narrow bore glass tubing. Glass taps are placed at A and B. A side tube passes out to a rubber bulb at D. The first portion of the main stem ends in the middle of a bulb at C. This arrangement facilitates the syphoning. The rubber cork at E fits into the vessel to be emptied, and is provided with a groove to let in air.



To commence the syphon action close A, squeeze D, and then at once close B. When A is opened enough fluid will pass up the tube to commence the action.

Compounds of Alkaline and Alkaline Earth Salts with Organic Bases.—F. Calzolari.—The hydrated salts of the alkalis and alkaline earths readily yield compounds with hexamethylene tetramine, *e.g.*, $LiI.4H_2O.C_6H_{12}N_4$, $CaCl_2.10H_2O.2C_6H_{12}N_4$, and with caffeine, *e.g.*, $SrI_2.8H_2O.2C_8H_{10}N_4O_2$ and $NaClO_4.C_8H_{10}N_4O_2$. All the compounds are crystalline; some are stable in air, while others, such as those containing calcium chloride, are hygroscopic. The salts of potassium and ammonium are anhydrous. All the halogen salts of calcium and strontium contain 2 molecules of hexamethylene tetramine to 10 molecules of water.—*Atti della Reale Accademie dei Lincei*, xxi., No. 9.

THE
ALKALINE WATERS OF THE LONDON BASIN.*

By JOHN C. THRESH, M.D., D.Sc.,
Medical Officer of Health to the Essex County Council.

(Concluded from p. 27).

THE question of the sources of the sodium salts is a problem at which I have been working for the last twenty years, and which has caused me to try numberless experiments. Last year, when referring to Bischof's "Chemical and Physical Geology," I came across a passage stating that a calcareous water passing through certain silicates of alumina containing potash and soda became softened, and directly afterwards I heard of a German process of softening water by filtration through an artificial zeolite, and the revivifying of the zeolite by treating it with brine. I tried an experiment with powdered soda-glass, and I found that after soaking it in brine it had a slight softening effect. I next found that certain granites, without soaking in brine, had a marked softening effect, and that when this power was lost it could be restored by treatment with salt. The results obtained with Montsorrel granite follow. (I have arranged my experiments in series commencing with granite. Each experiment quoted is merely typical of many others, which, as they simply confirmed the results given, do not require further mention).

Experiment 1.—Half a kilogrm. of granite dust was packed in a percolator, and tap-water of 17° of hardness passed through. The hardness was not appreciably affected.

Experiment 2.—Packed about 1 kilogrm. of coarse granite dust in the percolator, and passed through water of 57° of hardness. The first 600 cc. which passed through was very turbid. I collected successive 200 cc. and estimated the hardness with the following results:—

4th 200 cc.	Hardness 19°
5th 200 cc.	Hardness 22½°
6th 200 cc.	Hardness 28°
7th 200 cc.	Hardness 30°

Water ceased to pass through.

Experiment 3.—I now added a little dilute hydrochloric acid to the granite, and stirred it up; water then passed slowly again. After the acidity had disappeared water with 40° hardness was passed through and came out with only 2°, but the hardness rapidly increased and the water passed through very slowly. I then mixed the granite dust with brine. After soaking a few hours the water passed fairly freely. Tap-water was passed through in successive half litres, and after the turbid point had been passed, to which I shall refer later, the hardness was estimated.

Original hardness of water 17°.

Hardness of successive half litres—5°, 0°, 0°, 0°, 0°, 1°, 2½°, 5°, 5°, 5°, 5°.

Water of 40° hardness was now substituted. Results with successive half litres—5°, 7°, 11°, 14°, 31°, 31°, 33°. The water ceased to pass, and the experiment was therefore stopped.

Experiment 4.—The granite was again soaked in brine, and it was found that the softening action was restored.

Different kinds of granite chippings and dust from the same quarries were tried with similar results, but the finer the material used the more marked was the reaction obtained. A whiter granite has been since tried, but its softening effect was found to be comparatively slight.

The turbidity to which I referred above is due to the formation of a "sol" or colloidal solution. It commences when nearly all the brine has passed through. The brine solution passes in a bright and colourless condition, and contains a good deal of lime and some magnesia in solution. Upon adding distilled water, until nearly all the brine has been washed through, the filtrate becomes very red and turbid. With the addition of more water the

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* A Paper read before the Essex Field Club March 30, 191 .

Table XI.—*Various Sources.*

	Coal measures.			Lincolnshire limestone.		Damaraland.	Denmark
	Rochdale.	Wolverhampton.	Oldham.	W. Peterboro.	Peterboro.	Micaceous Clay.	sands on chalk.
Calcium carbonate	6·8	38·0	7·5	20·2	2·8	44·5	13·5
Calcium sulphate	—	—	—	—	—	—	—
Calcium chloride	—	—	—	—	—	—	—
Magnesium carbonate ..	5·5	12·3	3·7	3·5	0·9	38·4	1·0
Magnesium sulphate . ..	—	—	—	—	—	—	—
Magnesium chloride . ..	—	—	—	—	—	—	—
Sodium carbonate	7·6	9·4	9·7	5·1	55·5	9·7	19·0
Sodium sulphate	5·9	79·9	6·5	10·3	13·2	9·1	0·3
Sodium chloride	3·0	17·5	2·0	8·9	65·5	5·3	5·1
Sodium nitrate	2·1	—	1·0	0·4	0·3	—	—
Potassium sulphate	—	—	—	—	4·6	—	—
Silica, &c...	0·7	0·9	1·1	2·5	1·2	3·0	1·1
Total	31·6	158·0	31·5	50·9	144·0	110·0	40·0
Hardness	14°	53°	12°	26°	4°	90°	15°

Table X.—*Various Sources.*

	Ashdown sands. Tunbridge Wells.	Skegness. W. greensand.	Kelso, N.B. phorphyrite.	N.R.S. Warrington.	Millstone grit.	
					Lancaster.	Hallam.
Ca carbonate	2·25	2·6	1·3	8·7	14·0	3·0
„ sulphate	—	—	—	—	—	1·0 ($BaCO_3$)
„ chloride	—	—	—	—	—	—
Mg carbonate	1·05	0·7	0·2	4·7	1·1	7·0
„ sulphate	—	—	—	—	—	—
„ chloride	—	—	—	—	—	—
Na carbonate	12·0	27·6	25·2	3·0	1·8	13·6
„ sulphate	5·2	4·0	2·0	3·1	2·8	—
„ chloride	5·0	4·0	3·4	3·0	3·8	10·5
„ nitrate	0·3	—	0·4	1·0	0·2	0·2
Silica, &c.	0·2	0·6	2·0	0·7	1·8	0·7
Total ..	26·0	39·5	34·5	24·2	25·5	36·0
Hardness ..	4°	3½°	2°	14°	16°	13°

Table XII.—*Comparison of Granite and Thanet sand.*

	Granite.	Thanet sand (24).	Thundersley sand.
Silica	67·16	86·55	83·74
Alumina ..	16·19	5·34	6 69
Ferric oxide	3·82	2·24	2·30
Lime	2·59	0·85	1·78
Magnesia ..	1·58	0·40	0·68
Potash ..	5·38	2·13	1·48
Soda	2·43	0·77	1·29
Water ..	1·02	1·90	2·04 (by diff.)
	100·17	100·18	100·0

Table XIII.

	Potassium and sodium expressed as chlorides.	Per cent soluble in dilute hydrochloric acid.	Silica soluble in Na_2CO_3 after acid treatment.	Insoluble residue.
Granite	11·5	10·2	3·4	86·4
Dagenham sand ..	3·9	8·6	4·9	86·5
Thundersley sand ..	4·7	7·8	2·3	89·9
Dedham sand	4·2	7·1	4·4	88·5
Dedham sand (coarse)	—	5·7	4·5	89·8
Dedham sand (clayey)	—	14·8	3·2	82·0
Thanet sand No. 24..	4·8	7·2	4·5	88·3
Thanet sand No. 140	4·5	6·8	6·0	87·2
Thanet sand No. 255	2·6	6·2	4·6	89·2

turbidity disappears, but if hard water in now passed through it comes out quite clear and softened.

About this time a boring was being made at Broomfield, near Chelmsford, and when the Thanet sand was reached I obtained some of it, but water would not pass through it when it was packed in a percolator. When shaken in water of 17° of hardness and filtered, the hardness of the water was reduced about 2°. Later, when pumping was in operation, a good deal of clean sand was brought up and deposited in the tank receiving the water. The following experiment was tried with this washed sand.

Experiment 5.—Packed about 200 grms. of the Broomfield sand in a cylinder and passed through it water of 57° hardness, collecting successive 100 cc. Results:—54°, 20°, 8°, 7°, 11°, 16°. The sand was now so compact that more water would not pass through it.

(*Note.*—Some expansion takes place in these experiments as on three occasions experiments were stopped on account of the glass cylinders becoming fractured).

Obviously the sand had a softening effect.

Experiment 6.—More of the sand was collected and washed with tap-water to remove the clayey matter, and when put in a percolator it reduced the tap-water 2° in hardness. It was then soaked in brine and washed with distilled water. About 200 grms. used.

Towards the end of the washing the liquid passing through the percolator became turbid and very similar to the turbid water which passed through the granite at the same stage. When this turbidity was disappearing water of 60° hardness was passed through and successive 100 cc. collected and examined. The results were 4°, 8½°, 9°, 10°, 11°, 10°, 8½°, 12°, 17°, 20°, 20°.

Experiment 7.—Took a kilogrm. of the washed sand, treated it with brine, and passed tap-water of 17° through in successive 200 cc. Results:—In the first five batches the hardness was 1° to 1·5°. Water of 60° was now passed through. The first 15 batches had a hardness of 1·5°, the 16th and 17th of 2°. As all the hard water was used up, tap-water was used again. With 14 successive 200 cc. the hardness increased to 11° and the 15th batch passed through unchanged. Altogether 7 litres of water were passed through.

Experiment 8.—The sand was again treated with brine and the tap-water passed through. The first 3 litres were completely softened, then the hardness increased gradually to 12° at the 14th litre. The 15th litre passed through unchanged.

The average hardness of the 14 litres was 5½°. One kilogrm. of sand therefore had removed lime (and magnesia) equivalent to 1·61 grms. of calcium carbonate. As will be seen later, the sand can remove more than this if a harder water is passed through.

Experiment 9.—The sand was next treated with acid, when it was found capable of removing more lime salt, but not nearly so much as when treated with brine. The acid and brine treatments were repeated and the sand again salted and its lime removing power tested. The total lime and magnesia removed corresponded to 2·09 grms. of calcium carbonate, indicating that the treatment which the sand had undergone had, if anything, increased its activity.

Experiment 10.—At the end of the above experiment more water of 57° was passed through, with the following extraordinary result. Successive half litres:—

Hardness 70°, 70°, 90°.
Showing that the sand was now giving up lime salts.

Unfortunately at this point my experiments had to be abandoned for a time, and the sand was inadvertently thrown away. Attempts to get a similar result again have so far failed.

Experiment 11.—From Heybridge, near Maldon, I was able to obtain some sand which was brought up by the pumps employed to try and clear a bored well. This sand allowed water to pass through freely, and did not require washing. Through about half a kilogrm., a water of 20° of hardness was passed, and the successive 100 cc.'s collected gave 2°, 2°, 2°, 2°, 2°, 4½°, 8°, 16°, 20° respectively.

Similar results were obtained with a sand from the new boring at Galleywood, near Chelmsford, but the sand had to be washed repeatedly with distilled water to remove the clayey matter, before it would permit of water being filtered through it.

Thanet sand from several other places has been examined, and in all cases it has exhibited the same power of softening water, to some extent after washing, and to a marked extent after salting. Some sand obtained for me from the outcrop close to Erith, by Mr. Barrow of the Geological Survey, was found to contain a considerable quantity of lime salts, chiefly sulphate, and when water was passed through it, it increased the hardness enormously. After washing and salting it acted like the sand from deeper sources.

Experiment 12.—Thanet sand from a boring at Dedham, North Essex, contained much coarser quartz granules, but it would not let water pass through until the clayey matter had been washed way. When washed and salted it proved as active as any other sand examined. The amount of lime and magnesia removed corresponded to about 2 grms. per kilogrm. of the sand.

Experiment 13.—Through some salted sand from Thundersley, a mixture of sea-water and Halstead chalk water was passed. The calcium and magnesium in the mixed water before and after treatment were estimated with the following results:—

	Calcium (mgrms.).	Magnesium (mgrms.).	Hardness per 100 cc.
Untreated ..	9·75	2·8	33
Treated ..	1·5	0·1	5

These results indicate that magnesia salts are more readily removed than calcium salts.

Experiment 14.—Some natural water containing both salts being on hand a quantity was passed through the same filter with the following results:—

	Calcium.	Magnesium.	Hardness.
Untreated ..	6·75	3·65	34
Treated ..	4·4	0·75	14

Again showing that a larger proportion of the magnesia salts were removed. This, however, does not appear always to be the case.

Recently I obtained a good quantity of Thanet sand from Dagenham (boring of the South Essex Water Co.) with which I made the following experiments:—

Experiment 15.—Washed about 20 grms. of the original sand with distilled water until the hardness was only 4°; then agitated it with 100 cc. of a water of 44°, and syphoned off the water. The hardness had been reduced to 20°. Shaken with another 100 cc. of the hard water the hardness was reduced to 28°.

Experiment 16.—A quantity of the sand was washed with tap-water, then mixed with brine about the strength of sea-water, and left exposed to the air for two or three days. The sand was then washed with distilled water, dried, and half a kilogrm. placed in percolator and water of 130° hardness passed through. Successive 100 cc. were collected. The hardness was decreased to 3°, but rose to 130° at the 10th 100 cc. The amount of lime and magnesia removed calculated as calcium carbonate was 0·744 grms. or 1·5 grms. per kilo. of sand, or 0·15 per cent.

The sand before the hard water was passed through yielded 4·83 per cent of the chlorides of sodium and potassium, and after the hard water had been passed through it yielded 4·61 per cent, a loss of 0·21 per cent. The amount of mixed chlorides represented by the 0·15 per cent of lime salts removed is 0·208 per cent.

It is obvious, therefore, that only a small fraction of the sodium and potassium salts present in the sand take part in this reaction.

Experiment 17.—The half kilogrm. of sand used in Experiment 16 was now salted with saturated brine, washed, &c. This time the washing water did not become turbid, but merely acquired a brown colour. Some calcium chloride was added to a very hard water and passed through the sand until no effect was produced on the hardness. Analyses gave the following results:—

	Calcium.	Magnesium.	Hardness.
Untreated	48·0	2·4	126 per 100,000 parts.
Treated..	19·1	1·4	52 ,,

As the amount of water passed through the sand was 2000 cc., this half kilogrm. had removed 28·9 mgrms. calcium and 1·0 mgrm. magnesium per 100 cc., equivalent to 1·52 grms. of calcium carbonate from the whole of the two litres of water, or 3·04 grms. per kilogrm. of sand. Soaking with strong brine therefore had rendered the sand more efficient than soakage in brine of the strength of the sea-water.

Experiment 18.—The sand used in Experiment 17 was now washed with slightly dilute hydrochloric acid, then with distilled water, and again salted. Hard water was passed through until it ceased to be affected. The reduction in hardness corresponded to the removal of 1·44 grms. of calcium carbonate or 2·88 grms. per kilogrm. of sand. The untreated sand only removed 3·04 grms., so that the matter removed by dilute acid had no appreciable effect upon the softening.

Experiment 19.—The sand used above was soaked in strong hydrochloric acid, then washed, salted, and washed free from salt. Upon passing hard water through it, the softening effect was very slight. The strong acid appeared to have removed the constituent to which the softening is due. The experiment has not been repeated or the result confirmed by using sand from other sources.

Experiment 20.—Some of the sand from Dagenham was lixiviated and divided into two portions, one the comparatively coarse sand and the other the finer portion which would just permit of percolation of water through it. Equal quantities were treated with brine, washed with distilled water, and then treated with successive 200 cc. of hard water. The results were as under:—

Calcium and Magnesium Removed per Kilogrm. of Sand.

Coarse sand .. .. = 3·00 grms. as calcium carbonate
Fine sand .. .. .. = 2·74 ,,

Experiment 21.—Half a kilogrm. of Thanet sand unwashed from Galleywood boring softened 600 cc. of water from 16° to 4°. It then became so compact that more water could not be passed through it. After washing and salting 1 kilogrm. removed the equivalent of 4·08 grms. of calcium carbonate.

So far the results of my experiments indicate :—

1. That the Thanet sand from beneath the London clay possesses the power of softening hard water by substituting sodium (and possibly potassium) salts for those of calcium and magnesium.
2. That the constituent to which this softening effect is due is not removed by treatment of the sand with dilute acid, but appears to be removed by treatment with strong hydrochloric acid.
3. That this property of softening water belongs both to the clayey and sandy matters.
4. That the softening effect is greatly increased by treating the sand with brine.
5. That the amount of alkali removable by this softening effect is only a small proportion of the total alkalis contained in the sand.
6. That (within certain limits) a sand which has ceased to soften a water of a certain degree of hardness will exert a softening effect upon a water of a greater degree of hardness, and will exert a hardening effect upon a water of a softer character.

A few analyses of Thanet sands have been made in my laboratories, and the results obtained are compared with an analysis of a sample of granite dust supplied to me, together with the analysis by Messrs. Lavender and Bateman.

A number of less complete analyses are given in Table XIII.

I am not competent to compare the mineralogical constituents of granite with those of the Thanet sands, and at present I merely direct attention to the fact that they have certain properties in common, which are probably due to a common constituent. Possibly some of the geologists present may be able to suggest what is the constituent. A sample of felspar (albite) has given disappointing results, and experiments have been commenced with mica. Whatever the constituent, it is certain that the alkaline carbonates and sulphates, found in the waters derived from the chalk and Thanet sands in the London Basin, are obtained from the sands by substitution of sodium for calcium and magnesium in the sulphates and carbonates of calcium and magnesium present in the water before it commences to percolate through the sands. The analyses submitted show that every sample of such water can be imitated by passing a chalk water either without admixture, or with an admixture of a small proportion of sea-water, through Thanet sand, which has retained its softening powers. If we assume, and such certainly appears to be the case, that the Thanet sands were deposited at the bottom of the sea, it is obvious that they would acquire the power to substitute sodium and potassium for the calcium and magnesium in any chalk water with which they came in contact afterwards, and thus soften the water. If any salt remained in the sand this would be taken up by the water and the chlorides would be proportionately increased. In the districts in Essex and elsewhere where these alkaline waters are found there are localities where the amount of salt in the water is excessive, and most of these, but not all, are near the coast or tidal rivers, and the question may arise whether the salt now found in such waters is derived from prior evaporation of the water from the original sea or from sea-water getting into the chalk at various places at the present time. My impression is that it is due to an actual admixture of sea-water getting into the chalk and sands around the coast and in the Thames and Stour estuaries, and that this tidal water gets more and more diluted with true chalk water the further it travels from these points. Thus, in the Tendring Hundred most of the waters contain a comparatively large amount of salt, and further away from this district the salt decreases. Towards the south of the county the chlorides are comparatively low, due to more copious admixture with water from the Hertfordshire chalk. I might mention that in all these areas the water derived from the chalk is practically identical with that derived from the Thanet sands; where there is any difference the salinity increases with the depth of the boring, *e.g.*, Layer Marney and Walton-on-the-Naze. At Chelmsford and Braintree I have been able to get waters from the two sources, and found them practically identical. At Ingatestone there was no water whatever in the Thanet sands, but the limited amount obtained from the chalk was a typical alkaline water. These waters contain no free carbonic acid, therefore whatever distance they may travel in the chalk no solution of the chalk occurs; hence, however, much of the water is pumped, the fissures do not enlarge and do not yield water more freely.

Engineers insist in continuing the borings made in Central Essex into the chalk, but there is no evidence of more water being obtained than would have been the case had the boring ended in the sands, whereas there is evidence that some of the sand water is lost. Thus at Writtle a certain amount of water was obtained from the Thanet sands, and when the boring pierced the chalk most of the water disappeared and the chalk had to be plugged to restore the supply. At Tollesbury, where a deep bore has just been made, the water level fell some 15 feet when the chalk was pierced, a sure indication of a loss of water. Experience elsewhere, which I am not at liberty to mention specifically, proves that the chalk absorbs rather than yields water in those areas where it is covered with a large thickness of London clay. In any case the waters have a common origin, and if the chlorides are derived from the sea they should be accompanied by bromides and the amount should be approximately the same in proportion to the chlorides as in sea-water. In sea-water, as before stated, I find that there is 1 part of bromine to from 274 to 378 parts of chlorine, and that in the alkaline waters the proportions vary, there being for 1 part of bromine from 225 to 442 parts of chlorine. Considering the difficulty of making anything like an accurate estimation of the bromine these figures are sufficiently close to indicate some relationship. The difficulty of making an exact determination led me to abandon temporarily further determinations until I had worked out a process which could be relied upon. This has proved far more difficult than I had anticipated, and I am not yet so certain of my results as to feel justified in giving others. I suspect that in sea-water there are other compounds of bromine besides bromides, and that there are traces of iodides and iodates or both. This, however, is a chemical question upon which I shall have something to say elsewhere.

Possibly it may be asked whether the softening effect of the Thanet sands is sufficient to account for the removal of nearly all the calcium and magnesium salts from the large volume of water taken from the sands. I think there can be no doubt about the answer. Taking Essex alone the area under which Thanet sands exist must be about 666,000 acres, and assuming the average thickness to be 12 feet (a very low estimate), and that each cubic yard contains 28 gallons of water, the water held in the whole of the sand will be about 360,000,000,000 gallons. But my experiments indicate that each cubic yard would completely soften 10 cubic yards of a chalk water 30° of hardness. The amount of water the Thanet sands are capable of softening on this basis is therefore 21,600,000,000,000 gallons.

Essex (Administrative County) has a population of over 1 million, and if liberally supplied with water it would use 30 million gallons per day, or 10,950 million gallons per year. The amount of Thanet sand under the county would completely soften the whole supply on the above basis for 2000 years, and partially soften for a much longer period. I have recently obtained sandy matter from the beds resting upon the Thanet sand to ascertain if they have similar properties. Mr. Whitaker recognised this sand as being from the Blackheath beds. The sand contained much clayey matter, but it undoubtedly had the same action as the sand resting upon the chalk. The mineral or minerals which possess the power of softening water are probably very widely diffused, and I should like if possible to definitely identify them.

My object in giving this paper to the Field Club is to get in touch with members who may be interested in the subject, and who may be able to assist me with advice, or who may be inclined to pursue some of the lines of investigation indicated. My time for such work is not only limited, but scrappy, and on occasions the work has had to be abandoned for a long time, and then taken up again as time permitted. The subject is of more than local interest, as these alkaline waters appear to occur in the most diverse formations from the Volcanic to the Upper Eocene, and in all parts of the world, and I hope that you may agree that its importance is sufficient justification for my having occupied so much of your time.

MARKING PORCELAIN AND SILICA CRUCIBLES, &c.

In the analytical laboratory there often is occasion to put permanent distinguishing marks upon crucibles, &c., which will stand ignition and mild treatment with acids and alkalis. The blue pencil or the brush and china paints which are frequently used for this purpose, the markings being burned in, often give results so crude as to be quite unsatisfactory, especially for articles that are before one's eyes daily for years. Moreover, the blue pencil marks and many china colours lack permanence, and when applied to silica wares do not adhere satisfactorily. Mr. P. A. Yoder, Assistant Chemist, Plant Physiological Laboratory, U.S. Bureau of Chemistry, has worked out two methods, one for marking with platinum and the other for the application of china paints, both by the use of rubber type. A description of these methods is given in a recently issued circular of the U.S. Bureau of Chemistry.

The Platinum Process.

The crucibles are cleaned by heating for half an-hour with nitric acid, one part concentrated acid to one part of water. A sizing is prepared consisting of a hot 5 per cent solution of gelatin. The parts of the crucibles to be marked are dipped into this sizing, and set aside to drain and dry. When the gelatin is dry, the desired number is stamped on with a solution of platinic chloride containing 12 to 15 per cent of platinum; *i.e.*, about 32 to 40 per cent of the hydrated crystallised chloroplatinic acid. The pad holding the solution may be made of six or eight folds of smooth linen or muslin, and need not be much larger than the type used. This pad is nearly saturated with a few drops of the platinic chloride solution. Too much of the solution causes blurring, and too little of it or too diluted a solution results in dim numbers. After the numbers are dry the crucibles are gently heated until the platinum is reduced, and the gelatin burned off. This is most conveniently accomplished in a muffle. Finally, the numbers are heated for one-half minute in the flame of the blast-lamp—*i.e.*, for one-half minute from the time it attains the temperature of the flame.

If the wares are cleaned and fired as directed, the markings adhere well. The figures become more prominent if burnished by use of a china painter's burnishing stone, if available, or of seashore sand, or less advantageously of a silica soap. The deposit is resistant to single acids, but not to alkalis. In some experiments library paste was substituted with good results for the gelatin sizing. Gold and mixtures of gold and platinum solutions may be applied similarly, but there is more danger of volatilising the gold chloride before reduction takes place, and thereby causing a spreading of the deposit. The resulting figures also are less conspicuous than when platinum is used. This method of getting the deposit of platinum or gold may possibly find use also in decorating chinaware. If the solution is applied with a brush, a quill, or a glass stylus, it may be more dilute. The same method applied to silica wares also gives very satisfactory results.

Application of China Colours by Use of Rubber Stamps.

Paints mixed in oil are not satisfactory for use with rubber stamps, because the type leaves on the porcelain a rim of thickened paint while the main surface of contact is relatively bare. The method finally adopted is to stamp the wares to be marked with a sizing or varnish similar to that which painters use for applying gold leaf. "Fat oil"—*i.e.*, partly oxidised linseed-oil, supplied by paint dealers—proved very satisfactory for this purpose. While this sizing is still sticky, the dry pigment is dusted on with a camel's hair-brush. After the varnish has set set the excess of pigment is wiped off, and the crucible is fired at a strong red heat, preferably in a muffle. The "fat oil" dries slowly. This is an advantage because then some time may be allowed between its application and the dusting on of the pigment for the irregular layer on the porcelain to draw out by surface tension into a smoother one. Standing over-night at room temperature, or for one hour in a drying oven at 100° C., suffices for the varnish to set. The pad used for "inking" the type may consist of several thicknesses of linen cloth, and is nearly saturated with this varnish. Too much varnish on the pad must be avoided, as it results in figures with ragged outlines. This varnish may readily be cleaned from the rubber type before it has set by use of a 10 per cent alcoholic solution of caustic potash applied with a small bristle brush.

Colour Tests.

Seeking a prominent colour and one resistant to both acids and alkalis, a series of tests was made with samples of overglaze blues, blacks, and reds supplied by a dealer and one blue prepared by the writer. These were stamped on to porcelain crucibles as above described. The heat used in firing was a red heat slightly lower than that at which the coloured figures on the white background disappeared (the radiation plus reflection from a coloured surface equalling that from a white surface). In one test they were brought from a dull red to the above temperature during the course of one hour and then cooled. This sufficed to make the blacks and the reds resistant to nitric acid (35 per cent) and to sodium hydroxide solution (10 per cent), but the blues were appreciably soluble in the acid. To make the blues resistant, they had to be fired to a higher temperature or held at the above maximum temperature for about an hour. To test the permanence of the markings, the acid and the alkali were each applied five minutes cold, followed by five minutes at a boiling temperature. Of the seven blacks tried, two—viz., a lettering black and a blue-black—gave especially good effects in that they yielded a very strong black. Of the same samples when applied to silica dishes and fired as indicated, both the blacks and the reds were again resistant to both nitric acid and alkali, but the blues, even when fired more strongly, came off very readily in nitric acid.

In these tests an electric muffle was used. In heating porcelain crucibles to a high temperature in gas muffles in which the muffle chambers were not thoroughly sealed off from the gas chambers, and occasionally also in the electric muffle, a brown stain developed on the porcelain. This could readily be removed by heating the crucible half a minute in the blast-flame, most conveniently in a suitable chimney.

In applying the rubber stamp to the crucibles it is difficult to avoid a sliding motion that blurs the imprint. This may be prevented by using a suitable guide or a steadying support. Mr. Yoder found it convenient to rest both the inverted crucible and the type holder on a smooth surface while making the impression. In numbering crucibles, &c., it is often advantageous to have the number on three sides so as to make it visible, no matter which way the crucible is turned.—*Chemical Engineer*, xv., No. 3.

A SUGGESTION FOR MINERAL NOMENCLATURE.*

By HENRY S. WASHINGTON.

Introduction.

THAT the science of mineralogy may be regarded as a branch of descriptive chemistry (but one which deals only with substances occurring in nature) is recognised in the prevalent mineral classifications, where the chemical composition is the primary and most important factor. The character of the negative (acidic) ion controls for the formation of the largest classes and sub-classes may be based on the character of the positive (basic) ion, in some cases preceded by separation into anhydrous and hydrated compounds. In all these sub-classes minerals which belong to the same acidic type are placed together. The ultimate smallest groups, which bring together minerals regarded as most closely related, are based on similarity in crystal form, dependent on isomorphous replacement, either entire or partial, and either in the negative or the positive portion of the molecule; while, again, dissimilarity in crystal form due to polymorphism of substances with the same empirical chemical composition serves to distinguish between groups chemically alike.

The crystal form, therefore, is a necessary diagnostic, as important for the formulation of our idea of any mineral as its chemical composition. As Miers expresses it ("Mineralogy," London, 1902, p. 2), for the definition of minerals "we are forced to employ at least two properties, namely, the chemical composition and the crystalline form; these two, when completely known, are necessary and sufficient for the definition and determination of any mineral." The less important characters, such as colour, structure, habit, state of aggregation, and minor details of chemical composition, are (or should be) used only to distinguish very subordinate (varietal) divisions, and, as Miers justly says, far too much importance has been generally assigned to them in naming minerals. Many cases will also occur to every mineralogist of minerals which stand alone and can only be referred to indefinite positions in the classes, dependent on the general character of the negative ion; that is, they show no intimate relations with other minerals through both their chemical and crystallographic characters and constitute the sole representatives of potential groups, which thus correspond to the monotypic genera of botany and zoology.

In this necessary utilisation of both chemical composition and crystallographic characters, the definition and classification of minerals differ from, and may justly be considered as in advance of, the classification and definitions of descriptive chemistry, which only take cognisance of the ultimate chemical composition of the substance as revealed by analysis, and its molecular structure as shown by its reactions, replacements, molecular weight, &c. To the chemist, $CaCO_3$ is only calcium carbonate, whether its crystal form is trigonal or orthorhombic, with correlated differences in specific gravity, optic characters, &c. To the mineralogist these two forms are different minerals, though the chemical composition is expressed by the same empirical formula.

This recognition of polymorphous or physically isomeric forms of the same empirical molecule as different substances and the converse relationship between substances of closely similar crystal form and of the same chemical type, though differing in composition through isomorphous replacement, is but a logical following out of the teachings of physical chemistry. It is an extension of the definition of "substance" to include, in addition to the chemical composition, the relations of the physical and chemical characters of matter to the conditions of equilibrium which control crystallisation. That the recognition of the essential difference between substances (in this sense) with the same ultimate chemical composition is valid and necessary is shown by consideration of such cases as diamond and graphite (C), pyrite and marcasite (FeS_2), or calcite and aragonite ($CaCO_3$). In these the differences in the physical characters, and to no less an extent in many of the chemical characters, as resistance to reagents, of the members of each pair are so great that they must be regarded as distinct substances. This would be true even from the purely chemical point of view, since the physical differences, especially those like specific gravity and specific heat, indicate differences in the molecular weight and very probably in molecular structure.

It may be noted here that among minerals there are few ascertained cases of chemical isomerism, in which the distinct physical and chemical characters, due to profound and persistent differences in the molecular structure, persist after the substance has been changed into an amorphous state, as by fusion or solution, and then re-crystallised (Groth, "Introduction to Chemical Crystallography," New York, 1906, p. 3). Numerous illustrations of this are furnished by organic chemistry, the most classical being that of urea and ammonium isocyanate. Among minerals it is difficult to prove the existence of such cases, though they unquestionably occur, and Groth ("Chemische Krystallographie," Leipzig, Pt. I., 1906, p. 155, and Pt. II., 1908, p. 258) regards pyrite and marcasite, and cyanite, sillimanite, and andalusite, respectively, as cases in point. Whether there is any essential difference between physical and chemical isomerism may perhaps be doubted, but further discussion of this topic is uncalled for here.

In spite of this advanced state of the classification of mineralogy, the nomenclature is in much the same condition as in the time of Pliny, when minerals were named after their qualities, localities, or uses, with the systematic termination *-ites* or *-itis* (modern *-ite*), the only innovations being the introduction of names after persons and certain other arbitrary terminations. Despite attempts to introduce binomial names, analogous to those of botany and zoology, or those based on chemical characters, systematic mineralogy has adhered closely to the nomenclature of the first century A.D. (*cf.*, Dana, "System Mineralogy," 1892, p. xl.).

As a consequence, mineral nomenclature, like that of the older rock classifications, is unable to express the facts of classification. Roots derived from names of places or persons can convey in themselves absolutely no idea of the mineralogical characters, and even those derived from chemical or physical characters are applicable to many different minerals. Thus, cuprite applies equally well to CuO as Cu_2O, and octahedrite would be an appropriate name for magnetite, franklinite, or fluorite. All such name roots are purely arbitrary in their mnemonic connotations, but at the same time, by long association, a large proportion of mineral name roots convey very definite ideas of the mineral and chemical characters.

Again, with the uniform and monotonous general use of a single termination (-ite), and the arbitrary and unsystematic employment of others, the characters and relations of minerals, and even of mineral groups, are concealed. No distinction is evident from the name between a rare or uncharacteristic varietal form of a certain mineral (as hiddenite or sagenite), and a large mineral group which may include many distinct minerals (as zeolite or chlorite). In the case of a few of the commonest and largest groups of related minerals we have names, fortunately distinctive because of their terminations, which may be applied to the group as a whole, as spinel, felspar, garnet, pyroxene, amphibole, mica; and the general usefulness and common application of these is sufficient evidence of the value of such group names. In other cases the difficulty of expressing relationships is got round and the need supplied by the word "group" after the name of a typical representative; as the pyrite, calcite, aragonite, olivine, and apatite groups. In all these group names the underlying idea which connects the members is adherence to a certain type of chemical formula, with isomorphous replacement,

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* From *American Journal of Science*, xxxiii., No. 194.

and, of equal importance, close similarity in the crystal form as shown by the system, axial relations, and often cleavage. As regards the crystal system, in the largest groups this similarity need not amount to identity, as in the felspars, pyroxenes, and amphiboles, but in general the idea of a mineral group implies identity of crystal system modified only in its details by the slight morphotropic changes consequent on isomorphous replacement.

It will thus be seen that a mineral nomenclature should be able to express in the name a fairly definite idea of the chemical composition and type of compound, as well as the crystal system, and at the same time indicate the relations to other minerals, and especially the membership of a mineral in its particular "group." It is the object of this paper to lay stress on the importance of the recognition in mineralogical classification of this idea of mineral groups, distinguished by close similarity in chemical composition and crystal form, and made up of distinct mineral members, and to suggest a nomenclature which will express these relations, based on the general principles of chemical nomenclature, but providing also for the recognition of the crystal form as an element of the classification.

(To be continued)

SILOXIDE.

"Siloxide" is a name which has been given to products prepared by fusing pure anhydrous silica with oxides of elements of the silicon-carbon group, as titanium dioxide or zirconium oxide. The new glass is said to be formed by the solution of these refractory oxides of an acid character in silicic acid, and it is stated to be more easily worked than pure quartz glass—in fact, it can be worked by the ordinary methods employed in glass manufacture (see French Patent 432,786, July 31st, 1911, of Wolf-Burckhardt and Borchers). Z-siloxide, or zirconium glass, and T-siloxide, or titanium glass, are now being manufactured at Frankfurt a/M, Germany.

While Z-siloxide and T siloxide are said to lack the silky lustre of quartz glass ("vitreosil"), yet it is stated (Thomas, *Chem. Ztg.*, 1912, xxxvi., 25) that they possess distinct advantages over the latter with respect to strength, resistance to devitrification, and resistance to the action of alkalis.

The best Z-siloxide with respect to strength is said to contain 1 per cent of zirconia, while that containing 0·5 per cent has the most satisfactory thermal properties. It is said that zirconium glass has a softening point not much different from that of quartz glass, but that it resists deformation better at high temperatures because of its greater viscosity. The manufacturers state that zirconium glass crucibles are far superior to those made of quartz material in their ability to resist the action of "oxide-bearing metals" during smelting operations; that zirconium glass can be used five or six times; and that it displays only in a very small degree the disagreeable property, inseparable from quartz material, of devitrifying at temperatures exceeding 1300° C. It is supplied in the form of tubes, slabs, concentrating vessels, crucibles, flasks, boxes, muffles, arched-tubes, balls, calottes, &c.

The titanium glasses (0·1 to 2 per cent of titanium) are said to have a somewhat lower resistance to compression than quartz glass, but to resist transverse fracture better than the latter. The T-siloxide now being marketed is said to be superior to even Z-siloxide with respect to thermal properties—to be more satisfactory when temperatures up to 1500° C. are to be used. Its properties are said to be otherwise the same as those of Z-siloxide. While it is stated by the manufacturers that zirconium glass may be had either transparent or opaque, no information on this point as to titanium glass was secured.—*Journal of Industrial and Engineering Chemistry*, iv., No. 4.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The Opening Meeting will be held at Washington, D.C., U.S.A., on September 4th, 1912; the other meetings, business and scientific, in New York, beginning Friday, September 6th, and ending Friday, September 13th, 1912.

Information for Visiting Members.

The Chemists' Club of New York City has generously placed at the disposal of visiting members to the Congress its facilities as a Bureau of Information, and has also consented to act as a local committee to minister to the comfort of visiting members arriving from abroad at the port of New York.

For members who are not citizens or residents of the United States, the examination of baggage and other personal effects is not connected with any great delay if the United States Government blanks or forms, which are made accessible to all passengers on all steamers, be properly filled out and left with the purser as directed. Foreigners touring the United States are permitted to bring into this country all such personal effects or professional equipment as are needful, but articles intended for barter, sale, or gift are subject to duty, as set forth on the United States Government blanks or forms above referred to.

The ss. *Cleveland* and *St. Louis* will be met on their arrival at the piers in Hoboken and New York respectively by committees from the Chemists' Club, who will gladly assist members of the Congress in all details of passing through the Customs House, of despatching their baggage to their hotels or their places of residence in the city, and of reaching their places of residence themselves, with as little delay or loss of time as possible.

Members arriving by steamers other than the *Cleveland* or *St. Louis* will be met by members of the Chemists' Club, if they will give timely advance notice of the steamer by which they are travelling, to the reception committee of the Chemists' Club, at 52, East 41st Street, New York City.

The Chemists' Club will also gladly arrange for reservations at the hotels upon request by foreign members; in making use of this offer on the part of the Chemists' Club, members of the Congress are requested to be as precise in the description of the accommodations that they wish as is possible; the Chemists' Club will thereupon endeavour to obtain accommodations most nearly approaching the requirements set forth by the member of the Congress, but the Chemists' Club is in no wise responsible for the selection made, merely acting as intermediary and to the best of its ability.

Telephone Service.

Members who desire telephone information about or from the Congress can receive the same on and after August 19th by calling the following telephone number:—If the member desires to speak in English call "8920 Morningside"; if in French call telephone "7999 Morningside"; if in German call "7895 Morningside"; and if in Italian call "8125 Morningside." Those answering the last three telephone numbers on behalf of the Congress will speak the language above indicated; the first telephone call given, namely, "8920 Morningside," is for English conversation only with the Congress.

Members who may wish to call the Chemists' Club on the telephone can do so by asking for "1916 Murray Hill."

Advance Registration.

Registration for members and for accompanying ladies, between August 26th and September 2nd, both inclusive, can be effected in person or by mail at the Chemists' Club, 52, East 41st Street, New York City, in the same manner as provided for at Columbia University on and after September 3rd, and as described in Announcement No. 3,

p. 92, but when mailing the registration coupon for *advance registration* it should be addressed to—Eighth International Congress of Applied Chemistry, Registration Bureau, Chemists' Club, 52, East 41st Street, New York City.

This arrangement will *not* be effective on September 3rd, 1912; on that date and thereafter registration can be effected at Columbia University *only*.

All members are requested *not* to register by mail until they are certain of their New York address during the Congress.

It will greatly facilitate matters if correct advance registration be effected by as many members as possible.

Change of Address during the New York Stay.

All members changing their addresses during their stay in New York are requested to notify the Registration Bureau of this change in writing at their earliest opportunity; otherwise needless confusion and delay may result which may be unpleasant for all concerned.

Members coming to New York from any point in the United States or Canada can, in most cases, take advantage of summer excursion rates, reaching New York viâ Washington, with a stop-over privilege there by applying to their local ticket agents. These rates are so nearly the same as those obtainable on the certificate plan that the gain, if any in the latter, does not make up for the restrictions and inconveniences the latter involves.

Visiting American members are requested to notify the secretary by postal card of their intention of attending the Congress, in order that preparations, which must be made in advance, may be on a proper scale; prompt attention hereto will be appreciated.—Respectfully,

EIGHTH INTERNATIONAL CONGRESS
OF APPLIED CHEMISTRY,
William H. Nichols, President.
Edward W. Morley, Hon. President.
Bernhard C. Hesse, Secretary.

25, Broad Street, New York City,
June 27th, 1912.

(To be continued).

NOTICES OF BOOKS.

The Analyst's Laboratory Companion. By Alfred E. Johnson, B.Sc. (Lond.), F.I.C., A.R.C.Sc.I. Fourth Edition. London: J. and A. Churchill. 1912.

This very useful book of tables and laboratory hints has reached its fourth edition, in which all the gravimetric and volumetric factors have been recalculated on the basis of the atomic weights adopted by the International Committee for 1912. Some parts of the guide have been very considerably enlarged; thus in the section on water and sewage, the account of the determination of nitrates by the phenol disulphonic acid method is far fuller than it was before, and some other important processes are described in outline. The new tables include those of the melting-points of metals, the coefficients of the absorption of gases in water, the amounts of dissolved oxygen in distilled water, &c., and the chief provisions of the recently issued Draft of the Public Health (Milk and Cream) Regulations, 1912, are included.

Bleaching and Dyeing of Vegetable Fibrous Materials. By Julius Hübner, M.Sc.Tech. (Manchester), F.I.C. London: Constable and Co., Ltd. 1912.

There are two points about this book which give it a special significance, quite apart from its value as a contribution to our knowledge of an important branch of technology. In the first place, although coming from the pen of a University professor, it is, above all, thoroughly practical, the needs of the technologist being the dominant consideration throughout; and, secondly, the author has recognised that it is not the part of the technical instructor to put the elements of science before the student, but to initiate him into the application of the principles that he has learnt in his school days, or in his preliminary course of work. Hence the book contains no attempt to give the student a working acquaintance with chemistry in a few lines, but he is supposed to come to his technical work properly equipped. All practicable methods of bleaching and dyeing are, it is claimed, at any rate briefly treated, different methods of applying the same dyestuff being frequently described. The method of classification adopted is such as would be found most convenient by the technologist, and ignores purely scientific considerations, and no attempt is made to discuss theory. On the other hand, such practical details as current market prices are frequently given. The diagrams are excellent. There are no valueless pictures of the external appearance of complicated machinery, but many diagrammatic sections, and these are sometimes printed in two colours in such a way as to make it quite easy to follow the actual passage of the material to be dyed through the machine, while information as to dimensions, speeds, working capacity, power, &c., is given whenever possible. The preface to the book is contributed by Prof. Raphael Meldola.

Lectures on Cellulose. By C. F. Cross. London: The Institute of Chemistry. 1912.

The two lectures contained in this book were delivered before the Institute of Chemistry at University College, London, in January and February of this year. The lecturer's aim was to give young chemists and advanced students an insight into the nature of the scientific work actually carried out in professional practice, and he put some rather novel points of view before his audience. In the first lecture he gave a sketch of the importance of the cellulose industry, and described normal processes of preparation, concluding with a special study of the chlorination process. The second lecture dealt with some types of carbohydrate colloids, and discussed some economic aspects of the cellulose industry.

An Investigation of the Coals of Canada. By J. B. Porter, E.M., D.Sc., and R. J. Durley, Ma.E. Assisted by Theophile C. Denis, B.Sc., Edgar Stansfield, M.Sc., and a Staff of Special Assistants. Volume I. Ottawa: Government Printing Bureau. 1912. (1 dol.).

This volume contains part of a detailed account of the economical investigation of the coals of Canada, begun in the autumn of 1906 at the McGill University, Montreal, and recently brought to a conclusion. The report of the investigation is to be issued in six volumes, of which this is the first. A large staff was employed under Dr. J. B. Porter, who was responsible for the organisation and general direction of the investigation, and who explains in the introduction to this volume the scope of the work and the main features of each division of it. A general survey of the coal fields of Canada is contributed by Mr. T. C. Denis, and methods of collecting samples, the process of coal washing, and the manufacture and testing of coke are exhaustively discussed. The book is excellently indexed, and is provided with many drawings of machinery and general illustrations of the plant of important coal mines.

Die Entdeckung des Radiums. ("The Discovery of Radium"). By Mdme. P. Curie. Authorised German Edition. Leipzig: Akademische Verlagsgesellschaft. 1912.

The speech which is reproduced in this booklet was made by Mdme. Curie in December, 1911, at Stockholm, when the Nobel Prize was conferred upon her. In the course of the speech she gave a short account of her work on the measurement of the radio-activity of uranium minerals and the separation of radium, and she discussed its properties and its position in the Periodic Table, as well as Rutherford and Soddy's theory of atomic disintegration. The illustrations given in the book include one of the French Radium Factory at Nogent-sur-Marne, and a very interesting photograph of the laboratory in which the discovery of radium was made, and which is described as a "shed with a faulty glass roof, and destitute of any convenience for chemical work."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

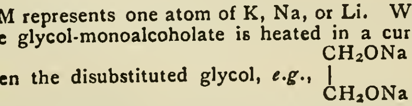
Note.—All degrees of temperaturs are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 23, June 3, 1912.

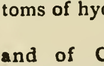
Detection and Determination of Fluorine in Minerals, Waters, and Living Tissues.—Armand Gautier and Paul Clausmann.—When very small quantities of fluorine have to be determined in an aqueous liquid, such as a potable or mineral water, the solution is first made slightly alkaline, crystallised sodium sulphate is added, and then a slight excess of barium chloride. The liquid is evaporated to dryness, the residue is taken up in the cold with just enough water to dissolve the soluble salts, an equal volume of alcohol at 96° is added, and the precipitate is washed by centrifugation with alcohol at 65°. The fluorine is separated from the residue by heating it with sulphuric acid in a special crucible made of gold and hermetically closed, and condensing the fluorine in pure potash. A siliceous mineral is powdered, and subjected to distillation with sulphuric acid without previous treatment. Organic matter has first to be ignited without loss of fluorine, and this is best effected in presence of lime or baryta.

Physico-chemical Volumetric Estimation of Substances Present in Natural Waters.—F. Dienert and A. Guillerd.—Dutoit has shown that if a curve is drawn, having for its ordinates the electrical resistivities, and for abscissæ the volumes of a reagent added to produce precipitation of a substance present in the water, the curve is quite smooth until the substance is completely precipitated, when there is a point of inflexion. The abscissa of this point corresponding to a known volume of reagent gives the weight of the substance precipitated. This method can be applied to the determination of lime, sulphuric acid, and magnesia, the reagents being potassium oxalate, barium acetate, and potassium ferrocyanide respectively.

Metallic Glycol-alcoholates.—E. Chablay.—At −50° glycol dissolved in liquid ammonia immediately decolorises a blue solution of alkali-ammonium, giving a white insoluble precipitate:—



$$(CH_2OH)_2+NH_3M=\begin{array}{l}CH_2OM\\|\\CH_2OH\end{array}+NH_3+H,$$

where M represents one atom of K, Na, or Li. When an alkaline glycol-monoalcoholate is heated in a current of hydrogen the disubstituted glycol, *e.g.*,  $\begin{array}{l}CH_2ONa\\|\\CH_2ONa\end{array}$ is obtained. The alkaline earths and lead yield only the disubstituted derivatives, in which two atoms of hydrogen are replaced by one of divalent metal.

Bromination of Cyclohexanone and of Cyclohexanol.—F. Bodroux and F. Taboury.—The direct action of bromine diluted with CCl_4 on cyclohexanone gives a yield of from 80 to 95 per cent of tetrabromocyclohexanone, according to the experimental conditions. In presence of acetic acid at the ordinary temperature the yield falls to 50 per cent, but if the liquid is boiled the reaction is energetic, and a considerable amount of 2.4.6-tribromophenol is obtained, besides a tarry product which the authors have not yet identified. Bromine dissolved in carbon tetrachloride attacks cyclohexanol; some HBr is set free, and the products are tetra and dibromocyclohexanone. When cyclohexanol is treated with bromine in boiling acetic acid the alcohol is destroyed, HBr is evolved, and some 2.4.6-tribromo-phenol is formed.

Dibromophenylisoxazolone and its Derivatives.—André Meyer.—4.4-dibromophenylisoxazolone may be prepared by gradually adding two molecules of bromine to one of phenylisoxazolone in acetic acid solution. It is a colourless compound, fusing at 76—77° without undergoing decomposition. It gives a hydrazone, $C_{15}H_{11}O_2N_3$, with phenylhydrazine, and this hydrazone is identical with benzene-azo-phenylisoxazolone; in the same conditions para-nitrophenylhydrazine yields *p*-nitrobenzene-azo-phenylisoxazolone. Semi-carbazide gives a semi-carbazone with the dibromo compound, and amines also eliminate bromine. Indigoïd derivatives can be obtained by the action of indoxylic acid or a solution of indoxyl.

Bromination of Hydroaromatic Compounds.—F. Bodroux and F. Taboury.—In presence of aluminium bromide, bromine reacts energetically with Δ' chlorocyclohexene to give hexabromobenzene. By a similar method the hydrocarbon obtained by the action of quinoline on 1.2-dibromocyclohexane is converted into C_6H_6. The hydrocarbon appears to be a mixture. Tetrabromocyclohexane is slowly attacked by bromine containing 1 per cent of aluminium in solution, the product being a mixture of several solid compounds, which the authors have not yet obtained in the pure state.

Nitro-derivatives of Diphenylene Oxide.—A. Mailhe.—The direct nitration of diphenylene oxide by means of fuming nitric acid gives a brown viscous mass, from which three compounds can be separated:—(i.) The dinitrated oxide; (ii.) the tetranitrated oxide; (iii.) the pentanitrated oxide. If these polynitro-derivatives are further treated with sulphonitric mixture containing excess of fuming nitric acid the hexanitrated compound is obtained; further nitration does not give a higher nitro-derivative, but the disulpho-derivative of the hexanitro compound.

Trimethyldiapoharmine.—V. Hasenfratz.—Apoharmine, $C_8H_8N_2$, combines with methyl iodide to give the iodohydrate of methylapoharmine, which is decomposed by potash into methylapoharmine, $C_8H_7N_2CH_3$. This base unites with methyl iodide to give the iodomethylate of methylapoharmine, $C_8H_7N_2CH_3.CH_3I$, from which a methylhydrate can be prepared by the action of silver oxide. By distilling this methylhydrate a new base is obtained; its formula is $C_{19}H_{22}N_4$, and it appears to be a trimethyl-derivative of a hypothetical diapoharmine, $(C_8H_8N_2)_2$. For this base the author proposes the name trimethyldiapoharmine. It behaves like a diacid base, giving a chloroplatinate, $C_{19}H_{22}N_4 2HCl.PtCl_4$, and a di-iodomethylate, $C_{19}H_{22}N_4.2CH_3I$. Thus Hofmann's reaction does not lead to the degradation of apoharmine, but to the formation of a complex base containing four atoms of nitrogen.

Atti della Reale Accademia dei Lincei. Vol. xxi., No. 9, 1912.

Condensation of Aldehydes with Phenyl Pyrrhol.—U. Colacicchi and C. Bertoni.—When equal weights of paraldehyde containing a little zinc chloride and *n*-phenylpyrrol are heated together for about two hours on a water-bath a brown insoluble mass is obtained. From this a yellow compound of formula $C_{12}H_{11}N$ can be isolated by means of ligroin. The equation is $C_{10}H_9N+C_2H_4O=C_{12}H_{11}N+H_2O$. Phenyl pyrrhol condenses similarly with formic and propylic aldehydes.

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AN APPARATUS FOR AUTOMATICALLY DECANTING AND WASHING PRECIPITATES.

By ERIC SINKINSON.

An apparatus has been designed for the purpose of automatically decanting and washing precipitates. The old laborious method of decanting and washing precipitates, requiring as it does the expenditure of much time and patience, is entirely superseded by the apparatus described below.

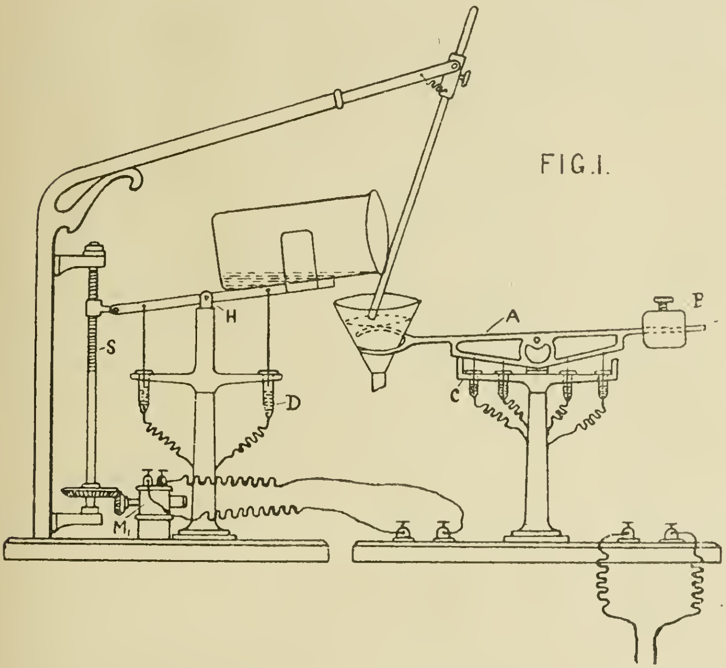

FIG. 1.

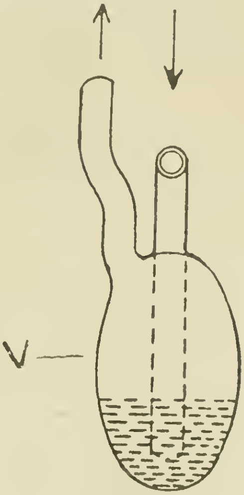

FIG. 3

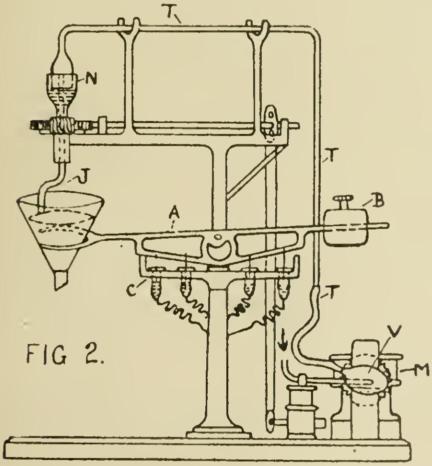

FIG 2.

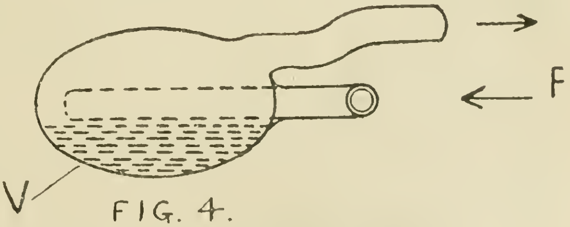

FIG. 4.

The decanting apparatus consists of two parts, one of which supports the funnel and the other the beaker containing the liquid to be decanted.

The funnel is supported in a ring at one end of a balance arm, A (see Fig. 1 in accompanying diagrams), at the other end of which is an adjustable counterpoise weight, B. By moving this weight backwards or forwards the amount of liquid in the filter-paper can be regulated at will to suit conditions.

When a sufficient amount of liquid has run into the filter, the funnel drops until arrested by the fixed support, C.

This support, C, serves to carry four mercury cups, which make and break certain electrical contacts, and so control the motors which regulate the supply of liquid to the filter.

The beaker is supported on a table hinged at H, the slope of which is regulated by the screw, S, which is in turn actuated by the motor, M.

As soon as the funnel drops, the motor is reversed until connection between battery and motor is finally broken at contact, D.

When the precipitate has finally been transferred from the beaker to the filter, the decanter is disconnected, and the washing attachment moved into position.

The washing liquid enters at the valve, V (Fig. 2), and passes along the tube, T, and out at the rotating jet, J.

In order that the jet may rotate, T being fixed, a mercury lock is introduced at N. The jet is rotated by a worm gearing actuated by a motor, M2.

The valve, V, shown separately in Figs. 3 and 4, is a small bulb containing mercury. Fused into it are two tubes, one reaching to the bottom through which the washing liquid enters, the other fixed at the top serves as an exit.

When in an upright position as in Fig. 3, the mercury traps the inlet tube, thus shutting off the supply to the jet. On rotation through 90° the valve takes up a position as in Fig. 4, setting up a free communication between inlet and outlet tube.

The apparatus works most satisfactorily, the washing of precipitates being carried out with greater precision than when done by hand.

A case covers the washer, so that no foreign material may get on to the paper during the process, as is liable in town laboratories in the ordinary way.

All that is necessary, therefore, is to connect the inlet tube to an ordinary wash-bottle supported on a stand, so that the water may gravitate to the jet, heat the water to boiling, and connect the terminals to a 4 volt accumulator.

The funnel with the precipitate to be washed is placed in the ring, the current switched on, the apparatus covered up, and left until a test shows the washing to be complete.

254, Crookesmoor Road, Sheffield.

A NOTE ON THE NON-EXISTENCE OF PERBROMIC ACID.

By P. W. ROBERTSON.

The original statement of Kammerer (*Journ. Prakt. Chem.*, xc., 190) that perbromic acid could be obtained by the action of bromine on perchloric acid was at first confirmed, but afterwards refuted, by Muir (*J. Chem. Soc.*, 1876, ii., 469). Wolfram (*Ann.*, 1879, cxcviii., 95) examined with some care the action of bromine on pure perchloric acid and its vapour, and came to the conclusion that it was unattacked, a result supported by the investigations of McIvor (Chemical News, 1887, lv., 203). Since then various unsuccessful attempts have been made to obtain perbromic acid or its salts. Thus, Cook (*Trans. Chem. Soc.*, 1894, lxv., 811) showed that potassium bromate on heating decomposed without the formation of the slightest trace of perbromate. Tanatar (*Ber.*, 1899, xxxii., 1013) found that the action of hydrogen peroxide on bromic acid was to reduce it to hydrobromic acid. Again, Müller and Friedberger (*Ber.*, 1902, xxxv., 2652) attempted to obtain perbromic acid by the electrical oxidation of bromic acid, but without success.

During the last ten years the author has been interested in this problem, and has endeavoured to prepare salts of perbromic acid by the following methods:—

1. By the action of bromine on potassium perchlorate in the presence of potassium bromide to remove any liberated chlorine. Even when the operation was performed in sealed tubes at temperatures as high as 250°, not the slightest change was observed.

2. By heating mixtures of potassium bromate and lead peroxide, it having been shown that lead peroxide facilitates the formation of perchlorate from potassium chlorate. Potassium bromide was found to be the only product of the reaction.

3. By the action of bromine on sodium periodate. When a solution of this salt was left alone with bromine for a week, or heated in sealed tubes to 100° for some hours, there was not the slightest liberation of iodine.

It seems that it must be finally concluded that perbromic acid and its salts are incapable of existence. The ordinary conceptions of valency can be employed to give structural formulæ for $HClO_4$ and HIO_4, although they do not explain why the $HBrO_4$ molecule does not exist. It seems probable that within a molecule there are in operation forces of attraction and repulsion, dependent upon the mass and nature of the component atoms, causing intramolecular vibrations of greater or less intensity. In the case, then, of a molecule such as $HBrO_4$, the vibrations would be so intense that such a system of atoms would not be capable of existence. Concerning the exact nature of the dynamic forces within even the simplest molecules little is known, and a theory which could predict the non-existence of such compounds as $HBrO_4$ or BrO_2 would be of fundamental importance.

VITAL EFFECTS OF RADIUM AND OTHER RAYS.*

By Sir JAMES MACKENZIE DAVIDSON, M.B., C.M.

(Concluded from p. 40).

Reaction.—Becquerel's accidental discovery that the presence of a tube of radium in the waistcoat pocket brought about a severe burn on the skin, demonstrated the physiological effect of this substance, and it only remained for the medical profession to find out in what cases such action would prove beneficial, and in what manner radium could be best applied. The effect upon the skin appeared to be very similar to that of the X-rays. At the time of the radium application no sensation is experienced, nor is anything abnormal observed for a varying period afterwards. In this respect the phenomenon which, in the case of the X-rays, has been referred to as the "latent period," is repeated. A certain amount of redness and discomfort—the latter in the form of a feeling of heat or burning—then make their appearance. This is the radium reaction, and its severity depends upon the duration of the primary dose. One essential difference between the X-rays and radium is that while the quality of the rays from a Crookes tube varies considerably from time to time, the output from the radium is quite constant, and therefore the duration of the application is the important factor in its use.

Biological Effects.—The biological effects of radium have been closely studied upon a large variety of organisms. Its influence upon plant development has been observed, among others, by Koernicke, who found (*Himmel und Herde*, October, 1904) that the general result of the exposure of seedlings was to cause retardation and eventually cessation of growth of stem and root. In some cases the growth was resumed after an interval; in others the plants never recovered. The first effect of the radium rays on dry bean and turnip seeds was to accelerate germination, but after a time the beans ceased to develop, although the turnips showed no signs of arrest - doubtless they would have done so had the exposure been prolonged. A tube of radium placed on a leaf will cause the irradiated area to lose its chlorophyll and to assume autumn tints.

Micro-organisms.—A considerable amount of research has been carried out upon micro-organisms. Anthrax microbes have been found not to develop at all if left for twenty-four hours in an atmosphere charged with radium emanations. In Metchnikoff's laboratory at the Pasteur Institute recently (*Archives d'Electricit Médicale*, Sept. 25th, 1911) it has been proved that certain toxins tend to lose their virulence after being made radiferous. When diphtheritic toxin was left for thirty days in contact with minute quantities of radium sulphate, the poisonous effect of the toxin was found to be much less rapid than in the case of the same toxin which had not been treated in this fashion. An interesting exception was noted in the tetanus toxin, upon which radium seemed to have no retarding influence.

The virus of rabies has been speedily destroyed when exposed directly to radium emanation, and Phisalix (Academy of Sciences, Paris, February 22nd, 1903) has demonstrated the sensibility of certain snake poisons to its action. Cobra poison, which is distinguished by its resistance to destruction by heat, is readily destroyed by

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* A Discourse delivered before the Royal Institution, February 2, 1912.

the radium radiation, and the observer found later that the virus of the viper can be destroyed in the same manner by the emanation. Not only so, but the radium which destroys the poison can also destroy with equal rapidity its antidote, quickly reducing the active properties of the anti-venomous serum of Calmette.

Fish and Mammals.—In aquatic life the effects of radium have also been investigated. Professor Coleridge Farr, of Christchurch, New Zealand (*British Medical Journal*, Oct. 14th, 1911), testing the artesian wells of that country, has found a destructive effect upon young fish and developing spawn in water containing radium emanation. Coming to the mammals, we find that radium exercises a rapid destruction upon the epidermis and the derma of young animals. In the early period of radium experiment it was discovered that, as in the case of the X-rays, young animals were killed far more readily than adults. Danysz (Academy of Sciences, Paris, December 28th, 1903) demonstrated this greater sensibility of the tissues, especially the epithelial tissues, of the young. According to this same observer also, under identical conditions of exposure to the action of radium rays, the skin of guinea-pigs is much more sensitive than that of rabbits, and a treatment sufficient to produce in the case of the guinea-pig a very extensive sore will only accelerate the growth of a rabbit's hair. Mice have frequently been made the subject of radium experiments. They have been found to be paralysed and to die after twenty days of uninterrupted exposure to radium placed at three inches distance from the mica window of their cage.

In all such cases it is worthy of remark that paralysis and death have been found to be due to internal hæmorrhages. The nerve cells have not shown any appreciable alteration. The central nervous system in all cases is, indeed, very resistant to radium action, but it suffers indirectly from the effects upon the vascular tissues.

Own Cases.—A wide field was opened up to radium, once its vital effect on living cells was demonstrated. The date of my own first application of radium to the treatment of disease was May, 1903. The case was a large rodent ulcer, just below the right eye, which was rapidly progressing in spite of X-ray treatment. Two glass tubes, each containing 5 mgrms. of radium bromide, were applied tentatively for a short time to the upper border of this ulcer, and the application was cautiously repeated in the course of two or three days. The improvement was so manifest that the tubes were applied in the same manner over the general surface of the ulcer, which finally healed perfectly without scarring, and has remained well during the nine years that have since elapsed.

The success encouraged me to try this method in the treatment of other cases of rodent ulcer, and with equally striking and satisfactory results. While incapable of effecting a cure in certain severe and old-standing cases, their progress was often arrested in a marked manner, and considerable improvement of the condition was attained.

Spring Catarrh.—Radium has also proved to have a markedly specific action upon a troublesome disease of the eyelids known as "spring catarrh." This occurs in young people, the upper eyelids more particularly being covered with rough tesselated granulations. The disease was quite incurable until I applied radium to a little boy sent to me by Mr. Arnold Lawson in February, 1906, and with the use of radium every case treated during the six years has been completely and painlessly cured. A matter also worthy of remark is that from the commencement of the treatment, even before any appreciable improvement is visible, the patients express themselves as feeling the eyes much more comfortable, and they are able to use them in their ordinary occupations during the period of treatment.

["Spring catarrh" case of Dr. Dawson Turner, of Edinburgh. Right eye treated by this method, other eye not. Notice difference. Case got well.]

In external diseases of the eye, radium has also proved to be of the greatest use (*vide* Lawson and Mackenzie Davidson paper.

Cure of Chronic X-Rays Dermatitis.—A further indication for radium therapy was discovered in the case of X-ray dermatitis. It was my misfortune to suffer from a chronic manifestation of this trouble, and three or four years ago a burnt patch on my head became ulcerated. One portion was so threatening as to suggest malignancy, which is, unfortunately, a common result of these lesions. As nothing that was tried would effect a cure, it became a question of excision, but before resorting to this I applied radium in glass tubes, and was agreeably surprised to find that it completely cured the condition.

The tube contained 20 mgrms. of pure radium bromide, and was left in position for twenty-five minutes. Nothing happened for twelve days, and then there occurred a certain amount of swelling and redness, the size of the black crust increased, and serum exuded from the side. This gradually subsided, and when the crust peeled off the normal healthy thin skin was found to be beneath it.

[Slide 1. Left hand with spot of X-ray dermatitis. 2. Same hand, with radium tube in position for treatment. 3. Hand showing reaction. 4. Hand cured, spot having disappeared. 5. Very severe case of X-ray dermatitis. 6, 7, and 8. Dr. Hall Edwards's hands.]

Apparatus.—For convenience of application, those who possessed a large quantity of radium spread it on surfaces protected by varnish. This enabled a large area to be treated, and, as the material interposed between apparatus and screen was slight, it allowed a considerable quantity of radiations to pass and impinge upon the skin. Dr. Dominici, of Paris, was the first to use dense metals, such as lead and platinum, also gold and silver, for screening purposes. By this means the less penetrating β-rays were stopped, and only the γ-rays and δ-rays of high penetrability were able to traverse the filter. Thus prolonged exposure became possible without injury to the skin, and the deeper parts that it was desired to affect could readily be reached. By means of these metallic filters, which can be made of different material and of different thickness, rays of any desired penetrability can be employed.

Embedding Radium.—A further procedure in the adaptation of radium to the treatment of tumours was to enclose the substance in small tubes of metal, such as platinum, and, an opening having been made deeply into the centre of the tumour, to lodge the tubes in that position, and allow them to remain embedded there for varying periods. Sometimes this has been combined with outside applications, so that the tumour has been attacked at once by radium rays from within and from without. Dr. Abbé, of New York, has made openings in this manner into malignant tumours, and has placed in position small celluloid tubes, into which the radium can be let down, and which can be easily removed, if desired, without any inconvenience to the patient,

Superficial Diseases.—A wide field has been found for the use of radium in the treatment of superficial diseases. It is very difficult to suggest a limit to the powers of the substance in this respect. Some diseases, of course, yield more readily than others. Lupus, which is tuberculosis of the skin, is very resistant to radium treatment, but a great many other skin diseases, as well as *small* cancers of the tongue and lip, can be cured, while large rapidly-growing tumours, like sarcoma, can be destroyed by the method of burying tubes within them. Here, again, the fact is illustrated that these rays seem to concentrate their attack upon the young and most rapidly growing cells. That is probably why sarcomas are so vulnerable to attack when compared with carcinomas, which are of slower growth. But in spite of its greater potency and convenience in application, the same thing has to be said of radium as was said of the X-rays, that it cannot in any sense be looked upon as a cure for cancerous growths of large size. It will inhibit the growth of these tumours and destroy them locally, but rarely completely, and it does nothing to prevent the usual secondary deposits.

[Rodent, and malignant wart on face. Dominici's and own cases, illustrating the effect of radium.]

Radium Emanation.—From the radium itself we pass to its emanation. The emanation is a heavy gas which can be dissolved in water, and be injected into the tissues, or can be confined in a metal tube and buried, the effect being practically the same as with radium itself. The emanation gives us 75 per cent of the energy which would be obtained if the radium from which it comes were embedded in its stead. The emanation, of course, can also be swallowed in solution and inhaled, and it is now much used in this manner. Several natural waters, such as those of Bath and other spas, contain radium emanation.

Emanation Effects.—The manifestations of the emanation are much the same as those of the radium itself, and its paralysing effect upon young animals is practically identical. When introduced into the system by inhalation, by injection, or by swallowing, the emanation seems to have a capacity for stimulating the body ferments. This holds true, probably, of many ferment actions in the body, although there are others in which the emanation appears to have no demonstrable influence. The excretion of sugar by diabetics, for instance, is stated to remain unaffected. In a lecture before the Berlin Medical Society, a year ago (January 18, 1911), Professor Wilhelm His, after dealing with cases of chronic rheumatism and uric acid gout, a large proportion of which had shown improvement under radium-therapy, said that, in fifteen cases out of eighteen under the influence of the radium emanation, the blood lost its uric acid within a few weeks. He pointed out that emanation behaves like every other gas which is not a normal constituent of the body, and is excreted to a very slight extent through the kidneys and to a large extent by means of the breath.

[Radium emanation standard.]

Sir William Ramsay has very kindly given me a "Standard" for the emanation. This little bottle contains 1/40,000 mgrm. of pure radium.

Selective Action.—I may be allowed to add a word or two about the actions generally of the radium in the body. In the diseases for which the rays possess curative properties their action is extraordinarily selective, so that, if the dosage is well timed they destroy the abnormal cells without destroying the normal. To find out in any given case which are the rays to use is an important matter, of course, for investigation, and as knowledge in this direction becomes more precise, the cures that may be set down to radium will be extended and made more certain.

Other Radio-active Substances.—The great disadvantage in this field of research is the scarcity of radium. As the knowledge of its utility is diffused, the demand for it increases, which seems to indicate that it must always remain exceedingly scarce and of a forbidding price. Naturally, therefore, those interested in its therapeutical properties are anxious to know whether among other radio-active substances there may be any which can take its place, and perhaps be more easily available to the profession, and, through them, to the public. Uranium, thorium, and actinium are radio-active, and have all been suggested in this connection, but they are too feeble to have real efficacy. The discovery by Otto Hahn of a substance known as meso-thorium, which is one of the disintegration products of thorium, and was found in the course of an attempt to separate radio-thorium directly from thorium, has aroused considerable expectation.

Meso-thorium is obtainable from the residues in the preparation of thorium for the manufacture of incandescent gas mantles. It emits the same rays as radium, and, weight for weight, is more powerful. As the supply of thorium is much larger than that of pitchblende, from which thorium is obtained, we may hope to have a larger supply of meso-thorium. It will cost much less, but, on the other hand, it has a short life of only about seven years as against radium which lasts 2500 years. It is being experimented with medically in Germany. I applied the tube now shown, which is equivalent to 10 mgrms. of pure radium, to a chronic patch of X-ray dermatitis on my hand, and a reaction followed fifteen days after application, and the result promises to be favourable.

[Show meso-thorium.]

Thorium Emanation from Radio-thorium.—Radio-thorium gives off thorium emanation richly. This is a heavy gas, lasting seventy-six seconds, giving off α-rays in profusion. These rays, impinging upon a sulphide of zinc screen, cause it to glow or fluoresce. Sulphide of zinc crystals sparkle and emit light when mechanically crushed or disturbed, and therefore the α-rays, striking these crystals, cause them to give out light. A remarkable spinthariscope effect is observed when the screen is viewed with a magnifying glass.

The emanation of radium will act like that of thorium, but, instead of lasting only seventy-six seconds, it will lose half its strength in about four days. Thorium emanation also resembles that of radium in giving rise to an "active deposit." This becomes concentrated on the negative pole in an electric field. A metallic surface can in this way be made intensely radio-active, giving forth the α-, β-, and γ-rays. The "active deposit" from thorium emanation lasts for several hours.

[Show thorium emanation from radio-thorium and screening effects. Blow emanation into sulphide of zinc screen, and also blow through long tubes.]

Conclusion.—There is a war in this world which ceases neither day nor night. It is the war against disease and death. Those engaged in this battle, whether they be in the crowded city or in the lonely swamp, are ever seeking some new weapons with which to meet the foe, and it has been my privilege to-night to explain, however imperfectly, some few of the most recent additions to the scientific armoury of medicine.

NOTES.

Radium, life	2500 years
Emanation, average life	5·57 days
Active deposit	About 3 hours
Thorium, average life	Unknown
Meso-thorium I., average life ..	7·9 years
Meso-thorium II., average life ..	8·9 years

Radiation, Beta, and Gamma Rays.

Radio-thorium, life	2·91 years
Alpha rays	—
Thorium X	5·35 days
Alpha rays	—
Actinium	—
Emanation	5·6 seconds

Rutherford gives the following :—

Thorium Series.

	Half-period of transformation.	Nature of radiation.
Thorium	15×10^{10} years	Alpha
Meso-thorium I. ..	5·5 years	
Meso-thorium II...	6 hours	Beta and Gamma
Radio-thorium ..	2 years	Alpha
Thorium X	3·6 days	Alpha
Emanation	54 seconds	Alpha
Active deposit—		
Thorium A . ..	10·6 hours	Beta
Thorium B . ..	1 hour	Alpha
Thorium C . ..	?	Alpha
Thorium D . ..	3 minutes	Beta and Gamma

VALUATION OF FLOR-SPAR.

By E. BIDTEL.

In the commercial analysis of fluor-spar the determinations usually required are calcium fluoride, silica, and calcium carbonate; in some particular cases lead, iron, zinc, and sulphur. We have received several calls for percentage of barium sulphate, but the most careful qualitative tests have failed to show the presence of this mineral, as will be shown later, in either what is known as Rosiclare or Fairview fluor-spar.

There is no practical method for the separation of fluorine from silica, and of determining fluorine direct in its ore, which answers the commercial requirements of a mine laboratory. The usual practice followed by most chemists is to determine the total calcium oxide, and to calculate from this the amount of calcium fluoride, after deducting the amount equal to the calcium carbonate present, this latter being determined from a separate sample in the usual way by absorbing the liberated carbonic acid in soda-lime tubes. This method would be correct if all the calcium present were combined with either carbonic acid or fluorine, and all the carbonic acid present combined with calcium. The first assumption is probably correct, as all our experiments go to prove this; but the latter we know is wrong, for lead carbonate, zinc carbonate, and iron carbonate are frequently present, especially in the gravel fluor-spar. Consequently, the calculated amount for calcium carbonate will be too high, and the calcium fluoride in consequence will be too low.

In view of the above error, I have found it better to dissolve all carbonates from the sample by acetic acid, leaving the calcium fluoride and silica as a residue on the filter ready for the determination of both silica and calcium fluoride. It must be remembered that calcium fluoride is slightly soluble in acetic acid. I have reduced this solubility to a factor which I use in my calculations. Generally the amount of calcium carbonate present is greatly in excess of the other carbonates, so that frequently it will be sufficiently accurate for commercial purposes to report the amount soluble in acetic acid after deducting the amount of calcium fluoride soluble in this acid as calcium carbonate. It is to be remembered that at this point there is opportunity for another small error, which, however, is limited, varying with the amount of base metals present; should they be present in considerable quantities the residue must be weighed, after drying at 110° C., to avoid an error caused by their oxidation. Ordinarily, however, this oxidation is so small that it need not be taken into account. In the separation of carbonates and ignition of residue, the loss will also include small amounts of water, volatile and organic matter. The residue left insoluble in acetic acid contains all the silica originally present in the ore. The silica is now determined by volatilising the same as silicon fluoride. The presence of sulphides of iron, zinc, and lead must be considered, and for this reason I have found it best to oxidise the sulphides in the residue by heating with mercuric oxide before evaporating with hydrofluoric acid. In this operation lead sulphide is entirely oxidised to lead sulphate, but the ferruginous zinc sulphide is but slightly acted upon, and remains unaffected by hydrofluoric acid, in so far as final results are concerned, as shown by analysis of synthetical samples of known percentages.

In regard to the determination of calcium fluoride, I avoid decomposing the sample and eliminate the calcium fluoride by treating the residue obtained from the silica determination with hydrofluoric acid to transform the iron oxide into iron fluoride, and extracting the same together with the lead and zinc by solution of ammonium acetate containing ammonium citrate. The method as used at present follows:—

Weigh into a small Erlenmeyer flask 1 grm. of the finely powdered sample, add 10 cc. of 10 per cent acetic acid, cover with a short-stemmed glass funnel, and heat on a water-bath for one hour, agitating from time to time. Filter through a 7 cm. ashless filter, wash with warm water four times, and burn off the filter-paper in a weighed platinum crucible at a temperature as low as possible. The loss in weight minus 0·0015 grm. (the amount of calcium fluoride soluble in acetic acid under the conditions named) is calcium carbonate.

Add to the residue in the platinum crucible about 1 grm. of yellow mercuric oxide in the form of an emulsion in water; break up any hard lumps that may have formed; evaporate to dryness, and heat to a dull red heat, cool, and weigh. Add about 2 cc. of hydrofluoric acid, and evaporate to dryness, repeating this operation twice, using 1 cc. of hydrofluoric acid in each of the last two operations. Add a few drops of hydrofluoric acid and some macerated filter-paper, as recommended by Dittrich, then a few drops of ammonium hydroxide to precipitate the iron, and evaporate to dryness. Heat to a dull read heat, cool, and weigh; the loss in weight is reported as silica. Now add 2 cc. of hydrofluoric acid, and a few drops of nitric acid, cover the crucible with its lid, and place on a moderately warm water-bath thirty minutes; remove the lid, and evaporate to dryness. If the contents of the crucible are not now perfectly white, evaporate again with hydrofluoric acid, add a few drops of hydrofluoric acid and 10 cc. of the solution of ammonium acetate (this ammonium acetate is prepared as follows:—Neutralise very carefully 400 cc. of 80 per cent acetic acid in a litre flask with strong ammonium hydrate; add 20 grms. of citric acid, and fill up to the mark with strong ammonium hydrate). Digest on a boiling water-bath for thirty minutes; filter, and wash by decantation with hot water containing a small amount of the ammonium acetate solution just described, then with pure hot water; ignite in the same crucible, and weigh. The residue should be perfectly white and should be pure calcium fluoride. To test this, add 2 cc. of sulphuric acid, heat to decompose the calcium fluoride, and evaporate the excess of sulphuric acid; repeat this operation, using 1 cc. of sulphuric acid. Now weigh the calcium sulphate, add 5 or 6 grms. sodium carbonate, fuse, and dissolve in hydrochloric acid in slight excess; should a white precipitate occur at this point it will indicate the presence of barium.

To prove this method I selected clear crystals of fluor-spar, pulverised the same, and purified it by treating with acetic acid, hydrofluoric acid, and ammonium acetate; the washed, dried, and ignited powder was decomposed by sulphuric acid, and the calcium sulphate weighed. By taking an average of six determinations 0·3875 grm. of this fluor-spar formed 0·67555 grm. of calcium sulphate equal to 99·97 per cent calcium fluoride. One grm. of this fluor-spar treated as described showed the following results as an average of twelve determinations:—

	Grm.
Loss in weight by treating with acetic acid	0·0015
Loss in weight by treating with HgO and HF ..	0·0002
Loss in weight by treating with ammonium acetate	0·0012

The amount of calcium fluoride lost in these different manipulations was 0·0029 grm., or 0·29 per cent, if we take 1 grm. for analysis. I now analysed mixtures of material of known percentage similar in composition to fluor-spar, and obtained the following results, using 1 grm. for analysis:—

	CaF_2.	SiO_2.	$CaCO_3$.	PbS.	ZnFeS.
Taken ..	85·11	6·66	5·59	1·50	1·14
Found ..	85·07	6·61	5·57		
Taken ..	80·05	7·71	7·92	2·50	1·82
Found ..	80·03	7·70	7·87		
Taken ..	78·45	8·32	10·40	1·40	1·43
Found ..	78·41	8·29	10·34		

Average samples of different carloads showed the percentage (1 grm. of material being taken for analysis). (See Table).

	Weighed as CaF_2.	$CaSO_4$ obtained by decomposition with H_2SO_4.	CaF_2 equal to $CaSO_4$.	Average plus 0·29 per cent.	SiO_2.	Average.	Soluble in acetic acid less 0·15 per cent.	Average.	CO_2.	$CaCO_3$ equal to CO_2.
1. Keystone ground.	99·07	172·75	99·06	99·31	0·44	0·45	0·20	0·24	0·116	0·26
	99·01	172·65	99·01		0·49		0·26			
	99·06	172·63	98·99		0·42		0·27			
2. A-1 ground . ..	96 81	168·80	96·80	97·09	1·47	1·45	0·88	0·88	0·35	0·80
	96·77	168·73	96·76		1·42		0·90			
	96·86	168·89	96·85		1·45		0·86			
3. Gravel	89·49	155·72	89·30	89·58	3·31	3·31	4·27	4·23	1·75	3·98
	89·35	155·69	89·28		3·33		4·17			
	89·38	155·71	89·29		3·29		4·25			
4. Gravel	86·76	151·00	86·59	86·97	4·90	4·93	4·72	4·68	1·95	4·43
	86·87	151·24	86·72		4·93		4·69			
	86·85	151·27	86·75		4·95		4·63			
5. Gravel	82·14	143·03	82·03	82·32	8·59	8·67	6·09	6·13	2·61	5·98
	82·13	143·00	82·00		8·70		6·18			
	82·08	143·10	82·06		8·71		6·12			
6. Unwashed sand .	66·02	114·80	65·83	66·14	13·76	13·77	15·52	15·58	6·83	15·52
	66·13	114·86	65·87		13·75		15·57			
	66·04	114·82	65·84		13·80		15·65			

The calcium sulphate obtained by decomposition of fluor-spar was fused with sodium carbonate, and the cake dissolved in hydrochloric acid. The solution was perfectly clear, showing a total decomposition of the fluor-spar and the absence of barium.

As our fluor-spar does not contain any gypsum and heavy spar, I did not investigate its influence on the calcium fluoride determination, but it is evident that small amounts of calcium sulphate will be leached out, if present, together with the carbonates. Barium sulphate is easy to detect, and can be determined as usual.

The only constituent of injurious influence would be any silicate containing calcium. F. Julius Fohs, in *Bulletin* 9 of the Kentucky Geological Survey, states the following silicates occurring associated with Kentucky fluor-spar:— Apophyllite, datolite, desmine, epidote, laumontite, and natrolite. Apophyllite and natrolite cannot be present in the fluor-spar because there are no alkalis to detect. The same with datolite. I could not find any trace of boron; desmine and laumontite cannot be present in any considerable amount, there being only very small amounts of aluminium in the spar.

I have made a support of aluminium which enables me to handle six crucibles at a time, and I can finish six analyses in ten hours.—*Journal of Industrial and Engineering Chemistry*, iv., No 3.

A SUGGESTION FOR MINERAL NOMENCLATURE.*

By HENRY S. WASHINGTON.

(Concluded from p. 46).

The System of Nomenclature.

As compared with the carbon compounds, minerals, and especially the silicates, present very great difficulties in the study of their molecular constitution. This is because of their high fusing points, non-volatility, insolubility, general chemical stability at ordinary or even very high temperatures (so that replacements of portions of the molecule are difficult), and impossibility of determination of the molecular weight, assuming that the term "molecular weight" is applicable to a solid body. Although we now realise the importance of this branch of mineralogy, and are beginning to recognise, especially among the silicates, the complex chemical constitution of many minerals and the existence of certain radicals or atomic groups analogous to those of organic chemistry, yet we are generally forced to be content with the expression of the chemical composition by simple empirical formulæ. The constitutional and graphic formulæ of but very few minerals can be given with any degree of confidence, and in the vast majority of cases we are absolutely in the dark.

Mineralogy is essentially in the condition of organic chemistry of the early days, when the composition of alcohol could only be expressed empirically as C_2H_6O, that of lactic acid as $C_3H_6O_3$, and that of urea as CH_4ON_2; whereas at present we can confidently express them by the constitutional formulæ $(C_2H_5)(OH)$, $(CH_3)(CHOH)(COOH)$, and $(CO)(NH_2)_2$, systematically known as ethyl alcohol, α-hydroxypropionic acid, and carbonyl amide, the last differing in constitutional formula from the isomeric ammonium isocyanate, $(CON)(NH_4)$.

Indeed, the theory of mineral constitution at present is in many ways analogous to the "theory of types" in organic chemistry, formulated by Gerhardt about 1850, as is seen in the general reference of the silicate minerals to simple silicic acids, H_2SiO_3, H_4SiO_4, $H_2Si_3O_7$, &c. Kekulé's "theory of linked atoms" has now superseded this in organic chemistry (*cf.*, C. Schorlemmer, "Rise and Development of Organic Chemistry," London, 1894, pp. 39, 69, and 155), and the applicability of this to mineral chemistry has only recently begun to be realised.

The study of the molecular constitution of minerals and attempts at the establishment of constitutional formulæ have been undertaken by Tschermak, Groth, Clarke, and many others, either through direct experiment or study of alteration products, but so far with doubtful success in most cases, and it will probably be many years before mineralogy attains to the knowledge requisite for formulæ like those of modern organic chemistry.

In three important papers Penfield (*Am. Journ. Sci.*, 1899, vii., 97; 1900, x., 19; 1907, xxiii., 23) established the complex character of the acidic portion of the tourmalines and amphiboles, and showed the effect of the mass action of the complex acid in controlling crystallisation, allowing replacement of the hydrogen atoms of the hypothetical acid by very different elements or radicals, and with different valencies, but without change in crystal form. He also speaks of these acids as tourmaline acid and amphibole acid, with the implication that an essential

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* From *American Journal of Science*, xxxiii., No. 194.

character of their salts is adherence to the particular crystal form of tourmaline and amphibole respectively.

More recently the problem of the constitution of some silicates has been studied by Tschermak, Baschieri, and others (Tschermak, *Sb. Ak. Wiss. Wien*, 1905, cxii., [1], 355; cxiv., [1], 455; 1906, cxv., [1], 217; E. Baschieri, *Proc. Verb. Soc. Tosc.*, 1907, xvi., 34; *Atti Soc. Tosc. Mem.*, 1908, xxiv., 133; Himmelbauer, *Sb. Ak. Wiss. Wien*, 1906, cxv., [1], 1184). These investigators have identified certain silicic acids, which they call after the mineral names, among them being:—Anorthitic acid (H_2SiO_3), albitic acid ($H_2Si_3O_7$), leucitic acid ($H_4Si_2O_6$), heulanditic acid ($H_{10}Si_6O_{17}$), granitic acid ($H_4Si_3O_8$), and datolitic acid ($H_2Si_2O_5$). Their method, it may be remarked, does not apparently permit of discrimination between a purely silicic or an alumo- or boro-silicic acid, and none of these workers suggests, like Penfield, that the acid or the acid name implies the crystal form of its salts.

It is suggested here that this concept of Penfield of silicate minerals as salts of mineral acids, in many cases of much greater complexity than is implied by the empirical formula, with the implication of the adherence of the salts to a characteristic crystal form, be extended to minerals in general and made the basis of a mineral nomenclature. From this point of view, silicate minerals would not be considered simply as salts of orthosilicic acid (H_4SiO_4), metasilicic acid (H_2SiO_3), disilicic acid ($H_2Si_2O_5$), and so forth; as substitution derivatives of normal aluminium silicates according to Clarke (which correspond to the old theory of types); or of multiples of silica according to Goldschmidt; but each group would be considered as salts of a particular silico- or alumino-silico-acid characterised by the particular crystal form and symmetry of its salts, and capable of isomorphous replacement either of its basic hydrogens or in the acidic portion.

This concept may be most appropriately applied to mineral groups, distinguished as at present by identity of chemical type and close similarity in crystal form, but it may be equally well applied to monotypic "groups," represented, so far as now known, by only one mineral, and which exhibit no evident near relationships, either chemical or crystallographic, as is the case with beryl and calamine. It is also clear that it would be applicable to minerals of simple as well as highly complex constitution. A further point, and one of great importance, is that a system of nomenclature based on this concept would be applicable whether the structural or constitutional formula, or even the exact chemical composition, of the mineral acid were known or not, as the salts of a given mineral acid (in this sense) would be identifiable and their relationship established by their conforming to a certain empirical chemical formula and crystal form. Thus the various pyroxenes and amphiboles are members of two different, but well-characterised, and universally recognised "natural" groups, though we are as yet almost wholly ignorant of their molecular constitution, knowing only that they may be referred, but do not necessarily belong, to the metasilicates, but are undoubtedly much more complex than is indicated by the empirical formulæ. We cannot even determine which group is the more complex.

Such a nomenclature would be rational and would be analogous to that of inorganic chemistry, of which mineralogy may be considered to be a branch, except that the crystallographic character is implied in the name and is an integral part of the definition. It might even be suggested that such a nomenclature as is here suggested is also applicable to artificial salts, and would be found especially useful with such highly complex compounds as the silicotungstates, phosphomolybdates, cobaltammine compounds, the various groups of which might be named after chemists who have been especially identified with their study.

While in advance of the present inadequate nomenclature, in that not only chemical and crystallographic characters but mineral relationships would be indicated, the suggested nomenclature would not, nor is it intended to, replace this for general use. The two would exist simultaneously, though used for different purposes, as the new nomenclature would lend itself readily to, and would probably aid in, the study and investigation of the molecular constitution of minerals and in other ways. In ordinary parlance and for usual purposes minerals, especially the common ones, would go by their present names, while when greater precision and exactitude were needed, especially in theoretical discussion, the suggested nomenclature could be used. Similarly, in inorganic and especially in organic chemistry, the common names are ordinarily used instead of the longer and more complex scientific names, which are systematic and indicate the chemical constitution.

For the purposes of such a nomenclature the large store of present mineral names may be drawn on for the necessary roots, since these roots would have in most cases sufficient mnemonic connotations to give directly an idea of the general chemical and crystal characters. Well known or fairly well known roots are sufficiently numerous to cover nearly the whole field of mineralogy. Though new minerals are being discovered with some frequency, representatives of entirely new mineral groups are comparatively rare, as many of the new minerals are referable to groups already known, and with increasingly exact knowledge of chemical composition and molecular structure, many minerals of hitherto unknown or uncertain affinities are being correlated with other groups, as the sodalites and the garnets.

It is suggested that the names of minerals (excepting for the present the elements and hydrocarbons) be formed similarly to those of oxides and salts in inorganic chemistry, as ferric oxide, sodium chloride, potassium sulphate, but with the crystal character implied in the name. Such mineral names will be binomial in general, composed of one term denoting the basic (positive) portion of the molecule, and another denoting the acidic (negative) portion. As the acidic portion is of major importance in classification it will be considered first.

The name of the mineral acid, or the acidic portion of its salts, will imply not only general chemical composition and type, but the crystal symmetry and general crystallographic relations of its salts, subject to the morphotropic changes due to isomorphous replacement.

The acid (negative) radical of a mineral group will be denoted by a root derived from the present name of a typical and appropriate member, preferably that best known or first named. To this root, in general shorn of its present termination (except for euphony or to avoid confusion with ordinary chemical salts), will be affixed the termination used in inorganic chemistry for the type of compound represented. For the mineral acid itself this termination would then be *-ic*, for a binary compound (oxide, sulphide, &c.) it will be *-ide*, for the sulpho-acid and analogous salts (*see Note*), and for the oxy-acid salts it will be *-ate*. As noted above, it will not be necessary to know the constitutional formula of the acid or mineral group to name it, as it may be defined by its empirical formula and crystal form.

(*Note.*—The regular termination *-ite* would be inadvisable for these, as liable to confusion with present names).

The water of crystallisation of hydrated mineral salts may in general be considered for the purposes of nomenclature as part of the negative portion of the molecule, since not only do nearly all hydrates differ crystallographically from the anhydrous salts, but the crystal form varies with the number of molecules of water present when several hydrates exist.

Such simple designations, implying always the crystal system characteristic of the salts of the mineral acid, will suffice for the negative (acidic) portion of isomorphous mineral groups in which the acid radical is identical in all (the base alone varying through isomorphous replacement), or for monotypic mineral groups. Thus, the members of the calcite, aragonite, and olivine groups are respectively salts of calcitic, aragonic, and olivinic acids, or calcitates, aragonates, and olivinates; while cyanite and calamine are the only known disthenate and calamate respectively.

When, however, in a group the chief element in the acidic portion is replaceable isomorphously, by different elements, as with the pyrite and apatite groups, or, as in the pyroxenes and felspars, there are marked differences in the crystal symmetry, the acidic portion remaining chemically the same, it becomes necessary to indicate these differences in the nomenclature. This may best be done in two ways, according to which of the cases is involved.

In the case of isomorphous replacement in the acidic portion the different compositions may be expressed by the use of appropriate prefixes to the acidic term used without a hyphen. Thus all members of the pyritohedrally isometric pyrite group would be pyrides, but pyrite and hauerite would be sulpyrides, and smaltite and chloanthite arsenpyrides. Among the silicates the presence of unusual or non-typical elements partially replacing silica may be expressed by similar syllables prefixed to the acidic name with a hyphen. Thus rosenbuschite and lavenite would be zirco-diopsidates. In some cases, when the isomorphous replacement in the acidic portion is complex, it may be advisable to use very much shortened syllabic forms for the various elements, as will be explained when the naming of the base is considered.

In the case of the more complex mineral acids, especially among the silicates, as the alumo-silicates or boro-silicates, in which only the subsidiary acidic element is isomorphously replaceable, the replacement will be indicated by the use of appropriate chemical syllables prefixed to the acidic term, used with a hyphen. Thus, if the garnets are regarded as salts of complex alumo-, &c., acids, they would be called alumi-garnetates, ferri-garnetates, and chromo-garnetates, and similarly members of the datolite group would be bori-datolates, alumi-datolates, or yttri-datolates, represented by datolite, euclase, and gadolinite. This will serve to distinguish such complex salts from those of mineral acids in which one characteristic element exists and is wholly replaced, as in the apatite group, which would be called phosphapatates, arsenapatates, and vanadapatates.

When the differences are those of crystal symmetry, as in the pyroxene and felspar groups, the general group names will be formed as above by a root derived from the present group name or best representative, followed by the terminations *-oic* for the acid, *-ode* for binary compounds, and *-ote* for sulpho- and oxy-salts. The various sub-groups, distinguished by differing but related crystal systems, will be designated by the use of the appropriate roots and regular terminations as described above. Thus all the members of the pyroxene group would be salts of pyroxenoic acid or pyroxenotes, while the orthorhombic members would be hypersthenates, the monoclinic diopsidates, and the triclinic rhodonates.

The rare cases among minerals of homologous series, corresponding to the paraffins and olefines of organic chemistry, in which each member differs from the preceding by a constant increase of a certain atomic group, must also be considered. These are best represented by the humite group, better called "series." The members of such a series may be designated as to the acidic portion by the use of the prefixes *uni-*, *bi-*, *ter-*, &c., to indicate the number of the varying radical, as will be shown later.

The base or bases present will be indicated by the use of the name or names of the positive element or elements, either as such or expressed by appropriate syllables when more than one base is present. It may be suggested that the relative importance of the several isomorphous bases present be indicated by a definite order in the syllables, and that the most important be placed last, the preceding ones being in the nature of modifiers. This can also be emphasised by using the full name for the most important base, and a contracted adjectival form, ending in *i* or *o*, for the others. When two bases are of equal importance, present in about equal molecular amounts, the combined full names may be used, though this last might better be reserved for definite double salts, as dolomite. Illustrating the above idea, forsterite would be called magnesium olivinate, most chrysolite ferro-magnesium olivinate, hyalosiderite might be magnesi-ferrous olivinate, and fayalite ferrous olivinate.

In many minerals, however, several bases are present, and in these cases, and even when there are only two, the designation of the base may become long and cumbrous. It may therefore be desirable to have all the bases represented by syllables as compact and condensed as possible, so long as this can be done without sacrificing clearness. For this purpose it is suggested that the first syllable of the element name may be used, joined together without linking vowels or hyphens, the order being significant of the relative importance, as above. Thus enstatite would be magnesium hypersthenate, bronzite fermag hypersthenate, and a highly ferrous hypersthene magfer hypersthenate.

With the increasing recognition of the presence of radicals in minerals, it becomes necessary, as a matter of convenience, to designate these by short terms, and here we may well follow the lead of organic chemistry, where we find such indispensable radical names as ethyl, butyl, phenyl, acetyl, derived from their most prominent compounds. Similarly we might designate the mineral radical, $Al(F,OH)$, essential in topaz, as topyl; $Mg(F,OH)$, present in the chondrodite series, as chondryl; and (BOH), which Penfield has shown to be present in tourmalines, as tourmyl. Such radical names would take the place of element names when present as bases.

The objection will, of course, be raised against the use of such syllables that they are barbarous, uncouth, and cacophonous. In reply to this it may be said that, while they will undoubtedly appear so at first, usage will gradually render them easy, natural, and less awkward. As a case in point may be cited the terminology of organic chemistry, where we find such words as carboxyl, aldoxim, azoxybenzol, glyoxal, phthalisoimide, and a host of others. The same objections could have been, and probably were, raised against these, but to express the lengthy and complicated names of organic compounds the chemist has found such syllables absolutely necessary. They are readily understandable and give an immediate insight into the composition of the substance, have wholly lost their original "barbarousness," and new ones are freely coined when needed.

Acid and basic salts present some difficulties, as it is not always possible as yet to determine the function of hydrogen or hydroxyl in minerals. When definitely known to be basic or acid salts they may be so designated, but in general they may be designated by special acidic names for the group, since the acidity or basicity almost always determines a crystal form different from that of the normal salt.

Names formed as suggested above have certain analogies with some of the present mineral names, in which isomorphous replacement is indicated by the use of chemical modifiers, as soda-microline, manganopectolite, cuprodescloizite, natrojarosite, plumbo-jarosite, and soda-mica. Even in these we can see the lack of system in present nomenclature, since these names belong to two distinct categories. In the one the modifier expresses only partial replacement of the characteristic element of the type mineral by an isomorphous one, as in the first three examples, which are presumably cases of solid solution and should be regarded as varieties of the type, or as intermediate between two extremes. In the last three cases there is *entire* replacement by the element denoted in the name, and such minerals are definite compounds and must be regarded as distinct species. For this reason natrojarosite and plumbojarosite are better entitled to recognition as distinct minerals than are soda-microcline (anorthoclase) or manganopectolite, and should have special names not formed on this plan, while paragonite has properly replaced the earlier soda-mica, which last should be used for a mica in which the potassium is only partially replaced by sodium.

The names of the suggested nomenclature are properly applicable only to minerals of the second kind just mentioned, that is to definite compounds, since it is essentially an inorganic chemical nomenclature, in which mixed crystals should be named by calling them mixtures of their components. In mineralogy the case is somewhat different, it is true, as such mixed crystals are often important and fairly well-defined mineral species, and names for them are necessary. Some latitude and discretionary power must, therefore, be allowed, and while all rather indefinite mixed crystals need not receive specific recognition or names, there will be many cases, especially when the mixture is of mineralogical importance, fairly constant in composition, or with some approximation to simple stoichiometric ratios, when names as above should be bestowed. To meet the common case of the indefinite or variable isomorphous replacement, it may be suggested that the syllable *ic* be added to the compounded elemental syllables used for the base. Thus the various hypersthenes and bronzites would be called collectively fermagic hypersthenates, and the lime-soda felspars would be calsodic albates.

Illustrations of the System.

It is impracticable to give here a complete illustration of the application of the system to all known minerals, so that only a few selected cases are given which will illustrate the points brought out above. It is purposed to publish elsewhere a fairly complete list, already prepared, which will serve as a basis for the suggested nomenclature.

Sphalerite Group.

Sphalerides, $R''(S,Se,Te)$, isometric, tetrahedral.

Sphalerite, ZnS	Zinc sulsphaleride
Metacinnabarite, HgS	Mercury sulsphaleride
Alabandite, MnS	Manganese sulsphaleride
Tiemannite, $HgSe$	Mercury selsphaleride
Onofrite, $Hg(S,Se)$	Mercury selsulsphaleride
Coloradoite, $HgTe$	Mercury telsphaleride

Pyrite Group.

Pyrides, $R(S,As,Sb)_2$, isometric, pyritohedral.

Pyrite, FeS_3	Iron sulpyride
Hauerite, MnS_2	Manganese sulpyride
Laurite, RuS_2	Ruthenium sulpyride
Smaltite, $CoAs_2$	Cobalt arsenpyride
Chloanthite, $NiAs_2$	Nickel arsenpyride
Sperrylite, $PtAs_2$	Platinum arsenpyride
Cobaltite, $Co(S,As)_2$	Cobalt sularsenpyride
Gersdorffite, $Ni(S,As)_2$	Nickel sularsenpyride

Marcasite Group.

Marcasides, $R(S,As)_2$, orthorhombic.

Marcasite, FeS_2	Iron sulmarcaside
Löllingite, $FeAs_2$	Iron arsenmarcaside
Safflorite, $CaAs_2$	Cobalt arsenmarcaside
Rammelsbergite, $NiAs_2$	Nickel arsenmarcaside

Hematite Group.

Hematides, R_2O_3, trigonal.

Corundum, Al_2O_3	Aluminium hematide
Hematite, Fe_2O_3	Iron hematide
Ilmenite, $(Fe,Ti)_2O_3$	Titanferri hematide
Geikielite, $(Mg,Ti)_2O_3$	Titanmagnesi hematide
Pyrophanite, $(Mn,Ti)_2O_3$	Titanmangani hematide

If the members of this group are considered to be aluminates, ferrates, &c., the appropriate names would be:—Aluminium alhematate, iron ferhematate, iron titanhematate, magnesium titanhematate, and manganese titanhematate.

Calcite Group.

Calcitates, R''_2CO_3, trigonal.

Calcite, $CaCO_3$	Calcium calcitate
Magnesite, $MgCO_3$	Magnesium calcitate
Dolomite, $CaMg(CO_3)_2$	Magnesicalcium calcitate
Ankerite $(Mg,Fe)Ca(CO_3)_2$	Fermag-calcium calcitate
Siderite, $FeCO_3$	Ferrous calcitate
Rhodochrosite, $MnCO_3$	Manganese calcitate

Felspar Group.

Felspathotes $\left\{\begin{matrix} R'AlSi_3O_8 \\ R''Al_2Si_2O_8 \end{matrix}\right\}$ monoclinic-triclinic.

(The constitution and relations of the felspars, lenads, and zeolites will form the subject of a subsequent paper).

Adular Sub-group.

Adularates, monoclinic.

Orthoclase, $KAlSi_3O_8$	Potassium adularate
Barbierite, $NaAlSi_3O_8$	Sodium adularate
Celsian, $BaAl_2Si_2O_8$	Barium adularate

Albite Sub-group.

Albates, $R'AlSi_3O_8$, triclinic.

Microcline, $KAlSi_3O_8$	Potassium albate
Albite, $NaAlSi_3O_8$	Sodium albate
Anorthoclase, $(K,Na)AlSi_3O_8$	Potassisodium albate

Anorthite Sub-group,

Anorthates, $R''Al_2Si_2O_8$, triclinic.

Anorthite, $CaAl_2Si_2O_8$	Calcium anorthate
Carnegieite, $Na_2Al_2Si_2O_8$	Sodium anorthate

Mixed Salts.

Oligoclase, Ab_2An_1	Caldisod anorth-albate
Andesine, Ab_1An_1	Sodcal alb-anorthate
Labradorite, Ab_1An_2	Soddical alb-anorthate

Pyroxene Group.

Pyroxenotes $\left\{\begin{matrix} R''_2Si_2O_6 \\ R''R'''_2SiO_6 \end{matrix}\right\}$ orthorhombic, monoclinic, triclinic.

Hypersthene Sub-group.

Hypersthenates, orthorhombic.

Enstatite, $Mg_2Si_2O_6$	Magnesium hypersthenate
Bronzite, $(Fe,Mg)_2Si_2O_6$	Ferromagnesium hypersthenate
Hypersthene, $(Mg,Fe)_2Si_6O_2$	Magnesiferrous hypersthenate

Diopside Sub-group.

Diopsidates, monoclinic.

Diopside, $CaMgSi_2O_6$	Calcimagnesium diopsidate
Hedenbergite, $CaFeSi_2O_6$	Calciferrous diopsidate
Wollastonite, $Ca_2Si_2O_6$	Calcium diopsidate
Augite, $\left\{\begin{matrix} mCaMgSi_2O_6 \\ n(Mg,Fe)(Al,Fe)_2SiO_6 \end{matrix}\right.$	Alfercalmag diopsidate
Acmite, $NaFeSi_2O_6$	Ferrisodium diopsidate
Jadeite, $NaAlSi_2O_6$	Alumisodium diopsidate
Spodumene, $LiAlSi_2O_6$	Alumilithium diopsidate
Pectolite, $HNaCa_2Si_3O_9$	Acid sodicalcium diopsidate

Rhodonite Sub-group.

Rhodonates, triclinic.

Rhodonite, $Mn_2Si_2O_6$	Manganese rhodonate
Babingtonite, $\left\{\begin{matrix} m(Ca,Fe)_2Si_2O_6 \\ nFe_2Si_3O_9 \end{matrix}\right.$	Ferricalcium rhodonate

Olivine Group.

Olivinates, $R''_2Si_2O_4$, orthorhombic.

Forsterite, $Mg_2Si_2O_4$	Magnesium olivinate
Monticellite, $CaMgSi_2O_4$	Calcimagnesium olivinate
Chrysolite, $(Fe,Mg)_2Si_2O_4$	Ferromagnesium olivinate
Fayalite, $Fe_2Si_2O_4$	Ferrous olivinate
Tephroite, $Mn_2Si_2O_4$	Manganous olivinate
Glaucochroite, $CaMnSi_2O_4$	Calcimanganous olivinate

Chondrodite Series.

Chondrodates, $R''_{2n-1}[R''(F,OH)]_2(SiO_4)_n$, orthorhombic.

Prolectite, $Mg[Mg(F,OH)]_2(SiO_4)$	Magnesium uni-chondrodate
Chondrodite, $Mg_3[Mg(F,OH)]_2(SiO_4)_2$	Magnesium bi-chondrodate
Humite, $Mg_5[Mg(F,OH)]_2(SiO_4)_3$	Magnesium ter-chondrodate
Leucophœnicite, $Mn_5(MnOH)_2(SiO_4)_3$	Manganese ter-chondrodate
Clinohumite, $(Mg_7[Mg(F,OH)]_2(SiO_4)_4$	Magnesium quadi-chondrodate

Datolite Group.

Datolates, $R''_3R'''_2Si_2O_{10}$, monoclinic.

Datolite, $H_2Ca_2B_2Si_2O_{10}$	Acid calcium bori-datolate
Euclase, $H_2Gl_2Al_2Si_2O_{10}$	Acid glucinum alumi-datolate
Gadolinite, $FeGl_2Y_2Si_2O_{10}$	Ferro glucinum yttri-datolate
Homilite, $FeCa_2B_2Si_2O_{10}$	Ferro calcium bori-datolate

Spinel Group.

Spinelates, $R''R'''_2O_4$, isometric.

Spinel, $MgAl_2O_4$	Magnesium alumispinelate
Hercynite, $FeAl_2O_4$	Ferrous alumispinelate
Gahnite, $ZnAl_2O_4$	Zinc alumispinelate
Magnetite, $FeFe_2O_4$	Ferrous ferrispinelate
Chromite, $FeCr_2O_4$	Ferrous chromispinelate

Apatite Group.

Apatates, $R''_5(F,Cl)[(P,As,V)O_4]_3$, hexagonal.

Apatite, $Ca_5(F,Cl)(PO_4)_3$	Calcium phosphapatate
Pyromorphite, $Pb_5Cl(PO_4)_3$	Lead phosphapatate
Mimetite, $Pb_5Cl(AsO_4)_3$	Lead arsenapatate
Svabite, $Ca_5F(AsO_4)_3$	Calcium arsenapatate
Vanadinite, $Pb_5Cl(VO_4)_3$	Lead vanadapatate

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

(Continued from p. 47).

In the following, the plans, so for as they relate to various functions of interest to chemists and taking place in affiliation or connection with the Congress, and so far as they have been definitely or tentatively fixed to date, are set forth for the information and guidance of members of this Congress.

Ladies accompanying members are heartily welcome at all social functions of the Congress, such as the receptions, teas, organ recitals, general lectures, banquets, and the like.

Entertainment.

Saturday, August 31.

Society of Chemical Industry.

8.30 p.m.—Informal reception at the Chemists' Club.

Verein Deutscher Chemiker.

9 p.m.—Informal gathering on the roof garden of the Hotel Astor, Broadway and Forty-fourth Street.

Sunday, September 1.

Religious Services—Reservations in suitable number for members of the Congress are made at the Cathedral of St. John the Divine, Cathedral Heights, and at St. Patrick's Cathedral, Fifth Avenue and Fiftieth Street. For other Sunday services consult the Sunday morning or Saturday evening papers.

Verein Deutscher Chemiker.

10 a.m.—Automobile trip from Grant's Tomb, Riverside Drive, through the parks, over the bridges, Prospect Park to Brighton Beach Casino; dinner at the Casino, with informal entertainment.

3 p.m.—Drive through Coney Island and along the Shore Road; return to New York City.

9 p.m.—Concert on the roof of the New Century Theatre.

Monday, September 2.

Society of Chemical Industry.

Labour Day, public holiday; excursions and other entertainments in and about New York City.

Verein Deutscher Chemiker.

10 a.m.—Business meeting and lectures at Havemeyer Hall, Columbia University. Dr. F. Raschig: The scientific and technical importance of tar-phenols. Dr. F. W. Frerichs: Thirty-two years in the United States as chemist and manufacturer.

1 p.m.—Dinner at the Claremont.

7.30 p.m.—Ladies' theatre party, followed by collation at the Ritz-Carlton Hotel, Madison Avenue and Forty-sixth Street.

8.15 p.m.—Gentlemen: Kommers, at a hall to be decided upon later.

Chemists' Club.

8.30 p.m.—Reception to members of the Congress speaking the Latin tongues at the Chemists' Club, 52, East Forty-first Street.

Tuesday, September 3.

Society of Chemical Industry.

9 a.m.—Meeting of the Council of the Society of Chemical Industry, Chemists' Club.

10 a.m.—Business and annual meeting in Rumford Hall, Chemists' Club, 52, East Forty-first Street.
Address of welcome by the Mayor of the City of New York.
Address by the Retiring President, Dr. Rudolph Messel.

12.30 p.m.—Complimentary luncheon, Chemists' Club.

Eighth International Congress of Applied Chemistry.

4.22 p.m., and at intervals thereafter—Special trains for Washington, D.C., leave Pennsylvania Terminal, Thirty-third Street and Seventh Avenue, and Baltimore and Ohio Railroad Stations at foot of Twenty-third Street and North River and at Liberty Street and North River.

9.45 p.m., and at intervals thereafter—Arrival in Washington, D.C.

Wednesday, September 4.

Eighth International Congress of Applied Chemistry.

11 a.m.—Inaugural meeting at Washington, D.C., presided over by the President of the United States.

2 to 4 p.m.—General excursions to the Capitol.

4.30 to 6.30 p.m.—Garden party on the lawn at the White House.

8 to 11 p.m.—Reception at the New National Museum.

Thursday, September 5.

9 a.m.—(At Washington, D.C.) Excursions to Art Galleries, Library of Congress, tour of Washington, or trip to Mount Vernon; this latter will occupy all the forenoon. Inspection of the Laboratories in Washington.

4.55 p.m., and at intervals thereafter.—Special trains leave Washington Terminal for New York.

American Institute of Chemical Engineers (at New York City).

7 p.m.—Banquet to members of the Institute and their invited guests at the Chemists' Club, 52, East Forty first Street, New York City.

10.55 p.m., and at intervals thereafter.—Arrival in New York from Washington.

(To be continued)

NOTICES OF BOOKS.

German Varnish-making. By Prof. Max Bottler. Authorised Translation, with Notes on American Varnish and Paint Manufacture, by Alvah Horton Sabin, M.S. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

The fact that varnish and paint-making is treated in a rather controversial spirit in this book rather adds to than diminishes its value, and the practical paint and varnish manufacturer who wants the opinion of an expert unbiased by tradition or the weight of current opinion will certainly get it in the notes added by the translator. In the German original, which has been translated in full, only German practice was discussed, and since in many respects it is not in complete accordance with that in America and other countries, although from the German point of view the book was entirely authoritative, the translator has added much fresh matter, and, in fact, there is almost as much interpolation as translation, while the original is frequently criticised and even corrected. The additions and the translation are distinguished by being printed in different type. Lengthy notes on the analysis of paints and varnishes have been added; these notes are to be regarded rather as a collection of somewhat inaccessible data than an outline of a complete method of analysis. The old Crockett formula book, which is of considerable historical interest, is reprinted in an appendix exactly as it was written in 1867.

Exercises in Chemical Calculation. By H. F. Coward, D.Sc., and W. H. Perkins, M.Sc. London: Edward Arnold. 1912.

The examples of chemical calculations which are given in this book have been drawn either from recent examination papers or from original articles containing results actually obtained in experimental work, and in the former case care has been taken to exclude or else modify any in which the data were utterly impossible from a practical point of view. Candidates for examinations should find this book very useful, as it contains plenty of examples in all branches of chemical calculations both for fairly elementary and advanced students. Short explanations of the principles involved in the examples are frequently prefixed, chiefly for the purpose of refreshing the student's memory about what he has already learnt, and some worked examples are also given. The use of logarithms is recommended, though it is not essential, and the student's attention is called to the importance of stating exactly the number of significant figures in the data and in the result.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperaturs are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 24, June 10, 1912.

Action of Sodamide and Alkyl Haloids on Benzoyltrimethylene.—A. Haller and Eug. Benoist.—When heated in benzene with sodamide, benzoylmethylene yields benzamide and a gas which is undoubtedly methyltrimethylene. When sodium benzoyltrimethylene is treated with allyl iodide the product is allylbenzoyltrimethylene, a liquid which boils at 136—137° under 16 mm.; with benzyl chloride the product is benzylbenzoyltrimethylene. The authors have determined the molecular refractions of the parent substance, its methyl and benzyl derivatives, and its carbonic ether, and have found that the difference between the observed and the calculated values varies from 0·7 to 1 unit. Hence the trimethylenic nucleus plays exactly the same part as an ethylenic bond when it is conjugated with the double bond of a ketonic oxygen atom.

Influence of Impurities on Activity of Aluminium.—E. Kohn-Abrest and M. Rivera-Maltes.—Aluminium which contains traces of mercury is exceedingly easily oxidised in damp air, water, and various liquids, and may be called active aluminium. Its activity is not influenced by the presence of small quantities of iron and silicon, such as are present in commercial aluminium which is called pure. The presence of copper, however, reduces the activity; thus 0·1 per cent of the metal is sufficient to make a sheet of aluminium containing mercury impervious to the action of water. In air the limits are somewhat different.

Hydrogen Silicides.—A. Besson.—Magnesium silicide, when treated with HCl, gives off mixed silicides of hydrogen containing PH_3 and H_2S, which latter impurities may be removed by means of Cu_2Cl_2 and KI respectively. During the reaction some of the silicon separates in the form of silico-oxalic acid, $Si_2O_4H_2$. The mixed silicides are unaffected by light; in presence of moisture they react with liquid ammonia, giving a substance of formula $Si_3O_7H_4$. The mixed gas when sufficiently dilute fumes in air without taking fire, the fumes consisting of a very light white solid of variable composition. After it has been kept for some hours at 100° its composition becomes practically constant, corresponding to the formula $Si_3O_5H_3$.

Decomposition of Copper Sulphite. - H. Baubigny.—When cupric sulphite is transformed into cuprous salt by auto-reduction, and in absence of excess of alkaline sulphite, the production of dithionic acid is only very slight, and the principal reaction is the formation of cuprous sulphite and sulphuric acid; the latter reacts with the unchanged cupric sulphite to give copper sulphate and sulphurous gas, which re-dissolves part of the sulphites, and may even exert a reducing action on the cupric sulphate. The reaction proceeds thus until the final product is insoluble cuprous chloride if cupric chloride was used, or cuproso-cupric sulphite if the copper salt employed was not a halogen salt.

Spontaneous and Progressive Destruction of Leaden Objects.—Camille Matignon.—Certain leaden objects, exposed in museums, are slowly oxidised, and are finally converted into more or less powdery matter consisting essentially of lead carbonate. Other specimens made of the same metal may undergo no modification, and thus "diseased" leads may exist, such that it is not possible to preserve them in a glass case of a museum. The investigation of the metal shows that chlorides are always present in diseased lead, and when chloride is added to a sheet of normal lead it becomes oxidised in the course of three years.

Decomposition of Uranyl Nitrate by Heat.—Paul Lebeau.—The decomposition of uranyl nitrate by heat begins at about 100°, the products being uranic hydrate and nitric acid, $(NO_3)_2UO_2.2H_2O = 2HNO_3 + UO_3H_2O$. At the melting-point of the salt the mass is partly dehydrated with formation of some anhydrous nitrate. The final product of heating the fused salt is a mixture of uranic anhydride and its hydrate.

Ethers of Dichlorsuccinic Acid and their Stereochemical Isomers.—G. Darzens and M. Séjourné.—αβ-Dichlorsuccinic acid ought to have as many isomers as tartaric acid. So far only two inactive isomers have been prepared, but the authors have prepared active ethers starting with *d*-tartaric acid, by the action of thionyl chloride on the tartaric ethers in presence of pyridine, and also from racemic tartaric acid they have obtained a new inactive dichlorsuccinic acid. All the dichlorsuccinic ethers readily lose a molecule of hydrochloric acid, giving rise to monochlorfumaric ethers.

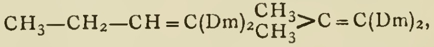
Isopropyldiphenylacetic Acid.—Mdme. Ramart-Lucas.—Isopropyldiphenylacetic acid,—

$$(C_6H_5)_2CH - C.(CH_3)_2.COOH,$$

can be synthesised by treating the nitrite of diphenylacetic acid with sodamide in benzene. NH_3 is evolved, and a sodium derivative is readily obtained. Isopropyl iodide reacts with this derivative to give the nitrite of the required acid, which may be obtained by saponifying it in a sealed tube with a mixture of hydrochloric and acetic acids. The acid melts at 163°. During the reaction a neutral product of formula $C_{16}H_{16}O_2$ is formed.

Chromogenic and Nitrogenous Substances in Fats.—G. Bouchard.—Brown gelatinous substances can be obtained by saponifying a fat with excess of soda, removing the soap formed, and neutralising the liquid with a mineral acid. The chromogenic matter which can be separated by means of petroleum ether has approximately the composition represented by the formula $C_{18}H_{28}O_4$. It is acid towards coloured reagents, and is a feeble reducing agent. The residue left after taking up the brown jelly with ether always contains nitrogen, and the author has found that nitrogen is always present in fats, the proportion in fats of animal origin being greater than in vegetable fats.

Leucobases and Dyes from Diphenylethylene.—P. Lemoult.—The author has prepared from Michler's ketone derivatives such as—



$$CH_3{-}CH_2{-}CH = C(Dm)_2 \quad {}^{CH_3}_{CH_3}{>}C = C(Dm)_2,$$

&c., where $Dm = -C_6H_4N(CH_3)_2$. These compounds dissolve in the cold in acetic acid, giving faint colourations which become much darker after heating for some minutes on the water-bath. The acetic solutions give also beautiful colourations with a little lead dioxide.

Cyclopentanic Glycols.—Marcel Godchot and Félix Taboury.—In the cyclopentane series two stereo-isomeric glycols exist, the *cis* and the *cis-trans* isomers. The authors have prepared the latter by oxidising cyclopentene with potassium permanganate, according to Wagner's method. The dehydration of α-cyclopentylcyclopentanol gives a new ethylenic compound cyclopentylcyclopentene, $C_5H_9{-}C_5H_7$.

MISCELLANEOUS.

Congress of Applied Chemistry.—It may be of interest to some of our readers who intend visiting the United States during the coming Congress of Applied Chemistry to learn that the Trustees of the Chemists' Club have decided to place at their disposal, free of charge, such of their laboratories as may be vacant, for any experimentation they may desire to make.

Institute of Chemistry.—*Pass List, July Examinations*, 1912.—Of thirty-five candidates who presented themselves for the Intermediate Examination, eighteen passed:—C. A. Adams, B.Sc. (Lond.); Miss D. J. Bartlett; L. O. Brekke, B.Sc. (Leeds); H. B. Brown; F. G. Conyers; E. D. Goddard, B.Sc. (Lond.); J. R. Gray; F. A. Hatch; M. Howie; D. W. Kent-Jones; E. Marsden; Miss E. G. Mocatta, B.Sc. (Lond.); E. A. Rayner, B.Sc. (Lond.); W. S. Ritchie, B.Sc. (Lond.); W. G. Saunders; D. E. Sharp, B.Sc. (Aberdeen); T. F. Smeaton; and W. A. Storey. Of thirty-seven candidates who presented themselves for the Final Examination, twenty-eight passed. In the Branch of Mineral Chemistry—C. R. Chown, A.R.C.S. (Lond.), B.Sc. (Lond.); H. Gilmour; W. P. Harmsworth; J. G. King; H. Knight; P. G. Knapman, B.Sc. (Lond.); and R. H. Truelove, B.Sc. (Lond.), A.R.C.S. (Lond.). In the Branch of Metallurgical Chemistry—E. O. Jones, B.Sc. (Lond.), A.R.C.S. (Lond.); W. A. C. Newman, B.Sc. (Lond.), A.R.C.S. (Lond.); and E. W. Yeoman, B.Sc. (Lond.), A.R.C.S. (Lond.). In the Branch of Physical Chemistry—J. I. Crabtree, B.Sc. (Vict.), and Miss A. M. Finney, B.Sc. (Birm.). In the Branch of Organic Chemistry—J. L. S. Allan; J. Crawford; G. J. Eastburn; J. H. Naylor, M.Sc. (Manc.); F. G. Rawling, M.Sc. (Leeds); S. Robertson; A. Wilson; T. A. Wilson; and T. Wright. In the Branch of the Chemistry of Food and Drugs, and of Water—S. W. Bunker, B.Sc. (Lond.); D. H. B. Cowman, B.Sc. (Lond.); A. Gemmell, B.S. (Edin.); C. L. Hinton; H. Raistrick, B.Sc. (Leeds); M. J. Robb, B.Sc. (Aberdeen); and S. B. Tallantyre.

City and Guilds of London Institute.—On the report of the Delegacy charged with the management of the City and Guilds (Engineering) College, the Council of the City and Guilds of London Institute on July 24th awarded the Diploma of "Associate of the City and Guilds of London Institute" to the following matriculated third-year students of the City and Guilds College who have completed a full course of instruction as prescribed by the Council. (An asterisk denotes entered as a second-year student):—*Civil and Mechanical Engineering*—A. S. Clay (Bramwell Medal), C. S. Stuart, R. W. Peake, A. K. Newland, A. G. Webb, J. E. Heinig, R. H. Williams, A. T. Sturgess, D. S. Baker, J. A. Mitchell, D. Wark, C. L. Hall, J. W. D. Cook, I. J. David, J. H. T. Wroughton, G. D. M. Gwynne Griffith, R. H. Warde, J. E. B. Potter, R. E. G. Dennys, C. A. E. Suckau, O. F. C. Bender, S. W. Allen-Magill, O. da S. Maia, R. C. L. Gagnier, J. A. R. Bromage, B. St. J. Newton, W. E. Bushby, W. A. Willox, E. S. M. Mounib, J. D. Chassereau, J. G. Eggar, S. F. Brooker, J. Gjems, W. L. Campbell,* F. T. Boyes, M. F. Dewidar, E. R. Desmarais, T. H. Gotch, R. E. Hammersley-Heenan, S. C. Crewdson, A. O. Morrison, L. Harris, W. R. Boyes, G. H. Reid,* R. R. B. Falcon, C. B. Prescott, C. L. H. Jackson, O. J. T. Runge, C. A. R. Dewey,* C. W. Lacey, J. N. D. Hammersley-Heenan, S. Grunspan, J. A. A. Manes, G. A. S. Dibley,* H. C. Harvey, W. A. M. Allan, J. A. S. Menezes, A. P. Daly, M. R. Lory, A. A. Linsell,* A. R. Weiss, B. Splitter,* E. O. Dunn, E. P. Naish, M. T. Dew. *Electrical Engineering*—F. L. Otter, J. Rosen, B. S. Lion, C. P. Smith* (Siemens Memorial Medal), E. A. Beavis, C. F. Pittman, T. H. Solomon, E. Hutchison, A. J. Dannhorn, A. C. Patel,* P. Varadachari, G. C. Clark, L. A. McDougald, C. J. Hews, M. H. J. Mitchell, H. C. Burrowes, G. T. McHatton, E. L. A. Mathias, D. Milner,* C. G. Panayotopoulos,* R. R. G. Mann,* A. M. Searle.* *Chemistry*—R. G. Parker.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Casein and Formalin.—May I ask for information describing the reaction between casein and formalin? I understand that a considerable amount of research into the structure and properties of the proteids has been prosecuted in Germany of late years, and would like to know whether anything has been done there or in this country to elucidate the following points:—(1) The formula of the reaction; (2) A solvent or solvents for the precipitate.—Cramond.

THE CHEMICAL NEWS.

Vol. CVI., No. 2750.

ESTIMATION OF DIRT IN MILK.

By W. F. LOWE, A.R.S.M., F.I.C.

It is seven years ago since I first took up the estimation of dirt in milk samples; there had been numerous complaints about dirty milk sold in Chester, and the Public Health Committee asked me if it would not be possible to estimate the dirt, so that proceedings could be taken against the milk sellers.

The first thing to be done was to obtain larger samples, and I got the food inspectors to take three pints, so that I received one pint, and could then use 500 cc. for the estimation.

I first tried the method given in Lehmann's "Methods of Practical Hygiene"; this was to place the well stirred-up milk in a glass cylinder and allow it to stand until all the sediment had settled; the milk was then drawn off with a syphon down to about 20 or 30 cc., the jar was filled up with water, allowed to settle, and the water syphoned off, and this was repeated until all the milk had been washed away. The sediment was then collected on a tared filter-paper, having first been examined under the microscope, dried at 100° C., and weighed.

This method was not very satisfactory, as a good deal of the sediment was evidently lost during the process, and I then tried a large separating funnel for the milk, and after standing all night drew off the sediment by the tap, mixed with only a few cubic centimetres of milk; it was diluted with water and washed directly on a tared filter-paper. A better method is to wash the sediment into a platinum dish and evaporate off the water, dry, and weigh; any sand can afterwards be estimated by burning up the residue.

From the examination of a number of slides of cowdung under the microscope it was evident that the sediment present was usually dung; in very dirty samples it can be seen to be dung by the naked eye, if the bottle containing the milk has been standing a little time, and is held up so that the bottom can be looked at from below. A powerful pocket lense is useful for this purpose.

Lehmann states that recent cowdung never contains more than 20 per cent of dry matter, and recommends that the weight of the dry sediment should be multiplied by five in order to give the actual quantity of dung present. This I found to be the case, as the dung usually lost about 80 per cent on drying at 100° C.

This, however, does not give a true representation of the amount of dung that has been originally present, as I found by the addition of weighed quantities of recent cowdung to milk only 11 to 12 per cent, or practically one-eighth of the amount added, could be recovered as dry sediment, the remaining 88 to 89 per cent having passed into the milk as moisture, extractives, and soluble salts, and the weight of dry sediment should be multiplied by eight.

As this method of estimation is not very satisfactory I next tried the estimation of the sediment by volume, and for this purpose a cylinder drawn out at the bottom was used; it was, in fact, a portion of a separating funnel, the tap of which had been broken; to this was attached, by rubber tube, a small glass tube about 2 inches long graduated in 0·01 c.c.; it was made out of a pipette, and was widened out at the top and closed with a rubber stopper at the bottom, and in order to prevent leakage a cap made from a bit of rubber tube and closed with a bit of glass rod was slipped over the end. Weighed quantities of recent cowdung were also examined with this apparatus, and it was found that the volume agreed very well with the weight of dung added to the milk.

The arrangement is almost the same as that of Dr. Houston, but I had been using it for a considerable time before his method was published, and it is one that would naturally suggest itself.

Dr. Houston's is about the most convenient apparatus for collecting the sediment, but a much less expensive, and one that answers very well, is the half litre conical bottle with the bottom removed, to the neck of which is attached a small graduated tube widened out at the top to fit the neck of the bottle. These can be obtained from the apparatus makers, but the graduated tubes usually supplied with them are only marked in 0·05 c.c. divisions and are closed at the bottom. It is better to have the tube graduated in 0·01 c.c. and to have the bottom open, so that it can be closed with a stopper or cap, as the sediment can then be easily removed.

After the sediment has settled, for which purpose it is allowed to stand over night, and its volume has been noted, the milk is poured off into its sample bottle, sufficient remaining in the little tube to retain the sediment. The tube is then detached and is filled up with water, and the sediment washed until free from milk; it is then run out through the bottom into a flat, thin watch-glass, and is examined under the microscope with a 1 inch or ⅔ inch objective, and some of it can be placed on a slide for higher powers.

The sediment usually consists of the undigested fibre of the food, and is mostly broken down vegetable tissue, stained yellowish is colour with bile, but in some cases it is mostly sand.

In order to prove the presence of bile in the sediment, and therefore to prove conclusively that it consisted of dung, I have made use of the modified Pettenkofer's test for bile acids (given in Watts's "Dictionary of Chemistry," vii., 188; it is also given in Allen's "Commercial Organic Analysis," second edition) used for testing urine for bile.

There are two ways in which this test can be applied to the sediment. In the first the sediment is filtered through a small filter-paper, and a fairly strong solution of cane sugar is run through; the paper and sediment are then thoroughly dried at 100° C., allowed to cool completely, and a drop of pure sulphuric acid run over the particles, when a fine cherry red to crimson colour will be seen, especially on holding the paper up to the light; the colour develops round the particles, and if they are very small a pocket lense is useful.

The other method is to dissolve a little cane-sugar in the watch-glass containing the sediment, and decant off the solution as completely as possible, and then dry the sediment on the watch-glass and apply the drop of sulphuric acid after cooling. This method is, I think, the better of the two, if not too much sugar is used, as it gives more time for observation, but if an excess of sugar has been used it coats the particles so thickly that the sugar may begin to char before the colour develops.

The colour produced by this test is said to be due to the action of furfural on cholalic acid. The glycocholic acid and the taurocholic acid of the bile salts undergo hydrolysis, and cholalic acid is one of the products, and it is the furfural produced from the sugar that gives the colour with the cholalic acid.

Mr. A. R. Tankard has suggested the use of grape-sugar, and I think it answers better than cane-sugar, as it does not char.

As to the limit for dirt in milk we have had convictions at Chester for as small an amount as 2 parts per 100,000 of milk, but this has been after a milk seller has been previously cautioned and there has been no improvement.

A prosecution is generally instituted when the amount reaches 3 parts per 100,000. In the counties of Flint, Denbigh, and Carnarvon, for which I am also the Public Analyst, a limit of 3 to 4 per 100,000 has also been taken.

The prosecutions and fines inflicted have had a very good effect, as the milk has improved wonderfully in this respect, and it is the exception now to receive a sample containing enough sediment to estimate. The effect can also be seen on the cows, as the cowkeepers have realised the necessity of keeping the cows clean, and one no longer sees them coming up to be milked plastered over with dung.

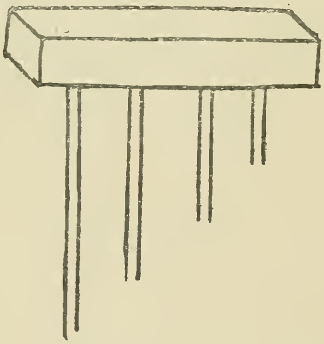
During hot weather it is well to add a few drops of formalin to the milk, but in cold weather, if the milk is recently taken, this is not necessary, and in cases where the milk is already sour it is best not to attempt to estimate sediment; but it is an important point, for in the case of a milk sample sent to the Government Laboratory for reference the sample will certainly be sour, and it will be a very different matter to estimate sediment in a bottle of solid curd as compared with one of fresh milk; at the same time the Government chemists have been able to confirm from such samples.

I have not gone into the bacteriological examination of milk, although in the first one or two cases taken into court Dr. A. E. Thomas, who at that time was Medical Officer of Health for Chester, examined the same milk for *B. Coli*, in order to give additional evidence of pollution. It is not difficult to examine for *B. Coli;* but after the matter had been gone into more fully it did not seem necessary to do so, and for further prosecutions the amount and nature of the sediment only has been relied on.

THE DIFFUSION OF ALKALIS AND ACIDS.

By W. R. FORBES, B.Sc.

The diffusion of alkalis may be shown by immersing in the liquid a gelatin tube containing phenolphthalein as indicator (Keeble, "Prac. Plant Physiology"). This method may be applied to study the rate of diffusion of alkalis and acids as follows:—Into a block of wood (see Fig.), mount a series of glass tubes of decreasing height. Fill these tubes with gelatin containing thymol and an indicator. In the case of acids methyl orange is used, and in that of alkalis phenolphthalein.



NOTE ON THE

SEPARATION OF FAT FROM SEWAGE.

By LEONARD CLEMENT, M.A.(Cantab), F.I.C.

A somewhat singular case of the separation of fat from sewage has recently come to the author's notice at the Sewage Works of the Nelson Corporation. The sewage of the town (1¼ million gallons per day dry-weather flow) gravitates into a rectangular brick chamber, from which it is lifted into septic tanks, &c., by means of centrifugal pumps. The pumps draw from a point at the bottom of the chamber and in the wall opposite to that in which the end of the main sewer is situated. The end of the sewer delivers at the top of the chamber, and is usually covered by sewage to the extent of a few inches. The capacity of the chamber thus utilised is only about 3300 cubic feet, and the direct distance between inlet and outlet 28 feet. The chamber, which is covered by the floor of the engine house, was cleaned out in February, 1902, and, until a few months ago, had not been examined since. On being opened, it was found to be almost completely filled with sand and other heavy debris, through which the sewage travelled by means of a comparatively narrow channel. A strong cheese-like odour permeated the atmosphere of the chamber, and the surface of the sewage was covered to a uniform depth of 6 inches with a yellow scum which was greasy to the touch.

A portion of this scum, after extraneous water had been allowed to drain away, gave on analysis the following figures:—

	Per cent.
Moisture	= 29·8
Fat	= 58·8
Foreign matter (by difference)	= 11·4

The dried fat-free residue gave, on ignition, ash amounting to 1·45 per cent of the whole sample. This ash consisted chiefly of sodium and calcium carbonate and the oxides of iron and aluminium.

That portion of the sample designated foreign matter comprised particles of the lighter bodies which usually characterise raw sewage, such as wood, coke, and the outer integuments of various seeds and fruits. It permeated the whole mass of the scum, indicating that the fat had separated from the sewage in small quantities, and had afterwards become consolidated into a comparatively coherent mass.

The freedom of the scum from any large proportion of nitrogenous matter is probably attributable to septic action over a long period of time, and also to the peculiar conditions of the case, which only permitted the separation of the very lightest particles in this way.

The extracted fat was brown in colour, opaque, and of very hard consistency, showing a strong tendency to crystallise. It gave the following analytical figures:—

Specific gravity at 54° C.	0·909
Melting-point	49·5° C.
Saponification number	199
Unsaponifiable matter..	5·3 per cent
Iodine value (Hubl.)	7 „
Reichert-Meissl number	0·3
Acid value	181

When some of the original scum was suspended in pure water in daylight it rapidly lost its odour and became covered with a dense growth of mould (a variety of mucorineæ), but no signs of such growths were visible when the scum was first removed from contact with sewage.

Cleaned of fat the chamber was closed down, and again examined after a period of rather less than three months. It then showed a scum of fat half-an-inch in thickness, but in this instance the particles had not united into a compact mass, and samples contained both more water and more nitrogenous matter than those collected three months before.

It seems likely that the separation of fat in this way is limited by the thickness of the fat scum above, since this, floating low in the sewage due to the admixture with water, prevents fresh particles of fat from rising out of the range of strong currents of sewage underneath. In which case a better yield of fat should occur if the scum is removed at more frequent intervals, or if the chamber is worked at a higher level so as to give a greater thickness of quiescent sewage above the level of the incoming sewer. Experiments in this direction are being tried.

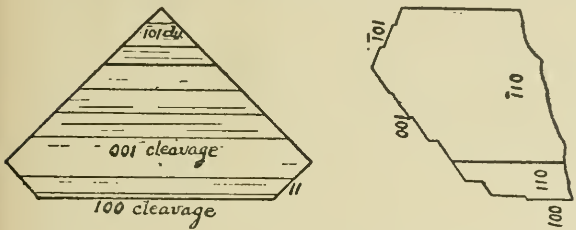
Corporation Laboratory, Nelson, Lancashire.

LORANDITE FROM THE RAMBLER MINE, WYOMING.

By AUSTIN F. ROGERS.

I am indebted to Mr. Berger, of Placerville, California, for an interesting specimen from the Rambler mine, near Encampment, in southern Wyoming. This specimen consists of dark fine-grained massive pyrite, upon which are implanted barite crystals and well formed crystals of orpiment. With the orpiment and barite are associated several orange-red realgar crystals and a single deep red crystal of what proved to be lorandite or thallium meta-sulpharsenite, $TlAsS_2$. This is the second known occurrence of lorandite, the original locality being Allchar in Macedonia (Krenner, *Abstract in Zeit. Kryst. Min.*, 1897, xxvii., 98).

The crystal mentioned is an imperfect one, of about 4 mm. size, bounded by the faces of a rhombic prism with interfacial angles of about 90° (calc., 93°) and by three cleavages in one zone, which is at right angles to the prism zone. Using Goldschmidt's orientation (*Zeit. Kryst. Min.*, 1899, xxx., 272—294), the prism faces constitute the {110} form and the three cleavages are parallel to {100}, {001}, and $\{\bar{1}01\}$. The accompanying figure (plan and side elevation) gives an idea of the crystal. All the faces but {110} are cleavages. The following angles measured on the reflection goniometer prove that the crystal is lorandite.



		Measured.	Calculated.
100(clv.) : 001(clv.) =	..	52°49′	52°27′
001(clv.) : $\bar{1}$01(clv.) =	..	51°17′	51°49′

The first mentioned angle was measured on a detached fragment, while the other angle was measured by mounting the matrix specimen on the goniometer, as it was feared that the crystal would go to pieces if detached from its matrix. The cleavage parallel to {100} is very perfect, that parallel to {001} good, and that parallel to $\{\bar{1}01\}$ fair. The lustre is adamantine on the cleavage faces, but the prism faces {110} are dull. Even if bright they could not be measured on account of the close proximity of the matrix.

Fragments are prismatic, non-pleochroic, and have parallel extinction. Lorandite is monoclinic, but the cleavages are in the zone of the ortho-axis and so have parallel extinction.

On charcoal lorandite fuses easily to a black globule, colouring the flame bright green. It gives a green flame when fused on platinum wire and alloys with the platinum. In the closed tube it fuses to black globules, giving a black and red sublimate and also minute colourless adamantine crystals of As_2O_3.

The lorandite is soluble in nitric acid, turning yellow. With chloroplatinic acid the solution gives a light yellow precipitate (Tl_2PtCl_6). After evaporating off the nitric acid, potassium iodide gives a yellow precipitate (TlI). The nitric acid solution with hydrochloric acid gives a white precipitate (TlCl).

With the spectroscope this white precipitate of thallium chloride gave a single bright line in the green. With a pure thallium salt the green line appeared at exactly the same position.

Although the blowpipe and chemical tests were made with a very limited amount of material consisting of minute detached fragments, the identity of the mineral with lorandite is well established. The spectroscope proves it to be a thallium mineral and the goniometrical measurements prove it to have the crystal form of lorandite. The blowpipe and chemical tests are confirmatory.—*American Journal of Science*, xxxiii., No. 194.

BENZOIC ACID AS AN ACIDIMETRIC STANDARD.

By GEORGE W. MOREY.

The study of the suitability of benzoic acid as a primary standard in acidimetry and alkalimetry was suggested by experience gained in the purification of benzoic acid to be used as a calorimetric standard. During that work it was found that benzoic acid could be titrated with standard alkali to a high degree of accuracy, and that this titration afforded the most rapid and accurate method of comparing the purity of various samples. Since pure benzoic acid has been furnished for some time by the Bureau of Standards as a calorimetric standard, it would of course be advantageous to use it also for a standard in acidimetry if found suitable.

Wagner (*Proc. Fifth Internat. Cong. Applied Chem.*, Berlin, 1903, i., 323), in a report presented to the Fifth International Congress of Applied Chemistry in 1903, mentioned benzoic acid among a number of other possibilities for the purpose named; and Phelps and Weed included it in a short study of the availability of several organic acids and acid anhydrides (*Am. Journ. Sci.*, 1908, xxvi., 141).

The method used in studying this problem was that of standardising a hydrochloric acid solution by several well-known and standard methods, and comparing the results so obtained with those obtained by standardising the same hydrochloric acid against benzoic acid. The methods chosen for the work were the distillation method of Hulett and Bonner, the gravimetric silver chloride method, comparison with a sulphuric acid solution standardised gravimetrically by the barium sulphate method, and comparison with the same sulphuric acid standardised volumetrically by the sodium oxalate method. All the materials used were prepared with the greatest care, and were carefully protected from the carbon dioxide of the air by suitable guard-tubes. Great care was taken to prepare and keep all solutions free from carbon dioxide, and each solution was tested from time to time for the presence of carbonate. All operations were conducted so as to be as free from error as possible. Weight burettes were used for all titrations, which were made in a 300 cc. flask through which passed a stream of air free from carbon dioxide. A 1 per cent solution of phenolphthalein was used as indicator in all the titrations.

Direct Standardisations of Hydrochloric Acid.—The hydrochloric acid was first standardised in its preparation, having been prepared by the method of Hulett and Bonner (*Journ. Am. Chem. Soc.*, 1909, xxxi., 390), which is based on the constancy of composition, at a definite atmospheric pressure, of the constant boiling mixture formed by hydrochloric acid and water. From the data given by Hulett and Bonner, the resulting solution was calculated to contain 0·0036396 grm. HCl per grm. solution, corresponding to a 0·1-N factor of 0·9980.

The next standardisation was by the silver chloride method with a 50 grm. sample. The hydrochloric acid in the filtrate and washings was determined with the nephelometer and the amount found added to that calculated from the weight of silver chloride. Four concordant determinations by this method gave the value 0·0036611 grm. HCl per grm. solution, corresponding to a 0·1-N factor of 0·9984.

The hydrochloric acid was standardised from the sulphuric acid by comparing the two solutions through a solution of sodium hydroxide. The mean of six determinations of the ratio HCl : NaOH was 1·0464; of four determinations of the ratio H_2SO_4, 0·8454; the ratio $H_2Cl : H_2SO_4$ was therefore 1·2378. For the gravimetric standardisation of the sulphuric acid a 50 grm. sample was taken. After igniting and weighing in the usual manner the precipitates were tested for occluded barium chloride by the method of Hulett and Duschak (*Zeit. Anorg. Chem.*, 1904, xl., 196), but the amount found was always less than 0·1 mgrm., a negligible quantity. The 0·1-N factor for the HCl calculated from these determinations was 0·9984.

The standardisation by means of sodium oxalate was made after a series of experiments made to compare various samples of sodium oxalate. While concordant results were obtained by strict adherence to a certain procedure in the transformation of the oxalate to the carbonate, it was found that slight variations in the rate or manner of heating might produce very discordant results. The 0·1-N factor calculated from the determinations with sodium oxalate was 0·9982.

Standardisation of Hydrochloric Acid by Benzoic Acid.—Because of the bulkiness of the sublimed benzoic acid, it was found convenient to fuse or compress it before weighing. Fusion has the advantage of diminishing the possibility of large surface effects. A platinum dish was filled with the sublimed benzoic acid, and the covered dish placed in an oven heated to about 140°. When melted the liquid was poured into a test-tube, and after solidifying the stick so obtained was broken into pieces of convenient size and preserved in a glass stoppered bottle. Samples so prepared can be kept indefinitely and used without preliminary drying.

About a grm. of this material was weighed and placed in a 300 cc. flask which had been swept free from carbon dioxide; 20 cc. of alcohol were added, the flask was stoppered and let stand until the sample had dissolved. Three drops of a 1 per cent solution of phenolphthalein were then added and the solution titrated directly with 0·1/N alkali, a current of air free from carbon dioxide bubbling through the solution until the titration was completed. The end-point chosen was that of a 7 per cent transformation of the indicator added, that being the end-point which should give the best results (Noyes, *Journ. Am. Chem. Soc.*, 1910, xxxii., 857). The effect of the alcohol on the end-point was determined in a blank experiment and the titrations corrected by this amount. This blank ranged from 0·06 to 0·08 cc.

In the first series of experiments a solution of barium hydroxide was used, this being the most convenient alkali to use when exclusion of carbon dioxide is necessary. The mean of four concordant determinations of the ratio $HCl : Ba(OH)_2$ was 1·3790. The mean of fifteen determinations, whose maximum difference was one part in 1600, gave the value 0·9984 for the 0·1/N factor of the HCl. In a second series of experiments the sodium hydroxide solution used in comparing the hydrochloric and sulphuric acids was used, for which the ratio HCl : NaOH was 1·0464. The mean of four concordant determinations was 0·9981.

Summary and Conclusion.—The results of the foregoing standardisations are summarised in the following table:—

Summary of Standardisations.

Method.	0·1/N factor for HCl.
Direct by Hulett and Bonner	0·9980
Direct by AgCl	0·9984
H_2SO_4—$BaSO_4$—NaOH—HCl ..	0·9984
H_2SO_4—$Na_2C_2O_4$—NaOH—HCl ..	0·9982
$C_6H_5CO_2H$—$Ba(OH)_2$—HCl	0·9984
$C_6H_5CO_2H$—NaOH—HCl	0·9981

The close agreement of these results proves the accuracy of the benzoic acid method. Moreover, benzoic acid has many advantages. Its high molecular weight permits the use of large samples, thus reducing the error of weighing; its stability and lack of hydroscopicity make it very convenient; and the method is rapid, since a single weighing and a titration are all the operations involved. These considerations, combined with the ease of obtaining it in a high state of purity, make benzoic acid an excellent material to use as a standard in acidimetry and alkalimetry.—*Journal of the Washington Academy of Sciences*, ii., No. 13.

THE USE OF MICE AND BIRDS FOR DETECTING CARBON MONOXIDE AFTER MINE FIRES AND EXPLOSIONS.*

By GEORGE A. BURRELL.

Introduction.

In connection with its investigation of the causes of mine fires and explosions, the Bureau of Mines is making a careful study of the methods that can be used with greatest efficiency for exploring mines containing smoke or suffocating or poisonous gases.

The presence of that poisonous gas, carbon monoxide (white damp), in the afterdamp of explosions and fires in mines has caused the death of a great many miners. An inspection of the reports of those explosions and mine fires in which men have been killed shows that this gas is often the cause of the majority of the fatalities. Haldane (C. LeN. Foster and J. S. Haldane, "The Investigation of Mine Air," 1905, p. 144) makes the statement that carbon monoxide poisoning is responsible for nearly all the fatalities. After a recent disaster at a mine in Pennsylvania in which twenty-one men were killed, the bodies of seventeen men showed no such marks of violence as would be produced by the concussion of an explosion. Tests of blood from some of these bodies clearly showed the bright pink hue caused by carbon monoxide. Not only have men present in mines at the time of disasters succumbed to this gas, but rescuers endeavouring to save their unfortunate comrades have perished also.

Of the gases produced in mines carbon monoxide is the most feared and the most difficult to detect. A miner's lamp gives warning of almost every dangerous condition of the atmosphere in a mine except the presence of this gas. Percentages of methane below those that form explosive mixtures can be detected by the appearance of the "cap" of the lamp flame, and a deficiency of oxygen is shown by the smothering of the flame in time for a retreat to be made before bodily harm can result. Carbon monoxide, however, may be present in deadly quantities in an atmosphere without the safety lamp detecting it, because a proportion much below that required to give a cap on a lamp flame is extremely poisonous.

Other gases occasionally found in mines in harmful quantity, such as hydrogen sulphide and oxide of nitrogen fumes, can be detected even in great dilution by their odour, so that fatalities from the presence of these gases in mines are few.

The author tested the value of a wick flame as a detector of carbon monoxide in comparison with its value as a detector of methane. A Wolfe safety lamp, constructed so that prepared mixtures of air and carbon monoxide could be fed into it at the base, was used. The minimum percentage of carbon monoxide (about 2 per cent) required to produce a visible cap was found to be almost identical with the required proportion of methane. Two observers could detect no difference in the colour or the height of the caps produced by this percentage of either gas; neither could they when 3 per cent of either gas was used.

In a mine some observers, especially after becoming accustomed to the darkness ("getting eyesight," as it is termed), may detect a cap when the air contains less than 2 per cent of methane, and it is possible to detect less

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* *Technical Paper* 11, Department of the Interior, Bureau of Mines; Joseph A. Holmes, Director.

than 2 per cent of methane by the use of special testing lamps. But the point brought out by the author's experiments is that low percentages of either methane or carbon monoxide scarcely give caps that distinguish one gas from the other. Moreover, it has been the author's experience that when a given percentage of carbon monoxide is present in the air of a coal mine, a larger percentage of methane is usually present, so that this gas would interfere with the detection of carbon monoxide by a lamp even if carbon monoxide enough to give by itself a characteristic cap were present. It is also true that in the afterdamp of mines carbon monoxide in quantity sufficient to produce a cap usually accompanies a deficiency of oxygen and an excess of nitrogen, so that the lamp is extinguished before it can show a cap. One result of this last fact, however, is that the indications of a lamp may sometimes prevent a man from going into an atmosphere containing carbon monoxide enough to be rapidly poisonous.

The gases that come out of the crevices in the coal bed immediately after shots of explosives may contain much carbon monoxide and hydrogen, besides methane, and when a lamp is held close to the crevices the carbon monoxide and hydrogen may cause the cap of the lamp flame to differ somewhat from the cap produced by methane alone. In exploring mines, however, the great danger to a rescue party is from small proportions of carbon monoxide—proportions so small that they have no visible effect upon the flame.

The author is aware that some mining men are of the opinion that a percentage of carbon monoxide below that which is immediately dangerous perceptibly brightens or lengthens the flame of a lamp, but he knows of no characteristic of carbon monoxide that would warrant such an opinion. A possible explanation of the brightening or lengthening, suggested by J. W. Paul, mining engineer of this Bureau, lies in the fact that a party exploring a mine containing afterdamp sometimes enters a place in which the proportion of oxygen in the air is larger than it was in the place previously explored, and as a consequence the wick flame burns for a while with increased intensity. As the oxygen content of an atmosphere decreases, the flame of an oil lamp burns more dimly until, at 17 or 17·5 per cent of oxygen, the flame is extinguished.

Occurrence of Carbon Monoxide.

Carbon monoxide has not been positively identified in the samples of what may be termed normal mine air collected by this Bureau, except in samples collected at the working faces where the air was vitiated by powder smoke. Samples of mine air from the ventilating current, from the main returns, and from splits have been examined, also samples from inclosed areas in which the air had been still; but although the apparatus used was accurate to 0·02 per cent, the author can not state positively that carbon monoxide was present in any of the samples. A series of tests is now being conducted in which air from sealed bottles containing coal that was freshly mined at the time of bottling is being examined for minute quantities of combustible gases other than methane. Although about twelve examinations have been made of samples taken one week apart, the presence of carbon monoxide has not been positively determined.

It appears that carbon monoxide is produced in mines in harmful quantity only through the agency of heat, or by the incomplete combustion of carbon that attends explosions, mine fires, the use of explosives, &c. The gas is produced by the imperfect combustion and dry distillation of coal dust in explosions, by the imperfect combustion of methane, by the burning of wood and coal with insufficient supply of oxygen, and by the contact of previously formed carbon dioxide with red-hot carbon, as when the flame of a blast or a gas explosion is projected into an atmosphere filled with the fine coal-dust. The last-named cause operates toward the formation of carbon monoxide when those explosives that contain within themselves sufficient oxygen for the complete oxidisation of their carbonaceous components are used in breaking down coal.

The carbon monoxide formed, with hydrogen and methane, collects in the open spaces and crevices behind a standing shot, and the miner is often burned by the flame that bursts forth when he carelessly puts his lamp close to a crevice or into an open space to examine the effect of a blast. Besides the danger that attends the burning of these crevice gases, trouble is often experienced from the gases that result from the use of improperly handled explosives in ill-ventilated parts of a mine. A series of experiments is being carried on by the Bureau of Mines to determine the gases that are produced by the firing of different explosives, and the extent to which the use of the explosives vitiates the air of the working places.

Properties of Carbon Monoxide.

Carbon monoxide is a colourless and inodorous gas with a specific gravity of 0·967. A litre of it weighs 1·2506 grms. at 0° C. and 760 mm. pressure (Rayleigh, *Proc. Roy. Soc.*, 1897, lxii., 204). It will not support combustion, but burns with a pale blue flame. The lambent flame above a grate in which anthracite or coke is burning is due to the combustion of this gas. Carbon monoxide is the main combustible ingredient of water-gas, of producer gas, and of blast furnace gas, which contain approximately 15 to 40 per cent of it, and is present, but in smaller proportion, in illuminating gas made by the destructive distillation of coal. It has not been identified as a constituent of the samples of natural gas examined by the Bureau of Mines, a fact that accounts for natural gas being less poisonous than water-gas, producer gas, or ordinary illuminating gas. Carbon monoxide in mixtures with air has a wide range of explosibility, from 16·5 per cent gas, lower limit, to 74·95 per cent gas, higher limit (*Journ. Soc. Chem. Ind.*, 1902, xxi., 395). Methane has explosive limits that lie between about 6·1 per cent gas, lower limit, and 12·8 per cent gas, higher limit (*Journ. Soc. Chem. Ind.*, 1902, xxi., 395). The lower limits cited have reference to complete combustion and to the ignition of the gas by an electric spark. Other modes of ignition, changes in temperature, the shape of the containing vessel, differences in pressure, and the presence of more or less water vapour may change the range of explosibility somewhat. The addition of a large quantity of carbon monoxide to explosive mixtures of methane and air would have the tendency to widen the upper limit of explosibility over that of methane alone.

Physiological Effect of Carbon Monoxide.

The oxygen absorbed from the air in the lungs is normally taken up by the blood in the form of a loose chemical combination with the red colouring matter (hæmoglobin) of the corpuscles, and in this form it is carried to the tissues where it is used. Hæmoglobin not only combines with oxygen, but also forms a far more stable compound with carbon monoxide, and when saturated with the latter it cannot take up oxygen. Hence, when the corpuscles in the blood of a living animal are saturated with carbon monoxide they cannot carry oxygen from the lungs to the tissues, and death must result. According to Haldane (*Journ. Physiology*, 1895, xviii., 200, 430, 463), carbon monoxide has no other effect than that resulting from its interference with the oxygen supply of the tissues, and apart from its property of combining with hæmoglobin it is physiologically indifferent, like nitrogen.

The affinity of carbon monoxide for hæmoglobin is about 250 times as great as the affinity of the latter for oxygen (J. S. Haldane, "Causes of Death in Colliery Explosions and Underground Fires," report to the Secretary of State for the Home Department, 1896). However, if oxygen is administered to a person not too far overcome it will completely replace the carbon monoxide in the hæmoglobin. In this respect pure oxygen acts about five times as rapidly as normal air, which contains approximately 21 per cent of oxygen. From air containing very small percentages of carbon monoxide, less than 0·1 per cent, the blood of a man does not take up enough of the gas to cause distress, unless the man breathes such air a long time. If the air contains larger proportions, the blood sooner or later reaches that stage of partial saturation with carbon monoxide that produces helplessness. Haldane (*loc. cit.*, p. 17) makes the following observation:—

> The blood of a man will take up about 2 pints of CO or oxygen. A man at rest breathes about 10 or 12 pints of air per minute, and experiment shows that of the carbon monoxide inhaled about 60 per cent is absorbed by the blood. If a man would breathe air containing 0·1 per cent of carbon monoxide he would absorb 0·007 pint per minute. It would then take him nearly 2·25 hours to absorb a whole pint, or produce one-half saturation of the blood, at which stage the limbs would become so weak as to cause them to give way when an effort was made to walk. A man who is walking, however, breathes about three times as much air as a man who is at rest, hence he might absorb a pint within an hour. With 0·2 per cent of carbon monoxide the time would be one-half as long, with 0·3 per cent one-third as long, &c.

If a man who has breathed mine air containing carbon monoxide and has retired to fresh air to recuperate again enters workings containing this gas before the carbon monoxide has entirely been displaced from his blood, he feels the effects of the gas in less time than when he entered the workings before.

The experience of those who have been partly poisoned by carbon monoxide seems to teach that usually much pain or distress does not precede collapse. One of the first symptoms is weakness of the limbs and dimness of eyesight. For some time after resuscitation, however, there may be severe headache, or even epileptic seizures and other serious ailments.

Poisoning by carbon monoxide can take place very suddenly. For instance, a man in a mine may quickly pass from a place containing such a small quantity of the gas that he has experienced no distress into a place containing a larger quantity where, because of the already partially saturated condition of the blood, he will quickly succumb. Also, the action of the poison may be accelerated by increased exertion, such as climbing a steep incline or ladder, or lifting heavy weights.

Chemical Tests for Carbon Monoxide.

The author has by the aid of a portable gas analysis apparatus made tests of the air in mines after explosions and fires, and has thus ascertained on the spot the composition of the atmosphere in the workings. Because of the time required to make such tests, and the need of the services of a person with some knowledge of gas analysis apparatus, chemical tests of the atmosphere in a mine immediately after a disaster are not made as often as they should be. Another reason for omitting them is that quick chemical tests for small quantities of carbon monoxide are not made as successfully as are chemical tests for methane, carbon dioxide, and oxygen.

Perhaps the best chemical test for carbon monoxide, in that other gases do not interfere and very simple apparatus is required, is by the use of blood diluted with water to a buff-yellow tint. This test, in the author's experience, is capable of distinctly showing as little as 0·03 per cent of carbon monoxide in the atmosphere. The method of procedure is as follows:—

One or two drops of blood drawn from the finger are diluted with water until equal portions of the solution placed in 100 c.c. test tubes have a buff-yellow colour. One of the tubes is taken into the mine, and at the place where the air is to be tested about 50 c.c. of the blood solution is poured out, the mine air taking its place. The tube is then corked, taken to the surface, and gently shaken for ten minutes. If the air contained carbon monoxide, the pink colour caused by the presence of carbon monoxide hæmoglobin is detected by comparing the solution with the normal blood solution in the other tube.

A fresh active solution of cuprous chloride may be used instead of blood for examining air for carbon monoxide. According to the author's experience, the use of such a solution, if the apparatus is precise and is properly manipulated, will show proportions of carbon monoxide harmful to a rescue party.

(To be continued).

THE PHYSICAL AND CHEMICAL PROPERTIES OF SOME ORGANIC AMALGAMS.*

By HERBERT N. McCOY and FRANKLIN L. WEST.

Although ammonium amalgam was first prepared a little over a century ago (Seebeck, *Ann. Chim. Phys.*, 1808, lxvi., 191), it remained until very recently the sole representative of its class. Shortly after its discovery, Davy (*Phil. Trans.*, 1810, c., 37) concluded that this unique substance was a compound of the pseudo-metal ammonium with mercury, and while this view was shared by many chemists, others believed the so-called amalgam was only mercury inflated with ammonia and hydrogen. The true metallic nature of the substance was finally proved beyond question by the researches of Le Blanc (*Zeit. Phys. Chem.*, 1890, v., 467), Coehn (*Zeit. Anorg. Chem.*, 1900, xxv., 430; *Zeit. Elektrochemie*, 1906, xii., 609), and G. M. Smith (*Journ. Am. Chem. Soc.*, 1907, xxix., 844). The experiments of Le Blanc also indicated very forcibly the possibility of the existence of substituted ammonium amalgams; and though Le Blanc concluded he had firmly established this point, yet the supposed new amalgams had so transient an existence under the conditions of his experiments that they were not isolated, and no evidence of their existence, other than that based on polarisation potentials, was obtained.

The preparation of two new synthetic amalgams has recently been described (McCoy and Moore, *Journ. Am. Chem. Soc.*, 1911, xxxiii., 273). These new substances are monomethylammonium amalgam and tetramethylammonium amalgam. The first of these is much like ammonium amalgam in its physical and chemical properties. The second differs markedly in several important particulars. As obtained by McCoy and Moore, it appeared as a crystalline mass mixed always with an excess of liquid mercury. It was of characteristic metallic lustre. At a temperature of zero degrees or lower it was fairly stable in the absence of moisture. Chemically it resembles the alkali amalgams, but is far more active than that of sodium. It reacts with water with great energy, and rapidly gives hydrogen and the corresponding base, tetramethylammonium hydroxide. From solutions of salts of copper and zinc, these metals are precipitated at once; while from solutions of salts of sodium and potassium the corresponding amalgams are formed. With a solution of ammonium chloride, the characteristic inflated mass of ammonium amalgam is produced. The very high solution tension indicated by these reactions was confirmed by direct potential measurements. The value obtained for similar conditions was about 0·6 volt higher than that found recently by Lewis and Kraus for sodium amalgam (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1459). The properties of the new synthetic amalgams presented so many novel and interesting features that the study of the subject has been continued by us with the results herewith presented.

The first object of the research was to find an improved method of preparation and preservation of tetramethylammonium amalgam which was at the same time the more interesting of the two new bodies and the more difficult to prepare. The method of McCoy and Moore consisted in the electrolysis of an absolute ethyl alcohol solution of tetramethylammonium chloride, using a mercury cathode and a silver plated platinum gauze anode. The silver

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* From the *Journal of Physical Chemistry*, xvi., No. 4.

united with, and so prevented secondary actions by, the liberated chlorine. The electrolysis was usually made at zero C. or at about −10° to −15°. It was found that absolute alcohol reacted with the amalgam rather rapidly even at zero, about 5 per cent being destroyed per minute (McCoy and Moore, *loc. cit.*). As this action during electrolysis decreased the yield very greatly, we designed a vessel (Fig. 1) in which the electrolysis could be conducted at the temperature of boiling liquid ammonia, −34°. At this temperature the action of the alcohol on the amalgam was much slower than at 0° C. We also found that a platinum anode could be substituted for the one of silver, as the chlorine set free no longer attacked the amalgam at this low temperature.

The glass vessel shown in Fig. 1 had outside dimensions of 13·5×5·5 cm. One of the side tubes of the jacket was joined by a rubber tube to a steel cylinder containing 50 pounds of commercial liquid ammonia. This jacket could be readily filled with liquid ammonia from the steel cylinder. After the vessel had become cold and coated externally with frost, the ammonia boiled away only slowly. The second side tube was joined to two large bottles partly filled with water for the absorption of the waste ammonia gas. The inner chamber of the vessel was closed by a close fitting rubber stopper carrying the electrodes and a tube filled with calcium chloride. The glass tube with the stopcock leading downward from the inner chamber was intended to allow us to draw off the amalgam without exposing it to the air. However, the usual procedure with this apparatus yielded so much solid amalgam that another method of removing the product proved more expedient.

The preparation of the amalgam was carried out as follows:—75 grms. of clean dry mercury were put into a piece of white muslin, 15 cm. square, and lowered into the vessel (Fig. 1). Forty cc. of absolute alcohol containing 1·5 to 2·0 grms. of dissolved salt were poured in, and the cloth made to stand up snugly against the damp walls of the vessel. The stopper and electrodes were adjusted, and the jacket filled with liquid ammonia from the tank. The electrolysis was usually conducted with an E.M.F. of 35 to 40 volts, which gave a current of 0·3 ampère. After the electrolysis the cloth, together with the semi-solid amalgam, was then raised above the solution, and the alcohol drained off while the whole was still in the electrolysis chamber, the low temperature of which prevented decomposition of the amalgam. The latter, while still held in the cloth, was rinsed in ice-cold carbon tetrachloride. This liquid has no action on the amalgam, and proved very effective in removing the alcohol and preventing decomposition by the moisture of the air. If kept at zero degrees under carbon etrachloride, the amalgam undergoes but little change in he course of several hours.

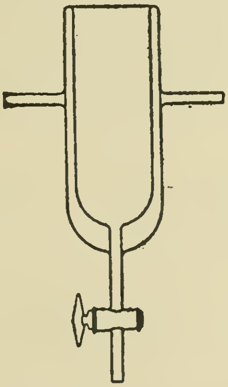


Fig. 1

Fig. 1.

As thus obtained, tetramethylammonium amalgam is a semi-solid mass of crystals and excess of liquid mercury, the former being but slightly soluble in the latter. By filtration with suction through a plug of cotton, the crystals are easily freed from most of the excess of mercury, and the amalgam is left as a solid crystalline metallic mass, weighing about 15 grms. During filtration the temperature must be kept at or below 10°, and the amalgam protected from the air by a layer of carbon tetrachloride. Unless otherwise stated all experiments which follow were made with *solid* amalgam which had been freed from excess of uncombined mercury.

Even at −34° the use of absolute alcohol as a solvent during electrolysis was not wholly satisfactory. By reason of the action of the alcohol on the amalgam, the yield of the latter was only about 15 per cent of that corresponding to the quantity of electricity passed through the cell. In the hope of finding a solvent that would give a better yield than did ethyl alcohol, fifteen other liquids were tried. Those selected were such as dissolved the salt and had high dielectric constants. Only two solvents gave appreciably better results, in some respects, than did ethyl alcohol; even these solvents had their disadvantages. Propyl alcohol acts on the amalgam more slowly than ethyl alcohol, but the solution has a lower conductivity, which necessitates the use of a smaller electrolysing current. Acetonitril behaves much like propyl alcohol. Very good preparations could be obtained from each of these solvents, but no decided advantage was to be gained by using either in place of absolute ethyl alcohol.

Almost all of the experimental work represented by this paper was carried out in an unheated room which had three large windows on each of two opposite sides. Most of the experiments requiring exposure of the amalgam to the air were made during the winter, so that with open windows the temperature of the room was usually between 0° and 10° C.

Physical Properties.—The amalgam is a silver-white granular solid. In its preparation, when the anode has been allowed to touch the cloth, large crystals will usually be found adhering tightly to the outside of the latter. These crystals will stand considerable pressure without breaking, and in cold dry winter weather their crystalline form is maintained for several minutes even though exposed to the air.

Density.—McCoy and Moore had observed that the solid amalgam floats on the excess of mercury, and stated that the density of the amalgam is somewhat less than that of mercury. We made determinations at zero degrees of the density of several solid preparations of tetramethylammonium amalgam by the pycnometer method, using carbon tetrachloride as the accessory liquid. The weight of the amalgam alone was in some cases found by direct weighing, with the material exposed to the air, when the weather was very cold and the air dry. An alternative method consisted in weighing a beaker containing amalgam covered with carbon tetrachloride, transferring the amalgam to the pycnometer, and finding the weight of amalgam removed by difference. The weight of the bottle filled jointly with amalgam and carbon tetrachloride, and again when filled with the latter alone, gave, together with a knowledge of the density of the carbon tetrachloride, the required data.

After each determination, the amalgam was immediately put into water, and the weight of the colloidal mercury thus obtained divided by the weight of the mercury, was taken as a measure of the concentration of the amalgam present (see McCoy and Moore, *loc. cit.*). The following results were obtained:—

Per cent colloidal mercury.	Density at 0° C.
0·0	13·6 (pure mercury)
1·2	11·8
1·0	11·7
1·0	11·6
2·0	11·1
2·4	10·6

Electrical Resistance.—The electrical resistance was measured by the Wheatstone bridge principle. Three resistance boxes were connected, as in the Post Office box bridge, by means of entirely negligible leads, and the lack of balance was detected with a sensitive D'Arsonval galvanometer. Even though the resistance measured was very small, yet with the ratio of 1000 to 1 in two of the boxes, the galvanometer was sufficiently sensitive to give an accuracy of one-fifth of 1 per cent.

The solid, but somewhat plastic amalgam was put into a funnel that was connected to a narrow U-shaped glass tube, and was drawn into the latter by means of a water aspirator. The tube was 37·7 cm. long and 0·047 sq. cm. in cross section. The entire manipulation was, in each experiment, carried out in a very cold room; during the electrical measurement the temperature of the amalgam was kept at 0° C. The resistance of the wires connecting the amalgam to the boxes was also measured with the ends of the wires placed near together in mercury, and this resistance subtracted from the total. The concentration of the amalgam was determined as above from the weight of the colloidal mercury produced when it was added to water. The following results were obtained, the specific resistance being expressed in ohms per linear cm. and 1 sq. cm. cross section.

Per cent colloidal mercury.	Specific resistance.
0·0	0·000094 (pure mercury)
2·0	0·000110
2·8	0·000110
5·0	0·000131
—	0·000133
—	0·000139

The per cent of colloidal mercury was not determined in the last two samples. The leads dipped a short distance below the surface of the amalgam, and it was therefore difficult to get at the true length of the column of material. This, together with the difficulty of working with the material, would not make the results given accurate to more than 1 or 2 per cent. It is to be observed that the higher the amalgam content, the greater is the resistance, and that the most concentrated amalgam has a resistance about one and one-half times that of mercury.

Electrical Behaviour of the Amalgams.—Coehn (*Zeit. Elektrochemie*, 1906, xii., 609) discovered that ammonium amalgam discharged a charged electroscope, but that the discharge takes place only if the electroscope is charged electro-negatively. We had no difficulty in confirming Coehn's observations on the discharge of negative electricity, and in addition, contrary to Coehn, we found that a small though decisive effect was always produced when the leaf of the electroscope was positively charged. We have also found that organic amalgams have similar properties. Monomethylammonium amalgam discharges both positive and negative electricity, the effect being, as in the case of ammonium amalgam, several times greater with negative electricity. On the other hand, tetramethylammonium amalgam discharges rapidly the positively charged electroscope, but has no effect when the electroscope is negatively charged.

The electrical behaviour of the last named amalgam is suggestive of that of the alkali metals and their amalgams. It is a well known fact that many metals give off electrons under the influence of ultra-violet light (Thomson, "Conduction of Electricity through Gases," Chap. X.). This action is the more pronounced the greater the electropositive nature of the metal. It is small with mercury, but is very marked with sodium and potassium. In case of the alkali metals, a strong source of ultra-violet light is unnecessary, even the light of a kerosene lamp is sufficient, while rubidium is still more sensitive, and gives off negative electricity in the presence of a red-hot glass rod. As the electrolytic solution tension of tetramethyl ammonium amalgam is about 0·6 volt greater than that of sodium amalgam and about equal to that of potassium amalgam (McCoy and Moore, *Journ. Am. Chem. Soc.*, 1911, xxxiii., 289), we might expect therefore that the organic amalgam would lose electrons under similar conditions. An account of our study of the electrical behaviour of synthetic amalgams follows.

The electroscope used was like that described by McCoy and Ashman (*Am. Journ. Sci.*, 1901, xxvi., 521), excepting that there was no condenser, C, nor plate L, to increase the electrostatic capacity. The instrument was one that had been used for several years in the Kent Chemical Laboratory, University of Chicago, for the quantitative measurement of radio-activity. The ionisation chamber is 20 cm. square and 14 cm. high; the gold leaf chamber, 9 cm. square and 10 cm. high. The gold leaf system is insulated by an amber plug, and carries at its lower end a circular brass plate or electrode 8 cm. in diameter. The motion of the leaf is observed through a pair of glass windows by means of a micrometer microscope. With the aid of two switches and a battery of small dry cells, the leaf could be instantly grounded or charged positively or negatively to about 300 volts. The discharge of the electroscope by an amalgam is most readily distinguishable from that by a radio-active substance in two noticeable particulars:—(1) The rate or discharge by the amalgam is erratically variable, (2) it also depends on the sign of the electric charge on the gold leaf system. However, the rate of discharge by an amalgam, though irregular, may be observed and measured in precisely the same way as in the case of a radio-active substance. This rate of discharge may readily be expressed in terms of that produced by a standard film of uranium oxide. Such a film, which produced an ionisation current of $2{\cdot}15 \times 10^{-11}$ ampères, as shown by comparison with one of McCoy and Ashman's standards (*loc. cit.*), was used throughout this work, and will be referred to as the "standard." In measuring the rate of discharge. the uranium film or the amalgam held in a shallow platinum dish was placed under the electrode on an earthed metallic support the distance of which below the electrode could be varied up to 8 cm. The micrometer scale of the reading microscope had 60 divisions; the standard discharged the electroscope at the constant rate of 42 divisions per minute. The natural leak amounted to about one-half division per minute.

(To be continued)

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

(Continued from p. 58).

Friday, September 6.

10 a.m. to 12 m. and 1 p.m. to 3 p.m.—Sectional meetings, Columbia University.

3.15 p.m. to 3.45 p.m.—Organ recital, Great Hall, College of the City of New York, Mr. Mark Andrews, Montclair, N.J., organist.

4 p.m.—Public lecture by Gabriel Bertrand, of Paris, France, entitled, "Du role des infiniment petits chimiques en chimie biologique," Great Hall, College of the City of New York.

5 p.m.—Informal tea at the College of the City of New York.

8 and 8.30 p.m.—Receptions to foreign members in attendance; Sectional smokers; Kommers to Section VIII.*b*, Pharmaceutical Chemistry, by the Apotheker Verein of New York City.

9 p.m.—Reception to meet the Japanese Delegates by Dr. and Mrs. Jokichi Takamine.

Saturday, September 7.

10 a.m. to 12 m.—Sectional meetings, Columbia University.

2 p.m.—Joint meeting of the Sections on Inorganic Chemistry, Physical Chemistry, Electrochemistry, and Agricultural Chemistry at the Auditorium of

the American Museum of Natural History, Seventy-seventh Street and Central Park West. Address by Samuel Eyde, of Kristiania, Norway, entitled, "Oxidation of Atmospheric Nitrogen and Development of Resulting Industries in Norway."

3.30 p.m.—Inspection of the American Museum of Natural History and informal tea.

8.30 p.m.—Reception at the Metropolitan Museum of Art in Central Park.

Ladies.—11 a.m.—Lecture or concert at Chemists' Club.

Sunday, September 8.

Religious Services—Reservations in suitable number for members of the Congress are made at the Cathedral of St. John the Divine, Cathedral Heights, and at St. Patrick's Cathedral, Fifth Avenue and Fiftieth Street. For other Sunday services consult the Sunday morning or Saturday evening papers.

Boat Excursion—Leaving Forty-second Street and East River at 10.30 a.m., down East River, around the Battery, up the Hudson as far as Newburgh and return. Refreshments will be provided. Return to New York City late in the afternoon.

Monday, September 9.

10 a.m. to 12 m. and 1 p.m. to 3 p.m.—Sectional meetings, Columbia University.

3.15 p.m. to 3.45 p.m.—Organ Recital, Great Hall, College of the City of New York, Mr. Mark Andrews, Montclair, N.J., organist.

4 p.m.—Public lecture by Carl Duisberg, of Elberfeld, Germany, entitled, "Die Neuesten Arbeiten und Probleme der Chemischen Industrie" (the lecture will be delivered in English), Great Hall, College of the City of New York.

5 p.m.—Informal tea at the College of the City of New York.

7 p.m.—Garden Party at Bronx Park.

8 p.m.—Meeting of the Council of the American Chemical Society, Rumford Hall, Chemists' Club.

Ladies.—10 a.m. to 1 p.m.—Auto trips seeing New York.

1 p.m.—Luncheon at the Claremont.

Afternoon.—At the Chemists' Club.

5 p.m.—Informal tea at the College of the City of New York.

Tuesday, September 10.

10 a.m.—International Commission for Uniform Methods of Sugar Analysis, Columbia University.

10 a.m. to 12 m. and 1 p.m. to 3 p.m.—Sectional meetings, Columbia University.

(This is the *last* Sectional Meeting at which resolutions which are intended to be put to the Congress at its meeting on Friday, September 13, can be introduced into any of the Sections; all resolutions must be offered in each of the four official languages, English, French, German, and Italian).

3.15 to 3.45 p.m.—Organ recital, Great Hall, College of the City of New York, Prof. Samuel A. Baldwin, of the College of the City of New York, organist.

4 p.m.—General Lecture by William Henry Perkin, of Manchester, England, entitled, "The Permanent Fireproofing of Cotton Goods," Great Hall, College of the City of New York.

5 p.m.—Informal tea at College of the City of New York.

5 p.m.—General meeting, American Chemical Society, at Chemists' Club.

8.30 p.m.—Reception and entertainment by the Chemists' Club to all members of the Congress at the Chemists' Club, 52, East Forty-first Street.

Ladies.—9.30 to 12.30.—Choice of one of the following three automobile trips:—1. Public Library, Tiffany's, Metropolitan Tower; 2. Aquarium, Down Town Section, Stock Exchange; 3. Metropolitan Museum of Art, American Museum of Natural History.—Lecture or concerts.

1 p.m.—Luncheon at the Chemists' Club.

(To be continued)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1912.

Dr. M. Onslow Forster, F.R.S., Vice-President, in the Chair.

Messrs. Bertram Lambert, Edgar A. Rayner, and J. W. Patterson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edwin John Amies, B.Sc., 10, Salisbury Road, Thorpe Hamlet, Norwich; William Llewelyn Bailey, Central Buildings, Matlock; Edmund Arthur Buckle, Beech Villa, Guest Road, Prestwich, Manchester; Ridsdale Ellis, B.Sc., 20, Queen's Square, Bloomsbury, W.C.; Arthur James Hale, B.Sc., 53, Gowrie Road, Lavender Hill, S.W.; Archie Haydon, 55, Grove Lane, Kingston-on-Thames, Surrey; Edward Hope, M.Sc., Lockingstoops, Lowton, Newton-le-Willows; Herbert Carr Roper, 42, Cavendish Place, Newcastle-on-Tyne.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. Francis Maxwell, 77, Lawrie Park Road, Sydenham, and Credit Foncier, Mauritius.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Thomas Allcock; Raymond Theodore Fred Barnett, B.Sc.; Charles James Vinall Bews, B.Sc.; Cyril Douglas Birks; William Henry Bowater; Harry Brindle; Alfred Varlow Campbell; Arthur Fred Campbell, M.Sc.; Bamacharan Chatterji, M.A.; Frank Lothian Cheshire; Leslie Melville Clark; Bhuparti Nath Das, M.A., B.Sc.; Gerard Irvine Davys, B.A., M.D., B.Ch., D.P.H.; George Cruden Dieffenthaller; Jatindra Mohan Dutta, M.A.; Donald MacEachern Fergusson; Alfred George Ernest Forster; Madanlal Jekisandas Gajjar, M.A.; Michael Francis Gallogly, B.A.; Robert Glegg, B.Sc.; Leonard Harding; Harold Hartley. M.Sc.; Henry Medley Hatherly; Max Henius, Ph.D.; Harold Heron; Edmund Haworth Holden, M.Sc.; Edward Lewis James; Edwin Oliver-James; William Jewell; Thomas John Keenan; Harold Eric Kuntzen; Harold McKee Langton, B.Sc.; James Leslie Auld Macdonald, B.Sc.; Nadirshaw Adarji Masani, M.A., B.Sc.; Percival Edward Meadon, B.A.; Frederick James Meister; Robert Charles Menzies; Sidney Morgan; George Ernest Pearson; Eric Keightley Rideal, B.A.; William Daveridge Hamilton Shaw, B.Sc.; Anakul Chandra Sircar, M.A.; William Thévenaz, D. ès Sc.; William Leonard Thomas; Percy Wharton Waters George Mason Williams.

Of the following papers, those marked * were read:—

*160. "*The Formation of Neon as a Product of Radio-active Change.*" By Sir William Ramsay, K.C.B.

The discovery that there is one hundred and eighty-eight times as much neon in the radio-active gas from the King's Well at Bath as in atmospheric air led to a repetition of experiments made by the author some years ago with Mr. Alexander Cameron, in which it was shown that when niton decomposes in presence of water, neon is one of the products. This conclusion has been questioned; the presence of neon has been ascribed to leakage of air into the apparatus; and Mr. Soddy has shown that it is possible to detect by the use of a spectroscope, the neon separated from 0·2 cc. of air. The author has now proved that a leakage of at least 4 cc. of air into the bulb, or during the processes of separation, would be necessary in order to account for the quantity of neon found; and as a proof that air had not leaked in, argon was tested for in the gases, and was found to be practically absent.

It is remarkable that although the water of the King's Well is fairly radio-active, neither free hydrogen nor free oxygen were present in the gases bubbling out of the water.

It is difficult to account for this, in face of the presence of a relatively large proportion of helium in the gases; the proportion is seventy-three times that normally present in air.

Discussion.

Prof. Travers said that some years ago, when he and Sir William Ramsay were searching for unknown inactive gases, they visited the Cauterets in the South of France, and collected samples of gas from several of the springs. The inactive fractions of these gases showed only the spectra of argon and helium. They were not, however, subjected to fractionation; and, later, when the methods of dealing with liquefied gases had been worked out, and neon had been discovered, the samples had been lost.

*161. "*An Analysis of the Waters of the Thermal Springs of Bath.*" By Irvine Masson and Sir William Ramsay, K.C.B.

Analyses were given of the gases escaping from these waters; they consist of carbon dioxide (36·0 cc.), nitrogen (954 cc.), argon (7·263 cc.), neon (2·334 cc.), and helium (0·297 cc.) per litre. There is no hydrogen or oxygen present. There is 0·78 times as much argon, 188 times as much neon, and 73 times as much helium as there is in atmospheric air. The gas also contained niton in a million litres, in equilibrium with 33·65 mgrms. of radium. An analysis was also given of the dissolved solids; the chief constituent is calcium sulphate, and it may be noted that lithium, strontium, and bromine are also present. There is also a trace of dissolved radium.

Discussion.

Mr. Chapman said that he gathered from the authors that the ratio of iron to lime was much larger in the recent than in the ancient deposits, and suggested that if that were the case it would appear to indicate that the water had undergone some appreciable change in respect of its mineral constituents.

Sir W. Ramsay replied that the surface formation was oolitic; but the water came from an unknown depth, and the nature of the rock was unknown. The nearest known deposits of pitchblende were in Cornwall, about 150 miles to the south-west. He also pointed out that persons with a delicate sense of smell had told him that the water had a faint odour of bleaching powder.

Mr. Masson said that comparison with two other analyses made during the past forty years showed that the composition of the mineral content of the water varied considerably.

*162. "*The Colour Intensity of Copper Salts.*" By Spencer Umfreville Pickering.

The colour intensity of copper in solutions of inorganic salts is practically a constant (taken as unity), and is unaffected by dilution. In cupri-compounds it is about 19 with the strongest solutions of which accurate measurements can be made, and generally diminishes on dilution, but is sometimes constant. These two values are explained as applying to bivalent and quadrivalent copper respectively, and the variation in colour intensity of all copper salts can be explained by their solutions containing the normal salt or the "cupri"-form of it (with quadrivalent copper) in varying proportions. Both these forms have been isolated and examined in the case of the glycerate and racemate. Such a view harmonises with the results of electrolysis, and with the coloration of iron and manganese when their valency is altered.

Discussion.

Dr. P. W. Robertson said that the work of Hantzsch and his collaborators had shown that the only trustworthy method of measuring the colour of a solution was to determine the absorption in different parts of the visible spectrum by means of a spectral photometer; to establish optical identity it was necessary also to show that the absorption curves concided in the ultra-violet. Cases were known where solutions differing appreciably in tint (the eye being extremely sensitive in certain portions of the spectrum), nevertheless gave on measurement absorption-coefficients practically the same; this was caused by a slight shifting of an absorption band. Other cases were known where solutions which appeared similar to the eye gave at the edge of the spectrum absorption-coefficients widely different; this was due to the appearance of a band just within the visual region. Finally, there were cases where a solution which obeyed Beer's Law—that is, which had an absorption-coefficient remaining the same on dilution—had a totally different colour when diluted or when examined in thin layers; this phenomenon was due to the existence of a flat band near the centre of the visible spectrum. These facts indicated that the direct vision method of comparing colour must be used with considerable caution.

Mr. Pickering said that objections existed to the spectroscopic method (Sidgwick and Tizard, *Trans.*, 1908, xciii., 195), as well as to the use of the tintometer. Sidgwick and Tizard's results established the practical identity of the blue coloration, and its practical independence of dilution in the case of the sulphate, chloride, bromide, and nitrate, but some solutions of copper salts were not blue at all. The independence of dilution in the case of the sulphate now appeared to be absolute. That Sidgwick and Tizard's results were affected by some source of error was shown by the fact that they indicated in the case of the organic salts a much higher value at infinite dilution than that actually realised now with very weak solutions. The change of valency of the copper atom without oxidation was similar to that recognised as occurring in the case of the halogens, nitrogen, oxygen, &c. The group $C(OH)_2$ would not necessarily confer strong acidic properties any more than in the case of other hydrates.

*163. "*Nitrites of the Mercurialkyl- and Mercurialkylaryl-ammonium Series.*" (Part II.). By Prafulla Chandra Ray, Nilratan Dhar, and Tincowry De.

From the measurements of their electric conductivities it is found that mercurihexamethylenetetra-ammonium and mercuriethylenediammonium nitrites belong to the ammonium type as they behave like the alkali nitrites.

*164. "*Studies of Dynamic Isomerism.* Part XIII. *Camphorcarboxylamide and Camphorcarboxypiperidide. An Illustration of Barlow and Pope's Hypothesis.*" By Walter Hamis Glover and Thomas Martin Lowry.

The preparation of these two substances was described in a preliminary note in 1910 (*Proc.*, xxvi., 162). By the slow evaporation of solutions in ethyl acetate, well formed crystals have now been prepared. The amide is monoasymmetric:—$a:b:c = 1·4736:1:1·7683$ or $0·7368:1:0·8841$; $\beta = 61° 2'$. The piperidide is orthorhombic and hemihedral:—$a:b:c = 1·5032:1:2·4320$ or $0·7516:1:1·2160$. Whilst there is only an approximate morphotropic relationship between these two compounds, a remarkable agreement is found to exist between the parameters of the amide and those of the less stable form of Forster's α-benzoylcamphor, thus:—

	Valency volume.	Equivalence parameters.
$C_{10}H_{15}O·CO·NH_2$ ..	68	3·627 : 4·923 : 4·352
$C_{10}H_{15}O·CO·C_6H_5$ ..	92	3·658 : 4·960 : 5·071

The significance of these relationships was discussed.

*165. "*Studies of Dynamic Isomerism.* Part XIV. *Successive Isomeric Changes in Camphorcarboxylamide and Camphorcarboxypiperidide.*" By Thomas Martin Lowry and Walter Hamis Glover.

Well formed crystals of camphorcarboxylamide, whether separated from ethyl acetate or from benzene, are almost inactive when freshly dissolved in alcohol or in benzene, but increase rapidly in rotatory power to $[\alpha]_{5461} = 100°$ in alcohol and 70° in benzene. The initial solubility of these crystals in heptane does not exceed 0·24 grm. per 100 grms. of solvent, as contrasted with 0·38 grm. for the minute crystals which separate from light petroleum. By similar methods the initial solubility of the piperidide is reduced from 2·06 to 1·64 grms. per 100 grms. of heptane.

Both substances give rise to inflected mutarotation curves. These are too complex to be accounted for by two successive unimolecular changes, and point to the existence of three or more isomeric changes involving four or more isomeric forms of each substance.

*166. "*The Continuous Fractional Distillation of Water.*" By William Robert Bousfield.

In accurate work on the conductivities of dilute aqueous solutions it is recognised that the water employed should approximately have a conductivity which is represented by $K_{18}=1\times10^{-6}$. In a former paper (*Trans.*, 1905, lxxxvii., 740) the author described an apparatus by means of which water of this order of purity could be produced by continuous fractional distillation from "tap water"; that is to say, the ordinary town-water supply. There were now described two forms of apparatus, constructed on the same principles, but simplified, and more easily managed. The first of these presents great advantages as a still for everyday use, yielding about 30 litres of water a day (working day and night), two-thirds of which as a conductivity of about 0·8, the remainder being distilled water of ordinary character. The foregoing result is produced without the use of chemicals. If a strongly alkaline solution of potassium permanganate is supplied with the feed-water at the rate of about ten drops a minute, water of a slightly lower conductivity can be continuously produced. The other apparatus, which may be referred to as the three-bottle apparatus, is suited for the continuous re-distillation of water under diminished pressure. By the use of this apparatus, water having a conductivity of 0·5 may be continuously produced by the re-distillation of the ordinary product of the first still.

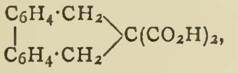
167. "*Studies on certain Aliphatic Hydroxy-acids.*" By Henry John Horstman Fenton and William Arthur Reginald Wilks.

The authors are continuing the study of the oxidation of various organic substances in presence of ferrous iron as catalyst, and of the properties and relationships of the products. An account was given of (1) the transformation of oxalacetic acid into dihydroxymaleic acid, (2) the isolation of bromo-oxalacetic anhydride (or bromo-hydroxymaleic anhydride), (3) the tautomeric dihydroxymaleic esters, (4) "aldehydo-glyceric" acid, and (5) the products obtained by condensation of these substances, and others, with carbamide.

168. "*Formation of Seven- and Eight-membered Rings from 2 : 2′-Ditolyl.*" By James Kenner.

In continuation of the work already described, on ring-formation with the aid of derivatives of 2 : 2′-ditolyl, it has now been found that the behaviour of $\omega\omega'$-dibromo-2 : 2′-ditolyl towards diethyl malonate and tetraethyl ethanetetracarboxylate is similar to that of *o*-xylylene dibromide (compare Kenner and Turner, *Trans.*, 1911, xcix., 2107).

*Dibenzo*cyclo*heptadienedicarboxylic acid*,—



$$\begin{array}{l} C_6H_4{\cdot}CH_2 \\ | \\ C_6H_4{\cdot}CH_2 \end{array}\!\!\!>C(CO_2H)_2,$$

forms prisms which melt at 205°, and decompose into carbon dioxide and *dibenzo*cyclo*heptadienemonocarboxylic acid*, m. p. 157·5°; the *methyl* ester of the latter acid is a highly refractive viscous liquid, b. p. 288°/181 mm., and gradually solidifies to radiate masses of thin plates.

*Tetraethyl dibenzo*cyclo*octadienetetracarboxylate* forms rhombic crystals, m. p. 108°.

The reactions of these and other derivatives from 2 : 2′-ditolyl are under investigation.

169. "*Contributions to the Chemistry of the Terpenes* Part XIII. *The Preparation of Pure Bornylene.*" By George Gerald Henderson and William Caw.

The best method of obtaining bornylene in quantity is to decompose methyl bornyl xanthate, which is easily prepared from borneol, by heating to a temperature not exceeding 200°, but the product contains a certain proportion of an isomeric terpene (either cyclene or camphene), and hitherto no satisfactory process of removing this impurity has been described. It has now been found that crude bornylene can be completely purified by treatment, under suitable conditions, with a limited quantity of hydrogen peroxide, and that the yield of the pure hydrocarbon is at least 60 per cent of the original material.

170. "*The Interaction of Bromine and the Sulphides of β-Naphthol.*" By Thomas Joseph Nolan and Samuel Smiles.

The interaction of bromine and the stable and unstable sulphides of β-naphthol was described. The former yields 2 : 6-dibromo-β-naphthol, whilst the latter furnishes dibromonaphthasulphoniumquinone, in which the substitution is homonuclear. The latter compound was also obtained by bromination of the sulphonium-quinone. It was concluded that the situation of the thio- and hydroxyl group in either sulphide is the same, and that the stable sulphide behaves as a true derivative of β-naphthol, whilst in the unstable sulphide the naphthalene nucleus behaves similarly to that in the sulphonium-quinone. Whether this peculiar behaviour of the latter compound is due to preliminary oxidation to the quinone will be decided by future experiments.

171. "*The Absorption Spectra of some Substances containing Two Benzene Nuclei.*" By John Edward Purvis and Nial Patrick McCleland.

A description was given of the absorption spectra of solutions of some hydrocarbons, ketones, amines, and ethers consisting of two benzene nuclei united by a chain of other groups. The mutual effect on one another of the two benzene nuclei and other oscillation centres in the molecule was discussed.

The bands observed in the vapour of anisole at various temperatures and pressures were also described, and compared with the solution bands.

172. "*The Influence of the Constitution of Tertiary Bases on the Rate of Formation of Quaternary Ammonium Salts.*" (Preliminary Note). By Ebenezer Rees Thomas.

Although some investigations have been carried out on the rate of combination of a few tertiary bases with various alkyl haloids, no accurate measurements have as yet been made of the rate of formation of quaternary ammonium salts from tertiary aromatic amines of the type $C_6H_5{\cdot}NXY$.

It was considered of interest to investigate the effect which the nature of the groups X and Y would have on the rate of such a reaction. No "heterospasis" or any such effect as Clarke describes (*Trans.*, 1910, xcvii., 416) was observed with carefully purified reagents. The reaction was carried out at 40° with N/10-absolute alcohol solution, the quaternary ammonium bromide being estimated gravimetrically as silver bromide.

The rates ($k\times10^{3}$ given in each case) for dimethylaniline (1·076), diethylaniline (0·094), methylethylaniline (0·660), methylallylaniline (0·324) with allyl bromide have been determined.

The results led to a study of dimethyl-*o*-toluidine (0·0573), dimethyl-*m*-toluidine (1·42), *p*-bromodimethylaniline (0·284), quinoline (0·0584), *iso*quinoline (0·450), pyridine (0·40), and 2-methylquinoline (0·0324). In some cases the reaction-velocity for benzyl bromide was also determined, and was in nearly every case related to that for allyl bromide in the ratio of about 6 : 1.

The effect of unsaturation of the attached groups on the residual affinities of the tervalent nitrogen atom has also been studied. The indications as to the influence of the strength of the base on its reactivity are not of a very definite nature, any such effect being in many cases completely masked by steric hindrance. The investigation is being continued and extended.

(To be continued).

NOTICES OF BOOKS.

Lord Kelvin: His Life and Work. By Alexander Russell, M.A., D.Sc., M.I.E.E. London: T. C. and E. C. Jack. New York: Dodge Publishing Co.

The author of this book, which is one of the "People's Books," had an intimate personal knowledge of the late Lord Kelvin, having been one of his students at Glasgow, and he has many interesting anecdotes to relate of him as a lecturer. He is also well equipped to write an account of Lord Kelvin's scientific work in the simplest and least technical language for the benefit of the general reader. The chapters on early electrical researches, submarine telegraphy and navigation, and electrical engineering are of absorbing interest, and the book gives a graphic and charmingly written account of a man whose extraordinary combination of gifts did indeed mark him out as a "prince of science."

Livingstone College Year Book, 1912. London: Livingstone College, Leyton.

The Livingstone College Year Book for 1912 contains the annual report of the work of the College issued at the end of 1911, as well as exceedingly interesting extracts from the letters of old students who are at work in all parts of the world; these extracts show the great value of the training given at the College to missionaries and others in elementary medicine and surgery. A short review of the year's progress in tropical medicine and some reviews of books are added.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperaturs are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 25, June 17, 1912.

Alkaline Periodates.—V. Auger.—Alkaline iodides in aqueous solution are oxidised by ozone, iodine being set free:—$2KI + O_3 + H_2O = O_2 + I_2 + 2KOH$. This reaction is immediately followed by the formation of hypoiodite:—$I_2 + 2KOH \rightleftarrows IOK + KI + H_2O$, and finally the hypoiodite is very rapidly transformed into iodide and iodate, so that the quantity of free iodine is always very small. Garzarolli-Thurnlackh states that some periodate is also formed, but the author has not confirmed this statement. When iodides act on periodates the reaction $3IO_4Na + 2NaI + 3H_2O = 2IO_6Na_2H_3 + IO_3Na + 2I$ occurs immediately. The reaction—

$$2IO_6Na_2H_3 + 2I = 3IO_3Na + 2INa + 3H_2O$$

commences at once, and about 50 per cent of the iodine formed disappears by the end of an hour. In an open vessel the basic periodate reacts with carbon dioxide, giving a neutral periodate, from which iodine is again set free: — $IO_2Na_2H_3 + CO_2 = CO_3NaH + H_2O + IO_4Na$; $IO_4Na + 2INa + CO_2 + H_2O = IO_3Na + I_2 + 2NaHCO_3$.

Use of Oxygen under Pressure to Determine the Total Carbon in Ferro-alloys.—P. Mahler and E. Goutal.—Combustion in a calorimetric bomb can be employed to determine the total carbon in ferro-alloys even of the most refractory nature. It is best to mix the specimen with three or four times its weight of metallic iron and half the total weight of lead or copper oxide, and to determine the carbon dioxide formed by absorption in standard soda solution, dilute sulphuric acid being employed for the titration of the soda. The determination of the carbon in the metallic iron and lead oxide is then repeated in exactly the same conditions, and the difference of the two results gives the carbon in the alloy.

Catalytic Hydrogenation of Benzylideneacetone.—G. Vavon.—Benzylideneacetone dissolved in ether or in ethyl acetate can easily be reduced by shaking it in an atmosphere of hydrogen in presence of platinum black. Ten atoms of hydrogen can thus be added to the molecule, the product being cyclohexylbutanol, $C_6H_{11}CH_2CH_2CHOHCH_3$. By stopping the reduction at a convenient moment, phenylbutanone, phenylbutanol, or cyclohexylbutanol can be obtained. The hydrogenation of the benzene nucleus by platinum black is not a reaction peculiar to benzylideneacetone. It can also be applied to benzylidene camphor, acetophenone, and the benzene hydrocarbons.

Derivatives of Hexahydrobenzoic Aldehyde.—Jules Frézouls.—Hexahydrobenzylidene acetophenone can be obtained by the condensation of hexahydrobenzoic acid and acetophenone in presence of sodium methylate, and the isomer, benzylidene-hexahydroacetophenone, by a similar method, starting with hexahydroacetophenone.

Bulletin de la Société Chimique de France.
Vol. xi.—xii., No. 12, 1912.

Action of Water on Active Aluminium.—E. Kohn-Abrest.—When aluminium made "active" by traces of mercury is oxidised by water in the cold, mixtures of hydrates of alumina are formed. The composition of the mixtures is modified by different causes, one being the duration of the contact of the oxide with water.

Syntheses by means of Mixed Organo-metallic Derivatives of Zinc.—α-Ethoxydialkylacetic Acids.—E. E. Blaise and L. Picard.—Phosphorus perchloride readily reacts with ethyl oxalate to give dichloroglycolic ether. The two atoms of chlorine in this ether are mobile, and readily react with mixed organo-metallic derivatives of zinc, being thus replaced by alkyl groups.

$$CO_2C_2H_5{-}CCl_2{-}O{-}C_2H_5 + 2R{-}Zn{-}I =$$
$$= ZnI_2 + ZnCl_2 + CO_2C_2H_5{-}CR_2{-}O{-}C_2H_5.$$

By the action of iodide of zinc methyl on dichloroglycolic ether the authors have prepared α-ethoxy-dimethylacetic acid.

Isomorphism in the Organo-metallic Series. Derivatives of Trivalent Elements.—Paul Pascal.—The thermic study of mixtures of triphenylamine and triphenylphosphine shows that these two compounds are perfectly isomorphic, and the same results are obtained with mixtures of triphenylarsine and triphenylstibine. Mixtures containing triphenylbismuthine exhibit isodimorphism.

Determination of Iodine in Iodides.—V. Auger.—Iodine in iodides, and especially in sea-weeds, can very readily be estimated by oxidising the iodide with $KMnO_4$ and determining the iodate formed. The solution containing the iodide is made alkaline with soda, a concentrated solution of permanganate is added, and the liquid is heated, acidulated with acetic acid, and treated with H_2O_2 till the MnO_2 disappears. Some dilute permanganate is then added, and finally H_2O_2 till the brown coloration is destroyed, 1 grm. of KI and 5 cc. of HCl are added, and the iodine formed is determined by means of hyposulphite.

Determination of Glycerin in Wines.—Constantin Beis.—100 cc. of the wine are neutralised with hydrated baryta and concentrated until a syrup is obtained. This syrup is mixed with sand, and the glycerin is extracted by means of acetone. After extraction the acetone is divided into two parts and evaporated. In one residue the sugar is determined by means of Fehling's solution, while the other residue is dissolved in five times its weight of water and powdered $Ba(OH)_2$ is added. After the solution containing the $Ba(OH)_2$ has been allowed to stand for some time, sand is added, and it is extracted with acetone at 50°. By evaporating the total filtrate at 50° the glycerin is obtained.

THE CHEMICAL NEWS.

Vol. CVI., No. 2751.

THE QUANTITATIVE SEPARATION OF LANTHANUM FROM YTTRIUM.

By C. JAMES and T. O. SMITH.

Hitherto the only method employed for the separation of the cerium earths from the yttrium earths has been the potassium sulphate treatment. This separation is based upon the fact that lanthanum forms a double sulphate with potassium which is insoluble in saturated potassium sulphate solution, while the corresponding yttrium compound is fairly soluble.

In addition to the above, Urbain has shown that by fractionally crystallising the rare earth magnesium nitrates in the presence of bismuth magnesium nitrate, the latter inserted itself between samarium magnesium nitrate and europium magnesium nitrate, dividing these elements quantitatively at this point.

He also states that by treating yttrium earth nitrates containing some cerium earth nitrates with magnesium nitrate and bismuth magnesium nitrate the separation of the two groups was effected.

Among other compounds which show diverging solubilities for these two groups are the sodium double sulphates, the formates, and the cacodylates.

For the quantitative study it was considered that the completeness of the separation could be better shown by employing lanthanum and yttrium, which approach the extremes of the series.

Solutions of the pure nitrates of lanthanum and yttrium were prepared and standardised by precipitation with oxalic acid in hot neutral solution. One cc. of the lanthanum nitrate solution contained 0·003570 grm. of La_2O_3. The yttrium nitrate solution contained 0·003482 grm. of Y_2O_3 per cc.

Fifty cc. portions of each solution were placed in a 250 cc. beaker and crystals of potassium sulphate added in excess. The solution was well stirred and allowed to stand twelve hours, again stirred, and set aside for a like period.

The precipitate of lanthanum potassium sulphate was filtered off and washed with saturated potassium sulphate solution. The yttrium was precipitated from the cold filtrate by pouring it into a dilute solution of boiling sodium hydroxide. After filtering and washing the yttrium hydroxide with boiling water, it was dissolved in hydrochloric acid, an excess being avoided, and the resulting chloride solution precipitated with oxalic acid. The oxalate was washed, dried, ignited, and weighed as Y_2O_3. The results were as follows:—

No.	Y_2O_3 taken.	La_2O_3 taken.	Y_2O_3 found.
1.	0·1741	0·1785	0·1516
2.	0·1741	0·1785	0·1517

These figures show that yttrium potassium sulphate is carried down along with lanthanum potassium sulphate. In the absence of lanthanum, and under similar conditions, no yttrium would be precipitated.

Sodium Double Sulphates.—Usually the sodium double sulphates are more soluble than the double sulphates of potassium. This fact seemed to present an advantage in this case. The solutions were measured out as in the previous instance, and because of the greater solubility of sodium sulphate this salt was added until the solution contained approximately 10 per cent. After standing twenty-four hours the lanthanum sodium sulphate was filtered off, and washed with a 10 per cent sodium sulphate solution. The yttrium in the filtrate was determined as before. The results were as follows:—

No.	Y_2O_3 taken.	La_2O_3 taken.	Y_2O_3 found.
1.	0·1741	0·1785	0·2646
2.	0·1741	0·1785	0·2613
3.	0·1741	0·1785	0·2600

The conclusions drawn from these results appear to indicate that an excess of sodium sulphate should have been used. However, even under these conditions the whole of the lanthanum was not precipitated, as the figures below show.

No.	Y_2O_3 taken.	La_2O_3 taken.	Y_2O_3 found.
1.	0·1741	0·1785	0·2570
2.	0·1741	0·1785	0·2583

Formates.—The next compounds possessing favourable properties were the formates. According to previous workers lanthanum formate dissolves in 420 parts of water while the corresponding yttrium salt dissolves in less than half its weight. By working with alcoholic solutions it was thought that the difference in solubilities might be considerably increased.

The mixture of standard nitrate solutions was precipitated with a slight excess of hot dilute sodium hydroxide. The hydroxides obtained in this way were washed with hot water and dissolved in diluted formic acid. The solution was evaporated until nearly all the water was removed. The residue was treated with 95 per cent alcohol, filtered, and washed with the same reagent. The formate was ignited to the oxide and weighed.

While lanthanum formate is practically insoluble in 95 per cent alcohol and yttrium formate fairly soluble, the analytical results show that yttrium is inclined to accompany the lanthanum.

Cacodylates.—The cacodylates were examined, and although their solubilities differ widely, were found unsatisfactory, owing to the following facts:—Lanthanum cacodylate has a tendency to become colloidal, and yttrium cacodylate is not quite insoluble in water. The use of alcohol does not improve the conditions.

Bismuth Magnesium Nitrate.—Urbain has stated, as previously mentioned, that lanthanum magnesium nitrate is insoluble in bismuth magnesium nitrate, and since yttrium forms no double nitrate it was assumed that a quantitative method might be obtained.

First of all, a qualitative test was made with regard to the solubility of the lanthanum double salt in concentrated nitric acid (sp. gr. 1·42) containing an excess of bismuth magnesium nitrate. It was found that the lanthanum was entirely insoluble. After this point had been proved, a mixture of 50 cc. of each standard solution was taken, evaporated to dryness, treated with 25 cc. of concentrated nitric acid saturated with bismuth magnesium nitrate, to which was added 10 grms. of bismuth magnesium nitrate and 1 grm. of magnesium nitrate. The mixture was warmed and stirred, a considerable amount of the bismuth magnesium nitrate going into solution. The solution was then set aside for twenty-four hours. The crystalline deposit was removed on a Gooch filter and washed with concentrated nitric acid saturated with bismuth magnesium nitrate.

The filtrate containing yttrium nitrate, together with some bismuth magnesium nitrate, was evaporated to dryness to remove all free acid. The residue was treated with 200 cc. cold water, and the bismuth precipitated with hydrogen sulphide. The bismuth sulphide was filtered off and washed with cold water. The filtrate was boiled to expel the excess of hydrogen sulphide, cooled, treated with ammonium chloride, made nearly neutral by means of ammonium hydroxide, and precipitated with oxalic acid. The oxalate was ignited to the oxide and weighed.

The Gooch crucible containing the lanthanum, together with the excess of bismuth magnesium nitrate, was washed into a beaker, saturated with hydrogen sulphide to remove the bismuth, and treated similarly to the yttrium. The results were as follows :—

No.	Y_2O_3 taken.	Y_2O_3 found.	La_2O_3 taken.	La_2O_3 found.
1. ..	0·08705	0·0892	0·08925	0·0883
2. ..	0·08705	0·0876	0·1785	0·1782
3. ..	0·1741	0·1752	0·1785	0·1731
4. ..	0·1741	0·1758	0·1785	0·1779
5. ..	0·1741	0·1767	0·1785	0·1764
6. ..	0·1741	0·1735	0·1785	0·1791

This method does not offer all that could be desired either in point of accuracy or ease of manipulation, but is offered because of its superiority over the older potassium sulphate method. For separating holmium, dysprosium, &c., from lanthanum the error would probably be greater owing to the fact that these elements have a slight tendency to form double magnesium nitrates. On the other hand, the separation should be much more perfect for the elements of the yttrium group possessing greater solubilities than yttrium itself.

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PURIFICATION OF MERCURY.

By W. R. FORBES, B.Sc.

Small quantities of mercury are conveniently purified by streaming through nitric acid and mercurous nitrate. Large quantities are purified by oxidation. Air is drawn through the metal, and the zinc and lead thus oxidised rise to the surface as a scum. The defect of this method lies in the fact that it is liable to leave a somewhat large proportion of metal unacted upon. An improved method is to first oxidise with air and then to shake with a quantity of charcoal powder which has been allowed to absorb a large amount of oxygen. This will materially improve the oxidation, and the charcoal will rise to the surface and carry the scum with it.

A NOTE ON THE DETERMINATION OF IODIDES BY DIRECT TITRATION.*

By J. W. TURRENTINE.

Bray and MacKay (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1193) have described a method for the determination of iodides in the presence of bromides and chlorides wherein the iodine is liberated from the iodides by standardised potassium permanganate, added titrimetrically, and is extracted as formed by shaking with successive portions of carbon tetrachloride. When the last of the iodine has been set free, the carbon tetrachloride extract is run off from the supernatant aqueous layer and is shaken with a solution of potassium iodide for the extraction of the iodine. The potassium iodide extract is titrated in the usual way with standard thiosulphate solution.

In the analysis of kelps for iodine a method was sought which would admit of the determination of small amounts of iodide with the minimum expenditure of time. For this purpose the initial liberation of the iodine was effected by standardised potassium permanganate and the amount of iodide thereby determined. The method then became strictly a direct titration of iodide in the presence of bromide and chloride. The results obtained were satisfactorily consistent, and the rapidity with which determinations could be made by means of it was such that this account of the method is deemed warranted.

The permanganate solution was standardised against solutions of potassium iodide of known concentration (1·0 grm. KI to 1000 cc. H_2O), the iodide of which had been purified by re-crystallisation and thorough drying.

Portions of the standard iodide solution were transferred, in graduated pipettes, to a 250 cc. dropping funnel ; 15 cc. of sulphuric acid solution (10 cc. conc. H_2SO_4 to 90 cc. H_2O) and 15 cc. of carbon tetrachloride were added. For the removal of reducing agents the carbon tetrachloride had been treated for several hours with iodine which was subsequently removed by shaking with sodium thiosulphate solution.

The solution of the permanganate was run in from a burette, and as the titration proceeded the liberated iodine was removed from the aqueous layer by shaking. With the decrease in the concentration of the iodide in this layer, the solubility of the iodine therein decreased, until, as the end of the titration was approached, the solution became entirely colourless. The persistence for one minute of the pink colour of the permanganate was taken as the end-point. The procedure was identical with that observed in the actual analysis.

At first the colour of the carbon tetrachloride layer caused some trouble in discerning the end-point, but with experience the trouble disappeared.

Bray and MacKay have pointed out that that in the direct titration of iodides by a permanganate solution there is an error introduced by the incomplete reduction of the last of the permanganate to a form intermediate between the heptavalent and the divalent condition. This would appear to be due to the decrease in the active mass of the iodide, since it is not observable in the presence of an excess of that substance. For a definite amount of the permanganate, then, the intermediate form of the manganese should not be present in the solution until after the iodide had been reduced to a definite concentration. When the concentration of the former is very low (as is normally the case as the end of the titration is approached), that of the iodide likewise would be very low before the reaction leading to the formation of the intermediate manganese compound appeared. In the titration, accordingly, the incomplete reduction does not occur until a definite and very low concentration of the iodide is reached. This point it follows—since the reaction is irreversible—must be independent of the original active mass of the iodide. For that reason the error should be a constant rather than a variable one ; and if the latter, certainly a correction could be introduced whereby it would be neutralised.

It was observed that values obtained for small amounts of iodide undergoing titration were relatively greater than those obtained for larger amounts. When the blank solutions were titrated in the absence of the iodide, it was found that a small amount of the permanganate (0·2 cc.) was reduced. As this was not observable in the absence of the carbon tetrachloride, the reduction of the permanganate was attributed to the carbon tetrachloride, or to some constituent thereof. When a correction was made for this error the values obtained from the titration of the various volumes of standard iodide were found to be concordant within the probable error of experimentation. These values are given in the accompanying table.

The range in values in iodide of the solutions titrated in the standardisation was the same as that which was expected to be found in the substances to be analysed. For that reason they cover only a small range. Whether the method is applicable to the determination of larger amounts of iodide can not be said, but *a priori* considerations indicate that it may be employed. It should only be necessary to remove the iodide with successive portions of carbon tetrachloride in order that that layer might not become too concentrated in iodine. Whether new corrections would have to be introduced or not could be determined experimentally.

The permanganate solution was standardised with solutions containing no chlorides or bromides, while the solutions analysed contained large amounts of chlorides and

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presumably some bromides. Bromides in small amounts are commonly found among the saline constituents of sea algæ. Whether they were present in the specimens analysed has not been determined. In this particular, then, the conditions existing during the standardisation were not strictly reproduced in the analysis. However, the authors whose method is here applied have explained the conditions under which chlorides and bromides are liable to introduce an error in the determination of iodide, and, it is believed, those conditions were strictly observed in the adaptation of the method to the analysis of kelps.

It is a truism that any titration method is reliable in which the solutions employed are standardised against the compound which is to be determined, provided the standardisation and the analyses be made under identical conditions.

No.	Cc. KI.	Cc. $KMnO_4$ corrected.	KI value per cc. $KMnO_4$ corrected.
1.	10	1·6	0·00625
2.	10	1·6	0·00625
3.	10	1·55	0·00645
4.	10	1·5	0·00666
5.	10	1·6	0·00625
6.	10	1·55	0·00645
7.	20	3·2	0·00625
8.	20	3·2	0·00625
9.	20	3·3	0·00606
10.	25	4·05	0·00617
11.	40	6·55	0·00611
12.	40	6·5	0·00615
13.	40	6·5	0·00615
14.	100	16·5	0·00602
		Mean	0·00624

THE USE OF MICE AND BIRDS FOR DETECTING CARBON MONOXIDE AFTER MINE FIRES AND EXPLOSIONS.*

By GEORGE A. BURRELL.

(Concluded from p. 66).

The Use of Mice and Birds.

Experiments with Mice.—In the author's opinion the use of birds and mice is superior to chemical tests for carbon monoxide, in that the test is quickly made, requires no technical experience, and is sufficiently exact.

Two or three mice or small birds can be placed in a cage and carried into the mine with an exploring party. Because the rate at which chemical changes occur in them is enormously greater than it is in a man, they show symptoms of poisoning far sooner. Haldane (*Colliery Guardian*, 1909, xcviii., 1251) states that a mouse weighing one-half an ounce consumes about fifteen times as much oxygen as one-half ounce of the human body would consume in the same time. With 0·1 per cent of carbon monoxide in the air, Haldane found that about two hours elapsed before giddiness, &c., began to appear in a man at rest, and, according to an analysis of the blood, exposure for another half-hour would have sufficed to produce practical disablement. A mouse became giddy in ten minutes. With 0·6 per cent of carbon monoxide in the air, all of the animals tried became helpless in two minutes and rapidly became comatose or died, whereas a person breathing the mixture was entirely unaffected even after ten minutes. An examination of this person's blood showed that it was one-fourth saturated.

In experiments at the laboratory of the Pittsburgh station of the Bureau of Mines white mice were placed in air containing the following percentages of carbon monoxide:—0·16 per cent, 0·2 per cent, 0·33 per cent, 0·46 per cent, 0·37 per cent, and 0·77 per cent. The mice were placed under a tight glass bell-jar having a capacity of 10 litres, into which carbon monoxide had previously been introduced. The atmosphere inside the jar was thoroughly mixed and sampled twice during the experiment, the samples being taken from different points in order to make sure that the content of carbon monoxide was uniformly distributed. The samples were analysed by combustion of the carbon monoxide in an apparatus with which duplicate analyses agreeing within 0·01 per cent could be performed.

An analysis of the air in the jar at the end of one hour showed that the oxygen content had been depleted 1 per cent, due to the breathing of the mouse, or not enough to affect the air. In air containing 0·16 per cent of carbon monoxide a mouse showed signs of sluggishness in about six minutes, but this sluggishness, judged by outward manifestations, did not increase to any great extent up to the time the mouse was taken from the jar two hours later. The animal's rate of breathing had dropped from a normal of 160 respirations to about 120 respirations per minute. The mouse did not evince such signs of distress as would serve, if the mouse were carried into an atmosphere containing carbon monoxide, to indicate in one hour's time the presence of 0·1 per cent of the gas.

In air containing 0·2 per cent of carbon monoxide a mouse suffered partial collapse in fifteen minutes, and showed decided symptoms of distress in eight minutes. At the end of an hour it had not lost all muscular power. It died in two hours.

In air containing 0·31 per cent of carbon monoxide a mouse suffered partial collapse in seven and one-half minutes, and showed decided symptoms in about four minutes; but thirty-five minutes had elapsed before it lost all muscular power and ability to turn over when placed on its back. After removal from the bell-jar the mouse was seemingly in normal condition again in about two hours.

In air containing 0·46 per cent of carbon monoxide a mouse gave decided signs of distress in two minutes, staggered around and showed partial collapse in four minutes, and in six minutes had lost all muscular power.

In air containing 0·57 per cent of carbon monoxide a mouse showed decided symptoms of distress in one minute, partly collapsed in two minutes, lost all muscular power in seven minutes, and died in sixteen minutes.

In air containing 0·77 per cent of carbon monoxide a mouse showed distinct signs of distress in one minute. It lost all muscular power in five and one-half minutes, and died in twelve and one-half minutes.

The experiments showed that in air containing the smaller percentages of carbon monoxide the mice displayed varying degrees of activity up to the time they exhibited pronounced distress. Of course, the value of the tests in exploring mines depends upon the warning that the mice give while they are being affected by the carbon monoxide, and it is especially desirable that their actions should indicate the presence of extremely small proportions of carbon monoxide, so that men will have ample time to retire from an atmosphere that contains such proportions of the gas. In the experiments it was found that in small quantities of gas, and under like conditions, one mouse might clearly exhibit signs of distress, whereas another might become comatose without showing distress so distinctly. Consequently, in using the test, the mouse should be closely watched, and a man not wearing breathing apparatus should retire at once from any part of a mine where the atmosphere distresses a mouse. It is advisable to carry at least three mice at a time into a mine, and to prod them slightly if they remain too quiet, in order to observe them in action.

A man when he exerts himself by carrying heavy objects, climbing ladders, or running, consumes in a given time more oxygen and also more carbon monoxide than when he rests. Consequently, a man at work might feel symptoms of carbon monoxide poisoning that would not be clearly shown by a mouse confined in a cage in the

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* *Technical Paper* 11, Department of the Interior, Bureau of Mines; Joseph A. Holmes, Director.

same atmosphere. In an atmosphere containing the small quantities of carbon monoxide usually found in mines after explosions and mine fires, a person may be able to go a long distance without experiencing much inconvenience. On the return trip, however, the symptoms may become so aggravated that considerable difficulty may be experienced in getting to the base of operations or to the surface.

Experiments with Birds.—Because mice may be slow in responding to the presence, in the mine air, of such small percentages of carbon monoxide as would cause distress to a man at work, experiments, similar to those performed with mice, were tried with birds. Canaries were confined in a bell-jar in atmospheres containing the following percentages of carbon monoxide:—0·09 per cent, 0·12 per cent, 0·15 per cent, 0·2 per cent, and 0·29 per cent.

After an exposure of one hour to an atmosphere containing 0·09 per cent of carbon monoxide, a bird was not affected to such an extent that it would, if carried into a mine, indicate by its actions the presence of that proportion of carbon monoxide. Only by close observation could one detect that the bird at the end of an hour felt slightly distressed.

With 0·12 per cent of carbon monoxide in the atmosphere of the bell-jar, a bird did not show clearly symptoms of being affected. In about fifteen minutes it had lost its liveliness, and thenceforth remained comparatively quiet. The bird did not fall from the perch, but close observation showed that it was decidedly weaker at the end of the hour than was the bird placed in air containing 0·09 per cent of carbon monoxide.

In air containing 0·15 per cent of carbon monoxide a bird evinced symptoms of slight distress in three minutes. It gasped, gradually became weaker, swayed, and at the end of eighteen minutes fluttered from the perch. At the end of an hour it had not lost all muscular power, but showed symptoms of extreme weakness.

In air containing 0·2 per cent of carbon monoxide a bird showed pronounced signs of distress in one and one-half minutes; it became very unsteady in three minutes, and fell from the perch in five minutes. After it was taken from the jar it regained its feet in two minutes, and appeared to be in normal condition in five minutes.

In air containing 0·29 per cent of carbon monoxide a bird fell from the perch in two and one-half minutes. When placed in fresh air again it had almost revived in five minutes.

Summary.

The following table shows the relative susceptibilities of mice and canaries to carbon monoxide poisoning:—

Effect of CO *on Mice and Canaries.*

Per cent CO.	Effect.
	Mice.
0·16	Very slight distress at end of hour.
0·2	Distress in eight minutes; partial collapse in fifteen minutes.
0·31	Distress in four minutes; collapse in seven and one-half minutes; lost muscular power in thirty-five minutes.
0·46	Distress in two minutes; collapse in four minutes.
0·57	Distress in one minute; collapse in two minutes; muscular power lost in seven minutes; death in sixteen minutes.
0·77	Distress in one minute; muscular power lost in six and one-half minutes; death in twelve and one-half minutes.
	Canaries.
0·09	Very slight distress at end of hour.
0·12	Weaker at end of hour than after exposure to 0·9 per cent.
0·15	Distress in three minutes; fell from perch in eighteen minutes.
0·20	Distress in one and one-half minutes; fell from perch in five minutes.
0·29	Fell from perch in two and one-half minutes.

These tests show that canaries may be better than mice as indicators of the presence of noxious gases in the atmospere of mines, since they more quickly show signs of distress in the presence of small quantities of carbon monoxide. In addition, the symptoms of poisoning in birds are much more clearly defined. A bird sways noticeably on its perch before falling, and its fall is a better indication of danger than is the squatting, extended posture that some mice assume without much struggling, attempts to walk, or other preliminary symptom of poisoning. Consequently, birds not only give more timely warning of the presence of small quantities of carbon monoxide, but exhibit symptoms that are more easily noticed by exploring parties.

Relative Susceptibility of Men and Birds.

In order to determine for himself the relative susceptibility of men and birds to the action of carbon monoxide the author performed the following experiment:—

A gas-tight chamber, having a capacity of 80 cubic feet, was constructed. Into this chamber sufficient carbon monoxide was introduced to produce an atmosphere containing 0·25 per cent of the latter. The author entered this atmosphere, taking with him canary birds and pigeons. The canary birds evinced distress in one minute, and fell from their perches in three minutes. The pigeons only showed slight signs of distress in eleven minutes. The author remained in the atmosphere for twenty minutes, and at the end of that time only suffered a slight headache, although later he became ill. The illness lasted several hours, and was accompanied by nausea and headache.

The experiment shows that small birds are much more susceptible to the action of carbon monoxide than are men, and demonstrates the desirability of using small birds, such as canaries, rather than larger ones, such as pigeons.

In company with other persons the author has also witnessed practical demonstrations of the usefulness of canary birds in exploring mines after explosions had occurred therein. The following analysis shows the composition of the air about 200 feet beyond the point at which a canary bird collapsed. The bird was carried by an exploring party without breathing apparatus. A miner's lamp would burn in this atmosphere, which is typical of those that have caused many deaths in rescue parties, and would give no warning of the presence of the deadly white damp.

Composition of a Mine Atmosphere Rendered Dangerous by White Damp.

Analysis of Atmosphere.

CO_2	1·49
O_2	18·25
CO	0·60
CH_4	1·25
H_2	0·29
N_2	78·12
	100·00

Analysis Differently Stated.

Air	Oxygen	18·25
	Nitrogen	69·07
	Carbon dioxide	0·03
Black damp	Nitrogen	9·05
	Carbon dioxide	1·46
Methane		1·25
White damp		0·60
Hydrogen		0·29
		100·00

A sample of the atmosphere was not obtained at the exact place where the bird collapsed, but was taken at the face of a heading 200 feet beyond, and close to what was supposed to have been the seat of the explosion. The exploring party was cautiously advancing along the heading when the bird collapsed. The members of the party immediately retreated without themselves feeling any distress. The bird quickly revived when placed in better air. About one hour later a helmeted party advanced to the face of the heading and collected the sample of air mentioned. The sample was obtained eighteen hours after the explosion and before ventilation had been restored in this part of the heading. The carbon monoxide content of the air at the place where the bird collapsed is problematical, but certainly was less than 0·60 per cent, because the air was purer at places in the heading farther back from the face. As a rough guess, the carbon monoxide content may be placed at 0·20 or 0·30 per cent.

The following analysis shows the composition of the atmosphere in an entry that had been more or less traversed by exploring parties for several hours prior to the taking of the sample :—

Composition of Atmosphere in an Entry Traversed by Exploring Parties.

CO_2	0·31
O_2	20·51
CO	0·04
CH_4	0·20
H_2	0·00
N_2	78·94
	100·00

One member complained of not feeling well at the time the sample was collected, but in prior exploration work he had probably breathed for several hours air containing small proportions of carbon monoxide. Hence, his symptoms were to be attributed to the cumulative effect of the air previously breathed rather than to the immediate action of the small proportion of carbon monoxide shown in the sample.

Another advantage of the use of birds in exploring mines remains to be considered. A mine atmosphere may be so deficient in oxygen as to extinguish a lamp flame and yet may not contain so little oxygen, or so much carbon monoxide, as to cause distress to birds. In exploring a mine after an explosion a party including members of the Bureau of Mines encountered an atmosphere that, as shown by analysis of a sample, contained the following gases :—

Composition of an Afterdamp.

CO_2	4·10
O_2	13·64
CO	0·00
H_2	0·00
CH_4	1·20
N_2	81·06
	100·00

The party was not equipped with breathing apparatus but carried safety lamps and birds. When it entered this atmosphere the lamps were extinguished (an oil lamp goes out in air containing less than 17 per cent oxygen), but neither the men nor the birds showed signs of distress.

In regard to the oxygen deficiency required to cause distress in men, Haldane says "The Causes of Death in Colliery Explosions and Underground Fires," Report to the Secretary of State for the Home Department, 1896, p. 15) :—

"When the oxygen percentage of air is gradually reduced by absorption of the oxygen, or (what is exactly the same thing) by addition of nitrogen, very little may be felt before the occurrence of impairment of the senses and loss of power over the limbs. If reduction is gradual, and the symptoms be carefully watched, it will be noticed that at about 12 per cent of oxygen, *i.e.*, with a reduction of 9 per cent, the respirations become just perceptibly deeper. At 10 per cent the respirations are distinctly deeper and more frequent, and the lips become slightly bluish. At 8 per cent the face begins to assume a leaden colour, though the distress is still not great. With 5 or 6 per cent there is marked panting, and this is accompanied by clouding of the senses and loss of power over the limbs, which would probably end sooner or later in death. It is probable that any sudden exertion made in air markedly deficient in oxygen may lead to temporary loss of consciousness, so that sudden efforts should be avoided in all cases where, through accident or necessity, a man is in an atmosphere which will not support light, and in such a position that he might fall into worse air or otherwise injure himself. When air containing less than 1 or 2 per cent of oxygen is breathed, loss of consciousness, without any distinct warning symptoms, occurs within forty or fifty seconds. Loss of consciousness in air deprived of oxygen is more rapid than in drowning or strangling, since in the former case not only is the supply of fresh oxygen cut off, but the oxygen previously in the lungs is rapidly washed out. Loss of consciousness is quickly succeeded by convulsions, which are followed by cessation of the respirations. The heart still continues to beat, in the case of cats and dogs, for from two to eight minutes ; in man this period is probably longer, for it seems to be the general rule that the larger an animal is the longer it will resist asphyxiation. So long as the heart is beating, however feebly, animation may be restored by artificial respiration. This may require to be continued for a considerable period, as the after effects of deprivation of oxygen are very serious, and the respiratory centre may not recover for some time."

The above statement shows why the atmosphere previously mentioned put out the lamps, but did not affect the men, and seemingly had little effect upon the birds. Of course men not wearing breathing apparatus should retreat at once from an atmosphere that extinguishes an oil-lamp flame and thus avoid the possibility of suddenly entering an atmosphere so deficient in oxygen that safe retreat would be difficult. For although birds would undoubtedly indicate in season a deficiency of oxygen sufficient to cause distress to men, if further advance were made, yet immediate retreat from an atmosphere in which a lamp does not burn assures a larger margin of safety.

Conclusion.

In bringing these tests to the attention of miners and mine officials the author makes no claim to originality in the use of birds or mice for the purpose of detecting harmful quantities of carbon monoxide in the air of a mine. Dr. Haldane strongly recommends their use. In this country, however, small animals have been used for the purpose described in comparatively few cases. For that reason and because the test is so simple and practical the author has added his observations to the work of Dr. Haldane in order to urge the general adoption of the test in this country. The fact that no series of tests of the comparative merits of birds and mice in atmospheres containing the entire range of small quantities of carbon monoxide had been made is a sufficient reason for the experiments described in the preceding pages. Further, the author's observations indicate that mice are hardly as sensitive to carbon monoxide poisoning as Dr. Haldane's experiments would indicate, and that small birds are better indicators of poisonous atmospheres than are mice.

Publications on Mine Accidents and Explosives.

The following Bureau of Mines publications may be obtained free by applying to the Director, Bureau of Mines, Washington, D.C. :—

Bulletins.

Bull. 17.—"A Primer on Explosives for Coal Miners," by Charles E. Munroe and Clarence Hall. 69 pp. 10 pls. Reprint of United States Geological Survey *Bulletin* 423.

Bull. 20.—"The Explosibility of Coal Dust," by George S. Rice, with chapters by J. C. W. Frazer, Axel Larsen, Frank Haas, and Carl Scholz. 204 pp. 14 pls. Reprint of United States Geological Survey *Bulletin* 425.

Bull. 26.—"Notes on Explosive Mine Gases and Dusts, with Special Reference to Explosions in the Monongah, Darr, and Naomi Coal Mines," by R. T. Chamberlin. 67 pp. Reprint of United States Geological Survey *Bulletin* 383.

Miners' Circulars.

Miners' Circular 2.—"Permissible Explosives Tested prior to January 1, 1911, and Precautions to be Taken in their Use," by Clarence Hall. 1911. 12 pp.

Miners' Circular 3.—"Coal-dust Explosions," by George S. Rice. 1911. 22 pp.

Miners' Circular 4.—"The Use and Care of Mine-rescue Breathing Apparatus," by J. W. Paul. 1911. 24 pp.

Miners' Circular 5.—"Electrical Accidents in Mines, their Causes and Prevention," by H. H. Clark, W. D. Roberts, L. C. Ilsley, and H. F. Randolph. 1911. 10 pp.

Technical Papers.

Technical Paper 4.—"The Electrical Section of the Bureau of Mines, its Purpose and Equipment," by H. H. Clark. 1911. 13 pp.

Technical Paper 6.—"The Rate of Burning of Fuse, as Influenced by Temperature and Pressure," by W. O. Snelling. 1911. 28 pp.

Technical Paper 7.—"Investigations of Fuse and Miners' Squibs," by Clarence Hall and S. P. Howell. 1911. 19 pp.

THE PHYSICAL AND CHEMICAL PROPERTIES OF SOME ORGANIC AMALGAMS.*

By HERBERT N. McCOY and FRANKLIN L. WEST.

(Continued from p. 68).

The behaviour of ammonium amalgam may be first considered. We made this amalgam by the electrolysis of an ice-cold aqueous solution of ammonium sulphate. In one experiment 80 grms. of mercury were used, and a current of 0·3 ampère was run for ten minutes. When the amalgam was placed in the electroscope and the gold leaf system charged negatively, the rate of discharge was so great that it could not be measured with much accuracy, but was approximately equal to six times the uranium standard. After several repetitions of this measurement with concordant results, the gold leaf system was charged positively; the rate of discharge was now much slower but still many times as fast as the minimum that could have been detected with certainty. The rate for the positive discharge was 0·26 that of the standard. At other times three other samples of ammonium amalgam were prepared and studied in the manner just described. The results were in all cases much like those recorded: a small rate of discharge of the positively electrified leaf and a twenty to fifty-fold greater rate for one negatively charged.

The rate of discharge of the electroscope by tetramethylammonium amalgam was studied in a large number of experiments. The detail of a few of these will fully illustrate the nature of the results observed:—1. A sample of the amalgam made in the manner already described and filtered from the excess of mercury was placed in the electroscope on a large platinum crucible lid. The positively charged gold leaf system was repeatedly discharged at a rapid rate. The motion of the gold leaf was very irregular and often jerky, in notable distinction to the behaviour when the discharge is caused by a radio-active substance. Five consecutive determinations of the rate of discharge in terms of that of the uranium standard as unity gave the following figures:—0·6, 1·6, 1·7, 2·9, 2·9, the charge on the gold leaf in all cases being positive. Immediately after the last of the above measurements, the gold leaf system was charged negatively; no discharge took place, although one one-hundredth of the rate shown in the last measurement with a positively charged system could not have escaped notice. After several minutes the sample still discharged a positive charge as fast as the uranium standard. This experiment was made on December 21st and therefore during cold weather, with the room unheated. Although the electroscope used was capable of giving activity measurements accurately to a small fraction of 1 per cent of the standard (see McCoy and Ashmann, *loc. cit.*) the erratic variability of the rate of discharge by tetramethyl-ammonium amalgam made it useless to express the results with greater apparent accuracy than they are here recorded. The enormous variation from one determination to another is therefore a real one and is not due to any appreciable inaccuracy of the method of measurement. This was further shown by the fact that substitution of the uranium film for the amalgam led, as is always found, to entirely concordant constant readings for the rate of discharge.

2. On February 20, 1911, a very good preparation of tetramethylammonium amalgam was made by a current of 0·32 ampère for 1·5 hours. At a room temperature of almost exactly zero the following rates of discharge of the positively charged electroscope were observed:—0·30, 0·16, 0·38, 0·06, 0·19, all in terms of the uranium standard as unity. The gold leaf system was then charged negatively, but no discharge occurred. With a positive charge the following additional rates were observed:—0·41, 0·10, 0·25. The last rate in each of the two series with this sample is much greater than the one immediately preceding it. In each case the sample was stirred immediately before the reading was taken. A similar effect was often noticed.

3. On March 1, 1911, a sample was made by a current of 0·4 ampère for one hour. This was filtered and placed in the electroscope. At a room temperature of 6° the following rates of discharge were observed in the six successive determinations made in the course of four or five minutes:—1·6, 7·0, 1·7, 3·3, 1·4, 0·38.

4. On May 4, 1911, a current of 0·3 ampère for two hours and five minutes gave a large yield of amalgam of excellent quality. The filtered product placed in the electroscope at a room temperature of 12° caused discharge of the positively charged gold leaf system at a very great rate, too fast to be measured. No effect was produced when the charge was negative. The large portion of this sample was covered with carbon tetrachloride and kept on ice until later in the day. The balance was used to find the effect on the rate of discharge of the distance between the amalgam and the electrode of the gold leaf system. The charge was positive in all cases. The successive rates of discharge were as follows:—Far, 1·8, 0·9; near, 1·8, 0·50; far. 0·14; near, 0·40, 0·14; far, 0·8; near, 0·12. The distances designated as far and near were 3·7 cm. and 1·5 cm. respectively. In spite of the fact that the rate was decreasing rapidly, it is easy to see that the effect is greater when the amalgam is near the electrode. The significance of this is discussed later. The portion of the sample kept on ice under carbon tetrachloride was tested after the lapse of about an hour; immediately upon being placed in the electroscope, the rate of discharge was enormous: as close an estimate as could be made indicated an activity twenty-five to thirty times that of the uranium standard. This very great activity continued for about five minutes. The temperature of the room was 12° at the time.

These experiments show conclusively that tetramethylammonium amalgam causes a discharge of positive electricity only. The rate of discharge is irregular for a given preparation under constant conditions and varies from one preparation to another. Temperature has an enormous effect on the activity of the amalgam. Thus in experiments 2, 3, and 4, the room temperatures were 0, 6, and 12 respectively and the maximum rates of discharge 0·38, 7·0, and 30 times the standard.

A large crystal that had been found adhering to the outside of the cloth on a cold dry winter day was placed in the electroscope. It showed no signs of decomposition for several minutes and it also had no effect on the charged

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* From the *Journal of Physical Chemistry*, xvi., No. 4.

eaf. It then slowly began to show evidence of decomposition, and also began to have a slight effect on the leaf, which increased to about 0·1 the rate of the standard and continued thus for several hours. This seems to indicate that the phenomenon is not an intrinsic property of the crystalline amalgam but is concomitant with its decomposition. On the other hand, it was frequently found that after the electrical activity had entirely ceased, the residue would give colloidal mercury with water, showing that decomposition was not yet complete.

With a positive charge on the leaf the amalgam discharges the electroscope very similarly to a true radioactive substance. There is not the slightest doubt, however, that the phenomenon is not one of radio-activity. A radio-active substance discharges both positive and negative charges at the same rate; moreover, this rate is not erratically variable and is not affected by temperature. An additional fact also differentiates the phenomenon from that due to radio-active ionisation; for the production of the maximum ionisation current, a given radio-active substance must be at least a certain distance from the electrode. This minimum distance is the range of the α-rays of the substance (Bragg, *Phil. Mag.*, 1904, [6], viii., 726). If the radio-active film is much nearer the electrode than the distance represented by the range of its α-rays, its rate of discharge is much less than the maximum. For moderate distances greater than the range the ionisation current is not appreciably lower than the maximum. In experiment 4 above we found that the rate of discharge by the amalgam was greater at 1·5 cm. than at 3·7 cm. As the ranges of the α-rays of radio-active substances lie between 2·6 cm. and 8·0 c.m. this is further evidence of the difference between the behaviour of the amalgam and a radio-active substance.

The facts so far mentioned indicate either (1) the liberation by the amalgam of electrons with velocities too low to cause ionisation of the air, or (2) the production of an electro-negatively charged gas. Since the escape of electrons from a metal is enormously accelerated by the action of ultra-violet light, we next studied the behaviour of the amalgam in this respect.

The effect of daylight on the rate of discharge of the electroscope by tetramethylammonium amalgam was shown by the following experiments. A large quantity of solid amalgam was placed in the electroscope and the door of the ionisation chamber left open and directed toward the window of the room. The rates of discharge were 0·30 and 1·7 times the standard. The brass door of the ionising chamber was then closed, thus leaving the amalgam in total darkness, and the following rates of discharge observed;—1·6, 2·9, and 1·1. The experiment shows that the phenomenon occurs in the dark as well as in the light. In fact many of the results already recorded were obtained when the amalgam was in complete darkness. In several experiments, magnesium ribbon was burned close to the open door of the ionisation chamber, and the light, rich in ultra-violet rays, allowed to fall upon the amalgam; but no acceleration of the rate of discharge was produced.

A more elaborate study of the effect of ultra-violet light on the behaviour of tetramethylammonium amalgam was greatly facilitated through the generous co-operation of Dr. J. R. Wright, of Ryerson Physical Laboratory of this University. At the time we were engaged in this research, Dr. Wright, working with Prof. Millikan, was investigating the effect of ultra-violet light upon aluminium. Dr. Wright's paper on the results has just appeared in the *Physikalische Zeitschrift*, 1911, xii., 338, under the title "The Positive Potential of Aluminium as a Function of the Wave-length of the Incident Light." For his own work Dr. Wright had a very powerful source of ultra-violet light produced by the spark discharge between zinc electrodes in parallel with eight Leyden jars and operated by the secondary current of a Seidel transformer, through the primary of which a current of 10 ampères at 25 volts was passed. Dr. Wright's installation also included a Dolezalek quadrant electrometer with the wires leading to it surrounded by earthed brass tubes. As this apparatus was admirably suited for the purpose of testing the effect of ultra-violet light on our amalgam we were very glad to have the privilege of its use in making the following experiments. For his courtesy in this respect and for his valued co-operation in the experiments, we wish to express to Dr. Wright our sincere thanks.

(To be continued)

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

(Concluded from p. 69).

Wednesday, September 11.

10 a.m. to 12 m. and 1 p.m. to 3 p.m. — Sectional meetings, Columbia University.

10.30 a.m.—Joint meeting of the Sections on Inorganic Chemistry, Physical Chemistry, Electrochemistry, and Agricultural Chemistry, at the College of the City of New York. Address by H. A. Bernthsen, of Ludwigshafen-on-Rhine, Germany, entitled, "Synthetic Ammonia."

3.15 p.m. to 3.45 p.m.—Organ recital at Great Hall, College of the City of New York, Prof. Samuel A. Baldwin, of the College of the City of New York, organist.

4 p.m.—Public Lecture by Giacomo Ciamician, of Bologna, Italy, entitled, "La Foto Chimica dell'Avvenire," Great Hall, College of the City of New York.

5 p.m.—Informal tea at the College of the City of New York.

8 p.m.—Entertainment at New York Hippodrome.

Ladies.—9.30 to 12.30 p.m.—Choice of one of the following three automobile trips:—1. Public Library, Tiffany's, Metropolitan Tower; 2. Aquarium, Down Town Section, Stock Exchange; 3. Metropolitan Museum of Art, American Museum of Natural History, lectures or concerts, or inspection of Hotel Waldorf-Astoria.

1 p.m.—Luncheon, Chemists' Club.

Thursday, September 12.

10 a.m. to 12 m. and 1 p.m. to 3 p.m.—Sectional Meetings, Columbia University.

(At this meeting all resolutions which have been offered prior to and during the afternoon session of Tuesday, September 10, must first be acted upon; no papers or other unfinished business, if any, can be taken up until all such resolutions have been finally disposed of by the Sections).

3.15 p.m. to 3.45 p.m.—Organ Recital, Great Hall, College of the City of New York, Prof. Samuel A. Baldwin, of the College of the City of New York, organist.

4 p.m.—Public lecture by Ira Remsen, of Baltimore, entitled, "Priestley in America," Great Hall, College of the City of New York.

5 p.m.—Informal tea, College of the City of New York.

Ladies.—9.30 a.m.—Boat excursions about New York Harbour.

1 p.m.—Luncheon, Chemists' Club. Afternoon lecture or concert at Chemists' Club.

7 p.m.—Grand Banquet, Hotel Waldorf-Astoria.

Friday, September 13.

10 a.m.—Meeting of the International Commission of Congresses of Applied Chemistry.

11.30 a.m.—Great Hall, College of the City of New York, final General Assembly of the Congress.

3 p.m.—Baseball game, New York v. St. Louis, Polo Grounds.

Society of Chemical Industry.

7 p.m.—Subscription Banquet, Hotel Waldorf-Astoria.

Saturday, September 14.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

10 a.m.—Inspection of Consolidated Gas Company, Astoria; Nichols Copper Company, Laurel Hill, New York.

2 p.m.—Corn Products Company, Shady Side, N.J.; Standard Oil Company; Bush Terminal Company, Brooklyn.

Sunday, September 15.

Religious Services—Reservations in suitable number for members of the Congress are made at the Cathedral of St. John the Divine, Cathedral Heights, and St. Patrick's Cathedral, Fifth Avenue and Fiftieth Street. For other Sunday services consult the Sunday morning or Saturday evening papers.

Monday, September 16.

9 a.m.—Excursion trains leave Pennsylvania Terminal for Chicago and the West.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1912.

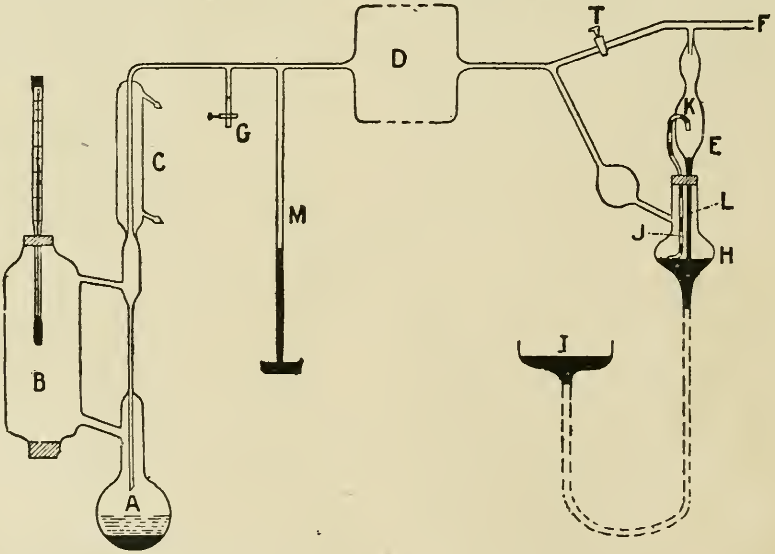
Dr. M. Onslow Forster, F.R.S., Vice-President, in the Chair.

(Concluded from p. 71).

173. "*An Easily Adjustable Vapour Thermostat.*" By James Fletcher and Daniel Tyrer.

The authors described a vapour-bath which can be maintained constant with very little trouble to 0·005°, and can be fixed at any desired point (say, between 30° and 130°) with the greatest ease. In principle it consists of a pure liquid boiling under a constant and adjustable pressure, which is controlled and maintained constant by a very efficient manostat. Practically any liquid of suitable boiling-point may be used. The boiling liquid is contained in the flask A (see diagram). The vapour passes into the compartment B, which may be of any particular form suitable; B also contains a thermometer, as shown. The vapour is then condensed in C, and returns as liquid to the boiling flask A. The end of the condenser C is connected, as shown, with an air reservoir D, of about 10 to 20 litres capacity (the larger the size of this reservoir the greater is the efficiency of the apparatus), and then to the manostat, E. The manostat being the most important part of the apparatus may be described at some length, and for the sake of clearness has been drawn in the diagram on a rather large scale. The tube F is attached to an efficient water-pump. The degree of exhaustion is first roughly adjusted by allowing air to enter by the side-tube and pinchcock G. The mercury rises into the bulb H out of the reservoir I until the level reaches the end of the tube J, when it stops and remains constant. If it passes this point it closes off the rest of the apparatus from the pump, and as air is entering through the side-tube G the pressure increases, and the level of the mercury in the manostat falls again. As soon as the end of the tube J becomes uncovered, the pump again comes into play, and rapidly reduces the pressure, causing the mercury level to rise again. When equilibrium is reached the level of the mercury remains constant, and a continual current of air and mercury passes up the tube J into the compartment K, from whence the mercury falls back into the bulb H by the tube L, and the air passes off through the pump. It will be clear that the difference in the levels of the mercury in H and I represents the pressure in the apparatus, and the adjustment of this pressure is made by merely altering the height of the reservoir.

For the proper working of the manostat it is necessary to have a large air supply to draw from; otherwise the mercury level in H rises and falls irregularly. This is the purpose of the air reservoir D. Although the level of the mercury in H may fluctuate slightly, the pressure recorded by the manometer M remains perfectly constant. In order to raise the temperature in B, the mercury reservoir I is raised, and to lower the temperature it is merely necessary to lower I.



For the efficient working of the apparatus attention mus be paid to the following details:—The reservoir should be shallow, so that if the vessel K partly fills with mercury, as sometimes happens, the difference in the mercury levels in H and I is not appreciably altered. The end of the tube J should be a narrow slit not wider than 0·5 mm, and bent horizontally. The width of this slit ensures that the greatest possible variation in the pressure is 0·5 mm., although the actual variation need not exceed 0·1 mm. In order to accelerate the initial exhaustion of the apparatus the tap T is provided as a by-pass, which at all other times must be closed. The connecting tubes should be of wide bore, so that the pressure at all parts of the apparatus is absolutely the same.

The boiling liquid used must be pure, and must boil quietly without bumping. It is found that bumping is prevented, however low the pressure, by placing in the flask A a layer of mercury as indicated. It is better to boil the liquid over a small free flame shielded from draughts. If the efficiency of the water-pump varies considerably, and if it is desired to have a very constant temperature, it is better to use two manostats connected together with an air reservoir and air inlet tube between them. The temperature can, however, be maintained constant to about 0·01° with one manostat.

Change of the atmospheric pressure affects the constancy of the temperature, and to a smaller extent change of the room temperature, owing to the alteration in the density of the mercury. These influences must be obviated by personal observation and adjustment.

If rubber stoppers are used, an alcohol should be employed as the boiling liquid, but with ground-glass connections lubricated with glycerol-dextrose mixture any liquid can be used. For temperatures ranging from 30° to 65° the authors recommend methyl alcohol, from 40° to 70° ethyl alcohol or benzene, and for higher temperatures toluene or xylene.

In experiments made with a Beckmann thermometer in B and with a double manostat, it was found that for short periods of time the temperature remained constant to 0·001°. For longer periods the variation is greater, but so long as the atmospheric pressure remains unchanged the temperature remains constant to about 0·005°.

This form of thermostat has many advantages over the usual large water-bath. It is more quickly adjustable, and need not be left going for long periods of time, as it is only a matter of a few minutes to start it again.

(We are indebted to the Chemical Society for permission to reproduce the accompanying illustration).

174. "*Contributions to our Knowledge of Semicarbazones. Part I. Semicarbazones of Phenyl Styryl Ketones.*" By Isidor Morris Heilbron and Forsyth James Wilson.

The authors have extended their investigations, of which a preliminary account has appeared (*Proc.*, 1911, xxvii., 325). They find that phenyl styryl ketone is apparently capable of yielding four semicarbazones, two white and two yellow, and adduce reasons for regarding these forms as stereoisomerides. The absorption spectra of the various modifications have been investigated, and the effect of ultra-violet light on the different forms has also been studied.

175. "*The Essential Oil of 'Nepal Sassafras' or 'Nepal Camphor' Tree.*" By Samuel Shrowder Pickles.

The essential oil from the wood of the Indian tree *Cinnamomum glanduliferum*, Meissn, has been examined, and found to have the following general characters:— $D_{15}/_{15}$ 1·1033; α_D 20 −0° 4″ (in a 1-dcm. tube); saponification value, 2·8; saponification value after acetylation, 7·0.

The oil is pale yellow, and possesses an odour resembling safrole with, however, a suggestion of anise. The yield obtained from the dried ground wood by steam distillation was 4·16 per cent. The oil is soluble in half its volume of 90 per cent alcohol, and in five volumes or more of 80 per cent alcohol.

An exhaustive examination showed the oil to consist mainly of safrole, myristicin, and elemicin. Other constituents, present in small quantities, are palmitic acid (m. p. 62·5°), esters of the lower fatty acids, and traces of phenols.

176. "*The Addition of Hydrocyanic Acid to Derivatives of Glutaconic Acid and Itaconic Acid.*" (Preliminary Note). By Edward Hope.

In extending the application of the method employed for the synthesis of β-methyltricarballylic acid (*Trans.*, 1912, ci., 899), the author has investigated the addition of hydrogen cyanide to the following substances:—Ethyl itaconate, ethyl teraconate, ethyl glutaconate, ethyl αγ-dicarbethoxyglutaconate, ethyl αγ-dicarbethoxy-α-methylglutaconate, and ethyl γ-cyano-αβ-dimethylglutaconate.

In the case of ethyl itaconate the reaction proceeds quantitatively with the production of *ethyl γ-cyanopropane-αδ-dicarboxylate*, $CO_2Et\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CN$, which boils at 171°/18 mm., and on hydrolysis gives an almost quantitative yield of tricarballylic acid. In the cases of ethyl teraconate and ethyl glutaconate, no appreciable addition of hydrogen cyanide has yet been observed to occur. Ethyl αγ-dicarbethoxyglutaconate and ethyl αγ-dicarbethoxy-α-methylglutaconate readily combine with the elements of hydrogen cyanide, yielding esters of very high boiling-point which probably possess the constitutional formulæ (I.) and (II.) respectively:—

$$\text{I. } (CO_2Et)_2\cdot CH\cdot CH(CN)\cdot CH(CO_2Et)_2.$$

$$\text{II. } (CO_2Et)_2\cdot CMe\cdot CH(CN)\cdot CH(CO_2Et)_2.$$

The ester (I.) on hydrolysis gives a large yield of tricarballylic acid and (II.) an equally good yield of the isomeric α-methyltricarballylic acids.

Ethyl γ-cyano-αβ-dimethylglutaconate readily combines with hydrogen cyanide with the production of *ethyl γδ-dicyano*iso*pentane-βδ-dicarboxylate*,—

$$CH_3\cdot CH(CO_2Et)\cdot CMe(CN)\cdot CH(CN)\cdot CO_2Et,$$

a viscid oil boiling at 200—206°/20 mm.

The general behaviour of these additive products and of others prepared by similar methods is under investigation, and it is hoped that these compounds will afford methods for preparing many hitherto unavailable substituted tricarballylic acids.

177. "*The Possible Limitation of Molecular Magnitude.*" By Holland Crompton.

No upper limit is usually assigned to molecular magnitude. E. Fischer has synthesised a polypeptide with the molecular weight 1212, and in the case of colloids molecular weights of the order 10^4, and even 10^6, are commonly spoken of. A difficulty arises, however, in admitting that molecular weights can exceed a certain value, unless the density increases as the molecular weight increases.

For suppose that a compound can exist, such as a protein, with a density at 0° not much greater than that of water, and with a molecular weight of rather more than 30,000, the grm.-molecule of such a compound at 0° would occupy about 30,000 cc. The grm.-molecule of a perfect gas under the standard conditions occupies only 22,400 cc., and we should therefore have a solid compound at 0° and under a pressure that cannot be less than one atmosphere, occupying a greater molecular volume than that of any gas.

That the molecules of liquids and solids should occupy greater volumes than those of gases under similar conditions, seems at first contrary to the usual conceptions of the gaseous, liquid, and solid states. It is true that at sufficiently low temperatures this condition must arise for all substances, but a simple calculation shows that for the majority of chemical compounds it would only occur at temperatures not far removed from the absolute zero.

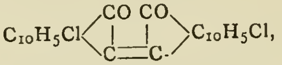
Two suggestions appear to be indicated. The first is that under the ordinary conditions there is an upper limit to molecular magnitude, and that for most substances, more especially colloids, the molecular weight cannot exceed a value of about 20,000. The second is that our ordinary kineto-molecular conceptions no longer apply when for a given temperature the molecular magnitude exceeds a certain critical value. The latter view seems most in keeping with our present knowledge, and perhaps serves to throw some light on the behaviour of colloids.

178. "*The Products of the Oxidation of Chloroacenaphthene with Chromic Acid.*" By Holland Crompton and Wilhelmina Rebecca Smyth.

Chloroacenaphthene was dissolved in about ten times its weight of boiling acetic acid, and then treated with from three to five times its weight of sodium dichromate. A vigorous reaction takes place, which is complete in about fifteen minntes. Three products are always formed, namely, chloroacenaphthenequinone, dichlorodiacenaphthylidenedione, and chloronaphthalene-1 : 8-dicarboxylic acid. The smaller proportion of dichromate favours the production of the first two, the larger proportion that of the third product. The yields are almost theoretical. The reaction product after being well washed with water is first boiled with a 10 per cent solution of sodium carbonate to remove the chloronaphthalene-1 : 8-dicarboxylic acid, and then heated with a concentrated solution of potassium hydrogen sulphite to extract the quinone. The residue after washing and drying is finally crystallised from xylene.

Chloroacenaphthenequinone, $C_{12}H_5O_2Cl$, is obtained from the potassium hydrogen sulphite solution by boiling this with sulphuric acid. It crystallises from acetic acid in yellow needles melting at 216° (corr.). The crystalline potassium hydrogen sulphite compound has the composition $C_{12}H_5O_2Cl,KHSO_3,2H_2O$. It gives a colourless *dioxime* with hydroxylamine, this compound gradually blackening on heating, but having no definite melting-point. With phenylhydrazine it gives a brilliant red *monohydrazone*, melting at 174° (corr.). No dihydrazone was obtained.

Dichlorodiacenaphthylidenedione,—



crystallises in small orange-red needles melting at 328° (corr.). It is very sparingly soluble in alcohol, chloroform, or acetic acid, but fairly so in boiling xylene, from which it can be crystallised. On reduction with hydriodic acid it gives chloroacenaphthene.

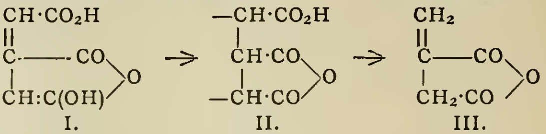
Chloronaphthalene-1 : 8-dicarboxylic acid has been already described (*Proc.*, 1908, xxiv., 241), but the melting-point of the anhydride is found to be higher than that previously given, and should be 213° (corr.). Salts of this acid were prepared and analysed.

179. "*The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part II. Solubility of Carbon Dioxide and of Hydrogen.*" By ALEXANDER FINDLAY and BUCCHOK SHEN.

In continuation of the work of Findlay and Creighton (*Trans.*, 1910, xcvii., 536), the authors have determined the solubility of carbon dioxide in solutions of ammonium chloride, potassium chloride, barium chloride, ferrous ammonium sulphate, sucrose, chloral hydrate, methyl-orange, peptone, propeptone, and hæmoglobin; and of hydrogen in solutions of dextrin, starch, gelatin, ferric hydroxide, and a suspension of metallic silver. It is found that the solubility of carbon dioxide in solutions of the salts mentioned above, and in solutions of sucrose and chloral hydrate, is in harmony with Henry's law, so that the behaviour found in the case of these solutions is different from that met with in the case of colloidal solutions. In the solutions of peptone, propeptone, and hæmoglobin the solubility of carbon dioxide is greater than in water, but decreases as the pressure is increased. This behaviour is explained on the basis of chemical combination. The solubility of hydrogen in solutions of dextrin, starch, gelatin, ferric hydroxide, and in a suspension of finely divided silver is, with the possible exception of the solutions of gelatin, in harmony with Henry's law.

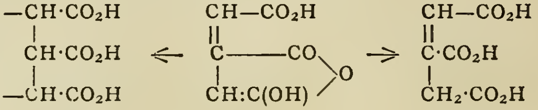
180. "*The Chemistry of the Aconitic Acids. Part I. The Labile Modification of Aconitic Acid and the Hydroxy-anhydro-acid.*" By NORMAN BLAND and JOCELYN FIELD THORPE.

The structure of the hydroxy-anhydro-acid mentioned in a preliminary communication (*Proc. Chem. Soc.*, xxviii., 131) has been found to be that represented by formula (I.), since it passes into the normal anhydro-acid (II.) when heated above its melting-point, and yields itaconic anhydride (III.) when heated at a higher temperature :—



I. M. p. 135°. II. M. p. 76°. III.

The hydroxy-anhydro-acid is converted into normal aconitic acid (IV.) by hydration with water, but yields labile aconitic acid (V.) when hydrated by strong alkali or by dilute alkali in the presence of casein :—



IV. M. p. 191°. V. M. p. 173°.

Derivatives of the hydroxy-anhydro-acid and of the labile acid were described.

181. "*The Action of Bromine on Cholesteryl Benzoate.*" (Preliminary Note). By CHARLES DORÉE and CHARLES STOTESBURY.

It was observed by Obermüller (*Zeit. Physiol. Chem.*, 1891, xv., 42) that cholesteryl benzoate, when treated in the cold with a solution of bromine in carbon disulphide, did not give the expected cholesteryl benzoate dibromide, $C_{27}H_{45}OBr_2 \cdot C_7H_5O$; instead, a monobromo-substituted derivative, $C_{27}H_{44}OBr \cdot C_7H_5O$, melting at 138° was obtained. The authors, in repeating this, find that during the bromination only a very slight evolution of hydrogen bromide takes place, and that the product contains two substances which differ in solubility and crystalline form. The more soluble one crystallises from acetone in needles melting at 139°, and appears to be identical with the derivatives mentioned above. The other is very characteristic, crystallising in large (frequently 1 cm. long), clear hexagonal prisms melting at 168°. The yield of this substance is increased if chloroform is used as the solvent. Analysis agrees with the formula $C_{27}H_{45}OBr_2 \cdot C_7H_5O$, and the investigation is being continued in order to ascertain whether this compound is the hitherto unknown benzoate dibromide.

182. "*A Theory of Fluorescence.*" By EDWARD CHARLES CYRIL BALY and RUDOLF KRULLA.

In every compound formed by virtue of primary valencies alone, the secondary valencies of the atoms are unsaturated. Every such atom must therefore form the centre of a field of force, but the independent existence of these fields must be metastable, and they must condense together with the escape of free energy. Such condensed systems of force lines can be opened by the influence of a solvent and of light. The opening up takes place in stages, each stage absorbing definite light waves. On the basis of this conception was put forward a theory of fluorescence, and experimental evidence was given in favour of it. Certain substances were shown in one solvent to emit fluorescent light of the same wave-length as they absorb in a second solvent.

183. "*Chemical Reactivity and Absorption Spectra.*" (Part I.). By EDWARD CHARLES CYRIL BALY and FRANCIS OWEN RICE.

The authors have considered the condensed force fields which must exist around the molecules of a compound, with regard to the phenomena of fluorescence (preceding abstract). With reference to the question of their chemical reactivity, it is evident that the reactivity of these closed systems must be vanishingly small, and that no molecules can enter into any chemical reaction until these systems have been opened up. There must be therefore at least two stages in any chemical reaction, one in which the closed system is opened up, and the other in which the reaction proper takes place. These two stages have been observed in the sulphonation of the benzene ring by means of absorption spectra, and the absorption curves show the stages in the sulphonation of anisole, *o*- and *p*-nitroanisole, quinol dimethyl ether, and other substances.

184. "*The Wet Oxidation of Metals.* Part II. *The Rusting of Iron.*" (Continued). By BERTRAM LAMBERT.

The work published by the author and a collaborator (*Trans.*, 1910, xcvii., 2426) on the corrosion of commercial forms of iron has been criticised by Friend ("The Corrosion of Iron and Steel," p. 65), "T. M. L." (*Nature*, 1911, p. 25), and "H. E. A." (*Science Progress*, 1911, 642). It is suggested (1) that all traces of carbonic acid had probably not been removed from the apparatus used; (2) that there is a serious objection to the use of quartz vessels, since the quartz might dissolve to a sufficient extent to play the same part as is usually attributed to carbonic acid by the supporters of the acid theory of corrosion; (3) that water prepared by distillation from strong solutions of barium hydroxide probably contains traces of carbonic acid.

The experiments have been repeated with additional precautions and refinements which have been devised to test the validity of these objections. The results of the experiments go to show that the objections have no foundation in fact, and that it may be considered as established beyond any reasonable doubt that commercial forms of iron will always undergo corrosion when exposed to the action of water and oxygen, even in the complete absence of carbonic acid or any other acid.

An electrolytic theory of the corrosion of iron, based on the differences in solution tension of different parts of the metal, was discussed.

Some further properties of pure iron were described, in particular its behaviour towards solution of copper salts. Pure iron can be exposed to the action of saturated solutions of copper sulphate or copper nitrate at the ordinary temperature without copper being deposited on the iron, but exposure to extremely dilute solutions of copper chloride will cause the immediate deposition of copper on the iron.

185. "*Colouring Matters of the Flowers of the* Cedrela toona." By ARTHUR GEORGE PERKIN.

These flowers, which constitute an Indian dyestuff of minor importance, yield a minute amount of a red crystalline colouring matter, $C_{15}H_{18}O_3$, identical with the nycanthin obtained by Hill (*Trans.*, 1907, xci., 1501) from the flowers of *Nycanthes arbor tristis*. This melts at 285—287°, and not 234—235°, as given by Hill, and in dyeing and other properties closely resembles, but is not identical with, the bixin of anatto (*Bixa orellana*). The presence of quercetin contaminated with a trace of an allied colouring matter as glucosides, and of a sugar, $C_{12}H_{22}O_{11}$, have also been detected, and to the former the main dyeing properties of the flowers appear to be due.

186. "*The So-called Manganese Trioxide.*" (Preliminary Note). By FREDERICK RUSSELL LANKSHEAR.

Franke's "pink gas" (*Journ. Prakt. Chem.*, 1887, [2], xxxvi., 31, 166; Thorpe and Hambly, *Trans.*, 1888, liii., 175) is conveniently prepared by allowing a 6 per cent solution of potassium permanganate in concentrated sulphuric acid to drop into a well-cooled mixture of 1 part of sodium hydrogen carbonate with 4 parts of anhydrous sodium carbonate. The evolved gases are led into a tube cooled in liquid air, where a pink solid mass soon forms. When the carbon dioxide has volatilised from this, an amorphous solid remains, which usually melts at about - 6°. It effervesces with sodium carbonate, is free from sulphuric acid, and dissolves quietly in water to form a brownish red solution, which, however, soon deposits manganese dioxide, leaving permanganic acid in solution.

The pink substance is also formed by the action of moist air on the invisible gas given off by the solutions of potassium permanganate in sulphuric acid. This gas has been aspirated through a tube cooled in liquid air, and found to be manganese heptoxide, Mn_2O_7.

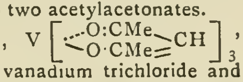
Determinations of the water in the "pink gas" give a mean ratio of about 15 molecules of water to 1 of manganese compound. The ratio of oxygen to manganese has been measured in two ways:—By measuring the volume of oxygen and the weight of manganese dioxide (estimated as Mn_3O_4) given on heating the pink substance, and by measuring the permanganic acid and the manganese dioxide produced (Chatard's process) when the pink gas is blown into water. The former measurement gave a ratio O/MnO_2 of 1·25 to 1; the latter 1·24 to 1. There is thus more oxygen in the substance than required by the formula MnO_3, and less than that demanded by Mn_2O_7.

In view of the facts that much water is present, that solutions of permanganate in sulphuric acid give off manganese heptoxide which forms the "pink gas" with moist air, and that the ratio of oxygen lies nearer that required by permanganic acid than by manganic acid, it must be concluded that the manganese-containing constituent of Franke's "pink gas" is merely hydrated permanganic acid with varying quantities of lower oxides or hydroxides, so that the existence of the oxide MnO_3 still requires demonstration.

187. "*Co-ordination Compounds of Vanadium.*" (Preliminary Note). By GILBERT T. MORGAN and HENRY WEBSTER MOSS.

Anhydrous vanadium trichloride reacts with acetylacetone in the presence of some reagent for removing hydrogen chloride to give rise to two acetylacetonates.

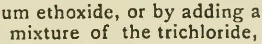
Vanadium teracetylacetonate,



$$\mathrm{V}\left[<\begin{matrix}\mathrm{O{:}CMe}\\ \mathrm{O{\cdot}CMe}\end{matrix}\geqq\mathrm{CH}\right]_3,$$

is produced either by treating vanadium trichloride and acetylacetone in alcoholic solution with the calculated quantity of sodium ethoxide, or by adding aqueous sodium carbonate to a mixture of the trichloride, acetylacetone, and chloroform, when the product dissolves in the organic solvent, and crystallises therefrom in transparent yellowish brown plates or prisms. The compound separates from alcohol or from acetylacetone in reddish brown prisms; it melts at 265—266°, and can be distilled without decomposition.

Vanadium oxybisacetylacetonate,—



$$\mathrm{VO}\left[<\begin{matrix}\mathrm{O{:}CMe}\\ \mathrm{O{\cdot}CMe}\end{matrix}\geqq\mathrm{CH}\right]_2,$$

results from the aërial oxidation of the preceding substance; it crystallises from ether or alcohol in well-defined hard transparent bluish green plates and prisms, which decompose and char on heating. Compounds corresponding with the preceding acetylacetonates have been prepared from benzoylacetone and vanadium trichloride.

The trichloride and pyridine combine either alone or in alcoholic solution to form a very soluble co-ordination compound dissolving in alcohol to an intensely purple solution. Ethylenediamine changes the green colour of alcoholic vanadium trichloride to a deep brown; the co-ordination product is very soluble.

Methylamine, dimethylamine, triethylamine, and benzylamine produce a similar colour change to brown in the green alcoholic solution of the trichloride; the products of these interactions are under examination. Vanadium trichloride dissolves in liquid ammonia, the product being soluble in water.

Although soluble in absolute alcohol to a green solution, anhydrous vanadium chloride is insoluble in dry ether free from alcohol.

The authors proposed to continue the investigation of co-ordination compounds containing vanadium as the central element.

188. "*Substituted Thiolazo-derivatives of Benzene.*" By JOHN JACOB FOX and FRANK GEORGE POPE.

Benzeneazophenylmethylmercaptole,—

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SMe,$$

and *benzeneazophenylethylmercaptole* have been prepared by the action of the corresponding alkyl iodides on the potassium salts obtained by the hydrolysis of the xanthic ester derived from aminoazobenzene. These substances resemble the corresponding ethers of benzeneazophenol, and yield hydrochlorides and hydrates.

p-*Nitrobenzeneazophenylmethylmercaptole* was obtained in small amount by the action of *p*-nitrobenzenediazonium chloride on phenyl mercaptan in alkaline solution, and subsequent treatment of the potassium salt of *p*-nitrobenzeneazophenylmercaptan with methyl iodide.

The band in the absorption spectrum of benzeneazophenylmethylmercaptole was found to occupy an intermediate position between the bands given by benzeneazophenetole and aminoazobenzene.

Extra Meeting of the Society.

At an Extra Meeting of the Chemical Society held on Wednesday, June 26th, 1912, at 8.30 p.m., Professor Percy F. Frankland, LL.D., F.R.S., President, in the Chair, Sir William Tilden delivered the Cannizzaro Memorial Lecture.

A vote of thanks to Sir William Tilden, proposed by Sir William Ramsay, seconded by Sir Edward Thorpe, was supported by the President, and carried with acclamation.

NOTICES OF BOOKS.

Allen's Commercial Organic Analysis. Volume VI. Edited by W. A. Davis, B.Sc., A.C.G.I., and Samuel S. Sadtler, S.B. Fourth Edition. London: J. and A. Churchill. 1912.

Volume VI. of the latest edition of *Allen's Commercial Organic Analysis* deals with the amines and ammonium bases, aniline, &c., and most of the principal vegetable alkaloids. The original arrangement of the subject matter has been retained and at the same time extensive additions have been made. The section on "Caffeine and its Allies" has been split into two, one dealing with tea and coffee only, and the other with cocoa and chocolate. The printing of the book can hardly be described as satisfactory; it is remarkable that such obvious mistakes as those occurring on pages 580 and 581 should have been overlooked, and there are other instances of want of care in the preparation of the book.

The Patent Law in Relation to Chemistry. By Ridsdale Ellis, B.Sc. London: Gill and Ellis. 1912.

The author of this pamphlet aims at giving his readers detailed information regarding the special circumstances attending the protection of chemical inventions, and from his long experience of patent procedure he is in a position to speak authoritatively on the Patent Law. The pamphlet discusses at some length the question as to what products and processes are patentable, explains the rights which are given by Letters Patent, and concludes with some useful hints on the drawing up of specifications.

Annual Report of the Board of Scientific Advice for India for the Year 1910-11. Calcutta: Superintendent Government Printing. 1912.

The Annual Report of the Board of Scientific Advice for India contains short reviews of the work done during the year in connection with Indian industries and agriculture. Researches in Applied Chemistry, Astronomy, Geology, Forestry, Botany, &c., have been performed, and in many cases brought to a successful conclusion, and the lists of publications are particularly full and show great activity on the part of investigators. The programme for 1911-12 is included, and a short report is given of the scientific and technical investigations conducted for India at the Imperial Institute during the year ending September 30, 1911.

Uber Neuere Thermodynamische Theorien. ("Modern Thermodynamical Theories"). By Dr. Max Planck. Leipzig: Akademische Verlagsgesellschaft. 1912.

This lecture was delivered in December, 1911, by Dr. Planck before a meeting of the German Chemical Society. The lecturer kept in mind the expert nature of his audience in handling his subject, although at the risk of telling some of them what they already knew well, he first gave an outline of the development of thermodynamics, so as to be able to show more clearly the relations between the older work and its later developments. The lecture contains a clear and succinct account of Nernst's theory, and explains fully the importance of its theory and its applications. The atomistic significance of the new theory, as far as it has at present been worked out, was discussed in the second part of the lecture.

Theory und Praxis des Mahlens. ("Theory and Practice of Beating"). By Clayton Beadle and Dr. Henry Stevens. Translated into German by Carl Franck. Berlin: Otto Elsner. 1911.

This book deals with a subject which has as yet been but little investigated from a scientific standpoint, and fills a gap in the literature devoted to paper-making. Since the German paper-maker also had at his disposal no handbook dealing with the theory and practice of beating, the translation into German will, no doubt, be cordially received in that country. The translator points out in a preface in what ways English practice differs from that commonly in vogue in Germany.

MISCELLANEOUS.

Becquerel Memorial Lecture. — The Becquerel Memorial Lecture will be delivered by Sir Oliver Lodge at the opening meeting of the next Session of the Chemical Society to be held on October 17th, 1912. Further details will be announced in due course.

Eighth International Congress of Applied Chemistry.—Important Notice.—It does not appear to be generally understood that members of the Congress, even if not able to attend the meetings, are nevertheless entitled to a copy of the *Proceedings*, which it is intended by the Executive Committee shall be issued as promptly as possible. All chemists are therefore invited to join the Congress, whether they intend proceeding to America or not. Membership can be completed on making application, accompanied by the subscription of £1, to Mr. William J. Matheson, 182, Front Street, New York City, U.S.A.

Valuation of Fluorspar.—(A Correction).—In my article on this subject (Chem. News, cvi., 53) I quoted incorrectly Mr. F. Julius Fohs' statement published in *Bulletin* 9 of the Kentucky Geological Survey, viz., "silicates occurring associated with Kentucky fluorspar." The word "Kentucky" should be omitted; it disturbs the meaning of the following discussion, changing the same to a depreciative criticism of Mr. Fohs' statement, which I did not intend to do. Mr. Fohs states that the silicates mentioned in my article occur occasionally associated with fluorspar, but not with Kentucky fluorspar.—Ernst Bidtel.

THE CHEMICAL NEWS.

Vol. CVI., No. 2752.

VERY HIGH TEMPERATURES.[*]

By JOHN ALLEN HARKER, D.Sc., F.R.S.

Exactly a century ago this month Michael Faraday entered the Royal Institution for the first time. He was then a youth of twenty, in the last year of his apprenticeship to a bookbinder in Blandford Street. Among the meagre records we possess of Faraday's early life we find the following:—

"I had the good fortune, through the kindness of Mr. Dance, who was a customer in my master's shop and also a member of the Royal Institution, to hear four of the last lectures of Sir Humphry Davy in that locality. The dates of these lectures were Feb. 29, March 14, April 8 and 10, 1812." It was Faraday's habit to occupy the seat in the gallery over the clock. He made very full notes of the lectures, and afterwards wrote them up, indexed, and bound them with his own hands into a volume of 300 pages, which is now preserved at the Royal Institution.

Some months later Faraday writes:—"Under the encouragement of Mr. Dance I wrote to Sir Humphry Davy, sending, as a proof of my earnestness, the notes I had taken of his last four lectures. The reply was immediate, kind, and favourable."

In March, 1813, apparently largely on the strength of the impression made upon Davy by this volume of notes, Faraday was engaged as assistant in the laboratory of the Royal Institution at a salary of 25s. a week, with two rooms at the top of the house.

The first lecture of Davy's course referred to was on "Radiant Matter," and dealt, among other things, with the action of electric sparks on gases. Ever since Volta's discovery in 1800 Davy had been occupied with the study of the pile and the effect of the new currents in producing heat and chemical change, thus leading up to his decomposition of the fixed alkalis and the isolation of potassium in 1807.

Following on this discovery, Davy proposed that a fund "should be raised by subscription for the construction of a large and powerful battery, worthy of a national establishment, and capable of promoting the great objects of science, and that this battery be erected in the laboratory of the Royal Institution." The sum required, a little over £500, was soon got together, and at the concluding lecture of the 1812 season the battery was put in action for the first time. We read in Davy's "Elements of Chemical Philosophy," iv., p. 110, an account of how he applied the battery to the running of an electric "arch" between two carbon rods. Parts of Davy's battery are still preserved at the Royal Institution.

I begin my lecture thus, merely to emphasise once more the truth of the adage of 3000 years ago:—"There is no new thing under the sun."

In 1912, when considering the subject of "very high temperatures," we can claim, comparatively speaking, to be capable of little more than Davy accomplished a century ago. In his arc he melted all the most infusible materials known to him, including lime and magnesia, which are among the most refractory materials in use at the present day.

Turning now from the historic to the present aspect of our subject, permit me to begin with a few elementary considerations as to our conception of temperature. I think I am correct in saying that everyone has some idea in his own mind of a temperature-scale, a kind of intuition which is generally a fairly useful one for practical purposes. Probably I am not exaggerating when I say that even men of science, who always think for their professional purposes of temperatures on the Centigrade scale, find themselves obliged to convert to Fahrenheit for an idea of the temperature of a room or of a summer's day.

I have endeavoured to give a graphic representation (Fig. 1) of the temperature scale as we know it, both in Centigrade and Fahrenheit degrees. You will notice the smallness of the interval between the extreme temperatures that prevail in the arctics and the tropics; and how restricted the "cold" region down to absolute zero is compared with the possibilities in the other direction. While, on the one hand, Kammerlingh Onnes by the evaporation of liquid helium under low pressure has succeeded in getting during the last few weeks to within 1·1° C. of absolute zero, the highest recorded terrestrial temperature—that of an electric arc under high pressure—falls short of the sun's estimated temperature by some 2000° C.

Some landmarks in our available range of temperature are given in Table I. It may be remarked that the three substances last quoted in the table are all in extensive use for electric lamp filaments.

Table I.—*Various Temperatures.*

	°C.
Absolute zero	−273
Helium boils (0·2 mm.)	−272
Helium boils (760 mm.)	−269
Hydrogen boils	−253
Oxygen boils	−183
Carbonic acid boils	−78
Mercury freezes	−39
Water freezes	0
Water boils	100
Tin melts	232
Lead melts..	327
Mercury boils	357
Zinc melts	419
Sulphur boils	445
Aluminium melts	657
Common salt melts	801
Zinc boils	918
Silver melts	961
Gold melts	1062
Copper melts	1083
Cast-iron melts	About 1100
Pure iron melts	1500
Fire bricks soften	1400—1800
Silica softens	1500—1600
Platinum melts	1750
Silver boils	1950
Tin boils	2270
Copper boils	2310
Lime and magnesia melt..	About 2400
Iron boils	2450
Tantalum melts..	2900
Tungsten melts	3000
Carbon melts	?

Table II. gives examples of various flame temperatures, which we have at our disposal.

Table II.

	°C.
Temperatures attainable in—	
Bunsen burner flame..	1100—1350
Méker burner flame	1450—1500
Petrol blow-lamp flame	1500—1600
Oxy-hydrogen flame..	About 2000
Oxy-acetylene flame..	About 2400
Thermit	About 2500
Electric arc..	About 3500
Electric arc (under pressure) ..	About 3600
Sun	About 5500

Some of the methods for measuring temperature with

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[*] A Discourse delivered before the Royal Institution, February 9, 1912.

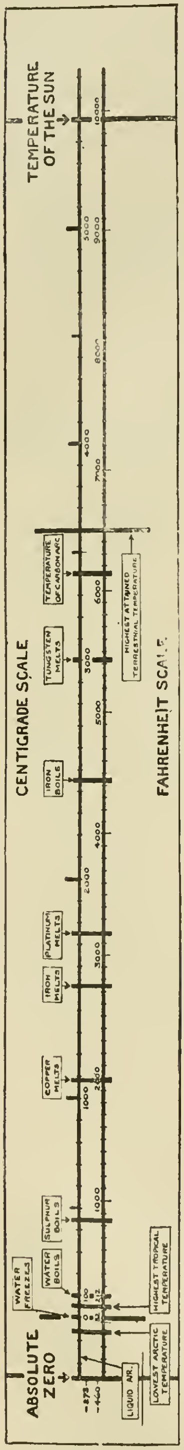


Fig. 1.

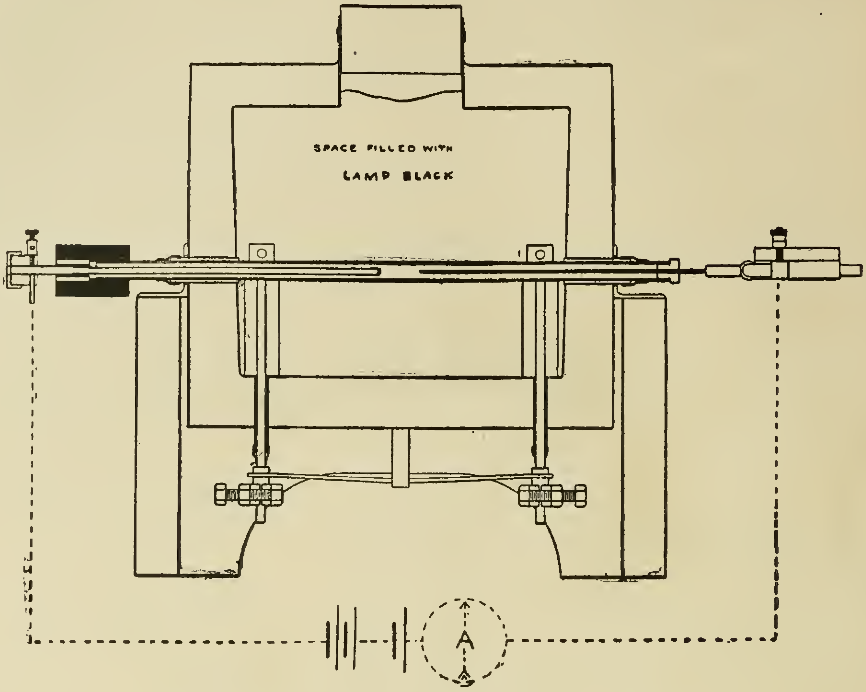


Fig. 2.—Small Model Straight Carbon-tube Furnace.

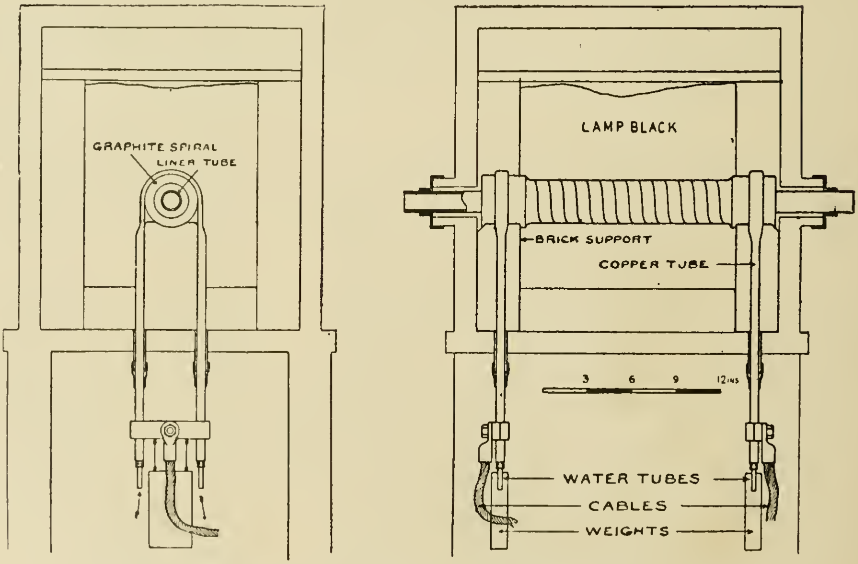


Fig. 3.—Carbon-tube Furnace with Graphite Spiral Heater.

their limitations are briefly recapitulated in Table III. I have only time to refer to one or two points. We have recently had the opportunity at the National Physical Laboratory of subjecting a number of mercury in silica thermometers to a critical examination. These thermometers, which are made in England, possess in a high degree the qualities of constancy, large range, and such complete freedom for temporary zero change that I feel safe in prophesying they will inevitably replace the present International standards, which are made of verre dur.

Table III.—*Some Indication of the present Range of Temperature Measuring Instruments.*

Method.	Range in °C.	
	Practical.	Extreme.
Expansion Thermometers—		
Gas thermometer.. ..	Up to 1200°	−272—1550°
Mercury in glass	−39—500°	−44—575°
Mercury in silica	−39—600°	−44—700°
Electrical Thermometers—		
Platinum resistance ..	−100—1100°	−250—1400°
Thermocouples—		
Platinum alloys.. ..	300—1400°	Up to 1750°
Base metals	−100—1100°	−250—1200°
Total radiation pyrometers	500—1400°	No upper limit
Optical pyrometers	600—3500°	No upper limit

In regard to high temperatures most of us rely to some extent on colour in estimating temperature. Table IV. gives a very fair notion of the temperature we may reasonably associate with the colour of a fire or muffle furnace (experiment shown). The intensity of the light varies according to well known laws which have been studied up to sun's temperature. If we know the law of variation we can measure the temperature by the use of some kind of photometer—which is what all optical pyrometers are.

Table IV.—*Temperature and Colour of a Fire.*

Colour.	Cent.	Fahr.
"Grey," lowest discernible temperature	About 450°	About 850°
Very dull red	About 500°	About 950°
Dull red	About 700°	About 1300°
Cherry red	About 900°	About 1650°
Orange	About 1100°	About 2000°
White	About 1300°	About 2400°
Dazzling white	Above 1500°	Above 2750°

For obtaining really high temperatures electric furnaces are our only resort. Small gas furnaces can reach 1600° with difficulty; large industrial furnaces attain 1800° C. in some instances.

Mr. Cook, of Manchester, has kindly lent me for this occasion a number of electric furnaces. These are constructed by winding tubes of fire clay or alumina with nichrome or platinum wire; the external lagging is of kieselguhr. Steady temperatures up to about 1000° and 1200° C. respectively can readily be got with power from a commercial circuit of 100 or 200 volts. With thicker wires and current at lower voltage these upper limits can be appreciably extended.

For higher temperatures we have to make use of carbon or graphite, and electric heating was first applied by such means in the form of the arc furnace. Such a furnace has many inconveniences—the heating is intensely local, and there may, for example, be a gradient of 2000° C. in a single inch. There is practically no temperature control, and there is every possibility of the final product becoming largely contaminated with carbon. Most of the early isolated so-called elements have since proved to be largely carbides.

Resistance heating is usually much more convenient, and this is the principle of carbon-tube furnaces, some essential features of which were employed by Prof. Dewar many years ago. They will stand rough use, and are much more controllable than the arc furnace. It is as easy to control a temperature of 2500° C. as one of a red heat.

Such furnaces usually have their end-terminals water-cooled, and are surrounded by lagging of lamp-black or charcoal.

The furnace tubes are either straight if made of carbon (Fig. 2), or spiral if made of Acheson graphite (Fig. 3). In the latter case they are provided with an internal liner-tube of carbon. There is no special difficulty in cutting the spirals from the solid; graphite, unlike amorphous carbon, is an extremely tractable substance to machine.

We have used these carbon resistance furnaces a great deal at the National Physical Laboratory, and Mr. Greenwood, at Manchester, carried out his experiments on boiling metals by the aid of such a furnace. The boiling of a metal (shown) forms a not-impossible lecture experiment, and a projected image of the surface of boiling tin displays all the usual phenomena of ebullition. The heating up of carbon is somewhat strikingly shown by passing a heavy current through a thin broad carbon strip provided with water cooled terminals (experiment shown). The stream lines of heat flowing from one terminal to the other are well illustrated at one stage of the heating.

Among other methods of electric heating are the induction furnace, which is of great value in refining crude materials, and the flame spark, in which it is possible to volatilise as refractory a substance as an incandescent gas mantle.

Some time ago we endeavoured at the National Physical Laboratory to make a furnace for very high temperatures without employing carbon. The introduction of the Nernst lamp was suggestive. It was found that a great number of substances could be made to act like a Nernst filament, *e.g.*, a piece of the stem of a churchwarden pipe, if sufficiently strongly heated, can be made to conduct electricity well enough to become incandescent. Carborundum crystal behaves similarly, and requires no initial heating (experiment shown); in this case the temperature can be raised high enough to volatilise off the silicon, which burns, forming a cloud of silica. A cascade furnace was constructed on these lines:—A tube made up of zirconia and a little yttria was raised by means of an insulated nickel winding to 500° or 600°, at which temperature the tube conducts sufficiently well to enable a heating current to be passed through it. There is no difficulty in melting platinum, for example, in such a furnace using a quite small heating current (about 2 ampères). A zirconia tube from such a furnace was taken out after it had been run for six months or so; it was then found to be quite translucent. The possibility of constructing in such a way refractory gas-tight materials at once suggested itself, and we proceeded to manufacture "pottery" at high temperatures. Great difficulties have been encountered in the experiments. Whereas, for example, the potter in baking his wares at temperatures up to 1300° C. looks for a shrinkage of 5 per cent or so, we were confronted with a shrinkage of 37 per cent. For the purposes of the fritting we employed carbon-tube furnaces of one of the types mentioned above. Now it sometimes happened that the outer surface of the zirconia tubes, instead of having the white and hard appearance of the rest, was found to be carburised and crumbly after baking. The action was not merely superficial, but extended to an appreciable depth. On the other hand, the inner surface of the tube, though freely open to the furnace atmosphere, was much less affected. The blackening occurred to a much less extent if the tube was shielded. It seemed as though particles, possibly electrified, were shot off from the carbon walls of the furnace across a space of some 5 or more mm. into the material of the refractory tubes. Dr. G. W. C. Kaye and I were led to investigate the cause of these phenomena, and yesterday we gave an account of some of the results to the Royal Society. I propose to devote the remainder of my lecture to a description of the methods employed and the results obtained in what proved to be a very interesting investigation.

(To be continued)

Action of Hydrazine on the β-Substituted Ethylenic Amino-ketones.—Emile André.—When hydrazine reacts with the β-amino substituted ethylenic amino-ketones the first product is a hydrazone, which then yields a pyrazol. Thus from dipropylamino-acetylstyrolene 3-methyl-5-phenyl pyrazol is obtained.—*Comptes Rendus*, clv., No. 1.

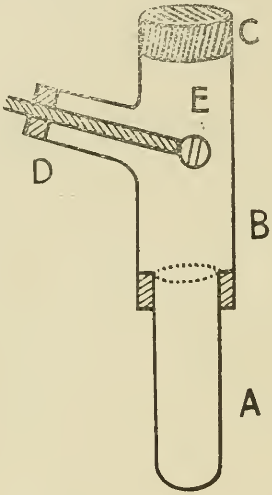
A HYGROMETRIC METHOD OF VAPOUR-PRESSURE DETERMINATION.

By W. R. FORBES, B Sc.

THE apparatus used is modified from a form described by Ewan and Ormandy (*Brit. Assoc.*, 1892). The dew-point is observed, and the corresponding vapour-pressure obtained from tables. The vapour-pressure at the temperature of the water-bath is thus obtained.

In the figure A is a copper "test-tube" to which is fitted a glass vessel, B, by means of a rubber band. Rubber corks close B at C and D.

D carries a glass rod to which a disc is attached; the disc being made of black glass crossed above and below by a silver band.



In observing the dew-point proceed as follows:—Note its first commencement on the upper surface of the disc, immediately reverse the disc, and note its formation on the second surface. This will eliminate slight errors due to evaporation.

The copper vessel ensures good heat conduction between the water-bath and the liquid.

THE PHYSICAL AND CHEMICAL PROPERTIES OF SOME ORGANIC AMALGAMS.*

By HERBERT N. McCOY and FRANKLIN L. WEST.

(Concluded from p. 79).

THE immediate object of our experiments was to find the nature and potential of the charge which the amalgam when insulated and in contact with very cold dry air might acquire under the influence of ultra-violet light. From the electroscope experiments we should expect such a charge to be electropositive. This also would be in accord with the behaviour of the alkali metals (Thomson, *loc. cit.*). The insulated amalgam was connected to the quadrant electrometer by a wire which passed with sulphur insulation through a brass tube 6 cm. in diameter. The terminal of this wire together with the amalgam and its support were shielded from the spark by means of large sheet metal screens. One of these screens had an opening 2 × 4 cm. which was covered by a piece of cardboard having an opening 2 mm. square. The light from the spark passed through this opening and illuminated the amalgam. The needle of the electrometer was charged to 120 volts and held its charge perfectly for hours. One pair of quadrants of the electrometer was earthed; a charge of 1 volt on the other pair gave a scale deflection of 3·4 cm. When the amalgam was absent and the spark going, the agitation of the needle due to static effects was not over 1 mm. on the scale. In the preliminary experiments the amalgam rested on a watch-glass supported by a vulcanised rubber stand.

Before making an experiment, all four quadrants of the electrometer were earthed; when all was ready, the earth connection of one pair of quadrants was lifted and this pair connected to the amalgam, appropriate switches being used. In all cases the amalgam took on a positive charge; a maximum potential of about 2·4 volts was usually reached in a few minutes. There was some doubt, however, whether the result was due to the ultra-violet light. It seemed possible that the amalgam might have acquired a positive charge spontaneously in the absence of the light.

In the final experiments the amalgam was contained in the glass tube represented by Fig. 2. This tube was 9 by 1·3 cm. and had a small side tube closed with a quartz glass window. The spark passed through the 2 mm. opening in the screen and through the quartz window and illuminated the amalgam. During an experiment, the lower part of the tube holding the amalgam was surrounded by ice and water.

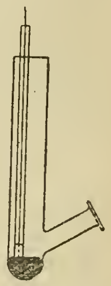


FIG. 2.

The first trial with the amalgam in the tube Fig. 2 was begun before the spark was started. During the first three minutes the positive potential of the amalgam rose slowly to 0·2 volt; the spark was now started and allowed to illuminate the amalgam. It seemed to have no effect on the rate of increase of potential. It was soon turned off without noticeable effect, for the amalgam continued to increase in positive potential until the electrometer deflection indicated 2·7 volts. In three subsequent trials in which the spark giving the ultra-violet light was not running, the amalgam took on potentials of 2·7, 2·8, and 3·8 volts respectively. The maxima were usually reached in five to ten minutes. The charge on the amalgam was positive in all cases. These results made it clear that the taking on of a positive charge by an insulated portion of tetramethylammonium amalgam is a spontaneous action which is not caused by the illumination with ultra-violet light. However, it is still possible that the ultra-violet light may be able to cause a smaller additional effect, which in our experiments in which the light also acted was masked by the larger spontaneous one.

The acquirement of a positive charge by the insulated amalgam can only mean that it loses spontaneously negative electricity. This fact is in complete accord with that of the discharge of the positively charged electroscope in the presence of the amalgam. The carriers of the negative electricity given off by the amalgam may be either (1) electrons or (2) ions, consisting of electronegatively charged molecules or larger groups or in general terms an electronegatively charged gas.

Photographic Experiments.—The difference between the activity of tetramethylammonium amalgam and that of the typical radioactive element uranium was clearly shown by the behaviour of each toward photographic plates. For the experiments Lumière Sigma dry plates were used. (This make is known to be rapid). These were exposed with all usual and necessary precautions for known periods to the action of the rays from a quantity of uranium oxide which discharged the electroscope about as fast as the average sample of the amalgam. A plate exposed to the uranium oxide for fifteen minutes showed distinctly a uniform black spot of the same size as the 3 cm. hole in the piece of sheet iron which shielded the balance of the plate from the action of the α- and β-rays of the uranium. Longer exposures gave blacker spots. One of

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* From the *Journal of Physical Chemistry*, xvi., No. 4.

the same kind of plates was also exposed, under strict photographic conditions, to the action of the amalgam in place of the uranium, all else being the same. Seven preparations of solid (filtered) amalgam were allowed to act on the plate successively in the course of twelve days. The total weight of the solid amalgam so used was 115 grms.; its preparation had required a total of 4·85 ampère hours. Upon development, this plate was found to be "fogged" in the centre, the intensity being about equal to that caused by thirty minutes' exposure to the uranium. The "fogged" portion of the plate was not sharply defined, corresponding to the hole in the sheet iron, as in the case of exposure to uranium rays. This fact suggested some other cause than the action of a radiation from the amalgam: possibly the dim red light used in the dark room or the action of mercury vapour during the long exposure. The first possibility was excluded by the fact that plates exposed to the red light for much longer periods than the total possible exposure to the same source in the amalgam experiment showed no effect at all upon development. On the other hand, a plate exposed for thirteen days to the action of pure mercury under the same conditions as used in the case of the amalgam showed a distinct circular spot, fully as dark, if not darker, than that on the plate which had been exposed to amalgam. These experiments show clearly that the apparent photographic action of the amalgam was due simply to mercury vapour and that the amalgam has no photographic activity.

The experiments on the electrical behaviour of the amalgam and the fact that this was not influenced by ultra-violet light, together with the negative results of the photographic experiments, are all best explained by the assumption that the amalgam gives rise to an electronegatively charged gas. In the electroscope the electronegative ions are attracted to the positively charged electrode and so discharge the gold leaf system. On the other hand, the negative charge of the ions comes from the amalgam; so that, if the latter is insulated, as in the quadrant electrometer experiments, it acquires a positive potential. The cause of the electrification of the air or gas is not certain although the following explanation seems probable. It is shown (in the following section) that the spontaneous decomposition of the dry amalgam gives, besides mercury, trimethylamine, and hydrocarbon gases, from 40—60 cc. resulting from a single preparation. Now Lenard has found that air bubbled through or shaken with mercury becomes negatively electrified (*Wied. Ann.*, 1892, xlvi., 584). From this it would seem very probable that the gases formed by the decomposition of the amalgam would escape from the interior of the mass in an electrified condition. It might seem that this explanation would require that the gas from every amalgam should have the same kind of electrification, whereas this is not the case. However, it is not improbable that mercury may behave like water which electrifies gases bubbled through it either negatively or positively according to the nature of the solution and the gas (Kelvin, *Proc. Roy. Soc.*, 1894, lvii., 335; Kosters, *Wied. Ann.*, 1899, lxix., 12). The fact already mentioned that the amalgam does not lose electricity except when it is decomposing is further evidence in favour of this view. Also the fact mentioned in an earlier paragraph, that the rate of discharge of the electroscope by the amalgam is greater when the latter is near the electrode, is entirely in accord with the view that a charged gas is given out by the amalgam, since, under such conditions, fewer of the gaseous ions will fail to reach the electrode. The effect would be very different if a radiation capable of causing ionisation were given out by the amalgam. Further evidence in this direction is also furnished by the following experiment.

A very good preparation of the amalgam that had been obtained with a current of 0·5 ampère for an hour and a-half was freed from excess of mercury and put in a small crystallising dish, 3¾ cm. in diameter and 1¼ cm. high, and placed in the electroscope with the gold leaf system charged positively. The discharge rate was 0·63 of the standard. A piece of aluminium leaf 0·0044 cm. thick was now quickly sealed with wax over the mouth of the dish. The covered amalgam had no effect whatever on the positively charged gold leaf system. The aluminium leaf was now removed and the amalgam again placed in the electroscope. The discharge rate was 0·19 of the standard. A second trial with the aluminium leaf over the amalgam resulted like the first, and when the leaf was again removed the discharge rate was 0·33 of the standard. This experiment was repeated on several different occasions with other preparations of amalgam with exactly similar results. It is thus seen that the charged particles that arise from the amalgam can not pass through aluminium leaf of the thickness used. On the other hand, this aluminium leaf would absorb only a small fraction of a β-radiation such as that of uranium, but would completely prevent the passage of gaseous ions of all sorts.

The carriers of electricity or the ions of a gas electrified by bubbling have much smaller velocities in an electric field and much smaller speeds of diffusion than have ions produced by radio-active radiations. The former sort of ions are therefore much more persistent than the latter, so that the gas remains charged for a relatively long time. It also retains much of its charge after passing through glass-wool, &c. The following experiments show that the negative electrification of the gas from tetramethylammonium amalgam is present as persistent ions. The rate of discharge of the electroscope by a sample of amalgam contained in a porcelain boat was determined in the usual way. The boat and amalgam were then brought into a straight "calcium chloride tube" outside of the electroscope and a current of air blown over the amalgam and into the electroscope, the air emerging near and toward the electrode, and the rate of discharge again noted. As a mean of four such independent experiments, it was found that the rate of discharge was 95 per cent as great in the second case as in the first. In a similar experiment in which uranium oxide was substituted for the amalgam, the rate of discharge by the air current was only 28 per cent of that when the uranium was in the ionisation chamber. It was also found, in several trials, that an appreciable part of the electrification of air blown over the amalgam would pass through a 6 cm. layer of glass-wool or a narrow copper tube 30 cm. long and 0·2 cm. in diameter, while if the path of the air current included both of these the electrification was all removed.

In β-ray radio-active changes, at least one electron is liberated by the disintegration of each atom. It is easy to calculate roughly how much electricity is contained in the electrified gas produced during the decomposition of the amalgam and to compare this quantity with that if each molecule of the amalgam decomposed gave off one electron. A quantity of amalgam, the decomposition of which would yield 50 cc. of gas of which 29 cc. would be trimethylamine, would on the average discharge the positively charged electroscope at a rate equal to that of the standard for a period of about ten minutes. Since the standard produces an ionisation current of $2·15 \times 10^{-11}$ ampère and 1 cc. of a univalent gas would represent 4 coulombs, it follows that only one electron is given off for every 10^{10} molecules of amine gas formed! This fact is itself sufficient to show that this phenomenon has nothing in common with that due to a radio-active transformation. If a few drops of water be added to the amalgam while it is in the electroscope, with the gold leaf system positively charged, the discharge becomes very rapid for about one minute and then suddenly stops. The duration of the rapid discharge depends on the quantity of amalgam present, and it is a particularly significant fact that the rate of electrical discharge is evidently dependent on the rate of decomposition of the amalgam.

The action of water on tetramethylammonium amalgam gives hydrogen and tetramethylammonium hydroxide (McCoy and Moore, *loc. cit.*). In the absence of water the amalgam decomposes spontaneously, giving a mixture of gases having the intense fishy odour characteristic of trimethylamine. The speed of decomposition varies greatly with the temperature. At zero it is very slow; at 25° it is much faster, the decomposition being practically complete in about an hour. A quantitative velocity determination was made by the use of a Lunge gas burette fitted with a water jacket through which water at the constant temperature of 27° flowed. A quantity of the amalgam, made and washed as usual but not filtered, was freed from carbon tetrachloride as thoroughly as possible by means of filter-paper and brought into the burette. Before introducing the amalgam, the burette and levelling tube were carefully dried and filled with dried mercury. As time went on, the amalgam began to decompose and the gas to accumulate in the burette over the amalgam; its volume at atmospheric pressure was read off at frequent intervals with results as shown in the following table:—

Velocity of Decomposition of Dry Tetramethylammonium Amalgam at 27°, K′ and K being Calculated by the Monomolecular Formula.

Time in minutes.	Volume of gas formed (cc.).	K′ $t_0=8$ mins.	K $t_0=13$ mins.
0	0·0	—	—
8	2·0	—	—
9	2·8	0·060	—
11·5	5·5	0·083	—
13	7·2	0·094	—
15	9·5	0·110	0·155
17	11·3	0·124	0·161
19	12·7	—	0·168
21	13·5	—	0·163
23	14·1	—	0·160
25	14·5	—	0·155
29	15·0	—	0·145
33	15·5	—	0·160
46	15·75	—	—
56	15·85	—	—
		Mean	0·158

During the washing and drying of the amalgam and its introduction into the burette, it was kept as cold as possible. Its temperature at the moment it was inclosed was therefore far below that of the water jacket, 27°. It must have required considerable time (perhaps ten minutes or more) for the amalgam to have reached this higher temperature. For this reason the velocity constant, K, of the rate of decomposition was calculated from the time thirteen minutes after the start. A calculation based on the eighth minute as zero gave the values under the heading K′, $t_0=8$ minutes. The results after the thirteenth minute show that the reaction is monomolecular. The initial velocity is very low owing to the low temperature of the amalgam at the start. A second disturbing factor at the start was due to the fact that the gas did not separate from the amalgam readily, due no doubt to its being present in the minute bubbles. This resulted in a swelling of the material without the appearance, for several minutes, of a gaseous layer. Two additional velocity determinations under similar conditions gave results essentially like that just discussed. In an attempted velocity determination at 0°, no gas had separated in the course of four hours, although some increase of volume of the amalgam seemed to have taken place. At the end of the fourth hour the temperature was raised to 25°, whereupon the decomposition occurred as usual and was complete in the course of an hour. The amalgam used in this experiment had been prepared by a current of 0·21 ampère for one hour and fifty minutes; the amount of mercury used was about four times the usual amount, the object being to obtain a more fluid product than usual.

The gas obtained by the spontaneous decomposition of this sample of amalgam measured 63·4 cc. It was transferred quantitatively to another burette over mercury and a known volume of 0·1 normal HCl introduced. The basic portion of the gas was absorbed by the acid solution; the volume remaining was 26·5 cc., corresponding to an absorption of 58·2 per cent. In several analyses the uncombined standard acid was titrated and a comparison made with the shrinkage in volume when the acid was added. For instance, in another experiment 40·15 cc. of gas shrank to 16·1 cc. when the acid was added. The shrinkage was thus 24·05 cc. The titration of the uncombined standard acid showed 9·47 cc. to have been neutralised by the 24·05 cc. of gas absorbed. If this gas were univalent, it should have required 9·53 cc. of the standard acid. Similar measurements in other analyses gave equally concordant results, and show that the gas absorbed is a univalent amine or a mixture of such amines.

The solutions of the amine hydrochlorides from several determinations were united, made alkaline with caustic soda, and the amines distilled off and absorbed in water. The solution was neutralised with hydrochloric acid, treated with platinic chloride and alcohol, and the resulting yellow precipitate washed thoroughly with absolute alcohol (Eisenberg, *Liebig's Ann.*, 1880, ccv., 142). In the analysis of the substance, 0·1308 grm. gave upon ignition 0·0470 grm. of platinum, equal to 35·93 per cent; trimethylamine chlorplatinate requires 36·94 per cent. Dimethylamine and monomethylamine chlorplatinates require 39·0 and 41·32 per cent of platinum respectively. In spite of the somewhat low value found, there is little doubt that the gas is trimethylamine.

The gas insoluble in the standard acid was analysed by means of the usual Hempel apparatus; 14·05 cc. of it was exploded with 41·4 cc. of pure oxygen. After the explosion 27·4 cc. of gas remained. This consisted of 16·16 cc. of carbon dioxide, soluble in 30 per cent KOH, and 11·24 cc. of oxygen, soluble, excepting a minute bubble, in alkaline pyroglycol. These results indicate that the decomposition of the tetramethylammonium radical occurs as follows:—

$$4Hg_x(CH_3)_2N \rightarrow 4(CH_3)_3N + 2CH_4 + C_2H_4 + XHg.$$

This reaction would give 57·1 per cent by volume of trimethylamine, while the experiment described gave 58·2 per cent of soluble gas and the average for eight additional experiments was 58·3 per cent. Each cc. of the amine-free gas should require 2·33 cc. of oxygen and produce 1·33 cc. of carbon dioxide. This particular experiment showed 2·15 cc. and 1·15 cc. respectively, while the mean of four such determinations gave 2·21 cc. and 1·20 cc. respectively. Theoretically also each cc. of the amine-free gas should require an equal volume of oxygen to unite with the hydrogen of the methane and ethylene; in the experiment the oxygen consumed, in excess of that needed for the carbon, was 1·01 cc. per cc. of original gas. However, a more thorough study of the decomposition products will be necessary before the reaction suggested can be considered as definitely established.

Monomethylammonium Amalgam.—McCoy and Moore made this amalgam by electrolysis of both aqueous and alcoholic solutions of its salts, and made potential measurements with it just as with tetramethylammonium amalgam. In the attempt to increase the yield we tried a large number of additional solvents. There was amalgam formation in methyl alcohol and glycerol solutions as well as traces in some of the others. Although the current is small with the glycerol, the crystalline character of the amalgam is well marked. However, water as solvent gives the best results. The amalgam decomposes rapidly in all cases during the electrolysis, giving off a gas with a strong ammoniacal odour, obviously monomethylamine. While the current is on, a dense white cloud persists in the electrolysing chamber. Neutral liquids, such as carbon tetrachloride or benzene, exercised no protective action on the amalgam, nor did low temperatures appreciably increase its stability. A fair preparation was obtained in one experiment at 75°, and that made at −34° was little, if any, superior to the one obtained when the temperature was kept at 0°.

Monomethylammonium amalgam increases greatly in volume as it undergoes spontaneous decomposition, in which respect it closely resembles ammonium amalgam. In each case the compact amalgam constitutes without doubt the alloy with mercury of the metallic form of the radical, while the distended material is only mercury inflated with the gaseous decomposition products. As stated in the introduction, monomethylammonium amalgam discharges the electroscope when the latter is charged either positively or negatively, the rate being several times greater for a negative charge. In several experiments a rate of discharge three to four times that of the uranium standard was observed for a negative charge on the gold leaf. The effect of the distance of the amalgam from the electrode of the electroscope was tried as in the case of tetramethylammonium amalgam. In one such experiment the rate was 1·6 times the standard for a distance of 1·5 cm. and 0·8 for 3·7 cm., the leaf being negatively charged.

Summary.

1. An improved method of making tetramethylammonium amalgam has been worked out, and the substance obtained in solid form. Determinations of its density and electrical resistance have been made.

2. The amalgam causes the discharge of a positively charged electroscope, behaving in this respect like a radioactive substance. That the phenomenon is not one of radio-activity was shown by the following facts :—A negatively charged electroscope is not discharged ; the rate of discharge of a positive charge is erratically variable, temperature having an enormous effect ; the rate is greater when the amalgam is closest to the electrode of the electroscope, thus showing the absence of an ionising radiation. A thin aluminium leaf placed over the amalgam prevents the discharge and so proves the absence of a β-radiation. The same conclusion is supported by the fact that the amalgam has no photographic activity. The phenomenon is distinguished from that shown by the alkali metals in that it is not appreciably influenced by ultra-violet light. The facts here summarised, as well as some others of minor importance, are best explained as follows :—The amalgam decomposes spontaneously into mercury and gaseous products. The gas escaping from the mercury in minute bubbles is negatively electrified, just as in the case of air bubbled through mercury as shown by Lenard. The ions of the negatively charged gas cause the discharge of the positively charged electroscope.

3. The spontaneous decomposition of the amalgam which takes place very slowly at 0° but quite rapidly at 25° seems to occur according to the equation : $4Hg_x(CH_3)_4N \rightarrow 4(CH_3)_3N + 2CH_4 + C_2H_4 + XHg$. The fact that a velocity determination of the speed of decomposition showed the reaction to be monomolecular indicates that the change takes place in stages.

4. The method of preparation and the properties of monomethyl amalgam were also studied.

5. The further study of the properties of organic amalgams, as described in this paper, has served to support the hypothesis that free radicals formed by the electrical neutralisation of the positive ions of salts would have metallic properties (McCoy and Moore, *loc. cit.* ; McCoy, *Science*, 1911, xxxiv., 138).

SILOXYD GLASS.

The U.S. Consul General at Zurich, Switzerland, reports the discovery by a Zurich inventor of a method of producing suitable apparatus for the chemical industry from electrically melted quartz.

According to the U.S. Consular Report, from which these notes are taken, the product is an improvement on quartz gut, or quartz glass, and is especially suited to the manufacture of pipes, tubes, receptacles, flasks, muffles, and other articles used in the production of chemicals, required to withstand a very high temperature and at the same time the effect of concentrated acids. Most of the articles used for such purposes have, until recently, been made of platinum, for the reason that a quality of glass that would meet the requirements had not been produced.

Articles made by the new process from electrically fused quartz because of the low coefficient of expansion, can be subjected to extreme changes of temperature without damage. It is now possible to make articles of large dimensions of this glass, such as socket pipes, acid bottles, and other vessels, that will hold as much as 25 gallons. This new material has been placed upon the market as "siloxyd" glass, and the process of manufacture has been patented in most of the European countries and in the United States.

Quartz glass, which has long been recognised as an important material in the manufacture of various articles employed in the chemical industry, and for which "siloxyd" is now being substituted where a severe test of temperature is required, was first discovered in 1839 by Prof Gaudin, who later produced from the same material some tubes and elastic threads which were exhibited at the Paris Exposition in 1878.

In 1889, Boys, who saw the possibilities of this remarkable substance, succeeded in making from quartz small tubes and other articles. Although there were many subsequent experiments, little progress was made in the development of the quartz glass industry until 1900, when Hereaus and Achendstone succeeded in making clear rock-crystal objects of sufficient sixe for scientific and mechanical purposes.

The raw material from which the glass is produced is washed quartz-sand, containing 95 per cent silicic acid, which is melted in an electric furnace in which the temperature rises to 2000° F. All the agencies known to the glass-working industry, including air, steam, gases, &c., can be applied, and it is now possible to melt and to mould into almost any desired form as much as 50 pounds of quartz. A remarkable quality of the quartz produced by the thermoelectric process is its resistance to acids. Even boiling acid, with the possible exception of hydrofluoric or phosphoric, will not corrode it. Quartz has the advantage of a coefficient of expansion about one-seventeenth that of the best glass suitable for chemical utensils and apparetns.

The chief objection to pure quartz glass as a material for apparatus used in the chemical industry is that it becomes brittle at high temperature, passing from the amorphous to the crystalline state with a diminution of strength. Until the discovery of Dr. Wolf-Burkhardt, authorities on the subject claimed that the addition of any other ingredient to the raw material would injuriously affect the quality of the melted quartz.

The new process consists in adding to the raw quartz solutions of oxides of zircon, titanium, and other metals difficult to fuse (or silicates of same to silicic acid), the resulting mixture giving on fusion a transparent glassy substance which fuses at a temperature of 1750°. The advantages claimed for this material over ordinary quartz glass are that its strength is 30 to 50 per cent greater than "quartz gut," tested by bending, and 10 to 30 per cent more tested by pressure, and that it is less brittle, because the devitrification is only about half that of quartz glass. It is also more resistant to basic metallic oxides.

The superior advantages claimed for "siloxyd" glass give to this new material a wide range of usefulness, especially for apparatus used in the acid industry and for laboratory purposes where socket pipes, tee pipes for acid conduits, evaporating basins, concentrating dishes, cooling vessels, special boxes, conical pipes, condensation utensils, balls for acid towers, &c., are required.—*Chemical Engineer*, xv., No. 5.

BLEACHED OATS AND BARLEY.*

The Department of Agriculture has received numerous inquiries relative to the application of the Food and Drugs Act to oats, barley, and other grains bleached with the fumes of sulphur. It appears that by this process grains which are damaged or of inferior quality may be made to resemble those of higher grade or quality, and their weight increased by addition of water. Such products, therefore, are adulterated within the meaning of the Food and Drugs Act of June 30, 1906, and can not be either manufactured or sold in the District of Columbia, or in the Territories, or transported or sold in interstate commerce.

It is represented, however, that grains which are weather-stained, or soil-stained, the quality of which is in no wise injured in other respects, are sometimes bleached with sulphur fumes. Pending the report of the Referee Board of Consulting Scientific Experts as to the effect upon health of sulphur dioxide, and the results of experiments being made by this Department as to the effect of sulphur-bleached grains on animals, no objection will be made to traffic in sound and wholesome grains which have been bleached with sulphur dioxide and from which the excess water has been removed, provided that each and every package is plainly labelled to show that the contents have been treated with sulphur dioxide. Bulk shipments should be properly designated on invoices. The terms "purified," "purified with sulphur," "processed," &c., are misleading, and not proper designations for these products.

Attention is also called to the fact that grains bleached with sulphur fumes may have their germinating properties very seriously impaired.

PROCEEDINGS OF SOCIETIES.

INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES.

The following announcement of the proceedings at the meeting of the International Association of Chemical Societies, held in Berlin in April, 1912, is made by order of the Council of the Chemical Society.

Extract from the Minutes of the Second Meeting of the Council in Berlin, April 11th—13th, 1912.

The following were present: —

(*a*) As full members of Council:—

W. Ostwald, President; H. Wichelhaus, Vice-President; P. Jacobson, General Secretary, for the Deutsche Chemische Gesselschaft.

A. W. Crossley, P. F. Frankland, Sir W. Ramsay for the Chemical Society (London).

A. Béhal, A. Haller, M. Hanriot for the Société Chimique de France.

Fr. Fichter, Ph. A. Guye, A. Werner for the Schweizerische Chemische Gesellschaft.

W. A. Noyes for the American Chemical Society.

N. S. Kurnakow, L. A. Tschugaeff, P. J. Walden for the Russian Chemical Society.

(*b*) As members of Council in an advisory capacity only: —

Ch. Marie for the Société de Chimie-Physique, Paris; Fr. Auerbach for the Deutsche Bunsen Gesellschaft; E. Cohen for the Nederlandsche Chemische Vereeniging; H. Goldschmidt for the Polyteknisk Forenings Kemikergruppe (Christiania); E. Biilmann for the Kemisk Forening, Copenhagen.

During the course of the meeting the following members included in section (*b*), namely, Messrs. E. Cohen, H. Goldschmidt, and E. Biilmann, joined the Council as full members in consequence of a decision to confer upon their respective societies the right of representation on the Council.

The following Members of Council, Messrs. Carrara (Società Chimica Italiana), Day (American Chemical Society), Oglialoro (Soc. Chim. Ital.), Paternò (Soc. Chim. Ital.), and Richards (Am. Chem. Soc.), notified their inability to attend the meetings.

The President of the Association, W. Ostwald, occupied the Chair.

The Chairman presented a Report on the development of the Association during the first year of its existence from April, 1911, to April, 1912. The Association, which originally consisted only of three Societies (the Société Chimique de France, the Chemical Society, London, and the Deutsche Chemische Gesellschaft), had grown considerably during the year—due, in part, to the acceptance of invitations to join the Association, and in part to the granting by the Council of applications for admission—and the Association now included representatives of almost all countries in which Chemical Societies exist.

During the meeting several requests for admission into the Association or for representation on the Council were granted. The membership of the Association at the close of the meeting may be seen from the following list of constituent Societies arranged in their order of admission:—

	Number o members.
*Société Chimique de France (April 25, 1911) ..	1024
*The Chemical Society (London) (April 25, 1911)	3132
*Deutsche Chemische Gesellschaft (April 25, 1911)	3352
Société de Chimie-Physique (June 15, 1911) ..	202
Deutsche Bunsen Gesellschaft für angewandte physikalische Chemie (June 19, 1911)	719
*Nederlandsche Chemische Vereeniging (July 14, 1911)	502
*Schweizerische Chemische Gesellschaft (August 3, 1911)..	287
*American Chemical Society (October 6, 1911) ..	5603
*Russian Chemical Society (October 22, 1911) ..	399
*Polyteknisk Forenings Kemikergruppe (Christiania) (October 27, 1911)	105
*Verein Osterreichischer Chemiker (October 28, 1911)	972
*Società Chimica Italiana (January 11, 1912) ..	648
*Kemisk Forening, Copenhagen (January 23, 1912)	137
Tokyo Chemical Society (March 18, 1912) ..	544
*Société Espagnole de Physique et de Chimie (April 10, 1912)	?
Total about	18,000

(The societies marked with an asterisk, as the representative societies of their respective countries, are each entitled to send three delegates to the Council; *cf.*, Articles IV. and V. of the Statutes).

"Suggestions for the Alteration and Amplification of the Statutes" were next considered. After discussion, alterations of Articles IV., V., and XII., concerning the method of voting (*a*) on the admission of new Societies to the Association, (*b*) on alterations in the Statutes, and also a supplementary Article XIII., dealing with the case of an equality of votes, were unanimously carried.

The statutes, as at present constituted, are given in Appendix I.

The meeting next proceeded to consider the reports of the Committees on the following questions: — (1) The Nomenclature of Inorganic Chemistry; (2) The Nomenclature of Organic Chemistry; (3) The Unification of Physical Constants.

In accordance with the decision of the Council at its first meeting in Paris on April 25th and 26th, 1911, the Societies represented on the Council had been requested to nominate committees for the consideration of these questions. The following Societies had accordingly each appointed three committees, all of which, eighteen in number,

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* Communicated by the United States Department of Agriculture, Office of the Secretary.

had presented reports:—Société Chimique de France; the Chemical Society (London); Deutsche Chemische Gesellschaft; Schweizerische Chemisch Gesellschaft; American Chemical Society; Russian Chemical Society.

The discussion turned mainly on the methods of organisation in connection with these questions, the consideration of the actual subject-matter being postponed until a later date. The meeting was called upon to decide as to whether the questions should continue to be dealt with by the national committees or whether the latter should be replaced by smaller international committees. The Council was of opinion that with regard to inorganic and organic nomenclature, the circumstances were different from those obtaining in the case of the unification of chemical and physical constants.

The following resolution concerning inorganic and organic chemical nomenclature was carried unanimously:—

"The national committees shall continue to exist for the present. Any Societies represented on the Council which have not as yet appointed committees shall proceed to do so forthwith."

"The reports of the committees are to be submitted to a process of sifting before the next meeting of the Council. The method of sifting to be adopted is a matter for arrangement between the officers of the Association and the committee's representatives on the Council."

In order to avoid any confusion arising out of the premature adoption and publication by authors of nomenclature suggested by their respective national committees, the following resolution was unanimously carried by the Council:—

"The Council expresses the hope that the introduction of new suggestions for nomenclature in place of existing terms will be avoided as far as possible until the question of nomenclature has been formulated by the Association. Authors' suggestions regarding nomenclature should be submitted to the existing committees for their consideration."

Chemical Societies are to be requested to publish in their respective journals this resolution, which is not meant to prejudice the publication of new suggestions when the necessity arises in consequence, for example, of the discovery of new types of compounds.

The composition of the existing committees on inorganic and organic chemical nomenclature is given in Appendix II.

With regard to the third question, namely, the unification of physical chemical constants, it was pointed out, both in the reports of the committees and during the course of the discussion, that a considerable amount of work had already been done in that direction by existing organisations; for example, the Deutsche Bunsen Gesellschaft, and the authors of "Tables of Physical Chemical Constants." It was therefore generally considered that there was no further need for the existence of the various national committees appointed by the Council. Accordingly an international Commission was nominated, composed of those Members of the Council who by their activities were most directly concerned with this question, namely, Messrs. Carrara, Cohen, Day, Goldschmidt, Guye, Ostwald, Ramsay, Richards, and Walden. This Commission should, as far as possible, work in agreement with other existing organisations appointed for the same purpose.

It was next announced by the President that the members of the International Committee on Atomic Weights—Messrs. Clarke, Thorpe, Urbain, and Ostwald—had expressed a wish to become incorporated with the International Association. Prof. Ostwald was requested by the Council to ask the existing members of the International Committee on Atomic Weights to draft statutes for the future organisation of this committee, and to submit these to the Council of the Association at its next meeting.

The Council next considered proposals for the further extension of the Association's activity.

Prof. Guye, who had pointed out the desirability of a uniform abbreviation of titles of journals, was appointed by the Council to take preliminary steps for the attainment of this object.

Prof. Ostwald brought forward arguments in favour of the unification of the size of printed scientific literature in accordance with the views expressed in his pamphlet entitled, "Die Weltformate" (Ansbach, 1911). The Council thereupon unanimously expressed the hope that all Chemical Societies would issue their publications in the "Weltformat" 16 × 22·6 cm. (these measurements referring to the cut copies), or in some form derived from this. The Council furthermore unanimously resolved that the publications of the Association should be issued in this form (16 × 22·6 cm.).

The suggestions by Prof. Ostwald concerning an international language called forth considerable discussion. The following suggestion was adopted unanimously:—

"The Council should appoint a committee to investigate the question of the mitigation of the difficulties arising from the existing multiplicity of languages employed in scientific literature."

Each Society represented on the Council is to nominate a delegate on this committee, the organisation of which was entrusted to the Swiss delegate.

Finally, the Balance Sheet for the general expenses of the Association during the past year was adopted; the sum spent amounted to 1200 mk. (£60), or about 6—7 pf. (approximately $\frac{3}{4}$d.) per member of all the constituent Societies.

The next meeting of the Council will take place in England in the middle of September, 1913. Sir William Ramsay was elected President. The officers of the Association are consequently the delegates of the Chemical Society (London), namely:—Sir William Ramsay, London (President); Prof. Percy F. Frankland, Birmingham (Vice-President); Prof. Arthur W. Crossley, London (General Secretary); who remain in office until the end of the next meeting. W. Ostwald (President until April, 1912); H. Wichelhaus (Vice-President until April, 1912)); P. Jacobson (General Secretary until April, 1912).

All communications should be addressed to Prof. A. W. Crossley, Chemical Society, Burlington House, London, W.

APPENDIX I.

Statutes of the International Association of Chemical Societies

(According to the Resolutions of April 26, 1911, and April 11, 1912).

Art. I. Il est fondé une Association Internationale des Sociétés Chimiques.

Art. II. Le but de l'Association est de former un lien entre les Sociétés chimiques du monde, pour s'occuper des questions ayant un intérêt général et international pour la Chimie.

Art. III. Toutes les Sociétés chimiques peuvent faire partie de l'Association après un vote favorable du Conseil (comp. Art. IV.). Le vote par correspondance est admis dans ce cas.

Art. IV. L'Association est dirigée par un Conseil formé d'un certain nombre de membres. Chaque pays ne peut être représenté dans le Conseil que par une seule Société chimique, que désignera trois représentants.

Art. V. Le Conseil actuel comprend les délégués des Sociétés fondatrices, c'est-à-dire de la Société chimique allemande (Deutsche Chemische Gesellschaft), de la Société chimique anglaise (Chemical Society, London), et de la Société chimique française (Société Chimique de France).

La représentation d'une autre Société dans le Conseil ne pourra être décidée que par celui-ci, et à la majorité des deux tiers des votants.

Art. VI. Le Conseil fixe à chaque réunion le lieu et l'époque de la prochaine session.

VII. Le Conseil nomme au début de chaque session un Président, qui est en même temps Président de l'Association, et qui entrera en fonctions à la fin de la session.

Art. VIII. Le Bureau est constitué par le Président, le Vice-Président, et le Secrétaire Général qui sont les délégués du même pays.

Art. IX. Le Président est chargé de convoquer le Bureau. Celui-ci veille à l'exécution des décisions prises par le Conseil; il fixe l'ordre du jour des Séances du Conseil et entretient des relations entre les diverses Sociétés. Le Président fait approuver les procés-verbeaux des séances. Seul, le procés-verbal de la dernière séance peut être approuvé par correspondance.

Art. X. Les moyens d'action de l'Association consistent:

En nomination de Commissions chargées d'étudier les questions qui leur seront soumises par le Conseil;

En publication dans les journeaux des Sociétés affiliées ou en tout autre mode de publication qu'il conviendra au Conseil de choisir;

En conférences ou Congrès.

Art. XI. Les frais généraux seront supportés par les Sociétés affiliées au prorata du nombre de leurs membres.

Toutes les dépenses autres que les frais généraux ne seront imputables aux diverses Sociétés que sous réserve d'un engagement personnel de ces Sociétés.

Le Secrétaire Général soumettra à chaque session à l'approbation du Conseil le compte-rendu financier de l'exercise écoulé.

Art. XII. Toute modification aux status exigera la présence de la moitié au moins de la totalité des membres du Conseil. Les décisions seront prises à la majorité des deux tiers des membres votants.

Art. XIII. Excepté les cas prévus par les Articles V. et XII., tout vote émis par le Conseil sera valable à la majorité absolue des votants.

A égalité de voix, celle du Président est prépondérante.

APPENDIX II.

Composition of the National Committees on Nomenclature.

I.—*For Inorganic Chemical Nomenclature.*

Deutsche Chemische Gesellschaft:—R. Lorenz (Chairman), Kettenhofweg 136, Frankfurt a M.; K. A. Hofmann, Witzlebenstrasse 26, Charlottenburg; A. Rosenheim, Alsenstrasse 3, Berlin NW.

Chemical Society, London: — Sir William Ramsay (Chairman), 19, Chester Terrace, Regent's Park, London, N.W.; J. C. Cain, 24, Aylestone Avenue, Brondesbury Park, London, N.W.; A. Harden, 2, Marlborough Road, Richmond (Surrey).

Société Chimique de France:—F. Bourion (Reporter), 21, rue Vauquelin, Paris; V. Auger, 25, rue Humboldt, Paris; R. de Forcrand, Montpellier; M. Delépine, 2, rue Alphonse-Daudet, Paris; D. Lebeau, 4, Avenue de l'Observatoire, Paris; E. Rengade, 10 rue Daguerre, Paris; G. Urbain, 69, Grande-Rue, à Bourg-la-Reine (Seine), Paris.

(Messrs A. Béhal, A. Haller, and M. Hanriot, the representatives of the Société Chimique de France on the Council of the International Association, are members of all the committees appointed by the Société Chimique de France).

Schweizerische Chemische Gesellschaft:—A. Werner, Freie Strasse 111, Zurich; V. Kohlschütter, Freie Strasse 3, Bern.

American Chemical Society:—J. L. Howe (Chairman), Wash. and Lee Univ., Lexington, Va.; Philip E. Browning, Kent. Chem. Lab., Yale University, New Haven, Ct.; E. C. Franklin, Hygienic Laboratory, Washington, D.C.; C. H. Herty, Univ. of N C., Chapel Hill, N.C.; H. M. Patterson, Xenia, Ohio; Owen Shinn, Dept. of Chemistry, Univ. of Penna., Phila., Pa.; A. L. Voge, Library of Congress, Washington, D.C.

Russian Chemical Society:—N. Kurnakow, Berg-Institut, St. Petersburg; A Gorboff, Chem. Laborat. of the Nicolai-Ingenieurakademie, St. Petersburg; L. Tschugaeff, Chem. Laborat. of the University, St. Petersburg.

II.—*For Organic Chemical Nomenclature.*

Deutsche Chemische Gesellschaft:—J. Jacobson (Chairman), Sigismundstr. 4, Berlin W. 10; C. Graebe, Westendstr. 28, Frankfurt-a.-M.; R. Pschorr, Humboldstr., 34, Berlin-Grunewald; R. Stelzner, Regensburger Str. 11, Berlin W. 50; J. Thiele, Goethestr., Chem. Institut, Strassburg i. Els.

Chemical Society, London:—W. P. Wynne (Chairman), The University, Sheffield; J. C. Cain, 24, Aylestone Avenue, Brondesbury Park, London, N.W.; A. J. Greenaway, The Orchard, Chertsey, Surrey; F. S. Kipping, University College, Nottingham.

Société Chimique de France:—L. Maquenne (Chairman), 19, rue Sufflot, Paris; G. Bertrand, 26, rue Dutoit, Paris; E. E. Blaise, Faculté des Sciences, Paris; P. Freundler, 6, Place Denfert-Rochereau, Paris; V. Grignard, Nancy; R. Marquis, 10, rue Charles-Divry, Paris; Ch. Moureu, 17, rue Sufflot, Paris; M. Sommelet, 4, Avenue de l'Observatoire, Paris; A. Valeur, 73, Boulevard, Montparnasse, Paris.

Schweizerische Chemische Gesellschaft:—A. Pictet, Rue Bellot 13, Geneva; Fr. Fichter, Neubadstr. 35, Bâle.

American Chemical Society:—M. T. Bogert (Chairman), Columbia University, New York; Ira Remsen, Johns Hopkins Univ., Baltimore, Md.; M. Gomberg, Univ. of Mich., Ann Arbor, Mich.; C. S. Hudson, Bureau of Chemistry, Washington, D.C.; T. B. Johnson, Yale University, New Haven, Ct.; J. F. Norris, Simmons College, Boston, Mass.; W. A. Noyes, Univ. of Illinois, Urbana, Ill.; J. B. Tingle, McMaster Univ., Toronto, Canada.

Russian Chemical Society: — A. Faworsky, Chem. Laborat. of the University, St. Petersburg; N. Zelinsky, Chem. Laborat. of the University, Moscow; W. Ipatiew, Artillerieakademie, St. Petersburg.

OBITUARY.

PROFESSOR H. O. JONES, F.R.S.

By the tragic death on August 15th of Prof. Humphrey Owen Jones, F.R.S., of Clare College, Cambridge, the career of one of the most promising and brilliant of the younger generation of the scientific world has been prematurely cut short. Prof. Jones and his wife, to whom he had been married only a fortnight, were killed while ascending the Aiguille Rouge de Pentéret above the Fresnay Glacier, not far from the spot where Prof. Francis Balfour lost his life in 1882.

Prof. Jones was born in 1878 near Aberystwith, and was educated at the University College of Wales and at Clare College, Cambridge. He took his B.Sc. (Wales) degree in 1897, M.A. (Cambridge) in 1903, and D.Sc. (London) in 1904. In 1900 he was placed in the First Class of Part II. of the Natural Sciences Tripos, with distinction in chemistry. He was elected a Fellow of the Royal Society this year, and was a member of the Royal Commission appointed to inquire into the advisability of using oil fuel in the Navy. Prof. Jones was a Fellow and Lecturer in Physics and Chemistry at Clare College, and had been for some years Demonstrator to Sir James Dewar, the Jacksonian Professor of Natural Experimental Philosophy at Cambridge. Both as a teacher of Chemistry and an indefatigable investigator he had rendered signal service to his University and to the science. His researches lay chiefly in the region of stereo-chemistry, and he had published a treatise on "The Stereo-chemistry of Nitrogen," besides many papers in the *Transactions* of the Chemical Society and the *Proceedings* of the Royal Society on nitrogen and sulphur compounds, and, with Sir James Dewar, on iron and metal carbonyls.

Mrs. Jones was herself a brilliant chemist, and was a research student at Newnham College, Cambridge.

NOTICES OF BOOKS.

Laboratory Test Cards. By John Don, M.A., B.Sc., F.I.C., and Hugh Jamieson, M.A., B.Sc.

These laboratory test cards are arranged in three sets, each set in a separate case containing 18 cards of 4 questions each. The first year set deals with measurement and matter, and the experiments suggested include such measurements of lengths and volumes, densities, pressures, &c., as can be performed with comparatively simple apparatus. The second year is devoted to heat, and the third to elementary inorganic Chemistry. With each set a card of short hints and answers is given. The cards will be very useful for students requiring revision in practical work, and on the whole the tests are well chosen, although they are rather unequal in difficulty, while a good deal of help or supervision by a demonstrator would often be required by the average student before he could perform the experiment outlined on the card. The student, however, should get a good deal of skill in manipulation, and a firm practical basis for his theoretical work if he worked through the cards, especially if he wrote careful and full accounts of his experimental work.

Lehrbuch der Chemischen Technologie und Metallurgie. ("Text-book of Chemical Technology and Metallurgy"). Edited by Dr. Bernhard Neumann. Leipzig: S. Hirzel. 1912.

This text-book has been written for the use of students in technical schools and colleges by a number of experts, each of whom is actually engaged in the industry he describes or has had special opportunities of acquiring a wide knowledge of it. The authors have endeavoured to omit obsolete matter and to burden the text with no unnecessary information, while at the same time keeping quite up to date. It does not seem to be within the bounds of possibility that any student would have time, or indeed find it profitable, to work through the whole book or even a quarter of it, and it might be wise to allow the student who had a good general knowledge of chemistry to specialise in his own particular branch of technology, confining his reading to that alone, rarher than attempting to get an acquaintance with practically all branches. However, as a work of reference for college libraries the book would be of value, and from this point of view its completeness would be a useful feature.

Grundlinien der Anorganischen Chemie. ("The Principles of Inorganic Chemistry"). By W. Ostwald. Third Edition. Leipzig: Wilhelm Engelmann. 1912. (18 M.).

The alterations in the third edition of this treatise are to be found chiefly in the earlier chapters, and are in accordance with what the author, and with him most experienced teachers of chemistry, believe to be the soundest methods of putting the science before the student. The two original introductory chapters have been expanded to five, dealing with General Principles, Substances and Mixtures, the Laws of Conservation, the Phase Rule, and Solutions, followed by the Phenomena of Combustion and Oxygen. The chief elements and their compounds are then taken up in the order of the earlier edition. These additions and the new chapter on radio-activity have increased the size of the book by nearly 100 pages. The text has been revised throughout, and such additions and corrections as have been rendered necessary by the advance of our knowledge of the science have been carefully made.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperaturs are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 26, June 24, 1912.

Control of the New Method of Determining Fluorine.—Armand Gautier and Paul Clausmann.—The authors have performed a number of control experiments for their new method of determining fluorine by dividing into two equal parts the substance in which the fluorine has been determined, adding to water a known weight of this substance, and ascertaining whether the weight of the fluorine added may be found by difference. The results were always quite satisfactory. Small quantities of fluorine can be detected by converting them into barium fluoride, free from silica, adding pure dilute sulphuric acid, and gently heating, the dish being covered by a glass disc previously varnished, and having a circular mark traced on it. The etching effect of the HF generated is easily visible to the naked eye.

Direct Hydrogenation of Diphenylethanes.—Paul Sabatier and M. Murat.—Symmetrical or αβ-diphenylethane is quantitatively hydrogenated at 220° by divided nickel, even if the latter is not active enough to hydrogenate benzene. The product is dibenzyl (fusing at 51°, boiling at 284°). When dibenzyl vapour and an excess of hydrogen are led over very active nickel, kept at 160° to 170°, the former is nearly totally transformed into dicyclohexylethane. Asymmetrical diphenylethylene is similarly transformed into αα-diphenylethane, which, however, is much more difficult to hydrogenate than dibenzyl. By means of four hydrogenations it can be converted into αα-dicyclohexylethane, $\begin{matrix}C_6H_{11}\\C_6H_{11}\end{matrix}{>}CH.CH_3$. This hydrocarbon has not been isolated before.

Stability of Hypoiodites.—V. Auger.—The hypoiodites of the alkalis are known to be very unstable even at 0°, and Lunge and Schoch's statement that calcium hypoiodite is an exception is based upon a mistake. The system $I + MeHCO_3 + H_2O$ does not yield hypoiodite, provided that the bicarbonate contains a sufficient quantity of CO_2 to prevent hydrolysis. If a dilute aqueous solution of alkaline bicarbonate is used in great excess hypoiodite is formed, being derived from the carbonate formed by the hydrolysis of the bicarbonate.

Uranic Anhydride and its Hydrates.—Paul Lebeau.—Uranic anhydride when prepared by the usual methods always retains water and nitrogen. In order to obtain it in the pure state it is necessary to heat it for some time to 500° in a current of oxygen. In contact with water it is directly transformed into uranic acid, $UO_2(OH)_2$. A concentrated solution of uranic nitrate dissolves appreciable amounts of uranic acid, and when it is evaporated at 100° it gives a residue which, after being treated with ether, is crystallised uranic acid. If the evaporation is performed *in vacuo* at the ordinary temperature and the residue is taken up with ether, the product is the hydrate of uranic acid, $UO_2(OH)_2H_2O$. In boiling water the latter is transformed into uranic acid.

Glycidic Ethers of β-Naphthanone, Naphthanoic Aldehyde, and Methylnaphthanylketone.—G. Darzens and H. Leroux.—β-Naphthanone readily condenses with ethyl chloracetate, giving good yields of a glycidic ether. Like all compounds of its class it is easily saponified by soda or potash, giving rise to a liquid which decomposes on distillation in a partial vacuum, the products being CO_2 and β-naphthanoic aldehyde. This new aldehyde is a colourless mobile liquid with a smell like camphor; it is readily oxidised in air, like benzoic aldehyde. The condensation of β-naphthanone with ethyl α-chlorpropionate gives an α-chlormethylated glycidic ether. The acid obtained by the alkaline saponification of this ether is solid and crystalline. It is decomposed by distillation with difficulty, the product being the new ketone, methyl-β-naphthanylketone.

New Azoic Dyes from Diphenylene-amine.—A. Mailhe.—Aniline readily unites with the oxide of diphenylene amine to give yellow crystals, and metatoluidine gives yellowish brown crystals. Other azoic dyes may be formed similarly, and, generally speaking, it may be said the oxide of diphenylene amine, like the oxide of phenylamine, can furnish azoic dyes which differ from the corresponding derivatives of aniline in having a brighter colour and a different absorption spectrum.

Vol. clv., No. 1, July 1, 1912.

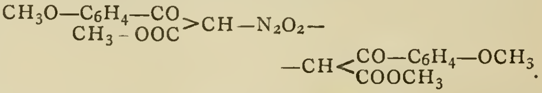
Synthesis of α-Phenyl-αβ-dimethylhydrocinnamic Acid.—Mdme. Ramart-Lucas.—α-Phenyl-αβ-dimethylhydrocinnamic nitrile can be prepared by making the magnesium derivative, obtained by the action of methylmagnesium iodide on α-phenylcinnamic nitrile, react with methyl iodide; or by methylating α-phenyl-β-methylhydrocinnamic nitrile with sodamide and methyl iodide. α-Phenyl-αβ-dimethylhydrocinnamic acid can be obtained by saponifying its nitrile with a mixture of acetic and hydrochloric acids at 180°. The acid melts at 181—182°, and is not identical with the acid, melting at 173°, found among the products of oxidation of the hydrocarbon derived by the dehydration of pseudo-butyldiphenylcarbinol.

Catalytic Hydrogenation of Benzylidene-acetophenone.—J. Frézouls.—When benzylideneacetophenone vapour is led with a current of hydrogen over nickel reduced at 250° and heated to 200° a colourless liquid is obtained, from which by fractional distillation dicyclohexylpropane is formed at 284°. When the nickel has been used for some hours the absorption of hydrogen appreciably diminishes, and the liquid then obtained is a mixture of a saturated and an unsaturated hydrocarbon, the proportion of the latter being increased as the activity of the nickel diminishes. Finally, a product distilling at 291—292° is obtained. This is diphenylpropane.

Syntheses of Nitriles of the Cyclanic Series.—V. Grignard and E. Bellet.—Nitriles of the cyclanic series may be obtained by the action of cyanogen on the organo-magnesium derivatives of the haloid cyclo compounds, $C_6H_{11}MgBr + CN-CN = C_6H_{11}CN + BrMgCN$. All the nitriles the authors have prepared thus have a strong disagreeable odour, like those of the fatty series. They may be reduced by sodium and alcohol to the corresponding amines. The same method applied to the solid hydrochloride of *l*-pinene gives a *d*-camphane-carbonic nitrile, which on saponification gives *l*-camphane-carbonic acid, fusing at 88—89°.

Syntheses by means of the Mixed Organic Metallic Derivatives of Zinc—α-Haloid Ketones.—E. E. Blaise.—The chlorinated ketones cannot be obtained by the action of the chlorides of the α-chloracids on the mixed organo-metallic derivatives of zinc, but they can readily be prepared by using the cycloacetals. α Oxyisobutyric acid gives the best results. This is best chlorinated by starting with the corresponding malonic acids, chlorinating in presence of carbon tetrachloride, and decomposing the chlor-malonic acid formed by heating it. The author has thus prepared ketones of the type $CH_2Cl-CO-R$ and $R-CHCl-CO-R$.

Ortho- and Para-methoxybenzoylglyoxylic Ethers.—A. Wahl and M. Doll.—By the action of nitrous vapours on methyl orthomethoxybenzoylacetate a small quantity of a white crystalline substance fusing at 141—142° may be obtained. It appears to be a dinitroso derivative of the oxime of formula—

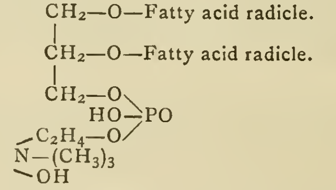


$$\begin{matrix} CH_3O-C_6H_4-CO \\ CH_3-OOC \end{matrix}\!>CH-N_2O_2-\;-CH<\!\begin{matrix} CO-C_6H_4-OCH_3 \\ COOCH_3 \end{matrix}.$$

When methyl paramethoxybenzoylacetate is treated similarly it yields anisoylglyoxylate of methyl. This very readily gives solid crystalline addition products with a great number of reagents. The authors have also prepared three new benxoylglyoxylates—the methyl, propyl, and isobutyl ethers.

MISCELLANEOUS.

Lipochrome and the Lipoids in Bread.—Where milk or milk-powder is used in making bread, especially that made with oatmeal, there may be a tendency to throw out lipochrome, the yellow colouring matter associated with lecithin under the general name lipoids, and hence from their association the latter and kindred substances of the formula—

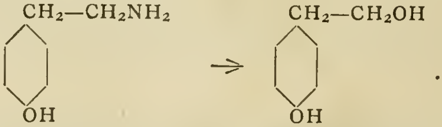


This happens after baking and keeping until stale, and is interesting from any further change the nitrogen and phosphorus groups may undergo.—J. C. Thomlinson, B.Sc.

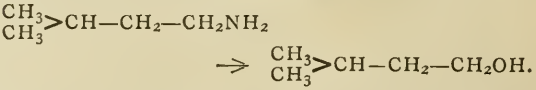
The Conversion of Amines into Alcohols by Yeasts and Moulds (*Revue Scientifique*, July 6th, 1912).—F. Ehrlich and P. Pistschinsika have shown that the various races of yeast are able to attack and utilise the primary amines. The assimilation is effected in the following manner:—

$$R.CH_2NH_2 + H_2O \rightarrow R.CH_2OH + NH_3.$$

In the same way the *p*-oxyphenylethylamine or tyrosamine of Armand Gautier is transformed by the yeast into tyrosol or oxyphenylethyl alcohol,—



Similarly, isoamyl-amine gives isoamyl alcohol,—



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>CH-CH_2-CH_2NH_2 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>CH-CH_2-CH_2OH.$$

The brewery and distillery yeasts employed in great excess do not attack amines so well as the wild and mycodermic yeasts. MM. Erlich and Pistschinsika have shown that moulds of the genus Oidium act on the amines in the same manner as the yeasts.—W. R. F.

THE CHEMICAL NEWS.

Vol. CVI., No. 2753.

VERY HIGH TEMPERATURES.*

By JOHN ALLEN HARKER, D.Sc., F.R.S.

(Concluded from p. 87).

Many experiments have been conducted, notably by Prof. O. W. Richardson, on the corpuscular emission of electricity from carbon at very low pressures, but scarcely anything is recorded for pressures approaching atmospheric. Positive ions and material particles are also discharged by carbon, as well as by hot metals, at suitable temperatures and pressures.

It is to be understood that in all the experiments now to be described the pressure remained atmospheric, and alternating current was employed for heating. Access of air to the interior of the furnace was prevented by windows at each end, perforated as required.

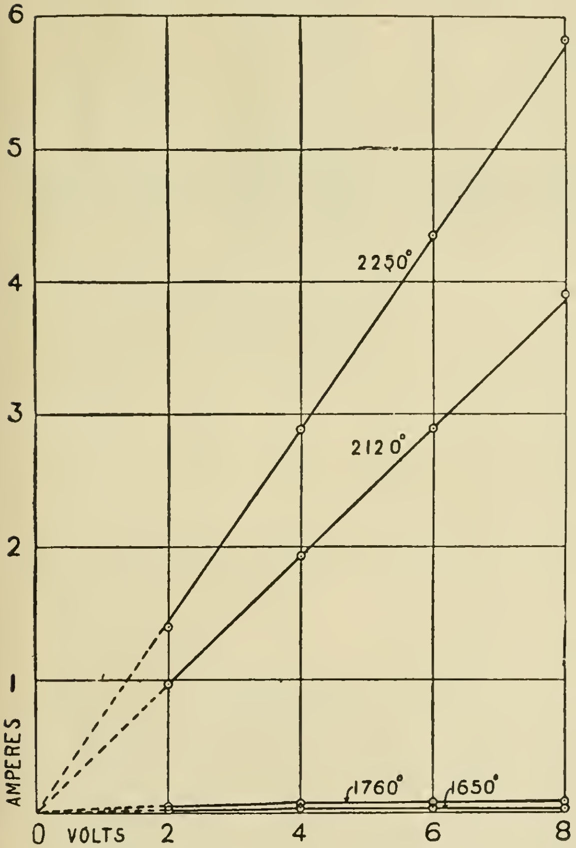


Fig. 4.—Relation between Ionisation Current and Applied Potentials for a 1 cm. Gap between the Electrodes.

In the early experiments we inserted within the carbon furnace tube two insulated carbon electrodes, one of them being hollow, so that a Siemens optical pyrometer could be sighted through it. The two electrodes were joined externally to an ammeter and a battery of cells (see Fig. 2), and we proceeded to determine current-voltage curves at various furnace temperatures. Some of these curves are shown in Fig. 4 for an electrode gap of 1 cm. No appreciable current could be detected below 1400° C. with applied potentials up to 8 volts, but as the temperature rose the current rapidly increased until at 2500° or more currents up to 10 ampères were recorded. At the lower temperatures the currents soon attain what appear to be saturation values. At higher temperatures there is a linear relation between potential and current. As the length of the gap increased the current diminished at a regular rate; but the decrease was small.

Fig. 5 exemplifies the exponential relation between temperature and current for a 1 cm. gap and an applied potential of 2 volts. The dotted straight line was plotted to axes of temperature and logarithm of current.

The magnitude of the currents made it evident that in spite of the high pressure the atmosphere of the furnace was ionised to an unusual degree at high temperatures, and we were led to investigate the effect of temperature alone. The battery was accordingly cut out, and one of the two carbon electrodes was mounted on a sliding carriage so that it could, at will, be moved in or out of the hot part of the furnace, *i.e.*, away from the fixed electrode or back towards it. The movable electrode would thus be temporarily cooler than the fixed electrode which remained steadily in the furnace. The ammeter in the circuit indicated a current which amounted to 2 milliampères at 1400° and nearly 2 ampères at 2500°; the cooler electrode was the positive one. The currents died away when the two electrodes attained the same temperature.

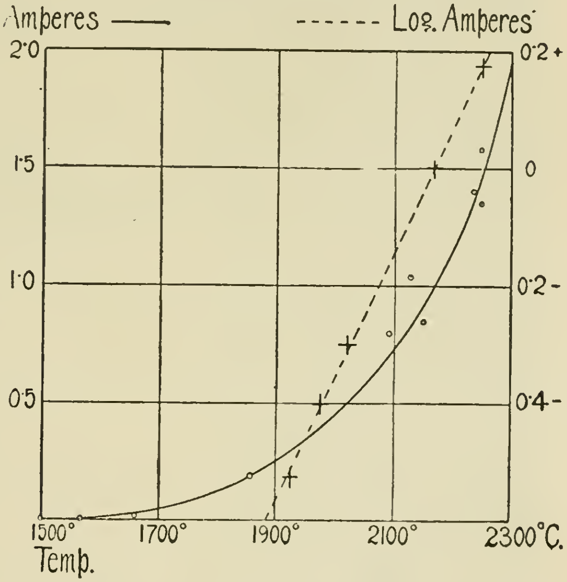


Fig. 5.—The Full Line Curve shows a Relation between Ionisation Current and Temperature for an Applied Potential of 2 Volts on a 1 cm. Gap between the Electrodes. The dotted straight line is plotted from the log. of the current and the temperature.

The production of an alternating current of very low frequency is thus rendered possible by the use of some periodic device. In one form of the experiment (shown) the movable electrode is attached to a crank which, rotated slowly by clockwork, performs the necessary dis-

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[*] A Discourse delivered before the Royal Institution, February 9, 1912.

placement of the electrode within the furnace. The ionisation currents produced are sufficient to make a nest of small glow-lamps light up brilliantly, the illumination waxing and waning as the movable electrode moves in and out.

We have been able to repeat some of these results with furnaces of a non-electric character.

In a further series of experiments, various modifications were introduced. The two electrodes were replaced by two co-axial tubes which were mounted within the furnace. The central smaller tube was of brass, through which a rapid current of water was sent; this formed the "cold" electrode. The surrounding larger tube of carbon constituted the hot electrode, and received its heat from the furnace. The electrodes were insulated as before, and into the annular space between them hydrogen or nitrogen was continually passed. No potential was applied, and the currents we obtained with a steadily rising temperature and a new carbon electrode are shown in Fig. 6. It will be seen that there was first a small "positive" current (which could be produced by positive ions crossing from the hot to the cold electrode), which soon changed into a much larger "negative" current (in the usual direction); the intensity of the latter dropped, and then showed a progressive increase with temperature. On taking down the apparatus we found that the brass tube was coated over most of its length with a thick and coherent deposit of carbon which had evidently crossed over from the hot electrode. Towards one end the deposit was rarer and whitish—presumably silica. We associate the maximum negative current of Fig. 6 with the passage of silicon and other impurities, which are volatilised at about 2000° C. out of the carbon electrode. On a second heating neither positive rays nor a negative maximum was detected, but the ionisation current increased steadily with temperature. The transference of carbon from the hot electrode to the cold may prove to be a complete explanation, not only of the contamination phenomena which gave rise to these experiments, but also of the comparatively large accompanying currents.

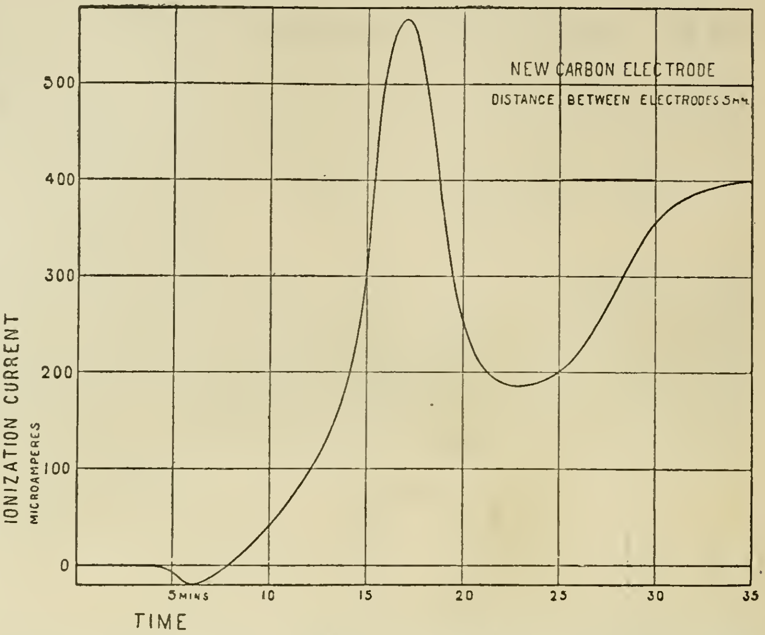


Fig. 6.—Relation between Ionisation Current and Time with a Steadily Rising Temperature. The "cold" electrode was water-cooled; the hot electrode was of new carbon. No potential was applied.

Fig. 7 illustrates the results obtained when steps had been taken to increase the difference of temperature between the hot and cold electrodes. The carbon was new, and the negative maximum again appears. Afterwards the furnace temperature was steadied, and the ionisation current also kept steady in consequence. It will be noticed that we were now dealing with currents amounting to large fractions of an ampère, and the experiments may fairly be regarded as providing a novel means of generating electricity. Their direct bearing on the problems of the electric arc and the carbon filament lamp is obvious, and we are continuing the research with a view to elucidating the many underlying phenomena.

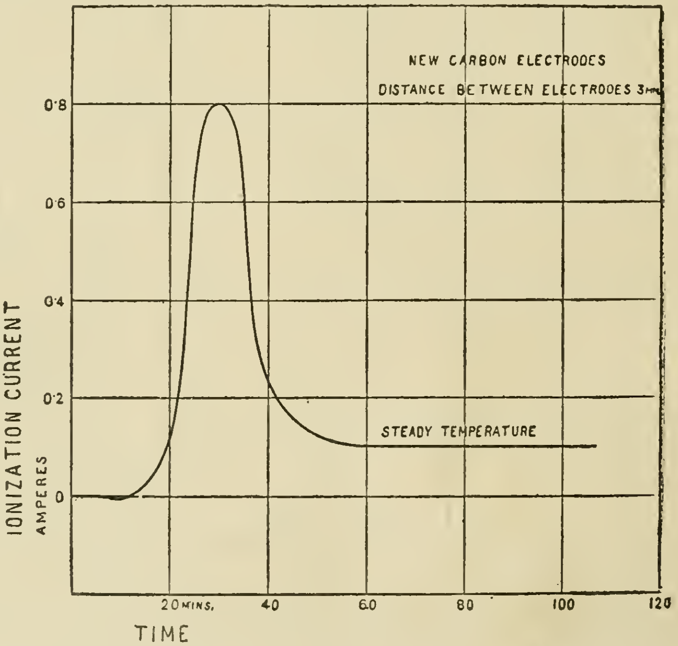
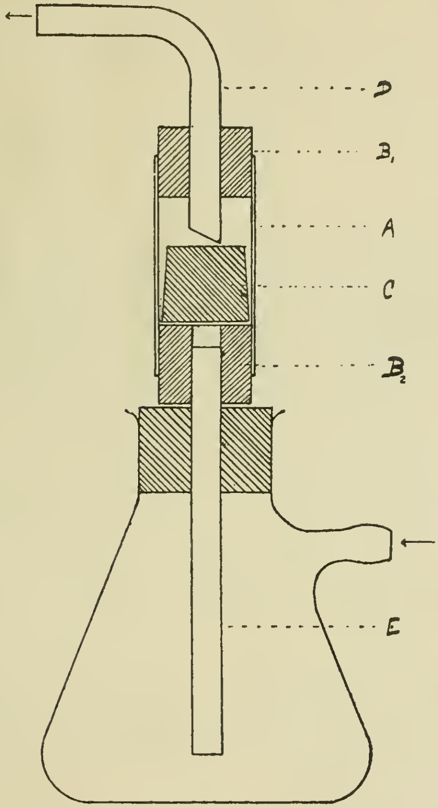


Fig. 7.—Relation between Ionisation Current and Time for Two New Carbon Electrodes, one Hot, the other Water-cooled. No potential was applied. The temperature was rising for the first fifty minutes, and was afterwards steady.

A SIMPLE VALVE FOR FILTER-PUMPS.

By H. B. HUTCHINSON Ph.D

Where the water pressure of a laboratory is fairly constant, the introduction of a safety flask between the pump and the apparatus is sufficient for all practical purposes. In those cases, however, where the pressure is liable to great variation, a safety flask is of little use in preventing water from sucking back into the apparatus, and a reliable valve becomes a necessity. Different forms of safety valves, suitable for laboratory work, are on the market, and not infrequently are expensive and inefficient. Various types of filter-pumps may be had with a special device for the prevention of sucking-back and for the maintenance of the vacuum, but these are far from satisfactory, while the ordinary form of slit-tube valve leaves much to be desired.



The apparatus described below has been in constant use in the Rothamsted Laboratory for some months, and has found general adoption. The valve consists of a stout glass tube (A) ½″—¾″ diameter fitted with two single-bored rubber corks (B$_1$ and B$_2$), between which is placed a solid rubber bung (C), with its wider end downwards, and fitting loosely into the tube.

A glass tube (D) with an oblique lower end is pushed through B$_1$ until it is about 1—2 mm. from the upper surface of the bung (C), and a second tube (E) is brought sufficiently far through B$_2$ to enable it to act as a support without bulging the upper surface of the cork.

The valve thus made may be used alone or may be attached to a small filter flask, as shown in the illustration. The latter way has the advantage of keeping the corks moist, but where the apparatus is intended solely as an air valve, a little dilute glycerol fulfils this function. The tube (D) is then attached to the pump, and E or the side tube of the filter flask is connected with the filtering or vacuum distillation apparatus. On account of its cheapness durability, and simple construction, it is hoped that the valve will be useful for general laboratory work.

The above device can be obtained from Messrs. A. Gallenkamp and Co., Ltd.

Rothamsted Experimental Station,
Harpenden.

THE ESTIMATION OF OXYGEN AND OCCLUDED GASES IN COPPER

AND A

CORRECTION TO THE ELECTROLYTIC ASSAY IN THE COMPLETE ANALYSIS OF COPPER.

By GEORGE L. HEATH.

The only strictly quantitative chemical reaction for the estimation of the oxygen in commercial copper was first proposed by Dr. W. Hampe, of Germany (*Zeit. f. Berg Hütten- and Salinen Wesen*, 1873; Fresenius, *Zeit.*, 1874). He subjected the finely divided metal to a gentle heat for a few minutes in a current of pure carbon dioxide, called the loss (a few mgrms.) moisture, and ignored it; the oxygen was then determined by the loss of weight, or water produced, on heating in a current of hydrogen at red-heat. His method was improved by simplifying the cleaning of the metal and by absorbing the traces of evolved sulphur in an ammoniacal solution of cadmium chloride (Archbutt, *Analyst*, xxv., 253; Hoffmann, *Trans. A.I.M.E.*, xxxiv., 671; Heath, *Journ. Am. Chem. Soc.*, xxvii., 313).

To secure the complete evolution of all gases from the metal, it is necessary to take a precaution not mentioned in any published description of the method. It is the purpose of this paper to correct the serious error in the old method and to report the result of a search for a means of estimating the occluded gases in cast refined copper (described by the author in *Journ. Am. Chem. Soc.*, xxvii., 313).

The loss on heating copper filings, or fine drillings, in hydrogen, until there is no further change in weight, is not entirely due to oxygen from cuprous oxide and sulphurous acid (*Journ. Elect. Chem.*, xvi., 707; *Chem. Abstracts*, 1911, p. 3384), but also includes the gases derived by the metal from the fuel and the refining in the furnace, and in addition, any trace of moisture, mechanically held, and finally is subject to the error to be explained.

I have found that, within the limits of an ordinary analysis, red-hot copper has practically no affinity for carbon dioxide. It has been proved that the gases which exist in cast metal (0·005 per cent or more) can be driven out of the same by replacing every trace of air in the glass tube with perfectly pure dry carbon dioxide, and then heating the copper in contact with the gas for twenty to thirty minutes. The loss in weight is due to evolution of the occluded H, with traces of CO, CO_2, N, and possibly argon.

The loss of weight found by heating subsequently in hydrogen *does not express the true oxygen* of the cuprous oxide present in the cast metal, for the metal retains, after long exposure to a current of hydrogen, nearly twice as much hydrogen in an occluded state, or solid solution, as was present in the absorbed gas of the cast metal; the original occluded hydrogen gas was driven out by the preliminary heating in carbon dioxide. This serious error has hitherto escaped attention. The hydrogen held back after heating in hydrogen should be finally expelled from the reduced copper by a current of pure carbon dioxide, exposing the hot metal to this gas for twenty minutes before cooling and weighing in air.

Carbon Dioxide.—Carbonic acid free from every trace of oxygen and other impurities cannot be produced as easily

	Sample No. 1.		No. 2.			No. 3.	No. 4.
	a.	*b.*	*a.*	*b.*	*c.*	"Low set."	Arsenical.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Occluded Gases and Combined Oxygen in Refined Copper.							
Absorbed gases—by heating in CO_2 ..	0·0064	0·0064	0·0074	0·0070	0·0070	0·0058	0·0077
Apparent loss—heating to constant weight in H gas and cooling in H gas	—	—	0·0523	0·0659	0·0579	—	0·0610
Additional loss by heating next in CO_2 ..	—	—	0·0156	0·0132	0·0139	—	0·0018
Total oxygen—by heating in H gas followed by CO_2 gas	0·0238	0·0254	0·0679	0·0741	0·0718	0·1664	0·0628
Summary of Complete Analysis.							
Oxygen and occluded gas averages . ..	—	0·0310	—	—	0·0784	0·1722	0·0705
Foreign metals in copper	—	0·0081	—	—	0·0066	0·0080	0·0146
Arsenic..	—	—	—	—	—	—	0·0674
Copper and silver	—	99·9560	—	—	99·9210	99·8120	99·8420
Total		99·9951			100·0060	99·9922	99·9945
Proof of Method for Oxygen, &c., by Analysis of Cu *from Ignition Tube.*							
Sulphur evolved and titrated	—	0·0006	—	—	0·0003	—	0·0011
Electrolysis (Cu and Ag)	—	99·9920	—	—	99·9930	—	99·9070
Foreign metals in Cu..	—	0·0081	—	—	0·0066	—	0·0820
Total		100·0007			99·9998		99·9901

from marble, or calcite, as by the method of Bradley and Hale (*Journ. Am. Chem. Soc.*, 1908, xxx., 1090). They use a paste of sodium bicarbonate and water in a 700 cc. flask surmounted with a separator tube. The generator is started half-an-hour before use and the gas allowed to flow through the purifying and drying tubes (to be described), as far as a three-way valve placed just before the ignition bulb tube containing the copper (*Journ. Am. Chem. Soc.*, 1908, xxx., 1090). If the gas is generated from marble, or calcite, it is even more necessary to absorb the trace of oxygen constantly given off from the mineral after the air is all driven out of the apparatus. If a trace remains, it will tint the red-hot metal at the point where it enters the bulb.

The carbon dioxide is purified and dried as follows:—(A) Casamajor generator with elevated pressure bottle, and small bottle on the table, containing the marble on a bed of large lead shot; the upper bottle is filled with hydrochloric acid (1 part to 2 of water). (A_1) Bulb of saturated neutral $KMnO_4$. (B) Glass-stoppered U-tube sealed at the bottom with a solution of silver sulphate. (C) Bowen's (potash) bulb filled with strong sulphuric acid, after which may be placed a short tube of anhydrous calcium chloride. (D) A tube of dry chromous chloride (recommended by J. O. Handy). (E) Tube of stick-phosphorus. (F) Two tubes of phosphorus pentoxide. (G) Short tube of dry calcium chloride. The expensive chromous chloride can be regenerated by passing a current of pure hydrogen through the tube at a gentle heat as long as any hydrochloric acid or moisture is given off.

By pulling out the second stopper in the tube B, the gas may be allowed to discharge into the air until the air is swept out of the generator, or it may be discharged under pressure from under a seal of 30 mm. of mercury, if generated from sodium bicarbonate by the method of Bradley and Hale (*Journ. Am. Chem. Soc.*, 1908, xxx., 1090). The gas should always be passed through the bulbs as far as a three-way valve placed in front of the ignition tube until a test on hot copper shows that the gas is pure, giving no discoloration whatever at the point nearest the generator.

Hydrogen Gas.—The part of the generator holding the pure granulated zinc should be rather small, in order that the air may more easily be swept out. The action should be started and the gas passed over the copper for fifteen minutes before lighting the burners. The purifying train is as follows:—A small washing bottle of 10 per cent KOH, saturated with KMnO. Bowen's bulb, conc. sulphuric acid, (C) palladium asbestos tube, heated by alcohol lamp, after air is expelled. (D) An Allihn 250 cc. washing bottle containing 100 cc. of water, 100 grms. of KOH (alcohol free), and 5 to 10 grms. of pyrogallic acid. (E) Two tubes of dry calcium chloride and the three-way valve in succession (C and D, alternative, tube of stick P, and two tubes of phosphorus pentoxide). (Handy proposes the following alternative:—(1) KOH; (2) conc. H_2SO_4; (3) $CaCl_2$; (4) heated palladium asbestos tube; (5) dry P_2O_5 opened up with glass-wool).

Preparation of the Copper Sample for Ignition.—If a lot of copper is very porous, or of unknown origin, it may be advisable to dry it at 100° C. in an atmosphere of pure carbon dioxide or nitrogen (instead of heating in ignition tube to a heat which would expel some of the gases—an operation recommended by Hampe originally). If the speed and size of drill are regulated to produce fine drillings without any heating and oxidation, or contamination from grease, it will not be necessary to clean the drillings with ether. The adoption of the Copper Specifications of the American Society for Testing Materials will secure a fair sample of any casting, although equally good results are assured by boring half way through from both top and bottom, and also from the sides. With very pure material an inch in depth is sufficient, the oxide having been previously removed by starting the hole through the surface skin with a larger drill.

As a prominent chemist has just noted:—"It is impossible to remove all the soapy lubricant, or organic matter, from wires by washing with alcohol or ether directly." In such cases it is suggested that the wire be cut in 3-inch pieces and digested for a few minutes with alcohol KOH, 1 per cent strength, as warm as possible without producing oxidation, then wash in water, alcohol, and ether successively. If a slight abrasion of the "skin" is not objectionable, the wire could be scoured, wet, with sharp silica (ground to pass a 40-mesh sieve), then washed with alcohol, &c. Extraction with petroleum ether (88° to 85° Bé.) in a Soxhlet tube will sometimes remove the offending material.

The ignition is performed in a hard-glass tube about 30 cm. long and 6 mm. internal diameter, which has one long bulb, or two round ones, at the centre. It is cleaned, ignited, weighed, and the 50 grm. sample fed into the tube very quickly in the following manner:—Slide a tight fitting rod into one end as far as the nearest bulb, and attach to the other end, by short tubing, a short-stemmed funnel, whose diameter equals that of the tube. By using a long platinum wire, and tapping the tube, the drilling can be packed in the bulbs, after which the tube is wiped with a dry warm cloth and allowed to stand ten minutes on the balance before weighing. When connected with the apparatus, the ignition tube rests on a lamp ring of 10 cm. diameter, and is protected from overheating by wrapping it with a fresh piece of thin asbestos paper, held in place by a short piece of stiff bent platinum wire.

Ignition of Copper.

For Absorbed Gases.—A short drying tube and jet tube can be attached to the rear end of the ignition tube through a glass three-way valve and the carbon dioxide passed through the tube system for thirty minutes to sweep all the air out of generator and tubes. The fan burner, or triple Bunsen burner, is then lighted, the copper kept at a full red-heat for twenty minutes, the tube cooled with an air blast, and the CO_2 replaced by air, which will require ten minutes. The tube is then wiped clean and allowed to stand on the scales ten minutes before weighing. The loss is due to gases from the cast metal.

For Total Oxygen and Sulphur.—Pass in hydrogen for fifteen minutes, then keep at a red-heat (not high enough to distil the metal into the glass) for one hour if the sample is filings, or two hours for coarse drillings. The necessary time should be ascertained in each laboratory by repeating an ignition on drillings of their standard fineness until the weight is constant. The three-way valve at the rear of the ignition tube should be turned during this heat so that the gases pass through a small U-tube, or bottle, containing 10 cc. of a solution of ammoniacal cadmium chloride (20 grms. per litre). Start the current of CO_2 through its own set of purifying tubes twenty to thirty minutes before the copper is all reduced, so that every trace of air shall be swept out of the tubes as far as the three-way valve in front of the copper. When the hydrogen has been passed long enough to complete the reduction of all oxides in the metal, turn off the hydrogen and pass in pure CO_2 for at least twenty minutes. Then cool the tube with an air blast until the copper is but slightly warm, replace the CO_2 with air, and weigh with the same precautions as before.

Sulphur.—About 70 cc. of water are placed in a No. 1 beaker, the cadmium solution and sulphide washed into it with the aid of dilute hydrochloric acid (1 : 1), and the sulphur is titrated at once with standard iodine (2 grms. of I per litre). 1 cc. of this solution = 0·0025 grm. of S.

(*Note.*—We use a specially prepared starch indicator which gives a very clear blue, with none of that disagreeable muddy red given by ordinary starch (*Am. Chem. Abstracts*, iv., 2617). The starch is allowed to stand over night, covered with cold water, containing 0·001 per cent of hydrochloric acid. The next morning the acid is carefully washed out and the starch dried for two hours in an air oven at 100° C. Five grms. of this prepared material is boiled with 500 cc. of water, filtered, or decanted from the sludge, and 15 drops of oil of cassia added before bottling, to render the solution permanent; 3 cc. of starch indicator are used in each test; a deduction is made for the iodine required to produce the end-point, as determined by a blank titration).

Experimental proof of the completeness of the reduction of the copper by ignition in hydrogen and carbonic acid may be obtained by a careful electrolytic assay of the reduced drillings. The sum of the per cent added to that of the other impurities as found by complete analysis will total 100 per cent without any oxygen, if the work and sampling are correct. In order to attain such a result it will be found necessary to take the sample for oxygen determination from the very same bottle of drillings employed for the complete analysis, that is for the electrolytic assay of the original cast copper. In sampling a casting the per cent of oxygen varies directly with the per cent of copper and silver, and is variable enough in different samples drilled in the same casting to prevent the results adding up exactly 100 per cent on complete analysis unless one sample is used for all tests.

There is slightly less occluded gas in low-set, or oxidised, cast copper than in copper which is well refined to standard grade. Highly refined metal which shows "true" overpoling (due not to sulphur, but to poling too high in the furnace) would certainly show a large increase in occluded gases, near the upper surface of the castings of chilled metal.

Since the occluded gases in cast copper are so small in weight, a sample of 100 grms. in a bulb of the style recommended by Dr. H. O. Hofmann would give a better result than the quantity I have specified.

Correction to Electrolytic Assay in Complete Analysis of Copper.

The exact electrolytic assay of refined copper as described elsewhere by the author gives results sufficiently accurate for valuation of the metal (*Journ. Ind. and Eng. Chem.*, iii., Feb., 1911), but the deposition on the cathode is not absolutely complete when a test of 1 cc. of electrolyte with hydrogen sulphide remains colourless.

As noted by W. C. Ferguson in a recent paper, we have also observed that about 0·005 per cent to 0·008 per cent remains in solution.

When an accurate complete analysis of the metal is desired, the author is accustomed to treat the electrolytes from the 5- or 10-grm. battery assays with hydrogen sulphide gas. The sulphides are collected on a filter, roasted directly in a porcelain crucible, treated with a few drops of nitric and sulphuric acids, diluted with a little water, and the copper deposited on a small weighed platinum strip and added to the principal cathode copper. Electrolytic deposits on platinum, as obtained by strictly following the method just quoted, have been found to be free from any appreciable quantity of absorbed hydrogen.

The methods already described might be used for gases in steel (*Ibid.*, iii., 372, June, 1911), by substituting nitrogen for carbon dioxide. Only of late has the effect of oxygen in steel received the attention it deserves.—*Journal of Industrial and Engineering Chemistry*, iv., No. 6.

QUALITATIVE DETECTION OF ALKALI BICARBONATES.

In preparing sodium carbonate from sodium bicarbonate for the standardisation of acids, it is desirable to have a means of ascertaining whether the bicarbonate is completely decomposed or not. The following test for bicarbonates in the presence of large quantities of normal carbonates was described by R. T. Haslam in the *Journal of the American Chemical Society*.

The test depends, first, on the fact that alkali bicarbonates, on the addition of calcium chloride, precipitate $CaCO_3$ with the liberation of carbon dioxide, and, second, that $CaCO_3$ dissolves somewhat in water containing carbon dioxide with the formation of calcium acid carbonate. If the calcium acid carbonate thus formed is neutralised with ammonium hydroxide, the $CaCO_3$ is of course re-precipitated.

Dissolve the substance to be tested in water that has been previously boiled to expel the carbon dioxide, and add $CaCl_2$ in excess. Allow this to stand four or five minutes, and filter off the $CaCO_3$. Then add a few drops of NH_4OH, and if the substance contained a bicarbonate, a precipitate of $CaCO_3$ is again obtained. With a large amount of bicarbonate the precipitation will take place in about one-half minute, while with a very small amount the time required may be eight to ten minutes. However, with no bicarbonate a perfect blank is obtained even after long standing.

This test will detect 0·1 per cent of $NaHCO_3$ in a normal sodium carbonate. The presence of ammonium salts vitiates the results on account of the solubility of $CaCO_3$ in such solutions.—*Chemical Engineer*, xv., No. 6.

FURTHER STUDY OF THE ATOMIC WEIGHT OF MERCURY, THROUGH THE ANALYSIS OF MERCURIC BROMIDE.

By C. W. EASLEY and B. F. BRANN.

Two previous contributions (*Journ. Am. Chem. Soc.*, 1909, xxxi., 1207; and 1910, xxxii., 1117) relative to the atomic weight of mercury described work which resulted, within narrow limits, in the same value of this constant. The methods employed, entirely different in character, dealt with the same material, mercuric chloride. While such a procedure probably indicated that the error of method was sufficiently small to be negligible, doubt pertaining to the nature of the material analysed was not removed. It remained, then, to prepare material of a different character, and it was decided to attempt a redetermination of the atomic weight from a study of the bromide since there seemed to be no reason why this compound should not be prepared in a pure state. It would be ideal to attack the question through the use of the oxide, but, from preliminary experiments, the preparation of this compound seems exceedingly doubtful.

The problem with the bromide presented many points of similarity to that of the chloride. Owing to the solubility of silver bromide in mercury salts, instead of treating a solution of mercuric bromide directly with silver nitrate, the mercury was first removed. This was accomplished in two ways, each leading to practically the same results:—First, by means of hydrazine hydrate in weak alkaline solution, and, second, with hydrogen peroxide under similar conditions. Like results from the use of the two reducing agents would seem to preclude the possibility of any considerable error arising from the use of either. The mean value of the atomic weight found does not differ essentially from the results reported in previous communications.

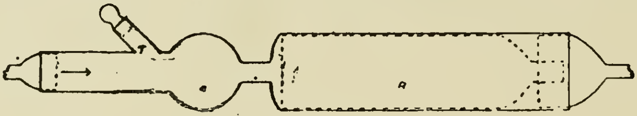


Fig. 1

Pure Mercuric Bromide.

It is well known that bromine may be readily made very pure by the methods of Stas (*Œuvres Complètes*, i., 587), and the modifications proposed by others (Richards, *Proc. Am. Acad.*, xxv., 199; Scott, *Journ. Chem. Soc.*, lxxvii., 649; Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1322), and, in a previous paper (Easley, *Journ. Am. Chem Soc.*, 1909, xxxi., 1216), several methods for the preparation of pure mercury were described. Thus, since the elements unite easily, it is possible to prepare the bromide of mercury without the intermediate use of water. This is probably important, as it was shown in the preparation of the chloride that that salt could not have had contact with water without the production of basic material during the subsequent process of sublimation. There was no reason to expect a different result with the bromide, so that recrystallisation of the salt was not resorted to, especially when the alternative and preferable procedure of bringing pure bromine and pure mercury together in an indifferent medium of nitrogen at the temperature of sublimation was practicable. The bromide thus prepared is probably free from the bromides of other metals. for the process was carried out at a temperature in the neighbourhood of 300°, conditions under which other compounds most likely to be present would not be perceptibly volatile.

In detail, the process consisted in passing a stream of nitrogen through liquid bromine, thus sweeping the vapour into a chamber containing mercury maintained at a temperature of 300°. The apparatus is shown in Fig. 1. The nitrogen was sent through a purifying and drying train constructed of glass alone, and the exit tubes were so arranged by means of branches and glass stopcocks that the gas could either first bubble through the bromine in a wash-bottle, or pass directly into the reaction chamber C, as shown in Fig. 1. Solutions of potassium hydroxide, some containing lead oxide in solution, were used for purifying the nitrogen, while the gas was dried by means of sulphuric acid in towers filled with glass beads. Phosphorus pentoxide, re-sublimed in a stream of dry air, by contact served to dry the liquid bromine. After pure mercury had been introduced through the tubulature, T, by means of a funnel reaching to the bottom of the chamber, C, the air in the apparatus was displaced by nitrogen, and this in turn by a mixture of nitrogen and bromine. The bulb was then heated to a temperature around 300°. The fact that the metal was covered with transparent colourless fused bromide showed that a sufficient excess of bromine was present. When the mercury was entirely converted and carried into the receiver, R, in the adjacent compartment, the latter was raised to a temperature of 235°, a point where the salt began to show a considerable vapour pressure. During the latter operation, nitrogen, without bromine, was passing through the apparatus, completely sweeping out the excess of bromine, and liberating, probably, any that might possibly have adhered to the salt at the lower temperature. Air-ovens, entirely separate from each other, were used for heating the compartments, and these were constructed of asbestos, with glass windows. The temperature was regulated by means of burners below the ovens. After cooling in the same atmosphere, dry air was admitted, and the salt was transferred by holding the receiving funnel, R, over the mouth of the weighing bottle and pushing the crystals into the latter with a well-rounded glass rod. At times the end of the receiver nearest the chamber, C, was heated to such an extent by conduction that a portion of the crystals fused and adhered somewhat to the glass. No attempt was made to dislodge such material, so that the collected salt must have been entirely free from silica and other matter originating in the glass. The transfer of the salt to the weighing bottle was made in air, for it was shown that exposure to the air of the laboratory did not sensibly affect its weight. In proof, a light tube, sufficiently small to rest on the balance pan, was sealed at one end to another tube of smaller bore through which either dry air or bromine vapour could be admitted. The other end was fitted with a hollow stopper which could be closed by means of a stopcock. A quantity of mercury was converted into the bromide within this tube, and as a stream of dry air was passing, it was effectually sealed, at one end by means of the flame and at the other by turning the stopcock. When counterpoised by a similar tube on the balance pan, the stopper was removed, and for the first time the salt was exposed to the air of the laboratory.

The salt collected in the receiver in beautiful needle-like masses. The fact that bromine was present in excess during the preparation, and that the bromine, mercury, nitrogen, and air were free from water, would preclude the formation of either calomel or basic salts. The complete solubility of the salt prepared by this method, in fact, shows no impurities of this character.

Preparation of Bromine.

Three samples of bromine were prepared, two being made by well-tried methods in which a solution of calcium bromide was depended upon to react with chlorine and fractional distillation, after transformation to hydrobromic acid, to remove the iodine. The bulk of the mercuric bromide was made with such bromine, but it was decided to use more exhaustive means in the purification of a third sample so that its value could not be doubted. The methods adopted were so laborious that only a small amount of this sample was obtained. The analyses showed that the mean atomic weight does not differ from the mean of any series in which a particular sample of bromine was used by more than one part in ten thousand.

Sample 1.—Commercial bromine was dissolved in a solution of calcium bromide which was prepared from marble and hydrobromic acid. The marble had not been exposed to the fumes of the laboratory, while the acid had been prepared from the original bromine by reduction. The bromine was distilled by placing the solution in a glass-stoppered flask whose side arm was sealed to the condensing system. All save the first fraction of this bromine was covered with sufficient water to form the constant boiling mixture of hydrobromic acid corresponding to the amount of bromine used. Hydrogen sulphide, from ferrous sulphide and dilute sulphuric acid, was next passed until nearly the whole of the bromine was converted into hydrobromic acid. Hydrochloric acid was removed from the gas by a train of wash bottles, the first of the series being filled with alkaline sulphides, and the final ones with pure water. When the sulphur had been separated by filtration through glass-wool, the acid was distilled, the free bromine and iodine passing over in the first fraction.

At this stage the purity of the bromine was investigated. Accordingly, a weighed amount of silver was converted into silver bromide by using some of the hydrobromic acid prepared above after it had been treated with a slight excess of ammonia. The silver was prepared following the ammonium formate method of Stas, with subsequent fusion on lime. Using all precautions, three determinations were made in which 18·32765 grms. of silver formed 31·89761 grms. of silver bromide. This results in a ratio of 57·457, whereas the theoretical one is 57·445. An excess of chlorine in the bromine is thus indicated. During the next process, however, in converting the acid to bromine, any free chlorine would be in contact with a solution of potassium and manganese bromides, and must have been effectually removed.

The oxidation of the acid to bromine was accomplished with potassium permanganate. Kahlbaum's highest grade was found to contain such small amounts of chlorine that several re-crystallisations removed all save the merest traces. In fact, tests on the mother-liquor of the last crystallisation showed a maximum of one part of chlorine in forty thousand parts of salt. The hydrobromic acid dropped from a separatory funnel upon the permanganate in a flask whose connections with the condensing system and funnel were all of glass. The contents of the flask were kept at a temperature such as would liberate the bromine. A first small fraction was discarded. The remainder was freed as much as possible from water by means of a separatory funnel, after which it was preserved in a bottle with phosphorus pentoxide, the preparation of which has been described before.

Sample 2.—This sample was prepared in the same manner as Sample 1 save for the fact that sulphur dioxide instead of hydrogen sulphide was used as the reducing agent. The gas was furnished from a cylinder containing the liquid, and was allowed to run through several wash-bottles containing sodium acid sulphite and then through pure water. This method obviates the contamination of the hydrobromic acid with precipitated sulphur, a source of considerable difficulty combined with loss of material whenever the hydrogen sulphide method was used.

Sample 3.—A quantity of Kahlbaum's best bromine was allowed to remain in contact with a solution of the potassium and manganese bromides which were saved in the process of oxidising the hydrobromic acid of Samples 1 and 2. The mixture was frequently shaken, and finally distilled. Reduction to hydrobromic acid was carried out as in Sample 2, but only the middle fraction of the distillate was retained. To a very dilute solution of this acid, pure silver nitrate was added, and the precipitate was washed many times, first with cold and then with hot water. Mercuric nitrate, prepared from mercury and halogen-free nitric acid, was added and allowed to remain in contact with the precipitate for forty-eight hours. A strong solvent action is thus exerted upon the silver halides (Morse, *Zeit. Phys. Chem.*, xxxviii., 705), and, as the solution of the nitrate was about normal, amounts of chlorine and iodine which analysis revealed in Sample 1 would have been removed when the residue was washed free from the mercuric nitrate. The silver bromide was next suspended in water, and converted to hydrobromic acid by well-washed hydrogen sulphide. A reserve supply of the silver bromide used up the excess of hydrogen sulphide. When the sulphide had been separated from the acid, the latter was distilled and oxidised to bromine precisely as in the case of the other samples.

Preparation of Mercury.

Sample 1.—This consisted of a small amount of mercury remaining from previous work (*Journ. Am. Chem. Chem. Soc.*, 1909, xxxi., 1217; see Sample 3). Its preparation has been described.

Sample 2.—The starting-point was the same mercuric chloride whose analysis, after sublimation, has already been reported (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1125). It was exceedingly pure. After sublimation in a stream of pure dry air, the salt was dissolved in water and treated directly with an ammoniacal solution of hydrogen peroxide. The resultant globule was given the same treatment as the one to be described under Sample 3.

Sample 3.—The same material used in Sample 2 served as the basis of this sample. The salt was re-sublimed, dissolved in a large amount of water, and treated with sulphur dioxide, thoroughly washed. The precipitated calomel was washed many times with pure water, and finally subjected to the action of ammonia. After washing out the excess of ammonia, a necessary process to prevent the formation of large amounts of soluble compounds (P. de Saint-Gilles, *Ann. der Chem.*, lxxxiv., 266) from which mercury could not be separated by the method used, sulphur dioxide was again added. During the latter process, the mass was maintained at a temperature of approximately 100°. Metallic mercury separated in globular form. The globule was washed with water, and then shaken with a dilute ammoniacal solution of hydrogen peroxide to remove all suspicion of reducible surface impurities. The metal was dried by quickly heating to the boiling-point. Traces of foreign material, of the nature of finely-divided silica, were separated by filtering the metal through a small funnel, the drawn-out stem of which was filled with fine glass threads. In spite of these precautions, after the metal had been converted to the bromide in the apparatus shown in Fig. 1 and the bromide had been distilled, there sometimes remained a slight residue. As no less than 15 grms. of mercury was ever used, and as the residue seemed unweighable, no error could have crept into the results from this source. No matter how long the residue was heated, no volatilisation was apparent. In several cases the residue was certainly silica. At another time, black material remained. This may have been a basic salt of mercury with an inappreciable vapour pressure at the temperature used. How it might have formed is not clear.

Reagents.

Hydrazine Hydrate.—Hydrazine sulphate was treated with an excess of sodium hydroxide, and the liberated hydrate was separated by distillation in a copper retort. The product was subjected to a second distillation in a system made entirely of glass. A product almost entirely free from chlorine resulted. When treated with silver nitrate, 0·00003 grm. of silver chloride was found in every grm. of the hydrate.

Hydrogen Peroxide.—Merck's 30 per cent solution of hydrogen peroxide was re-distilled and diluted to an approximately 3 per cent solution. In every 100 cc. used, an amount of chlorine corresponding to 0·00007 grm. of silver chloride was found and duly corrected for.

Sodium Hydroxide.—Very pure sodium was converted into the hydroxide by standing on platinum gauze over a platinum dish in a water-laden atmosphere free from carbon dioxide. The required quantity of hydroxide for one determination was prepared at a time, and a portion of this material was always examined for chlorine. When treated in the nephelometer with silver nitrate (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235), the different samples showed varying amounts of silver chloride, but in no case was an amount present exceeding 0·0001 grm. per 5 grms. of sodium hydroxide.

Other Reagents.—The water, nitric acid, and ammonia were all re-distilled, the first twice from permanganate solution. All were chlorine-free. Silver nitrate was made from the metal and acid, and the solution was evaporated to dryness. The metallic silver was prepared by the action of ammonium formate on silver nitrate.

The Method of Analysis.

The plan pursued consisted in treating a weighed amount of mercuric bromide in solution with sodium hydroxide, adding such an amount of a reducing agent as would precipitate the mercury, leaving the bromine in the form of bromide ions. The mercury being filtered off, and the solution being rendered alkaline, silver nitrate was used to form silver bromide, which was weighed. The value of the ratio $HgBr_2 : 2AgBr$ is thus determined.

In order to keep the amount of solution at a minimum, the bromide was not entirely dissolved in water when the calculated amount plus 0·25 or 0·30 grm., of sodium hydroxide was added. The object was not to unduly dilute the reducing agents, in which case more mercury might remain in solution, and also to avoid the filtration of large quantities of solution. This practice, on the other hand, lengthened the time required for the completion of the reaction, since the undissolved crystals of bromide could give rise to an amount of oxide only proportional to their surface. With hydrazine hydrate, the reduction proceeded with relative rapidity at room temperature, but in the case of hydrogen peroxide a temperature of 70° was required to have the reaction progress at a moderate rate. The oxide sucessively formed remained as a crust on the crystals until reacted upon by the reducing agent. Hydrazine hydrate was employed in some of the preliminary work on the analysis of mercuric chloride, but no actual analyses were made. It has proven a most effective reagent in the case of the bromide, the mercury forming with perhaps less unglobulised material than in the case of hydrogen peroxide. This, perhaps, is explained by the fact that the reaction is completed more quickly, and therefore less silica is formed by the action of the slightly alkaline solution. Again, the temperature was lower. The rate of the reaction was so regulated that the nitrogen was expelled quietly, carrying no spray beyond the catch system. A very small amount of mercury must have remained in solution, as invariably silver bromide was detected after an excess of silver nitrate had been added. The determination of this dissolved material will be described later. The amount of silver bromide in this condition never exceeded 0·001 grm. per litre of solution. When the reduction was complete, the contents of the flask were brought to the boiling-point in order to decompose the greater portion of the peroxide. This was done even in the experiments where hydrazine hydrate was used, for the excess of the latter was destroyed by the addition of hydrogen peroxide.

The flask, with the system for introducing the reagents and the tube for the escape of the liberated gases, is shown in Fig. 2. It is of the Erlenmeyer form, holds 500 cc., and is made of Bohemian glass. The tube passing through the ground-glass stopper is branched above. Through one branch the reagents are added, and the amount added at any time is gauged by means of the stopcock; through the other, the liberated gases pass. In the latter arm the tubing is bent so as to form a trap, T, beyond which it is widened and filled with beads kept wet with pure water. As the trap is always full of water, a most effective means of preventing loss through spray is at hand. Any material collecting on the inner walls of the branches found its way into the flask during the rinsing process at the completion of the reduction. It was found very difficult in the work on the chloride to entirely separate the mercury from the solution. The extremely fine particles refused to be globulised, and some of these particles either passed through the filter-paper of the most compact texture or crept over its side. The present work was not unlike the previous case in this respect. Better results were obtained by decreasing the rate of filtration by placing a globule of mercury in the apex of the filter. The difficulty was not entirely overcome, however, so that more than one filtration was often necessary. In spite of the character of the paper used, some shreds were loosened and passed into the filtrate, owing perhaps to the hot slightly alkaline solution. The amount was very small, but it was found later in the fused silver bromide as a small patch of surface scum. It was impossible to determine its amount accurately, but there is little doubt but that the correction would be exceedingly small. All danger of losing any of the solution by leakage from the lip of the flask during filtration was avoided by the use of a protecting cup around the neck of the flask as shown in the figure at C. The cup was thoroughly rinsed after all traces of solution had been removed from the flask itself. It is safe to say that there was no appreciable loss of material due to the process of filtration. Many rinsings were made, no danger of adding too much water being feared, since there is less danger of including material in the precipitated silver bromide if the solution is dilute. The solution was filtered directly into a flask of Jena glass,

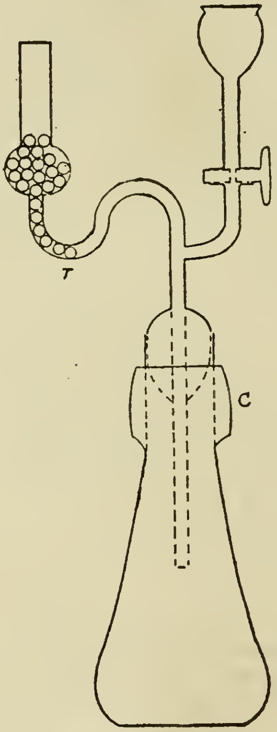


Fig 2.

and was acidified with an amount of nitric acid slightly in excess of that found necessary from the known excess of sodium hydroxide used at the outset. A slight excess over the theoretical quantity of silver nitrate was added to precipitate the bromine. Both the bromide and silver solutions were approximately tenth-normal. After standing over night in the glass-stoppered flask, the solution could be easily separated from the precipitate by the use of the Neubauer crucible. Only a small portion of the silver bromide found its way into the crucible during the filtering process, the greater portion remaining in the flask so that the washing might be more effective. The first stage of the latter process consisted in making eight or ten additions of water containing a slight amount of silver nitrate and nitric acid, decanting each in turn. About the same number of washings were then made with water containing nitric acid alone. The latter washings contained dissolved silver bromide. The amount was determined in the nephelometer, and found to average 0·0002 grm. per litre. When the precipitate had been completely transferred the crucible with its contents was dried in an air-oven, protected from outside fumes, at a temperature ranging from 150—160°, after which it was weighed. The greater portion of the precipitate being transferred to a weighed porcelain crucible and fused, the expelled water was determined by another weighing. The fused mass was transparent, save for a small patch due to filter shreds referred to above, and greenish yellow in colour. No difference appeared in the results whether a fused sample contained the above mentioned impurity or not, so that the error from this source is too small to be feared. Since tests on the contaminated portions for silver were negative, it is doubtful if any chemical change had resulted. More likely, the shreds merely entangled and kept separate small portions of silver bromide.

A correction, of small though positive value, became necessary through the observation that bromine was present in the filtrate, after the separation of the silver bromide, even after an excess of silver nitrate was added. This never amounted to more than 0·001 grm. of silver bromide per litre, generally considerably less, but a measurable quantity was invariably present. In most cases, the atomic weight would hardly be changed one unit in the second decimal place by this factor, but it was determined in every case to guard against larger error. A similar result was found in the analysis of mercuric chloride. At that time it was assumed to be due to the presence of mercury salts in solution. While no other supposition is put forward here, it is difficult to understand how such small quantities of mercury as are present (none has been shown in tests) could have such a strong solvent action. It is not impossible that some of the finely-divided mercury escaped notice, and was dissolved by the very dilute nitric acid added to neutralise the solution. That bromine was present, however, was proven by carrying out a blank test at the same time the solution was examined. The two sets, one with the solution the other with pure water, were treated alike in every detail, and although halogens were always found in the blank due to the reagents, yet larger amounts were always found in the solution. The method of determination consisted in the precipitation of the heavy metals in slightly ammoniacal solution by means of hydrogen sulphide. A small amount of alum in the solution assisted in securing a clear filtrate. Boiling served to drive off most of the hydrogen sulphide, and the remainder was oxidised to sulphuric acid by means of hydrogen peroxide. On acidifying the solutions, tests for the presence of halogens were made with the aid of the nephelometer.

As an illustration of the relative value of the corrections necessary in finding the amount of silver bromide which results from a given weight of mercuric bromide, we may take experiment No. 9. In this case, 11·28487 grms. of mercuric bromide gave rise to 11·75970 grms. of silver bromide, the latter weight being the sum of various factors as follows:—

Weight of silver bromide dried at 150—160°		11·76077
Weight of silver bromide in filtrate (1225 cc.)		0·00025
Weight of silver bromide in wash-water (1020 cc.)		0·00020
		11·76122
Water in silver bromide dried at 150—160° (loss on fusion)	0·00134	
Silver chloride, due to chlorine in hydrazine hydrate	0·00002	
Silver chloride, due to chlorine in sodium hydroxide..	0·00016	
		0·00152
Corrected weight of silver bromide		11·75970

The weighings were made by the method of substitution by the use of a delicate Sartorius balance, and the weights found in air have been converted to weights in a vacuum by the use of the following corrections:—

+0·000067 grm. per grm. of mercuric bromide.
+0·000041 grm. per grm. of silver bromide.

The platinum plated weights were carefully calibrated, and the corrections duly applied.

The Results.

No. of experiment.	Sample Hg.	Sample Br.	Weight of $HgBr_2$.	Weight of AgBr.	The atomic weight (*a*) of Hg.
1.	1	1	8·93958	9·31480	200·63
2.	1	1	14·36691	14·96940	200·64
3.	2	1	10·13638	10·56230	200·61
4.	2	1	9·94452	10·36218	200·62
5.	3	1	12·60142	13·13051	200·63
6.	3	1	12·16157	12·67122	200·65
7.	3	2	11·19762	11·66809	200·62
8.	3	3	16·16607	16·84235	200·68
9.	3	2	11·28487	11·75970	200·59
10.	3	2	17·25074	17·97597	200·61
11.	3	3	14·20924	14·80685	200·61
			Mean		200·64

(*a*) These results are calculated with the values Br, 79·92; Ag, 107·88 (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 1642).

Any discussion of the results would practically be a repetition of that in the paper on the chloride. No evidence has been unearthed in the present work to allow a different view of the result. Hydroxen peroxide was used as the reducing agent in eight experiments of the series; in Experiments 9, 10, and 11, hydrazine hydrate served this purpose. The mean result by each method is practically the same. This is strong evidence that there is little error connected with the removal of the mercury from mercuric bromide. The results are slightly but uniformly lower, however, in the cases where hydrazine hydrate was used. This would indicate that all the bromine from mercuric bromide had not been measured when hydrogen peroxide was used, or, on the other hand, that foreign matter was weighed in the other series. The latter assumption would seem to be the more probable, if either carries any weight, for hydrazine hydrate, if any remained after the treatment with hydrogen peroxide, might reduce the silver nitrate, and thus give an apparently large amount of silver bromide. This seems unlikely, however, for the solution was purposely made more strongly acid in this case than where the peroxide was used in order to counteract such a tendency. The effect is certainly small, and should be connected with the accuracy of the second rather than the first decimal place.—*Journal of the American Chemical Society*, xxxiv., No. 2.

THE EXTRACTION OF POTASH AND ALUMINA FROM FELSPAR.

By H. W. FOOTE and S. R. SCHOLES.

Felspar, being the only common American mineral containing potash in quantity, offers an interesting problem in its decomposition into salts of potassium and aluminium. The work that has been done on this problem has been reviewed by Cushman and Hubbard (*Journ. Am. Chem. Soc.*, 1908, xxx., 779). In their own work these authors have considered the possibility of decomposing finely powdered felspar by treatment with various reagents, particularly under the influence of the electric current. They found that hydrofluoric acid caused an amount of decomposition far above the theoretical, due to the hydrolysis of the fluorides by the action of the current, allowing the hydrofluoric acid to be used over and over again. For instance, in the direct action of hydrofluoric acid on the mineral, some potassium fluoride is formed, which hydrolyses on electrolysis and regenerates hydrofluoric acid at the anode. This acid is free to attack more felspar, and the process goes on until the action is practically complete.

In some preliminary work (carried out several years ago by one of us with Mr. N. A. Martin), which was never published, it was found that at a temperature well above 100°, under pressure, hydrofluoric acid behaved as a catalytic agent in the presence of an aqueous solution of sulphuric acid, and considerable decomposition could be produced.

No.	Felspar. Grms.	CaF$_2$. Grms.	H$_2$SO$_4$. Grms.	H$_2$O. Grms.	Temperature.	Hours heated.	Al$_2$O$_3$ in one-tenth aliquot. Grm.	Decomposed. Per cent.
1.	10	0·0	10	10	200°	23	0·0209	11·2
2.	10	0·5	10	5	140—150°	20	0·0723	38·7
3.	10	0·5	10	20	140—150°	20	0·1266	67·7
4.	10	0·5	10	10	140—150°	20	0·1362	72·8
5.	10	0·5	10	10	140—150°	40	0·1633	87·3
6.	10	1·0	10	10	140—150°	20	0·1662	88·9
7.	10	1·0	10	10	100°	20	0·1355	72·4

We have carried out a number of experiments, the results of which are given above, and have found that under certain conditions decomposition is nearly complete. The hydrofluoric acid appears to be a catalytic agent in this case in the same sense that nitrogen tetroxide is a catalytic agent in the lead-chamber process for sulphuric acid; that is, to explain the action, it is necessary to assume that felspar is attacked, forming some intermediate compound, perhaps silicon fluoride, which hydrolyses in the presence of water at a high temperature, regenerating hydrofluoric acid. Alumina and potash pass into solution at the same time, and can be recovered as sulphates.

In our experiments we used a sample of very finely ground felspar rock.

The material was analysed by the ordinary methods, and found to have the following composition:—

	Per cent.
SiO$_2$	67·12
Al$_2$O$_3$	18·70
K$_2$O	10·84
Na$_2$O	3·12
CaO	0·46
H$_2$O	0·44
	100·68

The calcium fluoride used to produce hydrofluoric acid in solution had all passed a 200-mesh sieve.

The experiments were carried out in sealed glass tubes. The mixtures attacked the glass slightly at the temperatures used, but not sufficiently to affect the general results. After the heating the contents of the bomb were treated with water to remove all soluble material and the solution transferred to a litre flask. Alumina was determined in an aliquot part, and from the result the percentage decomposition could be calculated. It was found by experiment that alumina could be determined in solution by direct precipitation with ammonia without first evaporating, since practically no silica was in solution. The results obtained are given in the accompanying table.

If the fluoride, in the above experiments, were all used merely to form silicon fluoride or hydrofluosilicic acid, the decomposition would be much less in every experiment than what was actually found. In that case, the largest amount of fluoride used would attack only about 6 per cent of the felspar, which is very much less than the smallest amount of decomposition observed.

No. 1 shows the comparatively small effect produced by sulphuric acid alone, even at a much higher temperature than in the experiments where fluoride was used. Nos. 2, 3, and 4 show the effect of varying the dilution of the sulphuric acid, using the same amount of fluoride in each. Of the three dilutions tried, the 50 per cent acid is the best for the purpose. No. 5 shows the diminishing speed of the reaction, as the time of treatment is increased. Comparing with No. 4 it seems that less than 15 per cent decomposition takes place in the second twenty hours. Increasing the amount of catalyser has more effect, as No. 6 shows, with nearly complete decomposition in twenty hours. Lower temperature very noticeably decreases the decomposition, as would be expected. No. 7 was identical in every respect with No. 6, except that the temperature was lower, and the amount decomposed fell from 88·9 to 72·4 per cent. It was found to be impracticable to heat the tubes containing fluoride much above 150°, as they invariably burst; so that we are unable to say at just what temperature decomposition would be practically complete within twenty hours.

Heating the mineral before it was treated in the closed tube has practically no effect. An experiment was carried out which duplicated No. 4 in every way except that the felspar was heated to redness for a half-hour before being placed in the bomb with the reagents. The per cent of decomposition was 70·7, a result nearly identical with No. 4.—*Journal of Industrial and Engineering Chemistry*, iv., No. 5.

Chemical and Mineralogical Examination of Beryls from Elba.—L. Maddalena.—The author has analysed specimens of beryl from Elba, Madagascar, &c., and has determined their physical constants. From the results it is evident that there is a relation between the sum of the alkalis, the index of refraction, double refraction, and density, the relation being approximately constant. There appears to be no difference either in chemical composition, optical properties, or specific gravity in the three types of beryl, as suggested by Duparc and others. Röntgen rays have no colouring effect on beryl.—*Atti della Reale Accademia dei Lincei*. xxi., No. 10.

IRON AND STEEL INSTITUTE.

Leeds Meeting, September 30th, October 1st, 2nd, 3rd, and 4th, 1912.

The Autumn Meeting of the Iron and Steel Institute (President—Arthur Cooper, Esq.) will be held at Leeds on Monday, Tuesday, Wednesday, Thursday, and Friday, September 30th and October 1st to 4th, 1912. An influential Reception Committee has been formed, with Lord Airedale as Chairman, the Hon. Rupert Beckett, D.L., as Treasurer, and Mr. J. F. Walker (Lord Mayor's Secretary) as Honorary Secretary.

The Provisional List of Papers expected to be submitted is as follows:—

On Nitrogen and Iron. By J. H. Andrew (Manchester).
Solubility of Cementite in Hardenite. By Dr. J. O. Arnold (Sheffield) and L. Aitchison (Sheffield).
Solubility or Diffusion of Hardenite in Ferrite. By Dr. J. O. Arnold (Sheffield) and C. Chappell (Sheffield).
Gases Evolved on Heating Steel to its Melting-point in a Vacuum. By G. Wesley Austin (Birmingham).
On Allotropy in General and that of Iron in Particular. By Dr. C. Benedicks (Stockholm).
New Type and Method of Construction of Large Gas Engines. By A. E. L. Chorlton (Manchester).
Thermal-magnetic Transformations of 25 per cent Nickel Steel. By Dr. E. Colver-Glauert (Sheffield) and Dr. S. Hilpert (Charlottenburg).
New Method for the Improvement of the Soundness of Steel Ingots by the Aid of Thermit. By Dr. Hans Goldschmidt (Essen/Ruhr).
Method of Producing Sound Ingots. By Sir Robert A. Hadfield, F.R.S. (Sheffield).
New Method of Revealing Segregation in Steel Ingots. By Sir Robert A. Hadfield, F.R.S. (Sheffield).
Magnetic Properties of Manganese and Nickel Steels. By Dr. S. Hilpert (Charlottenburg) and Dr. W. Mathesius (Worcester, Mass., U.S.A.).
Question of the Existence of Commercial Hyper-eutectic White Iron Free from Manganese. By Dr. H. M. Howe (New York).
Steel Works Yields. By P. Longmuir (Sheffield) and W. H. Robinson (Sheffield).
Some Aspects of Wire Drawing. By P. Longmuir (Sheffield).
Manufacture of Open-hearth Steel, with Reference to Improvement in Yield. By F. W. Paul (Glasgow).
Rolling-mill Practice in the United States. By J. Puppe, D.Ing. (Breslau).
Growth of Cast Irons after Repeated Heatings. Parts V. and VI. By Professor H. F. Rugan (New Orleans, U.S.A.).
Iron Ores and Mineral Resources of Chili. By Charles Vattier (Santiago, Chili).

The Provisional Programme of the Meeting is as follows:—

Monday, September 30th.

Arrival of Members at Leeds. The Secretaries' Office will be open at the Hall of the Philosophical and Literary Society, Park Row, from 2 p.m. until 7 p.m., for the registration of names and the issue of programmes, badges, and cards of invitation.

Tuesday, October 1st.

Welcome by the Lord Mayor of Leeds at the opening Meeting in the Hall of the Philosophical and Literary Society. A selection of papers will subsequently be read and discussed.

The afternoon will be devoted to visits to works in Leeds.

Group A.—Visit to the works of Messrs. Kitson and Co., Ltd. (Airedale Foundry), and to the Steam Plough Works of Messrs. John Fowler and Co., Ltd.
Group B.—Visit to the works of Messrs. J. Buckton and Co., Ltd. (Wellhouse Foundry), and to the works of Messrs. Hathorn, Davey, and Co., Ltd. (Sun Foundry).
Group C.—Visit to the works of the Hunslet Engine Co., Ltd., and to the works of Messrs. Manning, Wardle, and Co., Ltd. (Boyne Engine Works).
Group D.—Visit to the works of Messrs. Hudswell, Clarke, and Co., Ltd. (Railway Foundry), and to the works of Messrs. J. and H. McLaren (Midland Engine Works).
Group E.—Visit to the works of Messrs. Walter Scott, Ltd. (Leeds Steel Works), and to the works of the Coghlan Steel and Iron Co., Ltd. (Hunslet Forge).

In the afternoon arrangements have been made to enable the Ladies taking part in the Meeting to visit Bolton Abbey.

In the evening a Reception will be held by the Lord Mayor and Lady Mayoress in the City Art Gallery, Municipal Buildings, Calverley Street. During the evening a lecture on "Art in Relation to the Iron Industry," will be given by Mr. Frank Rutter, B.A. (Curator of the City Art Gallery) in the Reference Library adjoinining the Gallery.

Wednesday, October 2nd.

Meeting in the morning at the Hall of the Philosophical and Literary Society for the reading and discussion of papers.

The afternoon will be devoted to visits to works in Leeds.

Group A.—Visit to the works of the Monk Bridge Iron and Steel Co. (Whitehall Road) and to the works of the City Electric Lighting Power Station.
Group B.—Visit to the works of the Farnley Iron Co., Ltd. (Farnley).
Group C.—Visit to the works of Messrs. Greenwood and Batley, Ltd. (Albion Works), and to the works of Messrs. W. Johnson and Sons, Ltd. (Castleton Foundry).
Group D.—Visit to works of Messrs. Fairbairn, Lawson, Coombe, and Barbour, Ltd. (Wellington Foundry), and Leeds City Tramway Power Station.
Group E.—Visit to the Crigglestone Collieries and Coking Plant of Messrs. The Otto Coke-oven Co., Ltd., near Wakefield.
Group F.—Visit to the works of Messrs. Taylor Bros. and Co., Ltd. (Clarence Iron and Steel Works, South Accommodation Road, Hunslet).

Arrangements have been made to enable the Ladies taking part in the Meeting to visit Fountains Abbey.

In the evening a Reception will be held by the University of Leeds in the University Buildings, College Road.

Thursday, October 3rd.

Meeting in the morning at the Hall of the Philosophical and Literary Society for the reading and discussion of papers.

In the afternoon the Members and the Ladies accompanying them have been invited by Lord and Lady Airedale to attend a Garden Party, at Gledhow Hall.

In the evening a special performance of the comedy entitled "At the Barn," by Anthony P. Wharton, will be given at the Grand Theatre.

Friday, October 4th.

An excursion will be made to North Lincolnshire and Immingham.

Visits to other Works in and around Leeds.

Invitations have been received from the following works, which will be open for the inspection of Members during the afternoons of Tuesday, October 1st, and Wednesday, October 2nd.

Ironworks and Engineering Works.—H. Berry and Co., Ltd., Croydon Works, Hunslet; Campbells and Hunter, Ltd., Dolphin Foundry, Hunslet; Thomas Green and Son, Ltd., Smithfield Ironworks; the Yorkshire Copper Works, Hunslet; Lawson and Co., Ltd., Hope Foundry; Mann's Patent Steam Cart and Wagon Co., Ltd., Hunslet; Robert Middleton, Sheepcar Foundry; Scriven and Co., Leeds Old Foundry; Thomas Smith and Sons, Old Foundry, Rodley.

Miscellaneous Works.—John Barran and Sons, Ltd. (Clothing Manufacturers); Chorley and Pickersgill, Ltd. (Printing Works); Alf. Cook, Ltd., Crown Point Works (Printing Works); J. Kaye and Sons, Ltd., South Accommodation Road; Morton and Joynt (Clothing Manufacturers), Hunslet; Joshua Tetley and Son, Ltd., the Brewery, Hunslet; Wilson Hartnell and Co., Volt Works (Electric Appliances); the Leeds Corporation Railless Traction Tramways.

The University Laboratories and Departments will also be opened for inspection by the Members and their Ladies on the afternoon of Wednesday, October 2nd.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperaturs are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 2, July 8, 1912.

Density of Nitrosyl Chloride.—Eugène Wourtzel.—The author has determined the weight of a normal litre at 0° of NOCl, a knowledge of which is important for the purpose of controlling the atomic weight of chlorine. The molecular weight referred to oxygen ($O_2 = 32$) was found to be 65·456, while if the atomic weights $N = 14{\cdot}008$ and $Cl = 35{\cdot}460$ are taken, the value is 65·468. The difference between these two values is within the limits of experimental errors.

Alloys of Platinum and Aluminium.—M. Chouriguine.—Platinum and aluminium readily form a series of alloys, which on micrographic examination are seen to contain little lamellæ of eutectic containing crystals of aluminium and the compound $PtAl_3$. The alloy corresponding to 70·4 per cent of platinum is perfectly homogeneous, and its formula is $PtAl_3$. This compound is unaltered in air, and does not dissolve in ordinary acids in the cold.

Chlorous Acid.—M. Lasègue.—By the action of sulphuric acid on barium chlorite a pure aqueous solution of chlorous acid can be obtained. When left to itself it readily decomposes, and if the decomposed solution is neutralised with baryta the chlorine divides itself into four portions:—Chlorate, chlorite, hypochlorite, and chloride of barium.

Gases of Aluminium.—Marcel Guichard and Pierre Roger Jourdain.—By studying different specimens of more or less altered aluminium it is found that the total quantity of gas evolved on heating *in vacuo* increases with the amount of alteration the metal has undergone. Altered specimens furnish a large proportion of CO_2, which is partly dissolved in the metal and partly fixed by the alumina formed by the action of air on the metal.

New Determination of the Atomic Weight of Uranium.—Paul Lebeau.—The author has determined the atomic weight of uranium by reducing by means of hydrogen a known weight of uranyl nitrate, and thus getting the ratio $(NO_3)_2UO_2.2H_2O : UO_2$. Hence the molecular weight of uranous oxide is obtained, and from it that of uranium. The results obtained in five experiments were very concordant, and apparently 238·5 is very approximately the atomic weight of uranium.

Electrolytic Determination of Manganese.—Henri Golblum and Hélène Gunther.—When solutions containing manganese and iron sulphates are electrolysed in presence of ammonium oxalate in certain conditions the manganese can be quantitatively precipitated on the anode. The precipitation depends essentially on the density of the current, which has a great influence on the purity of the deposit of MnO_2. A moving electrode has to be employed, and a current of 2 amp. and 3 volts with a rotation of 700 times per minute gives satisfactory results.

Catalytic Preparation of Ether Salts of Cyclanols and Organic Acids.—J. B. Senderens and J. Aboulenc.—From the results furnished by formic acid it may be concluded that the etherification of the cyclanols by the homologues of this acid in presence of H_2SO_4 is completed at temperatures which are much lower than those at which cyclenes begin to be formed, and hence the production of these hydrocarbons may be avoided by heating the mixtures of cyclanol and acid as little as possible, instead of boiling, as is usually done in the authors' method of catalytic etherification.

Action of Hydrogen Peroxide on Acetothienone and α-Thiophenic Acid.—Maurice Lanfry.—Hydrogen peroxide acts on acetothienone both in the cold and on boiling, the result being the destruction of the thiophenic molecule, the action being most rapid on boiling. No trace of thienylglyoxylic acid or thiophenic acid, the usual products of the oxidation of acetothienone, is observed. The same results are obtained with acetothienone, though oxidation occurs less readily. With all thiophenic products a small quantity of gummy matter with an aromatic odour is formed.

Berichte der Deutschen Chemischen Gesellschaft, Vol. xlv., No. 9, 1912.

Occurrence of Formaldehyde in Plants.—Theodor Curtius and Hartwig Franzen.—According to Baeyer's assimilation hypothesis plants reduce carbon dioxide first to formaldehyde and this then condenses to give carbohydrates. Attempts have been made to prove the occurrence of formaldehyde in plants, but always unsuccessfully. The authors have now proved its presence in beech leaves by first driving off the volatile acids, then oxidising the aldehydes present by means of silver oxide, and proving that formic acid is among the products of the oxidation. Thus Baeyer's hypothesis is confirmed.

Tetraformal-trisazine as a Reducing Agent.—K. A. Hofmann and Douglas Storm.—Tetraformal-trisazine, $C_4H_{12}N_6$, may be obtained by allowing ice-cold formalin to drop into hydrazine hydrate. It forms silky crystals containing two molecules of water. It may be used in analytical chemistry as an acid and alkali-free reducing agent, which acts less strongly than hydrazine. Thus with silver nitrate in excess its aqueous solution gives a white precipitate, which on being gently warmed gives a silver mirror. The structural formula is very probably—

$$\begin{array}{c} HN.CH_2.N.CH_2.NH \\ H\dot{N}.CH_2.\dot{N}.CH_2.\dot{N}H. \end{array}$$

Direct Preparation of Organic Peracids.—J. d'Ans and W. Frey.—Organic acids react with hydrogen peroxide to give the corresponding peracids, and organic acid anhydrides behave similarly. Thus peracetic, perpropionic, and perbutyric acids have been prepared. The first is a clear liquid which is exceedingly explosive. A 50 per cent solution of performic acid has also been prepared. Boric acid-acetic acid anhydride reacts quantitatively with hydrogen peroxide to give peracetic acid. Ketene reacts with hydrogen peroxide, the product being peracetic acid, which with more ketene gives diacetyl peroxide.

NOTES AND QUERIES.

Petroleum, Oils, &c.—"Enquirer" is desirous of ascertaining what books are published on this subject in the French and German languages.

THE CHEMICAL NEWS.

Vol. CVI., No. 2754.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Dundee, 1912.

INAUGURAL ADDRESS OF THE PRESIDENT,

Prof. E. A. Schäfer, LL.D., D.Sc., M.D., F.R.S.

Introductory.—It is exactly forty-five years ago—to the day and hour—that the British Association last met in this city and in this hall to listen to a Presidental Address. The President was the Duke of Buccleugh; the General Secretaries, Francis Galton and T. Archer Hirst; the General Treasurer, William Spottiswoode; and the Assistant General Secretary, George Griffith, who was for many years a mainstay of the Association. The Evening Discourses were delivered by John Tyndall "On Matter and Force," by Archibald Geikie "On the Geological Origin of the Scenery of Scotland," and by Alexander Herschel "On the Present State of Knowledge regarding Meteors and Meteorites." The Presidents of Sections, which were then only seven in number, were for Mathematics and Physics, Sir William Thomson—later to be known as Lord Kelvin; for Chemistry, Thomas Anderson; for Geology, Archibald Geikie, who now as President of the Royal Society worthily fills the foremost place in science within the realm; for Biology, William Sharpey, my own revered master, to whose teaching and influence British physiology largely owes the honourable position which it at present occupies; for Geography, Sir Samuel Baker, the African explorer, who with his intrepid wife was the first to follow the Nile to its exit from the Albert Nyanza; for Economic Science, Mr. Grant Duff; and for Mechanical Science, Professor Rankine.

Other eminent men present were Sir David Brewster, J. Clerk Maxwell, Charles Wheatstone, Balfour Stewart, William Crookes, J. B. Lawes, and J. H. Gilbert (names inseparable in the history of agricultural science), Crum Brown, G. D. Liveing, W. H. Russell, Alexander Williamson, Henry Alleyne Nicholson, William Allmann, John Hutton Balfour, Spencer Cobbold, Anton Dohrn, Sir John Lubbock (now Lord Avebury), William McIntosh, E. Ray Lankester, C. W. Peach, William Pengelly, Hughes Bennett, John Cleland, John Davy, Alexander Christison, Alfred Russel Wallace, Allen Thomson, William Turner, George Busk, Michael Foster (not yet founder of the Cambridge School of Physiology), Henry Howorth, Sir Roderick Murchison, Clements R. Markham, Sir William (afterwards Lord) Armstrong, and Douglas Galton. Many of those enumerated have in the course of nature passed away from us, but not a few remain, and we are glad to know that most of these retain their ancient vigour in spite of the five-and-forty years which separate us from the last meeting in this place.

Selection of Subject of Address.—For the Address with which it is usual for the President to open the proceedings of the annual assembly, the field covered by the aims of the British Association provides the widest possible range of material from which to select. One condition alone is prescribed by custom, viz., that the subject chosen shall lie within the bounds of those branches of knowledge which are dealt with in the Sections. There can be no ground of complaint regarding this limitation on the score of variety, for within the forty years that I have myself been present (not, I regret to say, without a break) at these gatherings, problems relating to the highest mathematics on the one hand, and to the most utilitarian applications of science on the other, with every possible gradation between these extremes, have been discussed before us by successive Presidents; and the addition from time to time of new Sections (one of which, that of Agriculture, we welcome at this Meeting) enables the whilom occupant of this Chair to traverse paths which have not been previously trodden by his predecessors. On the last two occasions, under the genial guidance of Professors Bonney and Sir William Ramsay, we have successively been taken in imagination to the glaciers which flow between the highest peaks of the Alps and into the bowels of the earth; where we were invited to contemplate the prospective disappearance of the material upon which all our industrial prosperity depends. Needless to say that the lessons to be drawn from our visits to those unaccustomed levels were placed before us with all the eloquence with which these eminent representatives of Geology and Chemistry are gifted. It is fortunately not expected that I should be able to soar to such heights or to plunge to such depths, for the branch of science with which I am personally associated is merely concerned with the investigation of the problems of living beings, and I am able to invite you to remain for an hour or so at the level of ordinary mortality to consider certain questions which at any rate cannot fail to have an immediate interest for every one present, seeing that they deal with the nature, origin, and maintenance of life.

Definition.—Everybody knows, or thinks he knows, what life is; at least, we are all acquainted with its ordinary obvious manifestations. It would therefore seem that it should not be difficult to find an exact definition. The quest has nevertheless baffled the most acute thinkers. Herbert Spencer devoted two chapters of his "Principles of Biology" to the discussion of the attempts at definition which had up to that date been proposed, and himself suggested another. But at the end of it all he is constrained to admit that no expression had been found which would embrace all the known manifestations of animate, and at the same time exclude those of admittedly inanimate, objects.

The ordinary dictionary definition of life is "the state of living." Dastre, following Claude Bernard, defines it as "the sum total of the phenomena common to all living beings" ("La vie et la mort," English translation by W. J. Greenstreet, 1911, p. 54). Both of these definitions are, however, of the same character as Sydney Smith's definition of an archdeacon as "a person who performs archidiaconal functions." I am not myself proposing to take up your time by attempting to grapple with a task which has proved too great for the intellectual giants of philosophy, and I have the less disposition to do so because recent advances in knowledge have suggested the probability that the dividing line between animate and inanimate matter is less sharp than it has hitherto been regarded, so that the difficulty of finding an inclusive definition is correspondingly increased.

Life not Identical with Soul.—As a mere word "life" is interesting in the fact that it is one of those abstract terms which has no direct antithesis; although probably most persons would regard "death" in that light. A little consideration will show that this is not the case. "Death" implies the pre-existence of "life"; there are physiological grounds for regarding death as a phenomenon of life—it is the completion, the last act of life. We cannot speak of a non-living object as *possessing* death in the sense that we speak of a living object as *possessing* life. The adjective "dead" is, it is true, applied in a popular sense antithetically to objects which have never possessed life; as in the proverbial expression "as dead as a door-nail," But in that strict sense such application is not justifiable, since the use of the terms dead and living implies either in the past or in the present the possession of the recognised properties of living matter. On the other hand, the expressions *living* and *lifeless*, *animate* and *inanimate*, furnish terms which are undoubtedly antithetical. Strictly and literally, the words animate and inanimate express the presence or absence of "soul"; and not infrequently we find the terms "life" and "soul" erroneously employed as if identical. But it is hardly necessary for me to state that the remarks I have to make regarding "life" must not be taken to apply to the conception to which the word "soul" is attached. The fact that the formation of such a conception is only possible in connection with life, and that the growth and elaboration of the conception has only been possible as the result of the most complex processes of life in the most complex of living organisms, has doubtless led to a belief in the identity of life with soul. But unless the use of the expression "soul" is extended to a degree which would deprive it of all special significance, the distinction between these terms must be strictly maintained.

Problems of Life are Problems of Matter.—For the problems of life are essentially problems of matter; we cannot conceive of life in the scientific sense as existing apart from matter. The phenomena of life are investigated, and can only be investigated, by the same methods as all other phenomena of matter, and the general results of such investigations tend to show that living beings are governed by laws identical with those which govern inanimate matter. The more we study the manifestations of life the more we become convinced of the truth of this statement, and the less we are disposed to call in the aid of a special and unknown form of energy to explain those manifestations.

Phenomena Indicative of Life; Movement.—The most obvious manifestation of life is "spontaneous" movement. We see a man, a dog, a bird move, and we know that they are alive. We place a drop of pond water under the microscope, and see numberless particles rapidly moving within it; we affirm that it swarms with "life." We notice a small mass of clear slime changing its shape, throwing out projections of its structureless substance, creeping from one part of the field of the microscope to another. We recognise that the slime is living; we give it a name—*Amœba limax*—the slug amœba. We observe similar movements in individual cells of our own body; in the white corpuscles of our blood, in connective tissue cells, in growing nerve cells, in young cells everywhere. We denote the similarity between these movements and those of the amœba by employing the descriptive term "amœboid" for both. We regard such movements as indicative of the possession of "life"; nothing seems more justifiable than such an inference.

Similarity of Movements in Living and Non-living Matter.—But physicists (G. Quincke, *Annal. d. Physik u. Chem.*, 1870 and 1888) show us movements of a precisely similar character in substances which no one by any stretch of imagination can regard as living; movements of oil drops, of organic and inorganic mixtures, even of mercury globules, which are indistinguishable in their character from those of the living organisms we have been studying; movements which can only be described by the same term amœboid, yet obviously produced as the result of purely physical and chemical reactions causing changes in surface tension of the fluids under examination (see Note 1). It is therefore certain that such movements are not specifically "vital," that their presence does not necessarily denote "life." And when we investigate closely even such active movements as those of a vibratile cilium or a phenomenon so closely identified with life as the contraction of a muscle, we find that these present so many analogies with amœboid movements as to render it certain that they are fundamentally of the same character and produced in much the same manner. (G. F. Fitzgerald, *Brit. Assoc. Reports*, 1898, and *Scient. Trans. Roy. Dublin Soc.*, 1898, arrived at this conclusion with regard to muscle from purely physical considerations). Nor can we for a moment doubt that the complex actions which are characteristic of the more highly differentiated organisms have been developed in the course of evolution from the simple movements characterising the activity of undifferentiated protoplasm; movements which can themselves, as we have seen, be perfectly imitated by non-living material. The chain of evidence regarding this particular manifestation of life—movement—is complete. Whether exhibited as the amœboid movement of the proteus animalcule or of the white corpuscle of our blood; as the ciliary motion of the infusorian or of the ciliated cell; as the contraction of a muscle under the governance of the will, or as the throbbing of the human heart responsive to every emotion of the mind, we cannot but conclude that it is alike subject to and produced in conformity with the general laws of matter, by agencies resembling those which cause movements in lifeless material (see Note 2).

Assimilation and Disassimilation.—It will perhaps be contended that the resemblances between the movements of living and non-living matter may be only superficial, and that the conclusion regarding their identity to which we are led will be dissipated when we endeavour to penetrate more deeply into the working of living substance. For can we not recognise along with the possession of movement the presence of other phenomena which are equally characteristic of life and with which non-living material is not endowed? Prominent among the characteristic phenomena of life are the processes of assimilation and disassimilation, the taking in of food and its elaboration (see Note 3). These, surely, it may be thought, are not shared by matter which is not endowed with life. Unfortunately for this argument, similar processes occur characteristically in situations which no one would think of associating with the presence of life. A striking example of this is afforded by the osmotic phenomena presented by solutions separated from one another by semipermeable membranes or films, a condition which is precisely that which is constantly found in living matter (see Note 4).

Chemical Phenomena Accompanying Life.—It is not so long ago that the chemistry of organic matter was thought to be entirely different from that of inorganic substances. But the line between inorganic and organic chemistry, which up to the middle of the last century appeared sharp, subsequently became misty and has now disappeared. Similarly the chemistry of living organisms, which is now a recognised branch of organic chemistry, but used to be considered as so much outside the domain of the chemist that it could only be dealt with by those whose special business it was to study "vital" processes, is passing every day more out of the hands of the biologist and into those of the pure chemist.

The Colloid Constitution of Living Matter. Identity of Physical and Chemical Processes in Living and Non-living Matter.—Somewhat more than half a century ago Thomas Graham published his epoch-making observations relating to the properties of matter in the colloidal state: observations which are proving all-important in assisting our comprehension of the properties of living substance. For it is becoming every day more apparent that the chemistry and physics of the living organism are essentially the chemistry and physics of nitrogenous colloids. Living substance or protoplasm always, in fact, takes the form of a colloidal solution. In this solution the colloids are associated with crystalloids (electrolytes), which are either free in the solution or attached to the molecules of the colloids. Surrounding and enclosing the living substance thus constituted of both colloid and crystalloid material is a film, probably also formed of colloid, but which may have a lipoid substratum associated with it (Overton). This film serves the purpose of an osmotic membrane, permitting of exchanges by diffusion between the colloidal solution constituting the protoplasm and the circumambient medium in which it lives. Other similar films or membranes occur in the interior of protoplasm. These films have in many cases specific characters, both physical and chemical, thus favouring the diffusion of special kinds of material into and out of the protoplasm and from one part of the protoplasm to another. It is the changes produced under these physical conditions, associated with those caused by active chemical agents formed within protoplasm and known as *enzymes*, that effect assimilation and disassimilation. Quite similar changes can be produced outside the body (*in vitro*) by the employment of methods of a purely physical and chemical nature. It is true that we are not yet familiar with all the intermediate stages of transformation of the materials which are taken in by a living body into the materials which are given out from it. But since the initial processes and the final results are the same as they would be on the assumption that the changes are brought about in conformity with the known laws of chemistry and physics, we may fairly conclude that all changes in living substances are brought about by ordinary chemical and physical forces.

Similarity of the Processes of Growth and Reproduction in Living and Non-living Matter.—Should it be contended that growth and reproduction are properties possessed only by living bodies and constitute a test by which we may differentiate between life and non-life, between the animate and inanimate creation, it must be replied that no contention can be more fallacious. Inorganic crystals grow and multiply and reproduce their like, given a supply of the requisite pabulum. In most cases for each kind of crystal there is, as with living organisms, a limit of growth which is not exceeded, and further increase of the crystalline matter results not in further increase in size but in multiplication of similar crystals. Leduc has shown that the growth and division of artificial colloids of an inorganic nature when placed in an appropriate medium, present singular resemblances to the phenomena of the growth and division of living organisms. Even so complex a process as the division of a cell-nucleus by karyokinesis as a preliminary to the multiplication of the cell by division —a phenomenon which would *primâ facie* have seemed and has been commonly regarded as a distinctive manifestation of the life of the cell—can be imitated with solutions of a simple inorganic salt, such as chloride of sodium, containing a suspension of carbon particles; which arrange and rearrange themselves under the influence of the movements of the electrolytes in a manner indistinguishable from that adopted by the particles of chromatin in a dividing nucleus. And in the process of sexual reproduction, the researches of J. Loeb and others upon the ova of the sea-urchin have proved that we can no longer consider such an apparently vital phenomenon as the fertilisation of the egg as being the result of living material brought to it by the spermatozoon, since it is possible to start the process of division of the ovum and the resulting formation of cells, and ultimately of all the tissues and organs—in short, to bring about the development of the whole body—if a simple chemical reagent is substituted for the male element in the process of fertilisation. Indeed, even a mechanical or electrical stimulus may suffice to start development.

The Question of Vitalism and Vital Force.—*Kurz und gut*, as the Germans say, vitalism as a working hypothesis has not only had its foundations undermined, but most of the superstructure has toppled over, and if any difficulties of explanation still persist, we are justified in assuming that the cause is to be found in our imperfect knowledge of the constitution and working of living material. At the best vitalism explains nothing, and the term "vital force" is an expression of ignorance which can bring us no further along the path of knowledge. Nor is the problem in any way advanced by substituting for the term "vitalism" "neo-vitalism," and for "vital force" "biotic energy" (see Note 5). "New presbyter is but old priest writ large."

The Possibility of the Synthesis of Living Matter.—Further, in its chemical composition we are no longer compelled to consider living substance as possessing infinite complexity, as was thought to be the case when chemists first began to break up the proteins of the body into their simpler constituents. The researches of Miescher, which have been continued and elaborated by Kossel and his pupils, have acquainted us with the fact that a body so important for the nutritive and reproductive functions of the cell as the nucleus—which may be said indeed to represent the quintessence of cell-life—possesses a chemical constitution of no very great complexity; so that we n/ even hope some day to see the material which composes it prepared synthetically. And when we consider that the nucleus is not only itself formed of living substance, but is capable of causing other living substance to be built up; is, in fact, the directing agent in all the principal chemical changes which take place within the living cell, it must be admitted that we are a long step forward in our knowledge of the chemical basis of life. That it is the *form* of nuclear matter rather than its chemical and molecular structure which is the important factor in nuclear activity cannot be supposed. The form of nuclei, as every microscopist knows, varies infinitely, and there are numerous living organisms in which the nuclear matter is without form, appearing simply as granules distributed in the protoplasm. Not that the form assumed and the transformations undergone by the nucleus are without importance; but it is none the less true that even in an amorphous condition the material which in the ordinary cell takes the form of a "nucleus" may, in simpler organisms which have not in the process of evolution become complete cells, fulfil functions in many respects similar to those fulfilled by the nucleus of the more differentiated organism.

A similar anticipation regarding the probability of eventual synthetic production may be made for the proteins of the cell-substance. Considerable progress in this direction has indeed already been made by Emil Fischer, who has for many years been engaged in the task of building up the nitrogenous combinations which enter into the formation of the complex molecule of protein. It is satisfactory to know that the significance of the work both of Fischer and of Kossel in this field of biological chemistry has been recognised by the award to each of these distinguished chemists of a Nobel prize.

The Chemical Constitution of Living Substance.—The elements composing living substance are few in number. Those which are constantly present are carbon, hydrogen, oxygen, and nitrogen. With these, both in nuclear matter and also, but to a less degree, in the more diffuse living material which we know as protoplasm, phosphorus is always associated. "Ohne Phosphor kein Gedank" is an accepted aphorism; "Ohne Phosphor kein Leben" is equally true. Moreover, a large proportion, rarely less than 70 per cent, of water appears essential for any manifestation of life, although not in all cases necessary for its continuance, since organisms are known which will bear the loss of the greater part if not the whole of the water they contain without permanent impairment of their vitality. The presence of certain inorganic salts is no less essential, chief amongst them being chloride of sodium and salts of calcium, magnesium, potassium, and iron. The combination of these elements into a colloidal compound represents the chemical basis of life; and when the chemist succeeds in building up this compound it will without doubt be found to exhibit the phenomena which we are in the habit of associating with the term "life" (see Note 6).

Source of Life. The Possibility of Spontaneous Generation.—The above considerations seem to point to the conclusion that the possibility of the production of life—*i.e.*, of living material—is not so remote as has been generally assumed. Since the experiments of Pasteur, few have ventured to affirm a belief in the spontaneous generation of bacteria and monads and other micro-organisms, although before his time this was by many believed to be of universal occurrence. My esteemed friend Dr. Charlton Bastian is, so far as I am aware, the only scientific man of eminence who still adheres to the old creed, and Dr. Bastian, in spite of numerous experiments and the publication of many books and papers, has not hitherto succeeded in winning over any converts to his opinion. I am myself so entirely convinced of the accuracy of the results which Pasteur obtained—are they not within the daily and hourly experience of everyone who deals with the sterilisation of organic solutions?—that I do not hesitate to believe, if living torulæ or mycelia are exhibited to me in flasks which had been subjected to prolonged boiling after being hermetically sealed, that there has been some fallacy either in the premisses or in the carrying out of the operation. The appearance of organisms in such flasks would not furnish to my mind proof that they were the result of spontaneous generation. Assuming no fault in manipulation or fallacy in observation, I should find it simpler to believe that the germs of such organisms have resisted the effects of prolonged heat than that they became generated spontaneously. If spontaneous generation is possible, we cannot expect it to take the form of living beings which show so marked a degree of differentiation, both structural and functional, as the organisms which are described as making their appearance in these experimental flasks (see Note 7). Nor should we expect the spontaneous generation of living substance of any kind to occur in a fluid the organic constituents of which have been so altered by heat that they can retain no sort of chemical resemblance to the organic constituents of living matter. If the formation of life—of living substance—is possible at the present day—and for my own part I see no reason to doubt it—a boiled infusion of organic matter—and still less of inorganic matter is the last place in which to look for it. Our mistrust of such evidence as has yet been brought forward need not, however, preclude us from admitting the possibility of the formation of living from non-living substance (see Note 8).

Life a Product of Evolution.—Setting aside, as devoid of scientific foundation, the idea of immediate supernatural intervention in the first production of life, we are not only justified in believing, but compelled to believe, that living matter must have owed its origin to causes similar in character to those which have been instrumental in producing all other forms of matter in the universe; in other words, to a process of gradual evolution (see Note 9). But it has been customary of late amongst biologists to shelve the investigation of the mode of origin of life by evolution from non-living matter by relegating its solution to some former condition of the earth's history, when, it is assumed, opportunities were accidentally favourable for the passage of inanimate matter into animate; such opportunities, it is also assumed, having never since recurred and being never likely to recur (T. H. Huxley, Presidental Address, 1870; A. B. Macallum, "On the Origin of Life on the Globe," in *Trans. Canadian Institute*, viii.).

Various eminent scientific men have even supposed that life has not actually originated upon our globe, but has been brought to it from another planet or from another stellar system. Some of my audience may still remember the controversy that was excited when the theory of the origin of terrestrial life by the intermediation of a meteorite was propounded by Sir William Thomson in his Presidental Address at the meeting of this Association in Edinburgh in 1871. To this "meteorite" theory (see Note 10) the apparently fatal objection was raised that it would take some sixty million years for a meteorite to travel from the nearest stellar system to our earth, and it is inconceivable that any kind of life could be maintained during such a period. Even from the nearest planet 150 years would be necessary, and the heating of the meteorite in passing through our atmosphere, and at its impact with the earth would, in all probability, destroy any life which might have existed within it. A cognate theory, that of *cosmic panspermia*, assumes that life may exist and may have existed indefinitely in cosmic dust in the interstellar spaces (Richter, 1865; Cohn, 1872), and may with this dust fall slowly to the earth without undergoing the heating which is experienced by a meteorite. Arrhenius ("Worlds in the Making," translated by H. Borns, 1908, chap. viii., p. 221), who adopts this theory, states that if living germs were carried through the ether by luminous and other radiations the time necessary for their transportation from from our globe to the nearest stellar system would be only nine thousand years, and to Mars only twenty days!

But the acceptance of such theories of the arrival of life on the earth does not bring us any nearer to a conception of its actual mode of origin; on the contrary, it merely serves to banish the investigation of the question to some conveniently inaccessible corner of the universe, and leaves us in the unsatisfactory position of affirming not only that we have no knowledge as to the mode of origin of life—which is unfortunately true—but that we never can acquire such knowledge—which it is to be hoped is not true (see Note 11). Knowing what we know, and believing what we believe, as to the part played by evolution in the development of terrestrial matter, we are, I think—without denying the possibility of the existence of life in other parts of the universe (see Note 12)—justified in regarding these cosmic theories as inherently improbable—at least in comparison with the solution of the problem which the evolutionary hypothesis offers (see Note 13).

The Evolutionary Hypothesis as applied to the Origin of Life.—I assume that the majority of my audience have at least a general idea of the scope of this hypothesis, the general acceptance of which has within the last sixty years altered the whole aspect not only of biology, but of every other branch of natural science, including astronomy, geology, physics, and chemistry (see Note 14). To those who have not this familiarity I would recommend the perusual of a little book by Professor Judd entitled "The Coming of Evolution," which has recently appeared as one of the Cambridge manuals. I know of no similar book in which the subject is as clearly and succinctly treated. Although the author nowhere expresses the opinion that the actual origin of life on the earth has arisen by evolution from non-living matter, it is impossible to read either this or any similar exposition in which the essential unity of the evolutionary process is insisted upon without concluding that the origin of life must have been due to the same process, this process being, without exception, continuous, and admitting of no gap at any part of its course. Looking therefore at the evolution of living matter by the light which is shed upon it from the study of the evolution of matter in general, we are led to regard it as having been produced, not by a sudden alteration, whether exerted by natural or supernatural agency, but by a gradual process of change from material which was lifeless, through material on the borderland between inanimate and animate, to material which has all the characteristics to which we attach the term "life." So far from expecting a sudden leap from an inorganic, or at least an unorganised, into an organic and organised condition, from an entirely inanimate substance to a completely animate state of being, should we not rather expect a gradual procession of changes from inorganic to organic matter, through stages of gradually increasing complexity until material which can be termed living is attained? And in place of looking for the production of fully formed living organisms in hermetically sealed flasks, should we not rather search Nature herself, under natural conditions, for evidence of the existence, either in the past or in the present, of transitional forms between living and non-living matter?

The difficulty, nay the impossibility, of obtaining evidence of such evolution from the past history of the globe is obvious. Both the hypothetical transitional material and the living material which was originally evolved from it may, as Macallum has suggested, have taken the form of diffused ultra-microscopic particles of living substance (see Note 15); and even if they were not diffused but aggregated into masses, these masses could have been physically nothing more than colloidal watery slime which would leave no impress upon any geological formation. Myriads of years may have elapsed before some sort of skeleton in the shape of calcareous or siliceous spicules began to evolve itself, and thus enabled "life," which must already have possessed a prolonged existence, to make any sort of geological record. It follows that in attempting to pursue the evolution of living matter to its beginning in terrestrial history we can only expect to be confronted with a blank wall of nescience.

The problem would appear to be hopeless of ultimate solution, if we are rigidly confined to the supposition that the evolution of life has only occurred once in the past history of the globe. But are we justified in assuming that at one period only, and as it were by a fortunate and fortuitous concomitation of substance and circumstance, living matter became evolved out of non-living matter—life became established? Is there any valid reason to conclude that at some previous period of its history our earth was more favourably circumstanced for the production of life than it is now? (see Note 16). I have vainly sought for such reason, and if none be forthcoming the conclusion forces itself upon us that the evolution of non-living into living substance has happened more than once —and we can be by no means sure that it may not be happening still.

It is true that up to the present there is no evidence of such happening; no process of transition has hitherto been observed. But, on the other hand, is it not equally true that the kind of evidence which would be of any real value in determining this question has not hitherto been looked for? We may be certain that if life is being produced from non-living substance it will be life of a far simpler character than any that has yet been observed—in material which we shall be uncertain whether to call animate or inanimate, even if we are able to detect it at all, and which we may not be able to visualise physically even after we have become convinced of its existence (see Note 17). But we can look with the mind's eye and follow in imagination the transformation which non-living matter may have undergone, and may still be undergoing to produce living substance. No principle of evolution is better founded than that insisted upon by Sir Charles Lyell, justly termed by Huxley "the greatest geologist of his time," that we must interpret the past history of our globe by the present; that we must seek for an explanation of what has happened by the study of what is happening; that, given similar circumstances, what has occurred at one time will probably occur at another. The process of evolution is universal. The inorganic materials of the globe are continually undergoing transition. New chemical combinations are constantly being formed and old ones broken up; new elements are making their appearance and old elements disappearing (see Note 18). Well may we ask ourselves why the production of living matter alone should be subject to other laws than those which have produced, and are producing, the various forms of non-living matter; why what has happened may not happen? If living matter has been evolved from lifeless in the past, we are justified in accepting the conclusion that its evolution is possible in the present and in the future. Indeed, we are not only justified in accepting this conclusion, we are forced to accept it. When or where such change from non-living to living matter may first have occurred, when or where it may have continued, when or where it may still be occurring, are problems as difficult as they are interesting, but we have no right to assume that they are insoluble.

Since living matter always contains water as its most abundant constituent, and since the first living organisms recognisable as such in the geological series were aquatic, it has generally been assumed that life must first have made its appearance in the depths of the ocean. (For arguments in favour of the first appearance of life having been in the sea, see A. B. Macallum, "The Palæochemistry of the Ocean," *Trans. Canad. Instit.*, 1903-4). Is it, however, certain that the assumption that life orginated in the sea is correct? Is not the land-surface of our globe quite as likely to have been the nidus for the evolutionary transformation of non-living into living material as the waters which surround it? Within this soil almost any chemical transformation may occur; it is subjected much more than matters dissolved in sea-water to those fluctuations of moisture, temperature, electricity, and luminosity which are potent in producing chemical changes. But whether life, in the form of a simple slimy colloid, originated in the depths of the sea or on the surface of the land, it would be equally impossible for the geologist to trace its beginnings, and were it still becoming evolved in the same situations, it would be almost as impossible for the microscopist to follow its evolution. We are therefore not likely to obtain direct evidence regarding such a transformation of non-living into living matter in Nature, even if it is occurring under our eyes.

An obvious objection to the idea that the production of living matter from non-living has happened more than once is that, had this been the case, the geological record should reveal more than one palæontological series. This objection assumes that evolution would in every case take an exactly similar course and proceed to the same goal—an assumption which is, to say the least, improbable. If, as might well be the case, in any other palæontological series than the one with which we are acquainted the process of evolution of living beings did not proceed beyond Protista, there would be no obvious geological evidence regarding it; such evidence would only be discoverable by a carefully directed search made with that particular object in view (see Note 19). I would not by any means minimise the difficulties which attend the suggestion that the evolution of life may have occurred more than once, or may still be happening, but on the other hand, it must not be ignored that those which attend the assumption that the production of life has occurred once only are equally serious. Indeed, had the idea of the possibility of a multiple evolution of living substance been first in the field, I doubt if the prevalent belief regarding a single fortuitous production of life upon the globe would have become established among biologists—so much are we liable to be influenced by the impressions we receive in scientific childhood!

Further Course of Evolution of Life.—Assuming the evolution of living matter to have occurred—whether once only or more frequently matters not for the moment—and in the form suggested, viz., as a mass of colloidal slime possessing the property of assimilation and therefore of growth, reproduction would follow as a matter of course. For all material of this physical nature—fluid or semifluid in character—has a tendency to undergo subdivision when its bulk exceeds a certain size. The subdivision may be into equal or nearly equal parts, or it may take the form of buds. In either case every separated part would resemble the parent in chemical and physical properties, and would equally possess the property of taking in and assimilating suitable material from its liquid environment, growing in bulk and reproducing its like by subdivision. *Omne vivum e vivo.* In this way from any beginning of living material a primitive form of life would spread, and would gradually people the globe. The establishment of life being once effected, all forms of organisation follow under the inevitable laws of evolution. *Ce n'est que le premier pas qui coûte.*

We can trace in imagination the segregation of a more highly phosphorised portion of the primitive living matter, which we may now consider to have become more akin to the protoplasm of organisms with which we are familiar. This more phosphorised portion might not for myriads of generations take the form of a definite nucleus, but it would be composed of material having a composition and qualities similar to those of the nucleus of a cell. Prominent among these qualities is that of catalysis—the function of effecting profound chemical changes in other material in contact with it without itself undergoing permanent change. This catalytic function may have been exercised directly by the living substance or may have been carried on through the agency of the enzymes already mentioned, which are also of a colloid nature but of simpler constitution than itself, and which differ from the catalytic agents employed by the chemist in the fact that they produce their effects at a relatively low temperature. In the course of evolution special enzymes would become developed for adaptation to special conditions of life, and with the appearance of these and other modifications, a process of differentiation of primitive living matter into individuals with definite specific characters gradually became established. We can conceive of the production in this way from originally undifferentiated living substance of simple differentiated organisms comparable to the lowest forms of Protista. But how long it may have taken to arrive at this stage we have no means of ascertaining. To judge from the evidence afforded by the evolution of higher organisms it would seem that a vast period of time would be necessary for even this amount of organisation to establish itself.

Formation of the Nucleated Cell.—The next important phase in the process of evolution would be the segregation and moulding of the diffused or irregularly aggregated nuclear matter into a definite nucleus around which all the chemical activity of the organism will in future be centred. Whether this change were due to a slow and gradual process of segregation or of the nature of a jump, such as Nature does occasionally make, the result would be the advancement of the living organism to the condition of a complete nucleated cell; a material advance not only in organisation but—still more important—in potentiality for future development. Life is now embodied in the cell, and every living being evolved from this will itself be either a cell or a cell-agregate. *Omnis cellula e cellulâ.*

Establishment of Sexual Differences.—After the appearance of a nucleus—but how long after it is impossible to conjecture—another phenomenon appeared upon the scene in the occasional exchange of nuclear substance between cells. In this manner became established the process of sexual reproduction. Such exchange in the unicellular Protista might and may occur between any two cells forming the species, but in the multicellular Metazoa it became—like other functions—specialised in particular cells. The result of the exchange is rejuvenescence; associated with an increased tendency to subdivide and to produce new individuals. This is due to the introduction of a stimulating or catalytical chemical agent into the cell which is to be rejuvenated, as is proved by the experiments of Loeb already alluded to. It is true that the chemical material introduced into the germ-cell in the ordinary process of its fertilisation by the sperm-cell is usually accompanied by the introduction of definite morphological elements which blend with others already contained within the germ-cell, and it is believed that the transmission of such morphological elements of the parental nuclei is related to the transmission of parental qualities. But we must not be blind to the possibility that these transmitted qualities may be connected with specific chemical characters of the transmitted elements; in other words, that heredity also is one of the questions the eventual solution of which we must look to the chemist to provide.

Aggregate Life.—So far we have been chiefly considering life as it is found in the simplest forms of living substance, organisms for the most part entirely microscopic and neither distinctively animal nor vegetable, which were grouped together by Haeckel as a separate kingdom of animated nature—that of Protista. But persons unfamiliar with the microscope are not in the habit of associating the term "life" with microscopic organisms, whether these take the form of cells or of minute portions of living substance which have not yet attained to that dignity. We most of us speak and think of life as it occurs in ourselves and other animals with which we are familiar; and as we find it in the plants around us. We recognise it in these by the possession of certain properties —movement, nutrition, growth, and reproduction. We are not aware by intuition, nor can we ascertain without the employment of the microscope, that we and all the higher living beings, whether animal or vegetable, are entirely formed of aggregates of nucleated cells, each microscopic and each possessing its own life. Nor could we suspect by intuition that what we term our life is not a single indivisible property, capable of being blown out with a puff like the flame of a candle; but is the aggregate of the lives of many millions of living cells of which the body is composed. It is but a short while ago that this cell-constitution was discovered; it occurred within the lifetime, even within the memory, of some who are still with us. What a marvellous distance we have travelled since then in the path of knowledge of living organisms! The strides which were made in the advance of the mechanical sciences during the nineteenth century, which is generally considered to mark that century as an age of unexampled progress, are as nothing in comparison with those made in the domain of biology, and their interest is entirely dwarfed by that which is aroused by the facts relating to the phenomena of life which have accumulated within the same period. And not the least remarkable of these facts is the discovery of the cell-structure of plants and animals!

Evolution of the Cell-aggregate.—Let us consider how cell-aggregates came to be evolved from organisms consisting of single cells. Two methods are possible—viz., (1) the adhesion of a number of originally separate individuals; (2) the subdivision of a single individual without the products of its subdivision breaking loose from one another. No doubt this last is the manner whereby the cell-aggregate was originally formed, since it is that by which it is still produced, and we know that the life-history of the individual is an epitome of that of the species. Such aggregates were in the beginning solid; the cells in contact with one another and even in continuity; subsequently a space or cavity became formed in the interior of the mass, which was thus converted into a hollow sphere. All the cells of the aggregate were at first perfectly similar in structure and in function; there was no subdivision of labour. All would take part in effecting locomotion; all would receive stimuli from outside; all would take in and digest nutrient matter, which would then be passed into the cavity of the sphere to serve as a common store of nourishment. Such organisms are still found, and constitute the lowest types of Metazoa. Later one part of the hollow sphere became dimpled to form a cup; the cavity of the sphere became correspondingly altered in shape. With this change in structure differentiation of function between the cells covering the outside and those lining the inside of the cup made its appearance. Those on the outside subserved locomotor functions and received and transmitted from cell to cell stimuli, physical or chemical, received by the organism; while those on the inside, being freed from such functions, tended to specialise in the direction of the inception and digestion of nutrient material; which, passing from them into the cavity of the invaginated sphere, served for the nourishment of all the cells composing the organism. The further course of evolution produced many changes of form and ever-increasing complexity of the cavity thus produced by simple invagination. Some of the cell-aggregates settled down to a sedentary life, becoming plant-like in appearance and to some extent in habit. Such organisms, complex in form but simple in structure, are the Sponges. Their several parts are not, as in the higher Metazoa, closely interdependent; the destruction of any one part, however extensive, does not either immediately or ultimately involve death of the rest; all parts function separately, although doubtless mutually benefiting by their conjunction, if only by slow diffusion of nutrient fluid throughout the mass. There is already some differentiation in these organisms, but the absence of a nervous system prevents any general co-ordination, and the individual cells are largely independent of one another.

Our own life, like that of all the higher animals, is an *aggregate life;* the life of the whole is the life of the individual cells. The life of some of these cells can be put an end to, the rest may continue to live. This is, in fact, happening every moment of our lives. The cells which cover the surface of our body, which form the scarf-skin and the hairs and nails, are constantly dying and the dead cells are rubbed off or cut away, their place being taken by others supplied from living layers beneath. But the death of these cells does not affect the vitality of the body as a whole. They serve merely as a protection, or an ornamental covering, but are otherwise not material to our existence. On the other hand, if a few cells, such as those nerve-cells under the influence of which respiration is carried on, are destroyed or injured, within a minute or two the whole living machine comes to a standstill, so that to the bystander the patient is dead; even the doctor will pronounce life to be extinct. But this pronouncement is correct only in a special sense. What has happened is that, owing to the cessation of respiration, the supply of oxygen to the tissues is cut off. And since the manifestations of life cease without this supply, the animal or patient appears to be dead. If, however, within a short period we supply the needed oxygen to the tissues requiring it, all the manifestations of life reappear.

It is only some cells which lose their vitality at the moment of so-called "general death." Many cells of the body retain their individual life under suitable circumstances long after the rest of the body is dead. Notable among these are muscle-cells. McWilliam showed that the muscle-cells of the blood-vessels give indications of life several days after an animal has been killed. The muscle-cells of the heart in mammals have been revived and caused to beat regularly and strongly many hours after apparent death. In man this result has been obtained by Kuliabko as many as eighteen hours after life had been pronounced extinct; in animals after days had elapsed. Waller has shown that indications of life can be elicited from various tissues many hours and even days after general death. Sherrington observed the white corpuscles of the blood to be active when kept in a suitable nutrient fluid weeks after removal from the blood-vessels. A French histologist, Jolly, has found that the white corpuscles of the frog, if kept in a cool place and under suitable conditions, show at the end of a year all the ordinary manifestations of life. Carrell and Burrows have observed activity and growth to continue for long periods in the isolated cells of a number of tissues and organs kept under observation in a suitable medium. Carrell has succeeded in substituting entire organs obtained after death from one animal for those of another of the same species, and has thereby opened up a field of surgical treatment the limit of which cannot yet be described. It is a well-established fact that any part or organ of the body can be maintained alive for hours isolated from the rest if the blood-vessels are perfused with an oxygenated solution of salts in certain proportions (Ringer). Such revival and prolongation of the life of separated organs is an ordinary procedure in laboratories of physiology. Like all the other instances enumerated, it is based on the fact that the individual cells of an organ have a life of their own which is largely independent, so that they will continue in suitable circumstances to live, although the rest of the body to which they belonged may be dead.

But some cells, and the organs which are formed of them, are more necessary to maintain the life of the aggregate than others, on account of the nature of the functions which have become specialised in them. This is the case with the nerve-cells of the respiratory centre, since they preside over the movements which are necessary to effect oxygenation of the blood. It is also true for the cells which compose the heart, since this serves to pump oxygenated blood to all other cells of the body: without such blood most cells soon cease to live. Hence we examine respiration and heart to determine if life is present; when one or both of these are at a standstill we know that life cannot be maintained. These are not the only organs necessary for the maintenance of life, but the loss of others can be borne longer, since the functions which they subserve, although useful or even essential to the organism, can be dispensed with for a time. The life of some cells is therefore more, of others less, necessary for maintaining the life of the rest. On the other hand, the cells composing certain organs have in the course of evolution ceased to be necessary, and their continued existence may even be harmful. Wiedersheim has enumerated more than a hundred of these organs in the human body. Doubtless Nature is doing her best to get rid of them for us, and our descendants will some day have ceased to possess a vermiform appendix or a pharyngeal tonsil; until that epoch arrives we must rely for their removal on the more rapid methods of surgery!

The Maintenance of the Life of the Cell-aggregate in the Higher Animals. Co-ordinating Mechanisms.—We have seen that in the simplest multicellular organisms, where one cell of the aggregate differs but little from another, the conditions for the maintenance of the life of the whole are nearly as simple as those for individual cells. But the life of a cell-aggregate such as composes the bodies of the higher animals is maintained not only by the conditions for the maintenance of the life of the individual cell being kept favourable, but also by the co-ordination of the varied activities of the cells which form the aggregate. Whereas in the lowest Metazoa all cells of the aggregate are alike in structure and function and perform and share everything in common, in higher animals (and for that matter in the higher plants also) the cells have become specialised, and each is only adapted for the performance of a particular function. Thus the cells of the gastric glands are only adapted for the secretion of gastric juice, the cells of the villi for the absorption of digested matters from the intestine, the cells of the kidney for the removal of waste products and superfluous water from the blood, those of the heart for pumping blood through the vessels. Each of these cells has its individual life and performs its individual functions. But unless there were some sort of co-operation and subordination to the needs of the body generally, there would be sometimes too little, sometimes too much gastric juice secreted; sometimes too tardy, sometimes too rapid an absorption from the intestine; sometimes too little, sometimes too much blood pumped into the arteries, and so on. As the result of such lack of co-operation the life of the whole would cease to be normal and would eventually cease to be maintained.

We have already seen what are the conditions which are favourable for the maintenance of life of the individual cell, no matter where situated. The principal condition is that it must be bathed by a nutrient fluid of suitable and constant composition. In higher animals this fluid is the lymph, which bathes the tissue elements and is itself constantly supplied with fresh nutriment and oxygen by the blood. Some tissue-cells are directly bathed by blood; and in invertebrates, in which there is no special system of lymph-vessels, all the tissues are thus nourished. All cells both take from and give to the blood, but not the same materials or to an equal extent. Some, such as the absorbing cells of the villi, almost exclusively give; others, such as the cells of the renal tubules, almost exclusively take. Nevertheless, the resultant of all the give and take throughout the body serves to maintain the composition of the blood constant under all circumstances. In this way the first condition of the maintenance of the life of the aggregate is fulfilled by insuring that the life of the individual cells composing it is kept normal.

The second essential condition for the maintenance of life of the cell-aggregate is the co-ordination of its parts and the due regulation of their activity, so that they may work together for the benefit of the whole. In the animal body this is effected in two ways: first, through the nervous system; and second, by the action of specific chemical substances which are formed in certain organs and carried by the blood to other parts of the body, the cells of which they excite to activity. These substances have received the general designation of "hormones" (ὁρμάω, to stir up), a term introduced by Prof. Starling. Their action, and indeed their very existence, has only been recognised of late years, although the part which they play in the physiology of animals appears to be only second in importance to that of the nervous system itself; indeed, maintenance of life may become impossible in the absence of certain of these hormones.

Part Played by the Nervous System in the Maintenance of Aggregate Life. Evolution of a Nervous System.—Before we consider the manner in which the nervous system serves to co-ordinate the life of the cell-aggregate, let us see how it has become evolved.

The first step in the process was taken when certain of the cells of the external layer became specially sensitive to stimuli from outside, whether caused by mechanical impressions (tactile and auditory stimuli) or impressions of light and darkness (visual stimuli) or chemical impressions. The effects of such impressions were probably at first simply communicated to adjacent cells and spread from cell to cell throughout the mass. An advance was made when the more impressionable cells threw out branching feelers amongst the other cells of the organism. Such feelers would convey the effect of stimuli with greater rapidity and directness to distant parts. They may at first have been retractile, in this respect resembling the long pseudopodia of certain Rhizopoda. When they became fixed they would be potential nerve-fibres and would represent the beginning of a nervous system. Even yet (as Ross Harrison has shown), in the course of development of nerve-fibres, each fibre makes it appearance as an amœboid cell-process which is at first retractile, but gradually grows into the position it is eventually to occupy and in which it will become fixed.

In the further course of evolution a certain number of these specialised cells of the external layer sank below the general surface, partly perhaps for protection, partly for better nutrition; they became nerve-cells. They remained connected with the surface by a prolongation which became an afferent or sensory nerve-fibre, and through its termination between the cells of the general surface continued to receive the effects of external impressions; on the other hand, they continued to transmit these impressions to other, more distant cells by their efferent prolongations. In the further course of evolution the nervous system thus laid down became differentiated into distinct *afferent*, *efferent*, and *intermediary* portions. Once established, such a nervous system, however simple, must dominate the organism, since it would furnish a mechanism whereby the individual cells would work together more effectually for the mutual benefit of the whole.

It is the development of the nervous system, although not proceeding in all classes along exactly the same lines, which is the most prominent feature of the evolution of the Metazoa. By and through it all impressions reaching the organism from the outside are translated into contraction or some other form of cell-activity. Its formation has been the means of causing the complete divergence of the world of animals from the world of plants, none of which possess any trace of a nervous system. Plants react, it is true, to external impressions, and these impressions produce profound changes, and even comparatively rapid and energetic movements in parts distant from the point of application of the stimulus—as in the well known instance of the sensitive plant. But the impressions are in all cases propagated directly from cell to cell—not through the agency of nerve fibres; and in the absence of anything corresponding to a nervous system it is not possible to suppose that any plant can ever acquire the least glimmer of intelligence. In animals, on the other hand, from a slight original modification of certain cells has directly proceeded in the course of evolution the elaborate structure of the nervous system with all its varied and complex functions, which reach their culmination in the workings of the human intellect. "What a piece of work is a man! How noble in reason! How infinite in faculty! In form and moving how express and admirable! In action how like an angel! In apprehension how like a god!" But lest he be elated with his psychical achievements let him remember that they are but the result of the acquisition by a few cells in a remote ancestor of a slightly greater tendency to react to an external stimulus, so that these cells were brought into closer touch with the outer world; while, on the other hand, by extending beyond the circumscribed area to which their neighbours remained restricted, they gradually acquired a dominating influence over the rest. These dominating cells became nerve-cells; and now not only furnish the means for transmission of impressions from one part of the organism to another, but in the progress of time have become the seat of perception and conscious sensation, of the formation and association of ideas, of memory, volition, and all the manifestations of the mind!

Regulation of Movements by the Nervous System. Voluntary Movements.—The most conspicuous part played by the nervous system in the phenomena of life is that which produces and regulates the general movements of the body—movements brought about by the so-called voluntary muscles. These movements are actually the result of impressions imparted to sensory or afferent nerves at the periphery—*e.g.*, in the skin or in the several organs of special sense; the effect of these impressions may not be immediate, but can be stored for an indefinite time in certain cells of the nervous system. The regulation of movements—whether they occur instantly after reception of the peripheral impression or result after a certain lapse time; whether they are accompanied by conscious sensation or are of a purely reflex and unconscious character—is an intricate process, and the conditions of their co-ordination are of a complex nature involving not merely the causation of contraction of certain muscles, but also the prevention of contraction of others. For our present knowledge of these conditions we are largely indebted to the researches of Professor Sherrington.

Involuntary Movements.—A less conspicuous but no less important part played by the nervous system is that by which the contractions of involuntary muscles are regulated. Under normal circumstances these are always independent of consciousness, but their regulation is brought about in much the same way as is that of the contractions of voluntary muscles—viz., as the result of impressions received at the periphery. These are transmitted by afferent fibres to the central nervous system, and from the latter other impulses are sent down, mostly along the nerves of the sympathetic or autonomic system, of nerves, which either stimulate or prevent contraction of the involuntary muscles. Many involuntary muscles have a natural tendency to continuous or rhythmic contraction which is quite independent of the central nervous system; in this case the effect of impulses received from the latter is merely to increase or diminish the amount of such contraction. An example of this double effect is observed in connection with the heart, which—although it can contract regularly and rhythmically when cut off from the nervous system, and even if removed from the body—is normally stimulated to increased activity by impulses coming from the central nervous system through the sympathetic, or to diminished activity by others coming through the vagus.

Effects of Emotions.—It is due to the readiness by which the action of the heart is influenced in these opposite ways by the spread of impulses generated during the nerve-storms which we term "emotions" that in the language of poetry, and even of every day, the word "heart" has become synonymous with the emotions themselves.

The involuntary muscle of the arteries has its action similarly balanced. When its contraction is increased, the size of the vessels is lessened, and they deliver less blood; the parts they supply accordingly become pale in colour. On the other hand, when the contraction is diminished the vessels enlarge and deliver more blood; the parts which they supply become correspondingly ruddy. These changes in the arteries, like the effects upon the heart, may also be produced under the influence of emotions. Thus "blushing" is a purely physiological phenomenon due to diminished action of the muscular tissue of the arteries, whilst the pallor produced by fright is caused by an increased contraction of that tissue. Apart, however, from these conspicuous effects, there is constantly proceeding a less apparent but not less important balancing action between the two sets of nerve-fibres distributed to heart and blood-vessels; which are influenced in one direction or another by every sensation which we experience, and even by impressions of which we may be wholly unconscious, such as those which occur during sleep or anæsthesia, or which affect our otherwise insensitive internal organs, *Regulation of Secretion by the Nervous System.*—A further instance of nerve-regulation is seen in secreting glands. Not all glands are thus regulated, at least not directly; but in those which are, the effects are striking. Their regulation is of the same general nature as that exercised upon involuntary muscle, but it influences the chemical activities of the gland-cells and the outpouring of secretion from them. By means of this regulation a secretion can be produced or arrested, increased or diminished. As with muscle, a suitable balance is in this way maintained, and the activity of the glands is adapted to the requirements of the organism.

Regulation of Body Temperature.—Most of the digestive glands are thus influenced, as are the skin-glands which secrete sweat. And by the action of the nervous system upon the skin-glands, together with its effect in increasing or diminishing the blood-supply to the cutaneous blood-vessels, the temperature of our blood is regulated and is kept at the point best suited for maintenance of the life and activity of the tissues.

Effects of Emotions on Secretion.—The action of the nervous system upon the secretion of glands is strikingly exemplified, as in the case of its action upon the heart and blood-vessels by the effects of the emotions. Thus an emotion of one kind—such as the anticipation of food—will cause saliva to flow—"the mouth to water"; whereas an emotion of another kind—such as fear or anxiety—will stop the secretion, causing the "tongue to cleave unto the roof of the mouth," and rendering speech difficult or impossible. Such arrest of the salivary secretion also makes the swallowing of dry food difficult: advantage of this fact is taken in the "ordeal by rice" which used to be employed in the East for the detection of criminals.

Regulation by Chemical Agents: Hormones. Internal Secretions.—The activities of the cells constituting our bodies are controlled, as already mentioned, in another way than through the nervous system, viz., by chemical agents (hormones) circulating in the blood. Many of these are produced by special glandular organs, known as internally secreting glands. The ordinary secreting glands pour their secretions on the exterior of the body, or on a surface communicating with the exterior; the internally secreting glands pass the materials which they produce directly into the blood. In this fluid the hormones are carried to distant organs. Their influence upon an organ may be essential to the proper performance of its functions, or may be merely ancillary to it. In the former case removal of the internally secreting gland which produces the hormone, or its destruction by disease, may prove fatal to the organism.

Suprarenals.—This is the case with the suprarenal capsules; small glands which are adjacent to the kidneys, although having no physiological connection with these organs. A Guy's physician, Dr. Addison, in the middle of the last century showed that a certain affection, almost always fatal, since known by his name, is associated with disease of the suprarenal capsules. A short time after this observation a French physiologist, Brown-Séquard, found that animals from which the suprarenal capsules are removed rarely survive the operation for more than a few days. In the concluding decade of the last century interest in these bodies was revived by the discovery that they are constantly yielding to the blood a chemical agent (or hormone) which stimulates the contractions of the heart and arteries, and assists in the promotion of every action which is brought about through the sympathetic nervous system (Langley). In this manner the importance of their integrity has been explained, although we have still much to learn regarding their functions

Thyroid.—Another instance of an internally secreting gland which is essential to life, or at least to its maintenance in a normal condition, is the thyroid. The association of imperfect development or disease of the thyroid with disorders of nutrition and inactivity of the nervous system is well ascertained. The form of idiocy known as cretinism and the affection termed myxœdema are both associated with deficiency of its secretion; somewhat similar conditions to these are produced by the surgical removal of the gland. The symptons are alleviated or cured by the administration of its juice. On the other hand, enlargement of the thyroid, accompanied by increase of its secretion, produces symptoms of nervous excitation, and similar symptoms are caused by excessive administration of the glandular substance by the mouth. From these observations it is inferred that the juice contains hormones which help to regulate the nutrition of the body, and serve to stimulate the nervous system, for the higher functions of which they appear to be essential. To quote M. Gley, to whose researches we owe much of our knowledge regarding the functions of this organ:—"La genèse et l'exercice des plus hautes facultés de l'homme sont conditionnés par l'action purement chimique d'un produit de sécrétion. Que les psychologues méditent ces faits!"

Parathyroids.—The case of the parathyroid glandules is still more remarkable. These organs were discovered by Sandstrôm in 1880. They are four minute bodies, each no larger than a pin's head, imbedded in the thyroid. Small as they are, their internal secretion possesses hormones which exert a powerful influence upon the nervous system. If they are completely removed, a complex of symptoms, technically known as "tetany" is liable to occur, which is always serious, and may be fatal. Like the hormones of the thyroid itself, therefore, those of the parathyroids produce effects upon the nervous system, to which they are carried by the blood; although the effects are of a different kind.

Pituitary.—Another internally secreting gland which has evoked considerable interest during the last few years is the pituitary body. This is a small structure no larger than a cob-nut attached to the base of the brain. It is mainly composed of glandular cells. Its removal has been found (by most observers) to be fatal—often within two or three days. Its hypertrophy, when occurring during the general growth of the body, is attended by an undue development of the skeleton, so that the stature tends to assume gigantic proportions. When the hypertrophy occurs after growth is completed, the extremities—viz., the hands and feet, and the bones of the face—are mainly affected; hence the condition has been termed "acromegaly" (enlargement of extremities). The association of this condition with affections of the pituitary was pointed out in 1885 by a distinguished French physician, Dr. Pierre Marie. Both "giants" and "acromegalists" are almost invariably found to have an enlarged pituitary. The enlargement is generally confined to one part—the anterior lobe—and we conclude that this produces hormones which stimulate the growth of the body generally and of the skeleton in particular. The remainder of the pituitary is different in structure from the anterior lobe, and has a different function. From it hormones can be extracted which, like those of the suprarenal capsule, although not exactly in the same manner, influence the contraction of the heart and arteries. Its extracts are also instrumental in promoting the secretion of certain glands. When injected into the blood they cause a free secretion of water from the kidneys and of milk from the mammary glands, neither of which organs are directly influenced (as most other glands are) through the nervous system. Doubtless under natural conditions these organs are stimulated to activity by hormones which are produced in the pituitary, and which pass from this into the blood.

The internally secreting glands which have been mentioned (thyroid, parathyroid, suprarenal, pituitary) have, so far as is known, no other function than that of producing chemical substances of this character for the influencing of other organs, to which they are conveyed by the blood. It is interesting to observe that these glands are all of very small size, none being larger than a walnut, and some—the parathyroids—almost microscopic. In spite of this, they are essential to the proper maintenance of the life of the body, and the total removal of any of them by disease or operation is in most cases speedily fatal.

Notes.

1. The causation not only of movements but of various other manifestations of life by alterations in surface tension of living substance is ably dealt with by A. B. Macallum in a recent article in Asher and Spiro's "Ergebnisse der Physiologie," 1911. Macallum has described an accumulation of potassium salts at the more active surfaces of the protoplasm of many cells, and correlates this with the production of cell-activity by the effect of such accumulation upon the surface tension. The literature of the subject will be found in this article.

2. "Vital spontaneity, so readily accepted by persons ignorant of biology, is disproved by the whole history of science. Every vital manifestation is a response to a stimulus, a provoked phenomenon. It is unnecessary to say this is also the case with brute bodies, since that is precisely the foundation of the great principle of the inertia of matter. It is plain that it is also as applicable to living as to inanimate matter."—Dastre, *op. cit.*, p. 280.

3. The terms "assimilation" and "disassimilation" express the physical and chemical changes which occur within protoplasm as the result of the intake of nutrient material from the circumambient medium and its ultimate transformation into waste products which are passed out again into that medium; the whole cycle of these changes being embraced under the term "metabolism."

4. Leduc ("The Mechanism of Life," English translation by W. Deane Butcher, 1911) has given many illustrations of this statement. In the Report of the meeting of 1867 in Dundee is a paper by Dr. J. D. Heaton ("On Simulations of Vegetable Growths by Mineral Substances") dealing with the same class of phenomena. The conditions of osmosis in cells have been especially studied by Hamburger ("Osmotischer Druck und Ionenlehre," Wiesbaden, 1902-4).

5. B. Moore, in "Recent Advances in Physiology," 1906; Moore and Roaf, *Ibid.*; and "Further Advances in Physiology," 1909. Moore lays especial stress on the transformations of energy which occur in protoplasm. See on the question of vitalism Gley ("Revue Scientifique," 1911) and D'Arcy Thompson (Address to Section D at Portsmouth, 1911).

6. The most recent account of the chemistry of protoplasm is that by Botazzi ("Das Cytoplasma u. die Körpersäfte") in Winterstein's *Handb. d. vergl. Physiologie*, Bd. I., 1912. The literature is given in this article.

7. It is fair to point out that Dr. Bastian suggests that the formation of ultramicroscopic living particles may precede the appearance of the microscopic organisms which he describes ("The Origin of Life," 1911, p. 65).

8. The present position of the subject is succinctly stated by Dr. Chalmers Mitchell in his article on "Abiogenesis" in the *Encyclopædia Britannica.* Dr. Mitchell adds:—"It may be that in the progress of science it may yet be possible to construct living protoplasm from non-living material. The refutation of abiogenesis has no further bearing on this possibility than to make it probable that if protoplasm ultimately be formed in the laboratory, it will be by a series of steps, the earlier steps being the formation of some substance, or substances, now unknown, which are not protoplasm. Such intermediate stages may have existed in the past." And Huxley in his Presidential Address at Liverpool in 1870 says:—"But though I cannot express this conviction" (*i.e.*, of the impossibility of the occurrence of abiogenesis, as exemplified by the appearance of organisms in hermetically sealed and sterilised flasks) "too strongly, I must carefully guard myself against the supposition that I intend to suggest that no such thing as abiogenesis ever has taken place in the past or ever will take place in the future. With organic chemistry, molecular physics, and physiology yet in their infancy and every day making prodigious strides, I think it would be the height of presumption for any man to say that the conditions under which matter assumes the properties we call "vital" may not, some day, be artificially brought together."

9. The arguments in favour of this proposition have been arrayed by Meldola in his Herbert Spencer Lecture, 1910, pp. 16–24. Meldola leaves the question open whether such evolution has occurred only in past years or is also taking place now. He concludes that whereas certain carbon compounds have survived by reason of possessing extreme stability, others—the precursors of living matter—survived owing to the possession of extreme lability and adaptability to variable conditions of environment. A similar suggestion was previously made by Lockyer, "Inorganic Evolution," 1900, pp. 169, 170.

10. First suggested, according to Dastre, by de Salles-Guyon (Dastre, *op. cit.*, p. 252). The theory received the support of Helmholtz.

11. The history of science shows how dangerous it is to brush aside mysteries—*i.e.*, unsolved problems—and to interpose the barrier placarded "eternal—no thoroughfare."—R. Meldola, Herbert Spencer Lecture, 1910.

12. Some authorities, such as Errere, contend, with much probability, that the conditions in interstellar space are such that life, as we understand it, could not possibly exist there.

13. As Verworn points out, such theories would equally apply to the origin of any other chemical combination, whether inorganic or organic, which is met with on our globe, so that they lead directly to absurd conclusions.—"Allgemeine Physiologie," 1911.

14. As Meldola insists, this general acceptance was in the first instance largely due to the writings of Herbert Spencer:—"We are now prepared for evolution in every domain. . . . As in the case of most great generalisations, thought had been moving in this direction for many years. . . . Lamarck and Buffon had suggested a definite mechanism of organic development, Kant and Laplace a principle of celestial evolution, while Lyell had placed geology upon an evolutionary basis. The principle of continuity was beginning to be recognised in physical science. . . . It was Spencer who brought these independent lines of thought to a focus, and who was the first to make any systematic attempt to show that the law of development expressed in its widest and most abstract form was universally followed throughout cosmical processes, inorganic, organic, and superorganic."—*Op. cit.*, p. 14.

15. There still exist, in fact, forms of life which the microscope cannot show us (E. A. Minchin, Presidential Address to Quekett Club, 1911), and germs which are capable of passing through the pores of a Chamberland filter.

16. Chalmers Mitchell (Article "Life," *Encycl. Brit.*, eleventh edition) writes as follows:—"It has been suggested from time to time that conditions very unlike those now existing were necessary for the first appearance of life, and must be repeated if living matter is to be reconstituted artificially. No support for such a view can be derived from observations of the existing conditions of life."

17. "Spontaneous generation of life could only be perceptually demonstrated by filling in the long terms of a series between the complex forms of inorganic and the simplest forms of organic substance. Were this done, it is quite possible that we should be unable to say (especially considering the vagueness of our definitions of life) where life began or ended."—K. Pearson, "Grammar of Science," second edition, 1900, p. 350.

18. See "On the Production of Elements," W. Crookes, Address to Section B, Brit. Assoc., 1886; T. Preston, *Nature*, vol. lx., p. 180; J. J. Thomson, *Phil. Mag.*, 1897, p. 311; Norman Lockyer, *op. cit.*, 1900; G. Darwin, Pres. Addr. Brit. Assoc., 1905.

19. Lankester (Art. "Protozoa," *Encycl. Brit.*, tenth edition) conceives that the first protoplasm fed on the antecedent steps in its own evolution. F. J. Allan (*Brit. Assoc. Reports*, 1896) comes to the conclusion that living substance is probably constantly being produced, but that this fails to make itself evident owing to the substance being seized and assimilated by existing organisms. He believes that "in accounting for the first origin of life on

this earth it is not necessary that, as Pflüger assumed, the planet should have been at a former period a glowing fire-ball." He "prefers to believe that the circumstances which support life would also favour its origin." And elsewhere :—"Life is not an extraordinary phenomenon, not even an importation from some other sphere, but rather the actual outcome of circumstances on this earth."

(To be continued)

SCIENTIFIC METHODS IN EARTHENWARE MANUFACTURE.

It has been said that the technology of the lower grades of pottery (common earthenware, Rockingham ware, majolica, faience, and stoneware) is comparatively simple ; this is undoubtedly correct, viewing the earthenware industry as it exists to-day, but it is also true that less advantage has been taken of scientific methods and research in earthenware manufacture than in other industries. Harkort has recently discussed (*Zeit. Angew. Chem.*, xxiv., 2348) the composition of earthenware bodies and its relation to scientific results ; it is from this contribution that the following material is taken.

The strength of earthenware is dependent, not as in porcelain on the fusion of felspar, but principally upon the close packing of the clay particles ; it follows, therefore, that a determination of strength merely by the "ring" of the articles leaves out of account such factors as thickness, shape, &c. The value of earthenware depends, to a large extent, upon the flawless adhesion of the glaze, and as a defect may not become apparent for a considerable period, a rapid method of testing is important. Harkort heats the test-pieces in an electric oven, in which the temperature is gradually increased, and quenches them in water from different temperatures. His observations, extending for a year, have demonstrated that test-pieces which will stand higher temperatures withstand ordinary variations of temperatures longer ; and that if no cracks are developed at a certain quenching temperature, a satisfactory deportment towards changes of temperature can be predicted. Seger attributed the formation of cracks and the splitting off of a glaze to a difference between the coefficients of expansion of the body and the glaze. Damaur made measurements on earthenware bodies and confirmed Seger's assumption ; he showed that the coefficient of expansion increased with an increase in the silica content, but was affected by the temperature of firing, if this is raised to the point of fusion. Harkort finds that silica lowers the expansion in glazes, but in sintered bodies the opposite effect is observed, since it retards the drawing together of the particles of clay substance ; and that when the silica is fine-grained, the bodies are less liable to have glaze cracks. By means of his quenching process, definite limits have been found for the ratio of clay substance to silica in earthenware bodies. A certain amount of clay substance must be present to yield an easily workable body, but the silica content must be such that the coefficient of expansion represents an applicable value. It is pointed out that while finely ground silica must be added as sand is eliminated from well washed clays, its addition has a tendency to weaken a body, and a high temperature of firing which would tend to strengthen would be disadvantageous from the point of view of the formation of glazed cracks, as the density developed promotes their formation. It is found that the larger the fire-shrinkage is, the smaller the coefficient of expansion, and the greater the sintering the larger the expansion. Additions of lime and felspar increase the strength of the biscuit ; the effect of the felspar is attributable to its fusion, but at that temperature deformation results, although this is not observed when lime is added in amounts up to 20 per cent ; lime alone softens a body, and the burning temperature is slightly increased.—*Journal of Industrial and Engineering Chemistry*, iv., No. 5.

SILOXIDE, AN UNRIVALLED SUBSTITUTE FOR QUARTZ GLASS.*

By Dr. Ing. FELIX THOMAS.

The properties of quartz glass are so well known to-day that it is quite unnecessary to give any detailed description of them. The widespread use of this product—as, for example, in chemical manufactures—shows what importance is attached to the typical properties of quartz glass, its power to resist the action of acids, and its insensibility to widely divergent changes in temperature. These and other advantages are particularly apparent in vessels constructed from pure rock-crystal, which, however, are at the present time still far too expensive for industrial use and are employed only in the laboratory and for a few special purposes ; I refer to the quartz glass mercury vapour lamp. The material commonly designated as "quartz glass"—(the term "sand glass" has failed to establish itself)—is, as is well known, pure, amorphous, but non-transparent silicic acid, which has all the outward properties of glass, but in chemical composition is of course not glass at all. Moreover, this opaque quartz glass, which at the present time is on the market principally as an English manufacture under the name of "vitreosil," has essentially all the prominent properties of molten rock-crystal, though in a somewhat less degree. In particular it lacks the high mechanical stability of the latter and is more liable to devitrification, that is to say, it shows a far greater tendency to pass at high temperatures from the amorphous to the crystalline state, whereby the valuable mechanical properties are almost entirely lost ; it is also extremely sensitive to the basic metallic oxides and alkaline earths, and of course especially so to alkalis proper.

(*Note.*—Mention may here be made of the interesting work of A. Blake dealing with the loss of stability caused by devitrification and the change of structure connected with it. Compare also "Die Glasindustrie," 1911, xxii., Nos. 43—45).

An endeavour had therefore to be made to discover a material in which the above-mentioned deleterious properties of quartz glass should be entirely, or at least partly, lacking. This was achieved in a certain degree by the smelting of glasses of a thoroughly acid character from mixtures of silicic acid with oxides of zirconium, titanium, &c., which were chosen principally because their high melting-point appeared peculiarly adapted to give from the outset to the new glasses one of the chief advantages of quartz glass, namely, a high degree of infusibility, and because in their ability to resist the action of acids they occupy almost the same place.

At the request of Privy Councillor Prof. W. Borchers, I undertook to experiment with the new glasses with a view to determining how their most important properties for technical and scientific purposes can be compared with those of quartz glass. Although these experiments are not yet concluded I feel constrained to publish here for the benefit of experts the surprising and significant results which have so far attended my investigations. For these glasses, which are made from a mixture of pure quartz and acid oxides possessing a high-melting-point, I have chosen the collective name of "siloxide," which implies a solution of oxides or their silicates in a surplus of silicic acid. (In a chemical sense these glasses are distinguished from glasses proper by the fact that they are formed from silicic acid and acid oxides, whereas glass as such consists of silicic acid and a preponderating amount of basic oxides). The experiments so far carried out extend on the one hand to zircon oxide-silicic acid, and on the other to titanium oxide-silicic acid, and in part also to the zircon oxide-titanium oxide-silicic acid group.

The method of experimentation and other details I propose to publish in a comprehensive treatise at the con

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* From the *Chemiker Zeitung*, 1912, No. 4.

clusion of my tests with the other oxides. At this point I will only make known the results so far as they are of practical interest and most clearly illustrate the advantages which the new material possesses over quartz glass.

1. *Zircon Oxide-Silicic Acid* (*Z-Siloxide, Zircon-glass*).

The objects experimented with consisted of tubes of different diameters (3—30 mm.) of a uniform length of 200 mm.; of cubes of different sizes; and rods having a cross section of 1 cm.^{2} and a length of 140 mm. These were handed to me by the holder of the patents for these glasses, Dr. Franz Wolf-Burckhardt, of the Electrothermal Works at Seebach-Zurich, through the Zirkonglas-Gesellschaft m.b.H. of Frankfort-on-the-Maine, which has taken over the sale of siloxide.

1. *External Properties, Colour, Finish, &c.*—The superficial appearance of the thin tubes of zircon glass is indeed not as alluring as that of the English vitreosil tubes with their silky surface, but this is the only point in which zircon glass falls short of vitreosil. In all other respects, so far as the experiments have yet been carried out, zircon glass has considerable advantages over vitreosil and also over the quartz glass of the Deutsche Quartz-Gesellschaft in Beuel, now in liquidation, whose products, so far as quality is concerned, were inferior to the English vitreosil. The zircon glass products have a dull finish and, if rich in zircon, a pale yellow colour. They appear to be denser and firmer than the ordinary quartz glass products, as is clearly shown when zircon glass is cut on corundum wheels, the wear and tear of these being much more remarkable.

2. *Resistance* (*a*) *to Bending.*—As a general truth, applying equally to all opaque quartz glass and to every kind of siloxide, I may state at the outset that the relative breaking strength (measured in kgs. per sq. cm.) of rods and tubes having diameters up to 8 or 10 mm. is considerably higher than in the case of similar bodies of greater diameters. Thus Wachenroder, for example (*Chem. Nahr.*, 1910, No. 10), puts the breaking strength of quartz tubes having an external diameter of 4 mm. at 860 kgs. per sq. cm., whereas those with a diameter of 7·5 mm. have a breaking strength of only 643 kgs. per sq. cm. I myself found in the case of tubes of the same material (vitreosil) with a diameter of 8·5 mm., a breaking strength of only 430 kgs. per sq. cm. In the above-mentioned work by Blake the relative breaking strength of glazed quartz glass rods having a rectangular cross section (1—3 mm. × 5—10 mm.) is given as 382 kgs., that of the silk-finished material (presumably also vitreosil) as only 281 kgs. Blake's observation that the silk-finished material shows the lowest degree of infrangibility coincides with my own experience. This material is in a state of tension similar to that of badly annealed glass; for instance, if a thin tube of vitreosil is laid somewhat roughly on a stone or iron plate, it usually snaps clean off at one point, just as if it had been cut. In some cases I observed that such a tube when so treated actually flew into several fragments and that the fractured surfaces were quite smooth and even. In most cases a few particles were hurled to some considerable distance. On subjecting such tubes to a strain on the bending machine I made the following observation:—If the specimens tested remained for several seconds under a strain less than that of their breaking-point, the fracture took place suddenly, without any alteration in the load, so that the ends of the tubes were hurled some decimetres away. I have therefore come to the same conclusion as Blake, that the brittleness of the silk-finished material is due to the fact that it is in a state of constant tension.

In order to arrive at figures for purposes of comparison I selected for experiment tubes of some 30 mm. external diameter, having first satisfied myself by some preliminary trials that a variation one way or another of a few mm. in he diameter causes no essential loss or gain in the relative eaking strengths; only in the case of very thin-alled tubes was the breaking strength especially unsatisactory, wherefore the values obtained were eliminated by computing the mean breaking strength. The results of the tests for bending strength are given in Table I. below. In this table V denotes vitreosil, a pure quartz glass manufactured by the Thermal Syndicate, Ltd., Wallsend, England; "Q" represents the pure quartz glass of Dr. Franz Wolf-Burckhardt, of the Electrothermal Works at Seebach-Zürich, Switzerland; ZS stands for zircon glass, a product of the last mentioned firm. The figures after ZS denote the percentage of ZrO_2 in the composition.

TABLE I.

Description.	Breaking strength in kgs./sq. cm. (*a*.)	(*b*).	(*c*).	Thickness of tube in mm. (*a*).	(*b*).	(*c*).
V	110	86		3	2·8	
Q	150	350	148	2·1	2·9	2·0*
ZS 0·1	350	274		3·3	3·2	
ZS 0·5	219	175		3·4	3·3†	
ZS 1·0	326	416	380	3·1	3·4	3·4
ZS 2·0	227	162		3·0	3·1‡	
ZS 2·5	255	183		2·1	1·9	

* Probably an exceptional value.
† Thin places in the tube.
‡ Broken at the end.

It appears that a tube of smaller thickness shows a smaller relative breaking strength than a similar tube of greater thickness, so that tubes of about 30 mm. diameter ought to have a thickness of not very little less than 3 mm., if they are to withstand the strains of flexure given above.

(To be continued)

MISCELLANEOUS.

The Royal Photographic Society of Great Britain.—The Annual Exhibition of the Royal Photographic Society is being held this year at the Galleries of the Royal Society of British Artists in Suffolk Street, Pall Mall, from September 2nd till September 21st. The Exhibition as usual is divided into two main sections, the pictorial and the scientific, and while the former is, and always will be the more popular, it is in the latter that improvements are most frequently made and shown, to be afterwards adapted to the use of the more popular side of the art. Among the exhibits calling for special attention, is one important from a practical and commercial point of view. It is, perhaps, not generally known, that the firms who print notes, cheques, bonds, and other financial documents are constantly engaged in a friendly rivalry to secure the inviolability of such things. One firm devises a method of engraving or printing calculated to baffle the skill of the enterprising forger, and the other firms at once proceed to devise methods of overcoming the difficulties which the new process presents to the copier, with the result that new improvements are made, and the forger's task is rendered still more onerous. The exhibit referred to shows the results obtained by a new process by which the whole of the ink on an engraving, no matter how old, may be transferred, without the use of a lens, to a glass plate from which a copper or steel plate can be made. This etched plate will yield prints indistinguishable from the original, as may be verified by inspection of the examples shown. The details of the process are, for obvious reasons, not made public, but are stated to be of extreme simplicity, calling for neither great manipulative skill nor expensive apparatus. A method of this kind cannot long be kept secret, and it behoves bankers and others concerned in the issuing and handling of valuable financial script to examine the samples shown, and take steps to ensure that the documents they employ are produced by a process which cannot be violated by this method. Colour photography moves slowly to the long wished-for goal of prints in natural colours upon paper. Two steps in this direction had been made quite recently, and prints are shown upon the walls.

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INAUGURAL ADDRESS OF THE PRESIDENT,
Prof. E. A. Schäfer, LL.D., D.Sc., M.D., F.R.S.

(Concluded from p. 119).

Pancreas.—There are, however, organs in the body yielding internal secretions to the blood in the shape of hormones, but exercising at the same time other functions. A striking instance is furnished by the pancreas, the secretion of which is the most important of the digestive juices. This—the pancreatic juice—forms the external secretion of the gland, and is poured into the intestines, where its action upon the food as it passes out from the stomach has long been recognised. It was, however, discovered in 1889 by von Mering and Minkowski that the pancreas also furnishes an internal secretion, containing a hormone which is passed from the pancreas into the blood by which it is carried first to the liver and afterwards to the body generally. This hormone is essential to the proper utilisation of carbohydrates in the organism. It is well known that the carbohydrates of the food are converted into grape-sugar, and circulate in this form in the blood, which always contains a certain amount; the blood conveys it to all the cells of the body, and they utilise it as fuel. If, owing to disease of the pancreas or as the result of its removal by surgical procedure, its internal secretion is not available, sugar is no longer properly utilised by the cells of the body, and tends to accumulate in the blood; from the blood the excess passes off by the kidneys, producing diabetes.

Duodenum.—Another instance of an internal secretion furnished by an organ which is devoted largely to other functions is the "pro-secretin" found in the cells lining the duodenum. When the acid gastric juice comes into contact with these cells it converts their pro-secretin into "secretin." This is a hormone which is passed into the blood and circulates with that fluid. It has a specific effect on the externally secreting cells of the pancreas, and causes the rapid outpouring of pancreatic juice into the intestine. This effect is similar to that of the hormones of the pituitary body upon the cells of the kidney and mammary gland. It was discovered by Bayliss and Starling.

Internal Secretions of the Reproductive Organs.—The re-productive glands furnish in many respects the most interesting examples of organs which—besides their ordinary products, the germ- and sperm-cells (ova and spermatozoa)—form hormones which circulate in the blood and effect changes in cells of distant parts of the body. It is through these hormones that the secondary sexual characters, such as the comb and tail of the cock, the mane of the lion, the horns of the stag, the beard and enlarged larynx of a man, are produced, as well as the many differences in form and structure of the body which are characteristic of the sexes. The dependence of these so-called secondary sexual characters upon the state of development of the reproductive organs has been recognised from time immemorial, but has usually been ascribed to influences produced through the nervous system, and it is only in recent years that the changes have been shown to be brought about by the agency of internal secretions and hormones, passed from the reproductive glands into the circulating blood. (The evidence is to be found in F. H. A. Marshall, "The Physiology of Reproduction," 1911).

Chemical Nature of Hormones.—It has been possible in only one or two instances to prepare and isolate the hormones of the internal secretions in a sufficient condition of purity to subject them to analysis, but enough is known about them to indicate that they are organic bodies of a not very complex nature, far simpler than proteins and even than enzymes. Those which have been studied are all dialysable, are readily soluble in water but insoluble in alcohol, and are not destroyed by boiling. One at least—that of the medulla of the suprarenal capsule—has been prepared synthetically, and when their exact chemical nature has been somewhat better elucidated it will probably not be difficult to obtain others in the same way.

From the above it is clear that not only is a co-ordination through the nervous system necessary in order that life shall be maintained in a normal condition, but a chemical co-ordination is no less essential. These may be independent of one another; but, on the other hand, they may react upon one another. For it can be shown that the production of some at least of the hormones is under the influence of the nervous system (Biedl, Asher, Elliott); whilst, as we have seen, some of the functions of the nervous system are dependent upon hormones.

Protective Chemical Mechanisms. Toxins and Antitoxins.—Time will not permit me to refer in any but the briefest manner to the protective mechanisms which the cell aggregate has evolved for its defence against disease, especially disease produced by parasitic micro-organisms. These, which belong with few exceptions to the Protista, are, without doubt, the most formidable enemies which the multicellular Metazoa, to which all the higher animal organisms belong, have to contend against. To such micro-organisms are due *inter alia* all diseases which are liable to become epidemic, such as anthrax and rinderpest in cattle, distemper in dogs and cats, small-pox, scarlet fever, measles, and sleeping sickness in man. The advances of modern medicine have shown that the symptoms of these diseases—the disturbances of nutrition, the temperature, the lassitude or excitement, and other nervous disturbances—are the effects of chemical poisons (*toxins*) produced by the micro-organisms, and acting deleteriously upon the tissues of the body. The tissues, on the other hand, endeavour to counteract these effects by producing other chemical substances destructive to the micro-organisms or antagonistic to their action; these are known as *anti-bodies*. Sometimes the protection takes the form of a subtle alteration in the living substance of the cells which renders them for a long time, or even permanently, insusceptible (immune) to the action of the poison. Sometimes certain cells of the body, such as the white corpuscles of the blood, eat the invading micro-organisms, and destroy them bodily by the action of chemical agents within their protoplasm. The result of an illness thus depends upon the result of the struggle between these opposing forces—the micro-organisms on the one hand and the cells of the body on the other—both of which fight with chemical weapons. If the cells of the body do not succeed in destroying the invading organisms it is certain that the invaders will in the long run destroy them, for in this combat no quarter is given. Fortunately we have been able, by the aid of animal experimentation, to acquire some knowledge of the manner in which we are attacked by micro-organisms and of the methods which the cells of our body adopt to repel the attack, and the knowledge is now extensively utilised to assist our defence. For this purpose protective serums or anti-toxins, which have been formed in the blood of other animals, are employed to supplement the action of those which our own cells produce.

Parasitic Nature of Diseases.—It is not too much to assert that the knowledge of the parasitic origin of so many diseases and of the chemical agents which on the one hand cause, and on the other combat, their symptoms, has transformed medicine from a mere art practised empirically, into a real science based upon experiment. The transformation has opened out an illimitable vista of possibilities in the direction not only of cure, but, more important still, of prevention. It has taken place within the memory of most of us who are here present. And only last February the world was mourning the death of one of the greatest of its benefactors—a former President of this Association (Lord Lister was President at Liverpool in 1896)—who, by applying this knowledge to the practice of surgery, was instrumental, even in his own lifetime, in saving more lives than were destroyed in all the bloody wars of the nineteenth century!

Senescence and Death.—The question has been debated whether, if all accidental modes of destruction of the life of the cell could be eliminated, there would remain a possibility of individual cell-life, and even of aggregate cell-life, continuing indefinitely; in other words, Are the phenomena of senescence and death a natural and necessary sequence to the existence of life? To most of my audience it will appear that the subject is not open to debate. But some physiologists (*e.g.*, Metchnikoff) hold that the condition of senescence is itself abnormal; that old age is a form of disease or is due to disease, and, theoretically at least, is capable of being eliminated. We have already seen that individual cell-life, such as that of the white blood corpuscles and of the cells of many tissues, can under suitable conditions be prolonged for days or weeks or months after general death. Unicellular organisms kept under suitable conditions of nutrition have been observed to carry on their functions normally for prolonged periods and to show no degeneration such as would accompany senescence. They give rise by division to others of the same kind, which also, under favourable conditions, continue to live, to all appearance indefinitely. But these instances, although they indicate that in the simplest forms of organisation existence may be greatly extended without signs of decay, do not furnish conclusive evidence of indefinite prolongation of life. Most of the cells which constitute the body, after a period of growth and activity, sometimes more, sometimes less prolonged, eventually undergo atrophy and cease to perform satisfactorily the functions which are allotted to them. And when we consider the body as a whole, we find that in every case the life of the aggregate consists of a definite cycle of changes which, after passing through the stages of growth and maturity, always leads to senescence, and finally terminates in death. The only exception is in the reproductive cells, in which the processes of maturation and fertilisation result in rejuvenescence, so that instead of the usual downward change towards senescence, the fertilised ovum obtains a new lease of life, which is carried on into the new-formed organism. The latter again itself ultimately forms reproductive cells, and thus the life of the species is continued. It is only in the sense of its propagation in this way from one generation to another that we can speak of the indefinite continuance of life: we can only be immortal through our descendants!

Average Duration of Life and Possibility of its Prolongation.—The individuals of every species of animal appear to have an average duration of existence. (This was regarded by Buffon as related to the period of growth, but the ratio is certainly not constant. The subject is discussed by Ray Lankester in an early work:—"On Comparative Longevity in Man and Animals," 1870). Some species are known the individuals of which live only for a few hours, whilst others survive for a hundred years. (The approximately regular periods of longevity of different species of animals furnishes a strong argument against the theory that the decay of old age is an accidental phenomenon, comparable with disease). In man himself the average length of life would probably be greater than the threescore and ten years allotted to him by the Psalmist if we could eliminate the results of disease and accident; when these results are included it falls far short of that period. If the terms of life given in the purely mythological part of the Old Testament were credible, man would in the early stages of his history have possessed a remarkable power of resisting age and disease. But, although many here present were brought up to believe in their literal veracity, such records are no longer accepted even by the most orthodox of theologians, and the nine hundred odd years with which Adam and his immediate descendants are credited, culminating in the nine hundred and sixty-nine of Methuselah, have been relegated, with the account of Creation and the Deluge, to their proper position in literature. When we come to the Hebrew Patriarchs, we notice a considerable diminution to have taken place in what the insurance offices term the "expectation of life." Abraham is described as having lived only to 175 years, Joseph and Joshua to 110, Moses to 120; even at that age "his eye was not dim nor his natural force abated." We cannot say that under ideal conditions all these terms are impossible; indeed, Metchnikoff is disposed to regard them as probable; for great ages are still occasionally recorded, although it is doubtful if any as considerable as these are ever substantiated. That the expectation of life was better then than now would be inferred from the apologetic tone adopted by Jacob when questioned by Pharoah as to his age:—"The days of the years of my pilgrimage are a hundred and thirty years; few and evil have the days of the years of my life been, and have not attained unto the days of the years of the life of my fathers in the days of their pilgrimage." David, to whom, before the advent of the modern statistician, we owe the idea that seventy years is to be regarded as the normal period of life (the expectation of life of a healthy man of fifty is still reckoned at about twenty years), is himself merely stated to have "died in a good old age." The periods recorded for the Kings show a considerable falling-off as compared with the Patriarchs; but not a few were cut off by violent deaths, and many lived lives which were not ideal. Amongst eminent Greeks and Romans few very long lives are recorded, and the same is true of historical persons in mediæval and modern history. It is a long life that lasts much beyond eighty; three such linked together carry us far back into history. Mankind is in this respect more favoured than most mammals, although a few of these surpass the period of man's existence ("Hominis ævum cæterorum animalium omnium superat præter admodum paucorum"; Francis Bacon, "Historia vitæ et mortis, 1637"). Strange that the brevity of human life should be a favourite theme of preacher and poet when the actual term of his "erring pilgrimage" is greater than that of most of his fellow creatures!

The End of Life.—The modern applications of the principles of preventive medicine and hygiene are no doubt operating to lengthen the average life. But even if the ravages of disease could be altogether eliminated, it is certain that at any rate the fixed cells of our body must eventually grow old and ultimately cease to function; when this happens to cells which are essential to the life of the organism, general death must result. This will always remain the universal law, from which there is no escape. "All that lives must die, passing through nature to eternity."

Such natural death unaccelerated by disease—is not death by disease as unnatural as death by accident?—should be a quiet, painless phenomenon, unattended by violent change. As Dastre expresses it, "The need of death should appear at the end of life, just as the need of sleep appears at the end of the day." The change has been led gradually up to by an orderly succession of phases, and is itself the last manifestation of life. Were we all certain of a quiet passing—were we sure that there would be "no moaning of the bar when we go out to sea"—we could anticipate the coming of death after a ripe old age without apprehension. And if ever the time shall arrive when man will have learned to regard this change as a simple physiological process, as natural as the oncoming of sleep, the approach of the fatal shears will be as generally welcomed as it is now abhorred. Such a day is still distant; we can hardly say that its dawning is visible. Let us at least hope that, in the manner depicted by Dürer in his well-known etching. the sunshine which science irradiates may eventually put to flight the melancholy which hovers, bat-like, over the termination of our lives, and which even the anticipation of a future happier existence has not hitherto succeeded in dispersing.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

DUNDEE, 1912.

By Prof. A. SENIER, Ph.D., M.D., D.Sc.,
President of the Section.

PART I.

The Nature and Method of Chemistry.—Perhaps there is no intellectual occupation which demands more of the faculty of imagination than the pursuit of chemistry, and perhaps also there is none which responds more generously to the yearnings of the inquirer. It is surely no commonplace occurrence that in experimental laboratories day by day the mysterious recesses of Nature are disclosed and facts previously quite unknown are brought to light. The late Sir Michael Foster, in his Presidential Address at the Dover meeting, said:—"Nature is ever making signs to us, she is ever whispering the beginnings of her secrets." The facts disclosed may have general importance, and necessitate at once changes in the general body of theory; and happily, also, they may at once find useful application in the hands of the technologist. Recent examples are the discoveries in radio-activity, which have found an important place as an aid to medical and surgical diagnosis, and as a method of treatment, and have also led to the necessity of our revising one of the fundamental doctrines of the theory of chemistry—the indivisibility of atoms. But the facts disclosed may not be general, or even seem important; they may appear isolated and to have no appreciable bearing on theory or practice—our journals are crowded with such—but he would be a bold man who would venture to predict that the future will not find use for them in both respects. To be the recipient of the confidences of Nature; to realise in all their virgin freshness new facts recognised as positive additions to knowledge, is certainly a great and wonderful privilege, one capable of inspiring enthusiasm as few other things can.

While the method of discovery in chemistry may be described, generally, as inductive, still all the modes of inference which have come down to us from Aristotle, analogical, inductive, and deductive, are freely made use of. A hypothesis is framed which is then tested, directly or indirectly, by observation and experiment. All the skill, all the resource the inquirer can command, is brought into his service; his work must be accurate; and with unqualified devotion to truth he abides by the result, and the hypothesis is established, and becomes part of the theory of science, or is rejected or modified. In framing or modifying hypotheses imagination is indispensable. It may be that the power of imagination is necessarily limited by what is previously inexperience—that imagination cannot transcend experience; but it does not follow, therefore, that it cannot construct hypotheses capable of leading research. I take it that what imagination actually does is—it rearranges experience, and puts it into new relations, and with each successive discovery it gains in material for this process. In this respect the framing of a hypothesis is like experimenting, wherein the operator brings matter and energy already existing in Nature into new relations, new circumstances, with the object of getting new results. The stronger the imaginative power the greater must be the chance of success. *The Times*, in a recent leading article on Science and Imagination, says:—"It has often been said that the great scientific discoverers . . . see a new truth before they prove it, and the process of proof is only a demonstration of the truth to others and a confirmation of it to their own reason." While never forgetting the essentially tentative nature of a hypothesis, still, until it has been tested and found wanting, there should be some confidence or faith in its truthfulness; for nothing but a belief in its eventual success can serve to sustain an inquirer's ardour when, as so often happens, he is met by difficulties well-nigh insuperable. In a well known passage Faraday says:—"The world little knows how many of the thoughts and theories which have passed through the mind of a scientific investigator have been crushed in silence and secrecy by his own severe criticism and adverse examination; that in the most successful instances not a tenth of the suggestions, the hopes, the wishes, the preliminary conclusions have been realised."

But a hypothesis to be useful, to be admitted as a candidate for rank as a scientific theory, must be capable of immediate, or at least of possible, verification. Many years ago, in the old Berlin laboratory in the Georgenstrasse, when our imaginations were wont, as sometimes happened, to soar too far above the working benches, our great leader used to say:—"I will listen readily to any suggested hypothesis, but on one condition—that you show me a method by which it can be tested." As a rule, I confess we had to return to the workaday world, to our bench experiments. No one felt the importance of the careful and correct employment of hypotheses more than Liebig. In his Faraday lecture Hofmann says of Liebig:—"If he finds his speculation to be in contradiction with recognised facts, he endeavours to set these facts aside by new experiments, and failing to do so he drops the speculation." Again, he gives an illustration of how on one occasion, not being able to divest himself himself of a hypothesis, he missed the discovery of the element bromine. While at Kreuznach he made an investigation of the mother-liquor of the well known salt, and obtained a considerable quantity of a heavy red liquid which he believed to be a chloride of iodine. He found the properties to be different in many respects from chloride of iodine; still, he was able to satisfy all his doubts, and he put the liquid aside. Some months later he received Balard's paper announcing the discovery of bromine, which he recognised at once as the red liquid which he had previously prepared and studied. Thus, though imagination is indispensable to a chemist, and though I think chemists should be, and let us hope are, poets, or at least possess the poetic temperament, still, little can be achieved without a thorough laboratory training; and he who discovers an improved experimental method or a new differentiating reaction is as surely contributing to the advancement of science as he who creates in his imagination the most beautiful and promising hypothesis.

It may never be possible to trace in civilisation's early records the exact period and place of the origin and beginnings of our science, but the historical student has been led, it appears to me, by a sure instinct to search for this in such lands of imaginative story as ancient Egypt and Arabia. For is there anything more fittingly comparable with the marvellous experience of a chemical laboratory than the wonderful and fascinating stories that have come down to us in "The Arabian Nights"? Those monuments of poetical building of which Burton, in the introduction to his great translation, says that in times of official exile in less-favoured lands, in the wilds of Africa and America, he was lifted in imagination by the jinn out of his dull surroundings, and was borne off by him to his beloved Arabia, where under diaphanous skies he would see again "the evening star hanging like a golden lamp from the pure front of the western firmament; the afterglow transfiguring and transforming as by magic the gazelle-brown and tawny-clay tints and the homely and rugged features of the scene into a fairy-land lit with a light which never shines on other soils or seas. Then would appear, &c." I cannot help thinking that the study of such books as this, the habit of exercising the imagination by reconstructing the scenes of beauty and enchantment which they describe, might do much to strengthen and sharpen the imaginative faculty, and greatly increase its efficiency as an indispensable tool in the hands of the pioneer who seeks to extend the boundaries of knowledge. *The Times*, in the leading article already quoted, says that, as with a Shakespeare, "it is the same with imaginative discoverers in science. . . . But the faculty is not merely a fairy gift that can be exercised without pains. As the sense of right is trained by right action, so the sense of truth is trained by right thinking and by all the labour which it involves. That is as true of the artist as of the man of science; and one of the greatest achievements of science has been to prove this fact and so to justify the imagination and distinguish it from fancy."

Again, let it not be forgotten that chemistry in its highest sense—that is, in its most general and useful sense—is purely a world of the imagination, is purely conceptual. And in addition to this, moreover, it is based, like all science, on the underlying assumption of the uniformity of Nature, an assumption incapable of proof. If we think of the science as a body of abstract general theory, and exclude for the moment from our purview its innumerable practical applications, and also all special individual facts not yet known to be related to general theory, then what remains are the more or less general facts or laws. These it is which give the power of prediction in newly arising cases of a similar character; the power of foresight by which the claim of chemistry to its position as a science is justified. Chemistry, as such, is a complicated ideal structure of the imagination, a gigantic fairy palace, and, be it noted, can only continue to exist so long as there are minds capable of reproducing it. Think of all the speculation—and speculation too of the highest utility when translated into concrete applications — about the internal structure of molecules. I venture to say that the most magnificent creations of the world's greatest architects are not more elaborate or more beautiful or more fairylike than the chemist's conception of intramolecular structure and the magical transformations of which molecules are capable; and yet no one has had direct sensuous experience of any molecule or atom, or possibly ever will. It is well from time to time to recall these truths and realise where we are. But although the conceptual nature of science is unquestionable, it certainly contains truth in some form as tested by deductive concrete realisation, by correctness of prediction, and during the last century or two has undoubtedly given to man a mastery over nature never before dreamt of.

A Brief Historical Retrospect.—The foundations of chemistry, as we now know it, were laid under the influence, the guidance, of three great theories:—First, the theory of the alchemists of the transmutation of metals by means of the philosopher's stone; second, the theory of phlogiston, connected so much with the names of Becher and Stahl, which held sway for some two centuries; third, the theory of combustion, the quantitative period of chemistry, inaugurated by the great Scottish chemist Black by his introduction of the balance. How this led to a veritable renascence of chemistry in the hands of Lavoisier and the other giants of that stirring period—the close of the eighteenth and commencement of the nineteenth centuries—is well known. Looking back at the warfare which was waged about these older theories, for and against them, one realises now that there were elements of truth on both sides; for have we not in the work of Sir William Ramsay and others the revival of transmutation, and does not the essential truth of phlogiston survive in the modern doctrine of heat? In one of Dr. Johnson's letters to Boswell there is a curious reference to transmutation. He says that a learned Russian had at last succeeded, but, fearing the consequences to society, he had died without revealing the secret.

After the discovery of oxygen and the beginnings of quantitative chemistry, the science was ready for Dalton's great discoveries respecting combination by weight; the corresponding discoveries by Gay-Lussac on combination of gases by volume, and, through the latter, for Avogadro's famous hypothesis. Dalton had indeed, by reviving an old Greek suggestion, proposed to explain his discoveries by his atomic theory, but neither this nor our molecular theory, though the latter was inherent in the laws of gaseous combination of Gay-Lussac and in Avogadro's hypothesis, were finally put upon their present basis until Cannizzaro took up the subject half a century later. Meanwhile Dulong and Petit had completed their studies of atomic heat, and Mitscherlich had pointed out the relation between isomorphism and molecular structure. When it is considered how little is known of solid or liquid structure, and that our present knowledge of molecules is only of gaseous molecules, it is fortunate that these methods of study of solids are available. The same may be said of the results of the work of Kopp and his successors on molecular volumes. Of other aids to fixing our conception of molecules and atoms I need only refer to the periodic law, the studies of the properties of dilute solutions, of electrolytic dissociation, and of surface tension of liquids.

Liebig, in his first inquiry, begun before he went to Gay-Lussac in Paris, proved that silver fulminate and silver cyanate, though distinct substances, had exactly the same composition; thus was opened that great chapter in the history of chemistry which Berzelius named isomerism. Perhaps nothing in chemistry has given rise in recent years to more intellectual and practical activity than isomerism. Wöhler's classical synthesis of urea, by the metastasis of ammonium cyanate, added another instance of isomerism, and Berzelius soon afterwards announced the isomerism of tartaric and racemic acids. Wöhler's synthesis of urea, followed, as it was, by numerous other laboratory syntheses, showed that substances which occur in living organisms are not different from those which may be prepared artificially, and the old distinction between inorganic and organic chemistry disappeared—there is, of course, only one chemistry. The words it is true have survived, but only for reasons of practical convenience.

After isomerism the next great step forward in the study of intra-molecular structure was the discovery of groups partially individualised which are capable of remaining intact through many reactions. Gay-Lussac had previously noticed the cyanogen group as common to cyanides; but it was the celebrated paper by Wöhler and Liebig on "The Radical of Benzoic Acid" which finally established the existence of compound radicles or groups such as benzoyl, and obtained for the theory of compound radicals the position in chemistry it now holds. Bunsen followed somewhat later with the discovery of cacodyl, and now such groups are almost innumerable. In many respects, by the experimental skill which it shows, the clearness of its logical method, and the beauty of its form and diction, this memoir is a model of what a scientific communication should be. I will read the opening paragraph, using Hofmann's translation:—"When a chemist is fortunate enough to encounter, in the darksome field of organic nature, a bright point affording him guidance to the true path by following which he may hope to explore the unknown region he has good reason to congratulate himself, even though he may be conscious of being still far from the desired goal." Of this memoir Berzelius, in a letter quoted by Hofmann (Faraday lecture), says:—"The facts put forward by you give rise to such considerations that they may well be regarded as the dawn of a new day in vegetal (organic) chemistry."

The history of the advance of chemistry since the days of the Giessen laboratory is bewildering in its extent. This has been largely due to the Giessen laboratory itself, which sent trained investigators, each carrying with him some touch of its master's magic, into all civilised lands. I cannot attempt to even catalogue the results here. One thing may be said, that chemistry is not worked out, as some have thought; but rather the opportunities of discovery seem greater and more promising than at any previous period.

PART II.

Sub-atoms, Atoms, Molecules, Molecular Aggregates; Valency.—Whether in the light of recent researches it may become necessary to give up that portion of Dalton's theory of atoms in which he regards them as undecomposable and indivisible; or whether we may consider them, as Prout suggested a hundred years ago, as different aggregates of sub-atoms of a uniform kind of matter, or whether they must be regarded as complexes built in the manner supposed by the electron hypothesis; also what should be our attitude towards the related problem of transmutation—all this I pass over, the more willingly that these subjects were discussed so recently by so high an authority as Sir William Ramsay in his Address to the Association last year at Portsmouth.

I assume that we are fairly satisfied with our present atoms and their respective weights, and this no matter how the atoms are constructed, and that we shall be satisfied with them so long as they disport themselves in chemical changes as indivisible entities. And, further, I assume that we are satisfied with our molecules and their respective weights, as determined by the application of Avogadro's hypothesis. Whether the molecular weight is obtained by direct determination of gaseous density or by taking advantage of the properties of dilute solutions, in either case the molecular weight which results is the weight of a supposed gaseous molecule, for the latter method depends for its justification on the former. All our molecular weights are weights of molecules in the gaseous state, or are supposed to be; they are not necessarily applicable to liquids, and much less to solids; solids and liquids may well consist of far more complex particles.

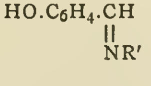
Gradually the central problem of chemistry has become more and more the study of the internal structure of molecules—of gaseous molecules. The enormous number and variety of the compounds of carbon, with which so many workers have enriched the science during the last hundred years, and the special adaptability of these compounds to the experimental study of molecular structure, has led investigators to make use of them rather than of the so-called inorganic compounds: thus out of inquiries into the intramolecular structure of these compounds arose and were developed the theories of types of Gerhardt, Williamson, and Kekulé. These are now, however, looked upon more as aspects of the general problem. More fruitful has been the study of the compound radicals or individualised groups of Wöhler and Liebig. But gradually these molecular structures have been regarded, in agreement with the views of Dumas, as complete wholes; like fairy temples, which from different points of view show different parts in relief, accentuating, it may be, this or that column or frieze or pediment. Kekulé's brilliant and suggestive theory of chain compounds and ring compounds did more than any other theory to guide and stimulate research in chemistry in recent times. Like Gay-Lussac's theory of gaseous combination, though built in the first place only upon a few facts, this theory has proved true of the thousands of others with which we have since become acquainted; there seems indeed to be a need of a new psychology to account for such truly marvellous foresight as is here exhibited. The atoms forming these varied structures were, however, regarded as being arranged in a plane, until the great discoveries of Pasteur made it necessary for chemists to extend their conceptions and to frame hypotheses of three dimensions. Thus has arisen in the hands of Le Bel and van 't Hoff and others our modern theories of stereo-chemistry. When isomerism occurs in an element Berzelius names it allotropy. It seems to me that now, when molecules of the elements do not differ essentially from molecules of compounds, there is no longer any distinctive meaning in the term, and that it might well be abandoned. I would like also to make another suggestion respecting nomenclature: that when we distinguish ring compounds as *cyclic* we might appropriately adopt the word *hormathic* (from the Greek word for a chain or a row) for chain compounds.

But in order to understand the linking of atoms in these molecular edifices some combining value had to be assigned to the different atoms. This idea of valency of the atoms was, no doubt, implied in Gerhardt's theory of types; but it did not gain much attention until later, when Frankland and Kolbé formulated an empirical theory of variable valency. Kekulé thought that atoms could not vary in their valency; but the alternative formulæ which he put forward to explain cases of difficulty would appear to be, rather, an attempted explanation of variable valency. It might be more correct to say that Kekulé's formulæ constitute an anticipation of Werner's theory of auxiliary valencies, the theory which seems to find most favour at the present day. Fixed valency can scarcely now be defended, in view of the existence of such compounds, for example, as the two fluorides and the two chlorides of phosphorus; the two oxides of carbon, ammonia and ammonium chloride; and, for example, the two series of compounds respectively of iron, mercury, and copper. Variable valency of atoms is empirically, at least, an established fact.

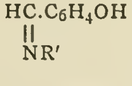
By the latest conceptions of variable atomic valency and its extension almost without limit—so that, for example, oxygen may be regarded as quadrivalent and even sexivalent—no doubt the existence of numerous compounds which previously presented difficulties can be explained. There are, however, others long known to chemists, such as double salts and the combination of water with salts, formerly called "molecular compounds," definite and individual, in which these views do not assist us. These compounds do not exist as gases, and unless they admit of experimental study by the methods of dilute solution, even their gaseous molecular weights cannot be ascertained.

It is noteworthy that in most of the instances recently investigated where variable valency has been assumed the compounds studied have been easily decomposable solids or liquids, and for one reason or another their gaseous molecular weights could not be determined. Many of these compounds, indeed, only exist at low temperatures. As instances of work of this kind I may mention Collie and Tickle on quadrivalent oxygen in dimethylpyrone derivatives; Gomberg on triphenylmethyl; Landolf on acetone di-hydrofluoride; Thiele and Peter on methyl-iodo-dichloride; and similar studies by Kehrmann, Willstätter and Iglauer, Bülow and Sicherer, Baeyer and Villiger, Archibald and McIntosh, Chattaway, Pfeiffer and Truskier, and others.

Another most interesting class of solids which are capable of existing in two isomeric forms distinguished from each other by such physical properties as density or colour are the Schiff's bases or anils. Some of these were studied by Hantzsch, who proposed to explain their existence by the Hantzsch-Werner stereo hypothesis:—



$$\begin{array}{l}HO.C_6H_4.CH\\ \qquad\qquad\ \ \|\\ \qquad\qquad NR'\end{array}$$



$$\begin{array}{l}HC.C_6H_4OH\\ \|\\ NR'\end{array}$$

But since only a few, and these not very satisfactory compounds, show this isomerism, which do not contain the hydroxyl group, other suggestions have been put forward to account for the isomerism, by Anselmino and by Manchot.

In my own laboratory, associated with Mr. F. G. Shepheard and also with Miss Rosalind Clarke, I have made a study of various Schiff's bases for the purpose of investigating the remarkable property which some of these bases exhibit of *phototropy*. By phototropy is meant the capability of reversible change of colour in solids depending upon the presence or absence of light. Incidentally, too, I wished to study another physical property which many Schiff's bases possess, in common with other substances, of reversible change of colour with raising or lowering of temperature. This property we have called *thermotropy*, and many old instances will be remembered of substances of simpler constitution which exhibit it; thus, when subjected to the temperature of solid carbon dioxide, ordinary sulphur becomes colourless, red oxide of mercury becomes yellow, vermilion becomes scarlet, and on return to the ordinary temperature the original colours reappear.

As has been pointed out in a recent communication by Biilman, it is most important in these discussions that we should be perfectly clear in the use of terms. I take it for granted that *isomerism* is a general term for compounds differing in some respects but having the same composition. If the molecules (gaseous) have the same weights they are *metamerides;* if of different weights they are *polymerides*. When solids crystallise in more than one form they are *polymorphous*. Now it does not seem reasonable to suppose that reversible colour changes such as those exhibited by phototropes or thermotropes involve such violent intra-molecular changes as the breaking and reconnecting of atomic linkages. For example, take the three bases, salicylidene-*m*-toluidine, which in the dark or immediately it is exposed to light is yellow, but on continued exposure to light quickly becomes orange, and changes back again to its original colour in the dark; salicylidene-*m*-aminophenol, which at ordinary temperatures is orange, but is much paler at the temperature of solid carbon dioxide, on raising the temperature to nearly the melting-point (128—9°) becomes orange red, and these changes take place in the reverse order again on cooling; salicylidene-*p*-aminobenzoic acid, studied by ourselves and by Manchot and Furlong independently, shows a wider range of thermotropic change between bright yellow and blood-red, and is also phototropic.

To explain such changes as these and the others of a similar nature previously referred to, I think some less drastic hypothesis should be sought than intramolecular breaking, and consequent metastasis or polymerisation. Though doubtless the hypothesis of Hantzsch and Werner could be invoked, or the modified hypotheses of Manchot or Anselmino, I think there should be some simpler explanation. Someone suggests polymorphism. Now polymorphism means that a change of crystalline form takes place which might doubtless connote change of colour. If one watches phototropic crystals changing colour under the influence of light from yellow to red, and notices that after remaining in the dark that the same crystals have changed back to the original colour, and, remember, that these changes can be repeated with the same crystals apparently without limit, it will not be considered likely that this phenomenon depends on a reversible change of crystalline form. In a communication to the Chemical Society some three years ago, Mr. Shepheard and I put forward the following suggestion:—"Evidence is accumulating of reversible isomeric reactions, like those described in this paper, which are indicated by physical differences, such as changes of colour. It is possible that these may be explained by hypotheses, similar to that of Hantzsch and Werner assuming intra-molecular rearrangement; but in the case of phototropy and thermotropy it should not be forgotten that the substances exhibiting these phenomena are solids. No one will doubt, however, that these differences of colour depend on isomeric change of some kind, but in the case of solids we know practically nothing of their molecules, not even of their relative molecular weights. The molecules of solids are probably far more complex than those of liquids or gases; indeed, they may be rather complex groups or aggregates of ordinary gaseous molecules, which would give rise to far more numerous possibilities of isomerism. It appears to us that phototropic and thermotropic reactions are more probably due to isomeric changes affecting the aggregation of molecules in solids than to intra-molecular change of molecules derived from a study of gases."

It seems to me that just as atoms may be structures built of sub-atoms of some kind, and just as molecules of gases are built of atoms variously linked together, that it is reasonable to conceive that molecules might combine to form aggregates, particularly when constituting solids; that as the sub-atoms may be conceived to have a combining valency, and the atoms are already accredited with this property, and in addition, as is supposed with Thiele's partial or Werner's auxiliary valencies, that molecules may have valencies also whereby to combine into molecular aggregates. It may be presumed that such aggregates are more complicated in structure, and thus may give rise to greater variety of isomerides, and be more readily transmutable than gaseous molecules. If such aggregates of gaseous molecules exist they might explain not only the easily changed isomerides recently studied, but also the large class of "molecular compounds" of the older chemists. I imagine someone saying that in suggesting this hypothesis—which by the way is not new, for it is mentioned in Ostwald's "Outlines"—I am violating the canon to which I have myself subscribed, as a condition of a scientific hypothesis, that it should be verifiable. Perhaps we carry our critical faculty sometimes too far. It is most highly scientific to doubt, but doubt which is merely destructive has little value; rather, with Descartes, it should lead on to construction, for he who builds even imperfectly is better than he who simply destroys. And I do not doubt that some way will be found to study solids and obtain data that will lead to the determination of their molecular aggregate weights. The study of molecular volumes of solid solutions; the remarkable results obtained by Pope and Barlow; Tutton's work on crystallography, and much besides, induce the hope that some day solids like gases will find their Avogadro.

PART III.

Pursuit of Chemistry Justified by its Useful Applicability.—In the pursuit of all this abstract theory, and still more so in the bewildering multitude of undigested individual facts, there is danger that important and fundamental, even moral, considerations may be lost sight of. For example take the fundamental question, Why should we pursue chemistry? No doubt it is considered by its votaries, those who seek in our laboratories to advance the science, that they are entitled to have provided for them, and will be rewarded by the provision of, the ordinary means of livelihood; but these, it will scarcely be denied, could generally be far better assured by other pursuits. It is suggested that intellectual discipline is a reason; but, I ask, for what purpose? Will anyone pretend that intellectual discipline without utilitarian object, without the possibility of using it for the betterment of society, is a worthy pursuit? I think not. But, in any case, none of us have devoted ourselves to chemistry merely for the sharpening of our wits. Again, someone suggests that chemistry and learning generally should be pursued for their own sake. In a recent most interesting and inspiring academic address Prof. Sir Walter Raleigh commends "those who seek nothing from knowledge but the pleasure of understanding" ("The Meaning of a University," Clarendon Press, 1911). If such a statement bears its most obvious meaning then, I venture to think that, in common with intellectual discipline without the intention of applying to a useful object the intellect so trained, such a reason is selfish, inadequate, and unworthy, and does not justify the pursuit of anything. No; research in chemistry apart from the possibility of applying it to the advantage of humanity cannot be defended. The mastery of the seemingly unlimited resources of Nature which chemistry achieves more and more, and its use to alleviate the misery and add to the happiness of mankind, is the only worthy and effective defence. And that this is the underlying ideal, in point of fact, that leads the chemist onward, not necessarily that he is always conscious of it, but always when he reflects, I think cannot be doubted. But, of course, no narrow idea of utility must be aimed at. Practically any chemical inquiry may lead to results of material advantage. Certainly nothing could be more mischievous than to make a narrow immediate utility the test. It would be easy to illustrate all this from the records of science, but instances in point are so well known that it is unnecessary.

On the other hand, it should not be forgotten that in making use of the manifold advantages derived from the growth of science, humanity, on its part, owes a great debt to scientific inquirers, and ought to feel it a sacred duty to do in return all in its power by support and encouragement to further scientific research. As Sir Walter Raleigh, in the address already referred to, says:—"It is so easy to use the resources of civilisation that we fall into the habit of regarding them as if they were ours by right. They are not ours by right; they come to us by free gift from the thinkers."

Some Concrete Applications of the Science.—That this advantage to civilisation has been, and is, the result of the pursuit and consequent advance of chemistry is happily a truth that is well known. There is scarcely an industry or a profession that has not been materially influenced or even created by the discoveries of chemistry, and therefore the welfare of nations is most intimately concerned in promoting its advancement. Now. it is common knowlege that no country has appreciated this to the same degree as Germany. It will, therefore, be worth our while to consider a moment the inauguration in Berlin, a year ago, of an entirely new institution, the Kaiser Wilhelm Institut, for the promotion and organisation of chemical research. This research is to be effected throughout the German empire, in the universities, the technical high schools, or in works, and it is supported mainly, at least at first, by subscriptions of the chemical manufacturers. An address of very great importance was delivered at its opening by Prof. Emil Fischer, than whom, perhaps, no one living has added more to the progress of chemistry. A translation of this address appeared in "Nature," and, with additions, has since been published in a convenient book form ("Chemical Research in its Bearings on National Welfare," London, 1912). In this address an authoritative account is given of the main contributions of chemistry to the national welfare, which even to those familiar with the subject must be astonishing in their importance, variety, and universality. It includes the applications of the science to problems of nourishment, to agriculture, and food supply; to engineering, metallurgy, cements; to clothing, artificial silk, or to colouring—dyes; to indiarubber production, both natural and artificial; to perfumery—artificial violet and other artificial floral perfumes, even that of the rose; to synthetic camphor; to drugs and synthetic materia medica, including the recent arsenic and selenium organic compounds which promise so much in the treatment of cancer and other fatal diseases; to radio-activity, to therapeutics, to the destruction of pathogenic microbes; to methods of sewage disposal; to the preparation of efficient explosives; and to many other useful objects. In connection with the manufacture of explosives the public should know that the ability to wage war is becoming more and more dependent on the work of chemists. When the supply of mineral nitrates is exhausted, or even before that event, the requisite nitrogen compounds will have to be provided in some other way, and almost certainly they will be obtained synthetically from the atmospheric gases which even now are becoming a commercial source.

The Time-spirit and Science.—But students of history know that there are certain periods that for some unexplained reason are specially fruitful in certain departments of intellectual or artistic development. Prof. Sir Walter Raleigh, for instance, a high authority on this subject, says:—"The human body, so far as we know, has not been improved within the period recorded by history; nor has the human mind, so far as we can judge, gained anything in strength or grace." Further, regarding literature:—"The question is not by how much we can excel our fathers, but whether with toil and pains we may make ourselves worthy to be ranked with them." Again:—"In the beautiful art which models the human figure in stone or some other enduring material, who can hope to match the Greeks? In the art of building who can look at the crowded confusion of any great modern city, with all its fussy and meaningless wealth of decoration, like a pastry-cook's nightmare, and not marvel at the simplicity, the gravity, the dignity, and the fitness of the ancient classic buildings? How can the seasoned wisdom of life be better or more searchingly expressed than in the words of Virgil or Horace, not to speak of more ancient teachers?" Thus all things are not progressing. The time-spirit now, and for some two centuries past, seems to have chosen to take under its particular guardianship the physical and natural sciences, their cultivation and applications, rather than philosophy or architecture or sculpture, or painting or literature. We shall do well to recognise this, and not waste our resources in striving to fight against it.

Present Indiscriminate Elementary Teaching and Neglect of Research.—Large sums of money are expended in this country on the diffusion of some knowledge of chemistry among all classes of scholars and students; in fact, scarcely anyone escapes from a smattering, largely undigested if not indigestible, either forced on them by regulations or by the allurement of bribes in the form of prizes, scholarships, or academic laurels. And if this is not good for scholars or students, it is worse for masters or professors. Our professors work "whole time" at this "stall-feeding" process, and if they happen to be strong men mentally and physically they may be able when weary with work to devote any overtime to—what I submit is far the more important matter for the State—the advancement of science by research. But this pursuit requires, for its successful prosecution, for resource and initiative to be at their best, that all the faculties should be in readiness in their fullest strength, freedom, and adaptability. How many, alas! are not strong men, and in their praiseworthy endeavours, notwithstanding, to contribute something to the achievements of their time succumb as martyrs to their devotion. The truth of this statement, I fear, is too well known to many of us here. In Germany this strain of elementary teaching is more recent, and is only now being felt. Prof. Emil Fischer in his address (*loc. cit.*) says of it: "During the last ten years a scheme of practical education of the masses has developed." "But this very education of the masses tends mentally to exhaust the teacher, and to a great extent, certainly to a higher degree than is desirable or indeed compatible with the creative power of the investigator, there prevails in modern educational laboratories a condition of overstrained activity." And again, "In the harassing cares of the day the teacher too readily loses that peace of mind and broad view of scientific matters necessary for tackling the larger problems of research." Laboratories, he says, are wanted "which should permit of research in absolute tranquillity, unencumbered by the duties of teaching." I have given these quotations from Prof. Fischer's address as indicating the matured judgment of a highly competent authority, communicated in the presence of the German Emperor on an historic occasion. His words are words of great weight and no country which regards its future welfare can afford to ignore them.

Sir Walter Raleigh (*loc. cit.*) says that every university is bound to help the poor . . . but that does not mean that a university is doing good if it helps those who have no special bent for learned pursuits to acquire with heavy labour and much assistance—just so much as may enable them to pass muster; on the contrary, it is doing harm. I would like to invite the attention of all who are seriously interested in the country's welfare to reconsider the present policy in the teaching of chemistry; and this applies also to other sciences. For the advancement of civilisation, for the increased welfare of the race by the technical applications of our science, it is not the indiscriminate teaching of the masses and the multiplication of examinations that is wanted, but the training of the few, of capable investigators. I do not propose necessarily that we should interfere with, or much less abandon, much of our present elementary teaching, and I know that elementary, largely technical, training in chemistry is needed for medicine and engineering; but I do propose that our first endeavour should be to secure under present conditions in the present college or works laboratories, or in laboratories to be specially provided, that capable men, of whom we have many, should be able to devote themselves to research without the worry of teaching and examining or of providing the ways and means of livelihood. There is, happily, reason to believe that this vital need is to some extent becoming known; for there have been several recent instances where a particular investigator has been afforded the means, financially, of prosecuting his particular researches in tranquillity. The diversion of endowments to such purposes, instead of their going to the foundation of additional school or undergraduate scholarships, cannot be too highly commended.

We may learn a lesson which bears on this from that remarkably prolific period of our science, the close of the eighteenth and the beginning of the nineteenth centuries. It was then no easy matter to pass the precincts of a chemical laboratory; only the fittest survived the ordeal. At the beginning of the nineteenth century the traditions of Berthollet and Lavoisier in Paris were kept alive by Gay-Lussac; in England those of Cavendish and Priestley by Davy; and Berzelius in Sweden worthily maintained the older school of Bergmann and Scheele. By a happy fate the interest of Alexander v. Humboldt was the means of both Liebig and Dumas being admitted to the intimacy of Gay-Lussac; and in Sweden Wöhler was fortunate to gain the confidence of Berzelius; and in London, Faraday that of Davy. The achievements of these men—Liebig, Dumas, Wöhler, and Faraday—is part of the history of science. To me it contains a lesson, in point, of great importance. The opportunity offered them was beset with difficulties. No bribes such as scholars or students expect to-day were offered them; they knew no examinations, and their available apparatus and laboratory equipment was of the smallest and crudest description; but they were eager students with whom the master was in sympathy, and it is common knowledge that they completed the foundations of our science. Now, I ask, considering the thousands of students whom we teach and examine to-day, are we doing as well in the interest of the country as our predecessors a century ago? Who can confidently answer in the affirmative? No; whatever else is done, the country needs the provision of men whose untrammelled energy should be devoted to original chemical research. Even as intellectual discipline the value of research is of the highest importance. In his Address to the British Association at Winnipeg, Professor Sir J. J. Thomson bears testimony to this. He says:—"I have had considerable experience with students beginning research in experimental physics, and I have always been struck by the quite remarkable improvement in judgment, independence of thought, and maturity produced by a year's research. Research develops qualities that are apt to atrophy when the student is preparing for examinations, and, quite apart from the addition of new knowledge to our store, is of the greatest importance as a means of education."

And the object and ideal is wrong also in our system of technical training. We aim too much at giving elementary instruction to artizans, which, though important in itself, can never take the place of the higher education of leaders or managers of industrial works. This is different in Germany, where, although the training of artizans is by no means neglected, the chief energy is directed to the training and teaching of the smaller class of managers. There is, too, in Germany a far more intimate relation between academic and industrial work, and the leaders in each often interchange posts. In one respect we have an advantage over Germany; it is important that this should be understood. The higher technical instruction across the Rhine has not been undertaken by the universities, but is carried out in separate institutions. With us the universities have gradually undertaken, in addition to the older technical subjects, theology, medicine, and law, the various branches of engineering and agriculture, and even commerce. This, it is to be hoped, will be extended so that the highly trained technologist may have the advantage of the undoubted humanising influence of the university.

Conclusion.—I have not attempted in this Address any complete survey of chemistry, either its growth in the past or its present condition, but I have endeavoured to give some account of the sort of thing chemistry is—of its method—and to maintain three theses:—1. That the logical method by which chemistry advances is not a simple one, and requires as one essential element the use of a highly developed imagination. To render this more efficient I have advocated special training. 2. Without violating, I hope, the canons of the proper use of hypothesis, I have proposed, in order to account for certain isomeric and other phenomena, the conception of solid molecular aggregates, although I am not able at present to indicate precise methods for its further investigation. These molecular aggregates are supposed to be formed by the combination of gaseous molecules just as the latter are formed by the combination of atoms. 3. As a matter of vital interest to the continued well-being of this country I have insisted strongly that our educational resources devoted to chemistry should be directed, in the first place and chiefly, to the highest possible training of promising students in the prosecution of research, and that the giving to the many of elementary instruction should be at least a secondary consideration.

Now, I do not wish to dictate how this last proposition could be best carried into effect. I think we should distinguish three classes of chemists, or technical chemists, whose domains would more or less overlap. Occasionally there will be a man, like the late Sir William Perkin, who would combine all three. The three classes are:—First, the pure chemist, devoted to scientific discovery only; second, the technical chemist, who prepares the discoveries of the pure chemist for the technologist, and has to determine such questions as economical production, and, for example, the conversion of colours into dyes; third, the technologist or works manager. These three classes should be in close relation to one another. By such a scheme we should probably overcome by education one of our most serious present difficulties—the ignorance of owners of works of the value of science.

It is a matter deserving most earnest consideration whether, under the propitious influence of our own time-spirit, it would be possible to organise research and develop it without interfering with its essential freedom and initiative, and this in each of the three classes I have mentioned, either by means of some of our existing institutions, or by the inauguration here of such an organisation as the Kaiser Wilhelm Institut in Berlin.

THE CHEMICAL NATURE OF URANIUM X, RADIO-ACTINIUM, AND THORIUM B.*

By ALEXANDER FLECK, B.Sc.

Marckwald and Keetman's statement that thorium and uranium X could not be separated was submitted to as thorough a chemical examination as possible. The chief method employed in the attempted separation of these two bodies was fractional precipitation, but in no case was it found possible to alter the concentration of the short-lived radio-element in thorium.

Similarly radio-actinium and thorium and thorium B and lead were found to be two pairs of chemically inseparable elements.

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* A Paper read before the British Association (Section B), Dundee Meeting, 1912.

ON THE DISSOCIATION OF PHOSPHORUS VAPOUR.*

By Prof. ALFRED STOCK and G. E. GIBSON, Ph.D.

Biltz and Victor Meyer have measured the vapour density of phosphorus at various temperatures. At lower temperatures the vapour density corresponds to the formula P_4. At high temperatures they were able to detect dissociation.

Victor Meyer's method is, however, not suitable for the quantitative investigation of dissociating vapours, since the degree of dissociation is altered by the addition of an inert gas.

The authors have determined the pressure temperature curves of phosphorus vapour at various volumes, using quartz apparatus and the quartz membrane manometer devised by Gibson (Diss. Breslau, 1911).

The vapour density corresponds to the formula P_4 up to about 700° C., above which dissociation takes place according to the equation $P_4 = 2P_2$.

There is no evidence of further dissociation at the temperatures investigated. The law of mass action applied to the new measurements decides against the equation $P_4 = 4P$.

The authors desire to thank Dr. Erich Stamm for valuable assistance in the course of the research, and to acknowledge receipt of a research grant from the Carnegie Trust, from which part of the expense of the investigation was defrayed.

THE DISTILLATION OF BINARY MIXTURES OF METALS *IN VACUO*.*

By A. J. BERRY, B.A.

Attempts have been made to isolate inter-metallic compounds in cases where one at least of the constituents is volatile by distilling alloys of the two metals containing an excess of the more volatile constituent in Jena-glass tubes, exhausted to the highest vacuum.

The success or failure of this method of isolating inter-metallic compounds clearly depends on two factors:—(1) The tension of dissociation of the inter-metallic compound must be practically *nil* at the temperature at which the distillation is effected; and (2) the partial pressure of the vapour of the more volatile constituent must fall abruptly at the composition of the alloy corresponding to the formula of the compound. It would, therefore, appear *à priori* that success is likely to be realised in cases where the intermetallic compound does not form solid solutions with either of its constituents. The magnesium-zinc alloys constitute a system of this kind; these two metals form the well-defined compound $MgZn_2$. The author has shown that this compound can be prepared by distilling alloys containing an excess of zinc beyond that required for the compound $MgZn_2$ (*Proc. Roy. Soc.*, A, 1911, lxxxvi., 67), the excess of zinc volatilising and the alloy of minimum vapour pressure consisting of the compound. It has further been shown that, under suitable conditions, this compound can be distilled without decomposition.

Attempts have been made to investigate the volatilisation of mixtures in which the compounds can form solid solutions with their constituents. Although no general conclusions have yet been reached, the following results have been obtained:—

1. Copper and cadmium are quantitatively separable by volatilisation of the cadmium.
2. Magnesium and cadmium yielded a non-homogeneous distillate.

THE

STUDY OF PLANT ENZYMES, PARTICULARLY WITH RELATION TO OXIDATION.*

The Committee have made considerable progress in the investigations which they have undertaken. The following is a list of communications by members of the Committee submitted to the Royal Society and published during the past year:—

(*a*) "Herbage Studies." I. "*Lotus corniculatus*, a Cyanophoric Plant," by H. E. Armstrong, E. F. Armstrong, and E. Horton.

(*b*) "Studies on Enzyme Action." XV. "Urease, a Selective Enzyme," by H. E. Armstrong and E. Horton.

(*c*) "The Distribution of Oxydases in the Plant and their *rôle* in the Formation of Pigment," by F. Keeble and E. F. Armstrong.

(*d*) "Studies on Enzyme Action." XVI. "The Enzymes of Emulsin, (i.) Prunase, the Correlate of Prunasin," by H. E. Armstrong, E. F. Armstrong, and E. Horton.

(*e*) "Studies on Enzyme Action." XVII. "Enzymes of the Emulsin Type, (ii.) The Distribution of β-Enzymes in Plants," by H. E. Armstrong, E. F. Armstrong, and E. Horton.

(*f*) "Studies on Enzyme Action." XVIII. "Enzymes of the Emulsin Type, (iii.) Linase, and other Enzymes in *Linaceæ*," by H. E. Armstrong and J. V. Eyre.

(*g*) "The Oxydases of *Cytisus Adami*," by F. Keeble and E. F. Armstrong.

Much preliminary work has been done in directions other than those considered in these communications, particularly with the object of throwing further light on the nature of the oxydases, the manner in which they act, and the part they play. The subject is one of great complexity and difficulty, and it is clear that it will be necessary to extend and multiply observations and experiments in a variety of fields if definite conclusions are to be arrived at. It is impossible to study the already voluminous literature of the subject and not be struck by the absence of proof that the oxydases are selective agents comparable with enzymes; at most it has been shown that their activity is of a catalytic order and usually limited, a particular oxydase apparently exercising its effect only within a certain group of componnds.

The Committee ask to be reappointed, with a grant of £30.

SILOXIDE, AN UNRIVALLED SUBSTITUTE FOR QUARTZ GLASS.†

By Dr. Ing. FELIX THOMAS.

(Continued from p. 119).

(*b*) *Pressure Resistance.*—The experiments carried out with the same materials (vitreosil excepted) with a view to pressure resistance had the results given in Table II. As test specimens, unless otherwise noted, cubes having an edge of 20 mm. with unglazed surface were employed.

Table II.

Description.	Pressure resistance appearance of first flaw. (*a*).	(*b*).	(*c*).	Actual breakage. (*a*).	(*b*).	(*c*).
Q ..	190 (?)*	470		1200 (?)*	921	
ZS 0·1	610	—	387	1103	914	905
ZS 0·5	502	468		923	763	
ZS 1·0	665	452	451	1830	1008	966
ZS 2·0	198	278	246	676	694	835
ZS 2·5	320	343		793	998	

* In the case of (*a*) observation uncertain.

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* A Paper read before the British Association (Section B), Dundee Meeting, 1912.

* Report of the Committee, consisting of Mr. A. D. Hall (Chairman), Dr. E. F. Armstrong (Secretary), Prof. H. E. Armstrong, Prof. F. Keeble, and Dr. E. J. Russell. Read before the British Association (Section B), Dundee Meeting, 1912.

† From the *Chemiker Zeitung*, 1912, No. 4.

TABLE III.—*Invariably* CO *Atmosphere.*

Description.	Temperature, °C.	Duration, in hours.	Degree of devitrification.	Ring.
V	1500	1	Flake ½ mm. thick; centres of crystallisation inside.	Inferior. Tube partly melted.
Q	1500	1	Flake ½ mm. thick; centres of crystallisation inside.	Inferior.
ZS 0·1..	1350	1	No trace of devitrification.	Fully preserved.
ZS 0·1..	1450	5	Fully devitrified; able to be crushed between the fingers.	None.
ZS 0·5..	1430	1	Tinged with white deposit, which was easily wiped away.	Fully preserved.
The same tube (*a*)	1500	1	Flake about ¾ mm. thick; tube not attacked by the oxide.	Good ring, therefore no crystallisation within.
ZS 0·5..	1500	1	Flake about ½ mm. thick.	Good ring.
The same tube ..	1650	1	More than half devitrified.	Strongly affected.
Q	1600	1	Strongly devitrified, also within.	Strongly affected. Tube very brittle.
ZS 1·0..	1500	1	Tinge, but within isolated centres of crystallisation.	Still pretty good.
ZS 1·0..	1700	½	Tube somewhat deformed, but still quite serviceable; no devitrification, of course, owing to the fact that the softening point had been passed.	Ring better than before the heating.
ZS 1·0..	1680	½	No devitrification; tube somewhat glazed.	Improved.
ZS 2·0..	1500	1	Somewhat more strongly devitrified than ZS 1·0 at 1500° C.	Fairly good.
ZS 2·0..	1680	½	Somewhat glazed, but no devitrification.	Good.
ZS 2·5..	1500	½	Two-thirds cross section devitrified.	Strongly affected.
ZS 2·5..	1500	1	More than three-quarters cross section devitrified.	No ring.

(*a*) Tube filled with metal filings rich in oxides.

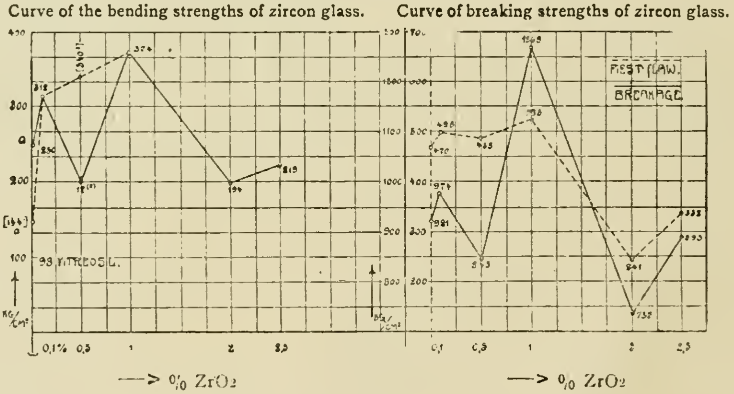


DIAGRAM I.

If the average values of these tables are represented in a system of co-ordinates we obtain the curves shown in Diagram I. for the pressure and bending strengths, which agree in showing that by the addition of 1 per cent of ZrO_2 to pure quartz glass the ability to resist pressure and bending is appreciably increased. Even 0·1 per cent has a quite perceptible effect in the right direction, whilst in both cases with 2 per cent we can affirm a minimum of strength which—so far at least as strain of flexure is concerned—far surpasses in value that of pure quartz glass.

3. *Devitrification.*—The extent of devitrification was determined by heating the tubes undergoing the test in an electrically heated tubular carbon furnace for one or two hours at the temperature best adapted to accelerate the devitrification and in the atmosphere most unfavourable to the material (CO). The objects were then removed from the furnace, and after cooling off in the air (in some cases after being chilled in cold water) the devitrified flakes were immediately measured. At the place of fracture it is easy to see how far the process of crystallisation has advanced, for at these points the material has completely lost its glassy characteristics. Blake's method of determining the intensity of the devitrification by measuring the loss of breaking strength was unfortunately beyond me, since the large number of tubes necessary for this purpose were not at my disposal.

The degree of devitrification can, however, be ascertained, qualitatively at least, without measuring the thickness of the devitrified flakes, by means of the "ring" given out by the object of experiment. Perfectly amorphous tubes have a clear resonant ring like that of hard porcelain; as the devitrification increases the sharpness of the tone is lessened, and with complete devitrification the tube rings as if it were quite cracked, which is actually the case since the tube now consists only of adherent tridymit-crystals. Moreover, with complete devitrification the tube can be crushed between the fingers, a clear proof of the thorough change of structure that has taken place. Of this less quantitative method of determining the degree of devitrification I have availed myself in the course of my experiments.

The results are summarised in Table III.

Thermally the best material is therefore that containing 0·5 per cent of ZrO_2, and in the second place comes that with 1 per cent. The latter material is, however, mechanically the most resistant, so that I recommend the choice of ZS 1·0 to satisfy mechanical claims, but ZS 0·5 for thermal purposes, while for both objects an intermediate mixture of about 0·75 per cent should be chosen.

4. *Resistance to Alkalis and Basic Metal Oxides.*—Experiments to determine the resistance of zircon glass to alkalis (solutions of soda and potash; caustic potash and caustic sodium lyes) are not yet quite finished, but apparently in this respect also zircon glass is superior to pure quartz glass. That it is also more able than quartz glass to withstand the basic metal oxides, is shown by the following observation made by a friend of mine, a gentleman who has worked a great deal both with quartz glass and zircon glass, and which I myself have repeated with the same result. A zircon glass tube placed in a magnesia tube or in a crucible coated with magnesia, and in direct contact with the magnesia, was not affected until it had been heated for half-an-hour in a temperature of 1500° C., and even then it was in every way fit for further use, whereas a quartz glass tube of the Deutsche Quartz Gesellschaft at Beuel, was almost instantly turned into slags.

5. *Softening Points. Miscellaneous.*—The softening points were determined by heating thin tubes of about 4 or 5 mm. in diameter and 40 mm. in length, the tubes being supported only at the ends, so that as soon as they began to soften they had to bend, a point which could be ascertained fairly accurately. The temperatures were measured with the Wanner pyrometer. The softening point of the pure quartz glass handed to me by the Zirkonglas-Gesellschaft m.b.H. at Frankfort-on-the-Maine was found to be 1734° C. with quick heating; that of the zircon glass averaged 1750° C. When slowly heated the quartz glass tubes began to lose their shape at about 1700° C. The difference in the softening points of the quartz glass manufactured by the Zirkonglas-Gesellschaft and its zircon glass is therefore inconsiderable. A fact of great importance, however, for many practical purposes is, that zircon glass loses its shape far more slowly than quartz glass, and that on account of its extreme viscosity.

Larger tubes can be heated for several minutes to the temperature at which softening begins to set in, without any risk of collapsing; they may perhaps somewhat lose their shape, but they will not be in any way unfit for use. Nevertheless zircon glass is very easy to work with the oxyhydrogen blowpipe, above all it gives no signs of the very troublesome bubbles met with in the case of the Beuel material; so that, for example, two zircon glass tubes can very easily be welded together without any formation whatever of blisters. Finally, still another property of zircon glass those will learn to appreciate who have to do with the cutting of tubes, &c.

In cutting the larger tubes, &c., on carborundum wheels, one has to set carefully to work, because quartz glass very easily flies apart, often, as I could frequently observe in the case of the larger tubes of Beuel quartz glass, fracturing along their entire length. Zircon glass can be treated somewhat more roughly without having to fear a fracture; the breaking out of larger pieces, even when the object worked is pressed with considerable force against the carborundum wheel, is comparatively rare. The small tubes can be cut, though perhaps less conveniently than quartz glass, with a triangular file.

(To be continued)

HARDWARE TRADE EXHIBITION, OLYMPIA.

"Ozonair" Stand Nos. 101 and 102.

On this stand a selection is shown of this Company's Ozonair Apparatus which is used in the production of absolutely pure ozone. Ozone, owing to its adoption on the Central London Railway, and in many important public buildings, has come to be generally known as a great aid to ventilation, purifying and freshening, as it does, the air in living rooms, offices, shops, theatres, hospitals, &c., by destroying the organic matter, smoke, fog, unpleasant odours, and other things which tend to contamination.

Ozone is also employed for the purification and sterilisation of drinking water supplies, whilst its industrial applications are very numerous. Amongst some of these may be mentioned the preservation of food for long periods, for helping the brewer to improve his yeast, and prevent contamination in his beer, and for bleaching and deodorising fats, waxes, &c. Ozone is now being employed in various therapeutical applications, and is a necessity for consumptive patients who have to reside in towns, instead of in the open air of the country.

The apparatus exhibited are examples of the principal portable types of ozone generators made by the company. An important feature of the apparatus is that in producing ozone no nitrous oxides are formed, and consequently there is no liability to harmful effects. Small machines are also exhibited which are more especially adapted for fixing permanently on to the wall; these are intended for use in shops, restaurants, smoking-rooms, lavatories, passages, small refrigerating stores, &c. Larger apparatus is also on view. These have been designed for use in public halls, factories, schools, markets, &c.

A full-sized plant is shown in operation as used in the ventilation of large buildings. Messrs. Ozonair Ltd. have now installed several hundreds of ventilation plants, so that the system is well worthy of careful consideration, especially as it is such an effective one. On the right-hand of the installation referred to is the inlet chamber for the fresh air which is taken from some convenient place outside the building. The air can be either cooled or heated in this chamber. It is then drawn through a special filter, which cleans it of all smuts and at the same time absorbs all the deleterious gases, such as ammonia and sulphurous acid, which are always present in the air of large cities, whilst the temperature of the air is reduced by a few degrees. This cleansed air is then driven into the mixing chamber of a motor driven fan, and thence distributed, by the aid of ducts through the building to be ventilated. Behind the fan and slightly above it an ozone generator is fixed. The air to be ozonised is drawn from outside through the generator, and thence into the mixing chamber of the main fan, so that all the air entering the building is properly ozonised, with the result that any stuffy or unpleasant smells in the building are neutralised and destroyed, rendering the atmosphere pleasant and sweet. The amount of air can be regulated at will.

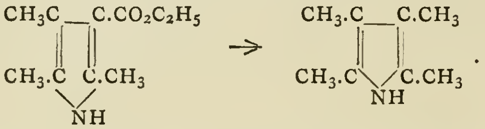
CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Atti della Reale Accademia dei Lincei.
Vol. xxi., No. 10, 1912.

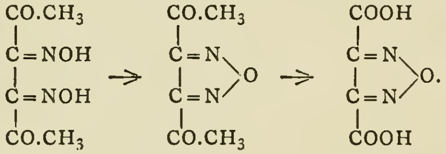
Chemical Action of Light.—G. Ciamician and P. Silber.—In presence of oxygen pyrrol is transformed by the action of light into a series of products which are carbonaceous and resinous, complex crystalline compounds $C_{12}H_{14}N_2O_5$, ammonium salts, and finally into succinic imide. The crystalline products may be separated into two portions, one more and the other less soluble in alcohol, which may possibly be regarded as derivatives of Dennstedt's tripyrrol, $C_{12}H_{15}N_3$. In the dark pyrrol undergoes a partial resinification, but the greater part of it remains unaltered.

Action of Sodium Alcoholate on Carbopyrrolic Ethers.—N. Colacicchi and C. Bertoni.—It has already been shown that sodium ethylate reacts with trimethylacetylpyrrol and the corresponding ketazine to give trimethylethylpyrrol. This action is due to the elimination of the acetyl group. The carboxyethyl group can be eliminated similarly but with more difficulty, and thus, for example, tetramethylpyrrol can be synthesised from 2 . 3 . 5-trimethyl-4-pyrrol carbonic ether, *i.e.*,—



New Transposition in the Pyrrol Group.— N. Colacicchi.—When the derivative formed by 2 . 4-dimethyl-3-acetylpyrrol with paraldehyde is heated, 2 . 4-dimethyl-5-acetylpyrrol is formed, and the author has now found that when 2 . 4-dimethyl-3-acetylpyrrol is heated in a closed tube to about 300° it is quantitatively transformed into the isomer with the acetyl group into the α-position.

Diacetylfurazane.—Luigi Alessandri.—When diacetylglyoxime is fused it readily loses water, and furnishes a product containing a molecule of water less than the original substance. Tha new derivative is a liquid which reacts readily with two molecules of phenylhydrazine, of hydroxylamine, and of semicarbazide; with potassium iodide it gives iodoform, and when oxidised with permanganate the resulting acid is identical with the furazanedicarboxyllic acid described by L. Wolff. The reactions are,—



The product described by Schmidt and Widmann and obtained by the action of fuming nitric acid on acetonylacetone is probably not a single substance.

MISCELLANEOUS.

British Association for the Advancement of Science. —The following were the Officers and Committee of Section B (Chemistry) at the Dundee Meeting of the British Association:—

President—Prof. A. Senier, M.D., Ph.D.

Vice-Presidents—T. Fairley, F.R.S.E.; Prof. A. Liversidge, LL.D., F.R.S.; Prof. H. Marshall, D.Sc., F.R.S.; Prof. J. C. Irvine, M.A., D.Sc., Ph.D.; Prof. A. F. Holleman, Ph.D.

Secretaries—E. F. Armstrong, D.Sc., Ph.D. (Recorder); C. H. Desch, D.Sc., Ph.D.; A. Holt, M.A., D.Sc.; J. K. Wood, D.Sc.

Committee—Prof. H. E. Armstrong, F.R.S.; P. C. Austin; W. Barlow, F.R.S.; Prof. H. Bassett; Dr. G. T. Beilby, F.R.S.; A. J. Berry; Dr. A. Compton; Dr. A. C. Cumming; Prof. A. E. Dixon, M.D.; Prof. H. B. Dixon, F.R.S.; Dr. J. V. Eyre; A. Fleck; Dr. G. E. Gibson; Dr. W. Goodwin; Dr. A. Harden, F.R.S.; A. Hynd; Dr. T. M. Lowry; Prof. C. R. Marshall; Dr. S. Mills; Dr. A. McKenzie; Prof. K. J. P. Orton; W. F. Reid; Dr. J. P. Scott; F. G. Shepheard; F. Soddy, F.R.S.; R. de J. F. Struthers.

The Papers brought before the Section were as follows:—

Prof. A. Senier—Presidential Address.
Prof. H. Marshall — Interaction between Thiocarbamide, Iodine, and Sulphur.
A. J. Berry—Distillation of Binary Mixtures of Metals *in vacuo*.
Dr. C. H. Desch—Report on Diffusion in Solids.
Dr. A. Holt—Absorption of Hydrogen by Palladium.
Dr. R. de J. Fleming Struthers—The Causes of the Induction Period.
A. Fleck—The Chemical Nature of Radium X, Radioactinium, and Thorium B.
A. Stock and G. E. Gibson—On the Dissociation of Phosphorus Vapour.
Dr. J. V. Eyre—Report on Solubility. The Enzymes of Linum. Variation in the Flax Plant with Locality.
A. Compton—Action of the Enzymes of Emulsin on Amygdalin and Vicianin.
Prof. F. Keeble and Dr. E. F. Armstrong—The Biochemistry of Flower Pigmentation.
Report of the Committee on Plant Enzymes.
Joint Discussion with Section A on the Atomic Heat of Solids, opened by Dr. F. A. Lindemann.
Prof. J. C. Irvine and A. Hynd—Synthetic Aminoglucosides.
Prof. J. C. Irvine and Miss B. M. Patterson—The Constitution of Mannitol Triacetone.
Prof. J. C. Irvine and Dr. J. P. Scott.—The Rotatory Powers of Partially Methylated Glucoses.
Dr. S. Mills—Acetyl-halogen Sugar Compounds.
Dr. A. Harden—Hexosephosphate.
Dr. E. F. Armstrong—Nomenclature of Optically Active Substances.
Discussion on the Migration of Groups.
Dr. A. McKenzie—The Walden Inversion.
Dr. K. J. P. Orton—The Conversion of Chloro-, Bromo-, and Nitro-amino-benzenes into the C-substituted Anilines and Anilides.
Dr. T. M. Lowry—Report on Dynamic Isomerism.
Dr. A. M. McKenzie and G. W. Clough—Interconversion of the Enantiomorphous Forms of Phenylmethylcarbinol.
Dr. J. K. Wood—The Optical Activity of Leucine in presence of Varying Amounts of Acid and Alkali.
Prof. A. F. Holleman and J. P. Wibaut — On the Nitration of the Chlorotoluenes.
Prof. C. R. Marshall—The Action of Bromine on Strychnine. Pentaerythritol Tetranitrate.
Prof. A. Senier—Phototropy and Thermotropy.
Reports of Committees:—Transformation of Nitroamines. Hydroaromatic Substances. Electroanalysis.

Announcement.—"Theories of Solutions," by Svante Arrhenius, director of the Nobel Institute of the Royal Swedish Academy of Science, Stockholm, is being published this week by Mr. Frowde for the Yale University Press. The volume constitutes the eighth of the series of Silliman Memorial Lectures at Yale.

Natural Gaseous Mixtures Rich in Helium.—Ch. Moureu and A. Lepape.—The examination of the mixtures of gases evolved by thermal springs at Sautenay, &c., reveals the presence of comparatively large quantities of helium, which has probably been formed by the disintegration of radio-active substances in the crust of the earth.—*Comptes Rendus*, clv., No. 3.

THE CHEMICAL NEWS.
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(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate is admitted to this Examination unless he has passed, or been admitted under the Statute referred to above as exempt from, a Matriculation Examination not later than that of the preceding January.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June. No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—(Vacant).

Lees Reader in Chemistry—(Vacant).

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. Jesus College Laboratory: D. L. Chapman, M.A. Queen's College Laboratory: Rev. G. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University, either by examination or by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures is published annually, in June, in a special number of the

Cambridge University Reporter, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge.

UNIVERSITY OF DUBLIN.

Trinity College.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C S.

Junior Demonstrator—H. K all, B.A.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students The Laboratories will open on October 1st. Lectures will commence on November 4th.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry.*—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(University of London).

Senior Professor of Chemistry—J. M. Thomson, LL.D. F.R.S.

Professors—Herbert Jackson, F.C.S., and P. H. Kirkaldy, F.C.S.

Lecturer and Demonstrators—S. W. Collins, B.Sc., L. E. Hinkel, B.Sc., and H W. Gill. B.Sc.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1912-1913 are Oct. 2, Jan. 8, and April 23.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till five daily, except Saturday

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

For fuller details the separate Syllabuses provided for each class should be consulted.

Evening Classes.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

(University of London).

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—R. W. Gray, Ph.D.; S. Smiles, D.Sc.; N. T. M. Wilsmore, D.Sc.; Katharine A. Burke, B.Sc.; W. C. McC. Lewis. D.Sc.; W. B. Tuck, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from September 3 to December 18; Second Term, from January 14 to March 19; Third Term, from April 22 to July 3.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 11. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and another hour to be arranged.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Courses of Physical Chemistry.

October to February: Tuesday and Thursday at 9. February to July: Tuesday and Thursday at 9.

The Courses comprise Stoichometry, the Liquid and Solid States of Matter, the Phase Rule, Thermochemistry, and in general the Application of Physical Methods to the Solution of Chemical Problems, Chemical Statics, the Electrolytic Dissociation Theory, Chemical Dynamice, and Chemical Thermodynamics.

Fees:—Courses, £5 5s.; Term, £2 2s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professors—Sir W. A. Tilden, D.Sc., F.R.S., and Sir T. E. Thorpe, C.B., F.R.S., &c.

Professor and Director of the Chemical Laboratories.—H. Brereton Baker D.Sc., F.R.S., &c.

Assistant Professors—M. O. Forster, Ph.D., D.Sc., F.R.S.; J. C. Philip, M.A., Ph D, B.Sc.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

Subject to agreement with the authorities of any College or other Institution, the Governing Body may by resolution recognise that College or Institution or any Department thereof, as being in association with the Imperial College for all or any of the purposes of the Charter, but no such resolution is to be valid or operative until allowed by the King in Council.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas have been awarded in the past to Students of the several constituent Colleges:—

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology.

The Associateship of the Royal School of Mines (A.R.S.M) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute (A.C.G.I.) will be awarded in Engineering (Civil and Mechanical), Engineering (Electrical).

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The 71st Session will commence on Oct. 2, 1912.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy is also accepted by the Conjoint Board.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Professor—A. Findlay, M.A., D.Sc. (Aberdeen), Ph.D. (Leipzig), F.I.C.

Lecturer and Demonstrator—T. Campbell James, M.A., Trinity College, Cambridge, D.Sc. (Wales).

Assistant Lecturer and Demonstrator—A. Brooke, Ph.D. (Strassburg).

Lecture Assistant—D. L. Phillips, B.Sc.

Student Assistant—C. W. Judd B.Sc. (Wales).

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 1st, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1910-1911, Course B). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 6 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £17. This composition fee enables the Student to attend any or all the Classes and Laboratories of the College.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 19, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturers and Demonstrators, Alice E. Smith, D.Sc., J. O. Hughes, B.Sc. Lecturer in Agricultural Chemistry, H. E. Jones, B.A., B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, B.Sc., and W. E. Williams, B.Sc.

The Session opens October 1st, 1912. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £5.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 15s. Advanced Lectures on Organic Chemistry, £1 5s.

Agricultural Chemistry.—Fee, £2 10s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Science Degree Course taken in one year, £4 4s.

The College Courses are arranged with reference to the Degree Courses of the University of Wales (of which the College is one of the Constitutent Colleges). The Courses in Science are also suited to the requirements of Students preparing for the Science Degree Course of the University of London.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.
Assistant Professor—E. P. Perman, D.Sc., F.C.S.
Demonstrator—R. D. Abell, D.Sc., Ph.D., F.I.C., F.C.S.
Professor in Metallurgy—A. A. Read, M.Met., F.I.C., F.C.S.

The Session commences October 1st, and terminates on June 27th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Inorganic Chemistry; Fee, £3 3s.

A course on Organic Chemistry wil be given in the Session 1913—1914.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in April, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

Department of Chemistry.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., D.Sc., F.I.C.; F. W. Rixon, M.Sc., PhD.

Lecturer in Inorganic and Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Hygienic Chemistry—F. Wallis Stoddart, F.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1912-1913 commences on October 1.

The Department of Chemistry is situated in the new wing of the University Buildings in Tyndall's Park, and was opened on October 1, 1910. The Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 ampères from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electro-metallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

Day Lectures.

General Courses.—1. General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. 2. General Organic Chemistry—Three Lectures per week during one Session and Laboratory work. 3. Physical Chemistry—Two Lectures per week for two Sessions and Laboratory work.

The Laboratories are open daily from 9.30 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—Intermediate Science—Course 1 and one day Laboratory per week. *Pass Degree*—Course 2 and 3, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree*—During the first year in the Honours School Courses 2 and 3, and the second and third, Course 3, and one or more of the following Special Courses as directed, *e.g.*:—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced Inorganic Chemistry, Applied Electro-chemistry, some part of Bio-chemistry.

The Colloquium and meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 1s. shall cover a perpetual registration for any number of Courses.

2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year.

3. The Fees for separate Courses of Lecturers in Faculty of Science shall be at the rate of £1 1s. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

Evening Lectures.

The Laboratories are opened from 6.30 to 9.30 p.m. on Tuesday during the Autumn and Spring Terms. Course 1 will be given on Wednesday at 8 to 9, and Course 2 or 3 on Friday at 8 to 9 p.m. during these Terms. The Lectures and Laboratory work in Course 1 will be similar to that given to Intermediate Students in the Faculty of Science, and that given in Course 2 or 3 to one of those given to Students studying for the Final Degrees in that Faculty.

Extract from Regulations as Regards Fees for Evening Students.

1. For Evening Students who enter on a curriculum for a Degree the Registration Fee shall be 5s., for a curriculum for a Certificate, unless the Student has matriculated, the fee shall be 10s. 6d.

2. Unless in any case otherwise prescribed, the Fees for Evening Classes in the Faculties of Arts and Science shall be 10s. 6d. for two terms, or for one term's attendance.

All communications to the University to be addressed to the Registrar. Information concerning Courses or Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

Chemistry.

Professor—J. Wertheimer, D.Sc., B.A., F.I.C., F.C.S.

Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.

Demonstrators—A. C. Higgs and E. G. Moody.

Assistant in Chemical Laboratory—S. Hayward.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught at the University College. The Engineering work of the University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, Sept. 30th.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators—Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Tinkler, D.Sc.; J. E. Coates, M.Sc.; E. P. Frankland, M.Sc.; Ernest Vanstone, M.Sc.

Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 1st, 1912.

The Chemical Department is housed in the new University buildings at Bournbrook.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a.m. Fee, £4 4s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10 30 a.m. Fee, £1 11s. 6d.

Second Year. — *Advanced Organic Chemistry.*— This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *Advanced Inorganic Chemistry.*— This course is devoted to the consideration of special branches of Inorganic Chemistry, and direction is also given as to the private reading which should be pursued by students. The class meets by arrangement once weekly during the Session. Fee, £1 1s.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A Course on Physical Chemistry. Fee, £2 2s.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Special Courses in General, Organic, and Physical Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6¼

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. Gardner, M.Sc.

Department of Chemistry and Dyeing.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc.

Assistant Professor of Chemistry—B. North, A.R.C.S. (Lond.).

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. H. Hodgson, M.A., B.Sc., Ph.D.; A. Jackson, B.Sc.; S. F. Stell, F.C.S.

Demonstrators in Chemistry—M. Fort, M.Sc.; H. Middleton, M.Sc.

Lecturer in Physics—J. A. Tomkins, A.R.C.S. (Lond.).

Demonstrator in Physics—F. Harcourt, B.Sc.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Demonstrator in Dyeing—T. Brooke.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Past Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing Course*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c. A completely equipped Practical Dyehouse and Finishing Rooms have now been added.

III. *Chemical Engineering.* Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science.* One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing.* Special Courses for Graduates in Chemistry, and for Drysalters, Colour Merchants, &c.

VI. *Textile and Dyeing.* Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board* (*M.R.C.S.*, *L.R.C.P.*), *London.*—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course.* Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Demonstrator—M. Kershaw, B.A., Ag.Dip. Cambs.

Assistant—H. Douglas Elkington, B.Sc., A.I.C.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc., F.R.S.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.

Assistant Lecturers and Demonstrators—W. Lowson, B.Sc., F.I.C.; W. H. Perkins, M.Sc., F.I.C.

Demonstrators—H. Calam, M.Sc.,; J. Marshall, M.Sc.; H. S. Patterson, B.Sc.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £5 10s.

2. Advanced Inorganic Chemistry. — (A) Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £4 10s.

3. Advanced Inorganic Chemistry. — (B) Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £4 10s.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee. £4 10s.

5. Honours Courses.—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £3 7s. 6d. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £2 5s. (*c*) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms.; fee, £3 7s. 6d. (*d*) Electro-chemistry: Tuesdays at 9.30 a.m.; £2 10s.

6. Chemistry of Food and Drugs.—Special class during the second term for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £3 3s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—£3 per half day of three hours per week.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S. F.I.C.

Assistant Lecturer—G. H. Frank, M.Sc., F.I.C.

Demonstrator—A. Woodhead, M Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dyestuffs.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Professor—E Stiasny, Ph.D.

Demonstrator—Harold Brumwell.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture at the University Farm.

Department of Coal-gas and Fuel Industries with Metallurgy.

Professor—J. W. Cobb, B.Sc.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, F.R S.

Professor of Physical Chemistry—F. G. Donnan, M.A. Ph.D., F R S.

Professor of Bio-chemistry—Benjamin Moore, M.A., D.Sc., F.R.S.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—Guy D. Bengough, D.Sc., M.A., A R.S.M.

Assistant Lecturers and Demonstrators—F. D. Farrow, M.Sc.; Francis W. Kay, M.Sc., Ph.D.; A. Rule, M.Sc., Ph.D.; R. E. Slade, M.Sc; J. Smeath Thomas, M.Sc.

Lecture Assistant—H. H. Froysell.

The Session commences October 3rd.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A General Introductory Course, including the principles of Organic, Physical, and Bio-chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Course J.—Applied Inorganic Chemistry, including Metallurgy. Fee, £2.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L.—Applied Electro-chemistry. Fee, £2 10s.

Also Pass and Honours Courses in Bio-chemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electro-chemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity or all manner of work and research in these subjects.

The Bio-chemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sheridan Muspratt Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1912, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Registrar not later than November 15. The Sir John Willox Chemical Scholarship, on similar lines, is open for competition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE
(In the University of Durham).

Professor of Chemistry—P. Phillips Bedson, M.A. D.Sc., F.I.C., F.C.S., J.P.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturer and Demonstrator—A. A. Hall, M.Sc., Ph.D.

Demonstrators—J. H. Paterson, D.Sc.; R. G. Forbestor, B.Sc.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

First Year Courses.—Division I.—This Course o Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 9th. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 8th. The class for Inorganic Chemistry meets at 3 p.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

Applied Chemistry—Tuesday, 5—6 p.m. Lectures on Fuel, Gas Analysis, Technology of Acid and Alkali. Fee, £3 10s. per Session.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc., A.R.C.M.; T. A. Savil, B.Sc. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects:—(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(*a*) Religious Knowledge, (*b*) Latin, (*c*) Greek, (*d*) Ancient History, (*e*) French, (*f*) German, (*g*) some other language to be approved, (*h*) Experimental Science or Physics or Chemistry, (*i*) Botany or Zoology, (*j*) Mechanics, (*k*) Extra Mathematics, (*l*) Geography.

(1.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iii.). Foreign Students may be exempted from the Matriculation Examination on report from the Board of Professors of Armstrong College, that they have already passed an examination equivalent to the Matriculation Examination of the University, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining. and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, October 3rd, 1912. Candidates should send in their names to the Secretary on or before September 13th.

Evening Lectures.—Under the auspices of the College and the Newcastle Section of the Society of Chemical Industry, special Courses of Evening Lectures will be given—Course of 5 Lectures by Dr. H. G. Colman, Gas Manufacture, to commence October 16th, 1912, and a Course of 5 Lectures by Dr. Desch on Metallography, commencing January 28th, 1913.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 30th. Candidates should send in their names to the Secretary on or before September 23rd.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Inorganic Laboratories—Harold B. Dixon, M.A., M.Sc., Ph.D., F.R.S.

Professor of Chemistry and Director of the Organic Laboratories—W. H. Perkin, Ph.D., D.Sc., F.R.S.

Senior Lecturers and Demonstrators—Arthur Lapworth, D.Sc., F.R.S.; C. Weizmann, Ph.D., D.Sc.; Norman Smith, D.Sc.; and E. C. Edgar, D.Sc.

Assistant Lecturers and Demonstrators—Robert Robinson, D.Sc.; F. P. Burt, B.Sc; F. R. Lankshear, B A., M.Sc.; Edward Hope, M.Sc.; and J. E. Myers, M.Sc.

Professor of Metallurgy—H. C. Carpenter, M.A., Ph.D.

Lecturer in Electro-Chemistry—J. N. Pring, D.Sc.

The Session begins October 1st, 1912.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

This course is intended for Students commencing the study of chemistry.

Introduction to Organic Chemistry.—Mondays, Wednesdays, and Fridays, at 9.30, during the Summer Term.

This course is designed to meet the requirements of Students preparing for the Intermediate B.Sc. Examination.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: One hour per week during the Michaelmas and Lent Terms. Applied Course: One hour per week during Michaelmas and Summer Terms.

B.Sc. with Honours in Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Directors of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

Departments of Chemistry and Metallurgy.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, D.Sc.; and R. Robison, Ph.D., B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on September 30th for Day, and on September 23rd for Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student attends a course on Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Brewing, Iron and Steel, and other Manufacturing Processes.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

The composition fee for full time in the Chemistry Department (lectures and laboratory) is £6 per term, and this fee covers all necessary apparatus and chemicals.

A composition fee of £6 per term is also charged for various complete courses, such as those required for the Institute of Chemistry, and for the degree examinations of London University.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, D.Sc., M.Sc.; W. J. Jarrard, B.Sc.; C. R. Young, B.Sc.; J. Kenner, Ph.D., B.Sc.

The Session will commence October 2nd.

Matriculation Course. — Tuesday and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B., Ch.B.—Monday, Wednesday, Thursday, and Saturday at 9.30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B Sc. Course in Chemistry.—Monday at 9.30 a.m. and Tuesday at 12.30 p.m. during second year, £3 3s.; Wednesday at 12.30 a.m., during two terms, Thursday at 10.30 a.m. and Friday at 10 30 a.m., during third year, £4 4s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon a Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one-half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Practical Chemistry which meets the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee, £5 5s.

An arrangement has been entered into with the Board of Education, London, S.W., which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s.

Department of Metallurgy.

Professor—J. O. Arnold, D.Met., F.R.S.

Senior Lecturers—F. K. Knowles, B.Met.; F. Ibbotson, B.Met., B.Sc.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The Department is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected. but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates are granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A steel works has been erected in connection with the Sheffield University at a cost of about £15,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works is also provided with a hammer capable of dealing with four-inch ingots Differential annealing furnaces and gas and electric hardening furnaces constitute part of the plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—Hugh Marshall, D.Sc., F.R.S.

Assistant Lecturers—J. K. Wood, D.Sc. and (Vacant).

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Session consists of three Terms:—The Martinmas Term begins early in October and ends before Christmas; the Candlemas Term begins early in January and ends about the middle of March; the Whitsunday Term begins in the middle of April and ends at the end of June.

Three Courses of Lectures are given, each extending through all three terms. The Junior Course, meeting four or five days a week (including Tutorial Meetings), is intended for beginners, and qualifies for Graduation Examinations in Arts (M.A. General), Science (First B.Sc.), and Medicine (First Professional).

The Intermediate and Advanced Courses, each meeting twice or thrice weekly, qualify for Degree Examinations in Arts (Special and Honours, respectively), and in Science (Final B.Sc. on Intermediate and Higher Standard, respectively).

All three are General Courses, including Inorganic, Physical, and Organic Chemistry.

The Laboratories are well equipped, and instruction is provided for students in Arts, Science (Pure and Applied), Medicine (including Public Health); provision is also made for students desiring to undertake Technological Work or Research.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Lecturer on Physical Chemistry—Francis W. Gray, M.A., D.Sc.

Demonstrators—Joseph Knox, D.Sc.; W. H. T. Williamson, B.Sc.

I. *General Lecture Course* (100 *Lectures*).— Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Physical Chemistry* (60 *Lectures*).—Three Lectures a week on Physical Chemistry, with Practical Demonstrations, are delivered during the Winter Session by the Lecturer, Dr. F. W. Gray. Fee, £2 2s.

III. *Inorganic Chemistry* (40 *Lectures*).—Two Lectures a week on Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. J. Knox. Fee, £2 2s.

IV. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £3 3s.

V. *Practical Course for Medical Students.*—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

VI. *Chemical Laboratory.*—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

University of Aberdeen and Aberdeen and North of Scotland College of Agriculture.

Agricultural Chemistry.

Professor—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; Alfred Hill, B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry* (*General Course*).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory.*—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—James Walker, LL.D., D.Sc., Ph.D., F.R.S.

Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; W. W. Taylor, M.A., D.Sc.; and J. E. Mackenzie, Ph.D., D.Sc.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, April to June.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Advanced Lecture Courses are given on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s.

Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry. Practical Examination:—Complex Qualitative Analysis; Preparations; Gravimetric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.
Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—A. Archibald Boon, B.A., D.Sc.; Andrew King, F.I.C.; Wm. Maitland, D.Sc.; F. D. Miles, B.Sc.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Analytical and Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University of Edinburgh as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Dr. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Day Classes open on October 8th, and the Evening Classes on September 30th.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

THE ROYAL TECHNICAL COLLEGE, GLASGOW.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A., LL.D.
Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.
Lecturer on Dyeing—A. B. Steven, B.Sc.
Lecturer on Sugar Manufacture—T. H. P. Heriot, F.C.S.
Professor of Metallurgy—A. Campion, F.I.C., F.C.S.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 24.

The main object of this College is to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade. It was founded by an Order in Council, dated November 26th, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College (established 1796), the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1912-1913 may be had from the Director, Mr. H. F. Stockdale,; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD.

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc.

The Session begins on October 14th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-seven Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 4th and following days. Twenty-two of these Bursaries are restricted to Men, one is open to Men or Women, and fourteen are restricted to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M.B., Ch.B. Degrees.; the regulations will be found in the "University Calendar."

Lecture Courses.

Three distinct Courses of Lectures are given, each extending over the three terms of the academic year.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam. on the Lower Standard and the Special Exam. for the M.A. Degree.

Third Year's Course.—Short courses of lectures on selected topics are given to Students preparing for the B.Sc. on the Higher Standard or the M.A. Degree with Honours.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £6 6s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Practical Physical Chemistry. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £6 6s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity to conduct original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry, 1851 Exhibition, and Carnegie Research Scholarships or Fellowships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., &c.

Lecturer on Organic Chemistry—A. W. Stewart, D.Sc.

I.—*Chemistry.*—The lectures are delivered at 12 o'clock on the first five days of each week, and terminate about the end of March. The course embraces the elements of Physical, Inorganic, and Organic Chemistry. Fee, £3 3s.

II.—*Advanced Chemistry.*—Inorganic and Organic. The lectures are given at such days and hours as suit the convenience of the class. Fee, £2 2s.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of Qualitative and Quantitative Analysis, Inorganic preparations, &c. The class is held on four days in the week during the second term for two hours each day. Fee, £3 3s.

IV.—*Practical Chemistry for Engineering Students.*—A special course is given during the third term. Fee, £3 3s.

V.—*Laboratory Pupils.*—The Chemical Laboratories are open from the second week in October to the beginning of July, on the first five days of the week, from 10 a.m.—5 p.m. (except during the vacations). Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for the whole Session. Facilities are provided for Students who wish to undertake research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Post Graduate Scholarships in Chemistry alone awarded annually of £50, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

UNIVERSITY COLLEGE, CORK.

A CONSTITUENT COLLEGE OF THE NATIONAL UNIVERSITY OF IRELAND.

Professor—Augustus Edward Dixon, M.D.

Demonstrators—John Taylor, M.Sc.; James L. McKee, B.A., Ph.D.

The College Session will commence in October, 1912, and end in June, 1913. All classes are open to male and female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.
2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.
3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.
4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.
5. Courses in Systematic and in Practical Chemistry for Students of Engineering.
6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c,, are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND.

UNIVERSITY COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M R.I.A.

Demonstrators—Robert B. Foster, Ph.D., and Miss R. Clarke, B.A.

Research Assistant—Frederick G. Shepheard, B.Sc., A.R.C.Sc.

The Session commences in September and ends in June.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple gravimetric quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical fatty and aromatic organic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's*

Courses.—Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photo-chemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Arts.—First Year's Course.—Same as Faculty of Science.

Faculty of Medicine.—First Year's Courses.—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates, and the chemical examination of urine. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—First Year's Courses.—Laboratory: Same as in Faculty of Science, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, first year.

The College offers a Scholarship in Chemistry for competition in alternate years of the value of £60, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Inorganic Chemistry, Elementary and Advanced; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Physical Chemistry; (5) Metallurgical and Technological Chemistry and Assaying; (6) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for three years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION

(F.I.C. AND A.I.C.).

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to elevate the profession of Chemistry, by setting up a high standard of scientific and practical proficiency for persons desirous of becoming professional consulting and technological chemists, public analysts, and chemical advisers, by examining Candidates, and granting certificates of competency, and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination (Fee, £5 5s.) are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Elementary Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. A Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *The Final Examination* (Fee, £5 5s.) *for the Associateship* (*A.I.C.*).—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—Mineral chemistry; metallurgical chemistry; physical chemistry; organic chemistry; chemistry of food and drugs, fertilisers and feeding-stuffs, soils, and water (including a compulsory examination in therapeutics, pharmacology, and microscopy); or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology. *Fellowship* (*F.I.C.*).—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council.

Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Bloomsbury Square, London, W.C. Past Examination Papers, 6d.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute for the Advancement of Technical Education.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Central Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons training to become Technical Teachers; 2. Persons preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in the various special subjects. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

City of London College, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School.

Battersea Polytechnic.—Principal, S. G. Rawson, D.Sc., F.I.C. Inorganic, Organic, and Technological Chemistry, John Wilson, M.Sc. (Vict.), F.I.C., and Assistants. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in various Technical subjects. (For further information see College Calendar).

Borough Polytechnic Institute, 103, Borough Road, S.E.—Chemistry Department under the Direction of C. Dorée, M A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro-chemistry and Electro-chemical Analysis. Special Courses of Lectures on various Technical subjects. (For further information see College Calendar).

Birkbeck College, Breams Buildings, Chancery Lane. —Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Wednesday, Sept. 25, when Sir Sidney Lee, D.Litt., LL.D., will give the Opening Address, at 7.30 p.m. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. Last session 49 students took Degrees in Arts and Science, 22 with Honours. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

Northern Polytechnic Institute, Holloway Road, N.—Principal, R. S. Clay, D.Sc. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of Education examinations. Prospectus sent free on application to the Secretary.

Northampton Polytechnic Institute, St. John Street, E C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Day and Evening Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus).

South Western Polytechnic, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of four years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 4d.

East London College, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D., F.R.S. Lectures and Practical Classes are held, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to Research and Post-graduate studies. Evening Classes for London University Degrees are also held.

Sir John Cass Technical Institute, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by H. Burrows, Ph.D., F.I C., G. F. Morrell, B.Sc., &c., G. Senter, D.Sc., &c., Arthur R. Ling, F.I.C., C. O. Bannister, A.R.S.M., Arthur Harden, D.Sc., J. S. S. Brame, and Wesley J. Lambert. The new Session of this Institute, which is specially devoted to technical training in Experimental Science and in the Artistic Crafts, will commence on Monday, September 23rd. The instruction in experimental Science provides systematic courses in Mathematics, Physics, and Chemistry for London University examinations in addition to the courses on higher technological instruction, which form a special feature of the work of the Institute. In connection with the latter, several new departures are being made for the coming Session. The curriculum of the Fermentation

Industries has been much developed, and now includes courses of instruction on Brewing and Malting, on Bottling and Cellar Management, and Power and Mechanical Plant in the Brewery, on the Micro-biology of the Fermentation Industries, and on the Chemistry and Technology of Hops, in addition to courses in Chemistry and Physics for those who have not sufficient previous knowledge of these subjects. In the department of Physics and Mathematics, a special course of Lectures and Demonstrations will be given on Colloids, which will deal with the methods employed in their investigation and their relation to technical problems; also a special course of Lectures on the Theory and Application of Mathematical Statistics, in which the application of modern mathematical methods of dealing with statistical data in social, educational, economic, and physical problems will be discussed, and opportunity given to students to investigate problems on their own account. In the Metallurgy department, in addition to the ordinary courses of instruction in general Metallurgy, special courses of an advanced character are provided on Gold, Silver, and allied metals, on Iron and Steel, on Metallography and Pyrometry, on Engineering Metals and Alloys, on Mining, Mine Surveying, and on Mineralogy. The special courses on Liquid, Gaseous, and Solid Fuels have also been extended, and, in addilion to a course of Lectures, will include laboratory work on Fuel Analysis and on Technical Gas Analysis. It is also of interest to note that included amongst the Language Classes is a course on Scientific and Technical German, the special object of which is to provide those engaged both in Pure and Applied Science with an opportunity of acquiring a knowledge of scientific and technical German. Full details may be obtained on application, or by letter to the Principal.

University Tutorial College, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Biology, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

East Ham Technical College.—Principal, W. H. Barker, B.Sc. Chemistry, A. E. Dunstan, B.Sc. Evening Classes and Secondary School.

Blackburn Municipal Technical School.—Chemistry: Robert H. Pickard, D.Sc.(Lond.), &c., assisted by Jos. Yates, M.Sc., F.I.C., Jos Kenyon, B.Sc., A.I.C. and W. Lewcock, B.Sc. Session opened Monday, Sept. 16. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

Leeds: Central Technical School, Leeds Institute, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in all subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by W. W. Burrell, M.Sc., J. B. Murray, A. McFarlane, and G. H. Rydall, B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by B. A. Burrell, F.I.C., F.C.S., and T. O. Thornton; Gas Manufacture, by W. E. Pettigrew; Oils and Fats, by J. A. S. Morrison, M Sc.; Magnetism and Electricity, Practical Physics, &c., by J. E. Tindall, B.A., B.Sc.; Bread-making and Flour Confectionery, by W. H. Quinn and J. C Hesselgrave; Photography and Process Work, by S. E. Bottomley and A. Guy Symmons Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Special three evening Course for Pharmaceutical Students, covering the "Minor" syllabus in three years, by J. H. Gough, Ph.C., F.C.S.; S. Parrish, B.Sc., A.R.C.S; and N. Walker. Session commenced Sept. 18th. See the Technical Handbook, 2d. (by post 5d.). Prospectuses of various Classes free on application to the Head Master, or to James Graham, Secretary for Education, Calverley Street, Leeds.

Redruth School of Mines (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application.

Municipal School of Technology, Sackville Street, Manchester.—Laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, Textile industries, Photography, Collotype and Photo-mechanical processes, Letterpress and Lithographic industries, and industries within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity. The School is established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can proceed to the Degrees of Bachelor and Master of Technical Science B.Sc. and M.Sc. Tech.). Special facilities are offered to graduate students desirous of pursuing advanced research in any department of Applied Chemistry and other branches of the Industrial Arts, and a Journal is published embodying the more important results of such researches. The possession of a University Degree is of increasing importance to young men who are seeking the more important positions connected with the Chemical Industries. The number of students seeking admission to the University Degree course in this School has never been so great as in the case of the Session opening on September 30th. The supply of students entering the Chemical Department, although it has been steadily increasing for some years, has not kept pace with the demand for those who have completed the degree course. Thus the number of applications for young men who have graduated in Chemistry from this school was last year much in excess of the number of students graduating in this department. A similar excess of the demand over supply is now being experienced in the Electrical Engineering Department, while a demand on the part of Mechanical Engineering firms for graduates in Mechanical Engineering is now beginning to make itself felt.

Wolverhampton Municipal Science and Technical School.—Principal, J D. Coales, D.Sc., M.I.E.E.; Inorganic and Organic Chemistry, Th. J. Murray, M.Sc., Ph.D.; Physics, A. T. Harrison, B.Sc.; Botany, Sidney Phillips, Ph.C. Human Physiology and Hygiene, H. J. Tench, A.R.S.I. Materia Medica and Pharmacy, F. W. Thompson, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students and Chemical Trades. Session commenced Monday, Sept. 16th. For other particulars and programme, apply G. F. Chell, Secretary.

Municipal Technical Institute, Belfast.—Principal, F. C. Forth, A.R.C.Sc.I. Chemistry, Prof. H. Wren, M.A., Ph.D., D.Sc., and Assistants. Day and Evening Courses. Session opened Sept. 16th.

BRITISH ASSOCIATION, DUNDEE MEETING.

Prof. A. Senier, Ph.D., &c., President of the Chemical Section, prefaced his Address with the following Obituary references:—

I am sure it will be agreeable to the feelings of the members of this Section that before beginning my Address I should refer to the great losses we have sustained by death since our gathering last year at Portsmouth.

An active member and Past-President has passed away by the death of Edward Divers, after a serious operation, undergone at his advanced age with characteristic fortitude. His devotion of his long life, in this country and Japan, to the advancement and diffusion of science, is indelibly inscribed in its records. But Divers was more than an investigator and teacher, he was a beloved centre of our social life, and was particularly happy when he could bridge over the distance between the young beginner in research and the older experienced master. He understood and had the sympathy of both.

In Henry Forbes Julian, one of the victims of the awful disaster to the *Titanic*, we have lost a valued contributor to our proceedings; though he was best known as a geologist and metallurgical engineer. It was, however, by chemistry under the inspiring influence of Sir Henry Roscoe that his first enthusiasm for science was aroused, Forbes Julian was a leading technical adviser in mining undertakings and his advice was much sought after, especially in South Africa and even in Germany.

Another tragedy, from the shock of which we have not yet recovered, has deprived science of the young and promising enquirer Humphrey Owen Jones. We know the dreadful details—he and his young wife—how they became sacrifices to the treacherous crags and snows of Mont Blanc.

And this, alas! is not all. On the very day of the fatal accident to Humphrey Jones, another young and promising chemist, John Wade, passed from us from the effects of a cycling accident. He was an enquirer of singular ability, and found time also to give us one of our deservedly most popular manuals of organic chemistry.

NOTICES OF BOOKS.

The Aynsome Annual, 1911. Edited by J. Stewart Remington. Ulverston: James Atkinson. 1912.

The papers of which this annual is composed have mostly been reprinted from the *World's Paper Trade Review* or the *Journal of Industrial and Engineering Chemistry*. They deal exclusively with subjects connected with the paper-making trade, and give a good idea of the value and importance of the work which is being done at the Aynsome Technical Laboratories at Grange-over-Sands. One article on the fibre of the baobab tree of Africa and India details the results of tests made with the fibre of the inner bark of the tree, which may be regarded as highly satisfactory from the point of view of the paper-maker. On the other hand, the possibility of using American saw grass on a commercial scale seems more problematical, and information as to cost of production, &c., is lacking. A comparatively long paper discusses the question of the formation of chemical compounds of cellulose and alumina resinate in sizing paper.

A Report on the Work of the Laboratories in 1911. By A. Lucas, F.I.C. Cairo: Government Press.. 1912.

This pamphlet gives a short account of the routine work done in the Egyptian Government Laboratories in 1911, with comments upon some cases of special interest or importance. The work included the analyses of many samples of papers, water, foods, &c., for the Departments of Finance, Public Works, War, and Education, and the total number of samples showed a decided increase upon last year. Tables of Statistics relating to the work done, the staff, &c., are added.

Revue de Chimie Appliquée. ("Review of Applied Chemistry"). Volume I. Number 1. Published by l'Association des Anciens Elèves de l'Institut de Chimie Appliquée de l'Université de Paris. March, 1912.

This new periodical is the official organ of the Association of old Students of the Institute of Applied Chemistry attached to the University of Paris. Judging from the first number it may be foretold that a useful future is before the Journal. It contains among other articles a paper on the wearing away of bronzes, already published in the *Revue de Métallurgie*, and another on the detection of horse flesh among flesh foods. Reviews and *résumés* of articles in current periodicals are included, and short abstracts of the meetings of the Académie des Sciences, the Society of Chemical Industry, and the Verein Deutscher Chemiker.

Berichte über die beiden ersten Tagungen des Conseil de l'Association Internationale des Sociétés Chimiques. ("Report of the Two First Meetings of the Council of the International Association of Chemical Societies").

This Report, issued by the Council of the International Association of Chemical Societies, contains accounts of the two meetings held in April, 1911, and April, 1912. At the first meeting the Association was founded, and the report explains its constitution and gives the provisional list of statutes, together with a short thesis by Professor Jacobson on the naming of organic compounds. In the account of the second meeting the revised statutes are given and the lists of members appointed on the three commissions for discussing the questions of a suitable nomenclature for organic and inorganic compounds, and of a system for unifying the notation used for physical constants. Short *resumés* of the reports of the commissions are added.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 3, July 16, 1912.

Natural Gaseous Mixtures Rich in Helium.—Ch. Moureu and A. Lepape.—Already noticed.

Anhydrous Nitrates of Uranyl and of Zinc.—M. Markétos.—When a hydrated nitrate is heated the product is generally a basic nitrate, and not the anhydrous salt. The latter, however, may be prepared by heating in an atmosphere of nitric acid. The author has thus obtained the nitrates of uranyl, $(NO_3)_2UO_2$, and of zinc, $(NO_3)_2Zn$, although the preparation is not easy; firstly, because the region of their stability is very limited, and, secondly, because special precautions have to be taken to ensure the absence of water vapour in the nitric acid vapours. Anhydrous uranyl nitrate is a white amorphous substance, exactly corresponding to the formula $(NO_3)_2UO_2$. It readily absorbs moisture from the air.

Yield in Grignard's Reaction.—Pierre Jolibois.—Grignard supposes that when magnesium is dissolved in an ethereal solution of ethyl iodide, $Mg{<}^{I}_{C_2H_5}$ is formed. The author has found that a secondary reaction always occurs if the experiment is performed without taking any precautions. This reaction may be represented by the equation $MgIC_2H_5 + C_2H_5I = MgI_2 + C_2H_4 + C_2H_6$. In the preparation of the organo-magnesium derivative the ethyl iodide must thus not be left in contact with the magnesium compound.

Oxidation of Parathymol. Dehydrodiparathymol. —H. Cousin and H. Hérissey.—The oxidation of parathymol, either by iron perchloride or by oxidising ferments, is comparable with that of thymol by the same agents; in both cases substances of analogous composition and having phenolic properties are obtained. Dehydrodiparathymol forms long colourless needles containing no water. It fuses at 96—97°. It is noticeable that orthothymol behaves quite differently towards oxidising agents, giving rise to substances which are not phenolic.

Leucobases and Dyes of Diphenylethylene. Preparation of Two Cyclohexylidenic Bases.—P. Lemoult. —The action of cyclohexyl-magnesium bromide on Michler's ketone gives the base $C_6H_{10}=C(Dm)_2$, where Dm represents $C_6H_4N(CH_3)_2$. This base forms large crystals, melting at 144°. With the tetraethylated homologue of Michler's ketone the product is $(C_6H_{10}=C(De)_2$, De being $C_6H_4N(C_2H_5)_2$.

MISCELLANEOUS.

Evening Education in London.—London's Evening Classes.—The London County Council announces that the Evening Classes held in Polytechnics, Technical Institutes, Schools of Art, Commercial Centres, and Evening Schools will shortly be re-opened. The programme which the Council has prepared includes classes to meet all kinds of needs. For students who are engaged in trades, there are held in the Polytechnics and Technical Institutes classes in all necessary subjects, Art and Craft Students will find full provision in the Schools of Art for the study of every branch of Art and Craftsmanship. For the large number of young men and women who are employed in business houses, the Commercial Centres provide comprehensive courses of study, including Languages, Book-keeping, and Shorthand, and advanced subjects such as Banking, Accountancy, Commercial Law. There are classes held in the evening schools to enable young people to improve their general education, and to begin the study of some special subject bearing upon their future employment. To girls and young women, classes in Cookery, Laundry-work, Home Nursing, Infant Care, Dressmaking, &c., are offered, whilst boys and young men can obtain instruction in Wood-work and Metal-work, and in Workshop Drawing and Calculations, to prepare them for entrance into the Polytechnics and Technical Institutes. The physical education of both sexes is not neglected; classes in Drill and Gymnastics being provided in every part of London. Increasing attention is being given to the teaching of English Composition, and, in short, no educational need has been overlooked. It becomes a duty which young people owe to themselves, their parents, employers, and the City to which they belong to attend the classes. The enrolment of students began on Monday, September 16th, and a leaflet giving full particulars as to where the classes are held, and as to fees (which it may be stated are very low) can be obtained at any of the Council's schools, and of the Education Officer, Education Offices, Victoria Embankment. It is hoped that the efforts of the Council to improve the education of the young people of London by means of these valuable classes will result in a large influx of new and earnest students in the session now at hand.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Sal-ammoniac.—Will some correspondent kindly inform us in what recent editions in literature we can find the most modern full details as to the production of sal-ammoniac. We should be glad to be put in communication with a technologist dealing with the subject.—W. and Co.

THE CHEMICAL NEWS.

Vol. CVI., No. 2757.

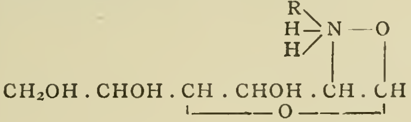
SYNTHETIC AMINOGLUCOSIDES.*

By J. C. IRVINE and A. HYND, M.A., B.Sc.

In recent publications (*Trans.*, 1911, lcix., 250; 1912, ci., 1128) the authors have described the preparation of bromotriacetylglucosamine hydrobromide and the use of this compound in preparing a methylglucosamine which was shown to be α-aminomethylglucoside. Further experiments have now indicated that bromotriacetylglucosamine is a general reagent for the preparation of α-aminoglucosides, as it enters into reaction with widely different types of hydroxy-compounds giving, in the first instance, acetylated aminoglucosides from which the acyl groups may be removed by hydrolysis.

So far as is known at present, the α-aminoglucosides thus obtained do not occur naturally, and they are distinguished from unsubstituted natural or artificial glucosides by their alkalinity, their capacity to form additive salts with acids, and their behaviour towards hydrolytic reagents. Some of the compounds are remarkably stable, and are only decomposed into a salt of glucosamine when strongly heated with concentrated acid. In such cases the compounds are also unaffected by enzymes, and form molecular complexes with metallic halides.

From these and other considerations, α-aminoglucosides of this nature are regarded as cyclic nitrogen compounds of the general type :—



Where R is a group of low molecular weight. As examples of this class we have α-aminomethylglucoside, α-aminoethylglucoside, and α-aminoamylglucoside.

A second type of α-aminoglucoside is formed when the group coupled with the glucosamine residue contains a benzene ring, as hydrolysis then proceeds normally with dilute mineral acids or with enzymes. Representative members of this class, to which the usual glucosidic formulæ may be applied, are α-aminohelicin and α-aminosalicin.

No general account of the preparation of α-aminoglucosides can be given, as the method has to be varied to suit individual cases. When the hydroxy-compound is readily volatile, a large excess may be employed, and the reaction is carried out in the presence of morphine, which removes the hydrogen bromide formed in the change. On adding the finely powdered bromotriacetylglucosamine hydrobromide, a considerable rise of temperature takes place, and the condensation is complete in a few minutes. The isolation of the acetylated aminoglucoside is then conducted as already described by us (*loc. cit.*).

In the case of high-boiling hydroxy-compounds the reaction may be carried out as described above, and the crude product precipitated by the addition of ether, or, when the solubilities permit, the condensation is conducted in dry ether containing pyridine, the solution being shaken with the solid bromo-compound for several hours. In such cases the product separates in the course of the reaction. These and other variations of the method were necessary when solid hydroxy-compounds were employed. The removal of the acetyl groups was effected by heating with methyl alcohol containing 1 per cent of hydrogen chloride. In the course of the research, nine aminoglucosides have been examined. The list includes morphine aminoglucoside, which is an alkaloidal derivative of a new type.

THE ROTATORY POWERS OF PARTIALLY METHYLATED GLUCOSES.*

By J. C. IRVINE and J. P. SCOTT, M.A., D.Sc.

During the past four years a number of partially alkylated sugars have been obtained by a variation of the method originally adopted by Purdie and Irvine in the preparation of tetramethyl glucose (*Trans.*, 1903, lxxxiii., 1021), and we are now in a position to add a series of partially methylated glucoses to the list of compounds of this type.

The method of preparation adopted can be expressed in general terms. Glucose was condensed with various residues which could subsequently be removed by hydrolysis; the unsubstituted hydroxyl groups were then methylated by the silver oxide reaction, and, on hydrolysis, a partially alkylated glucose was obtained. It was thus possible to protect selected groups from methylation, as shown in the following examples :—

Monomethyl Glucose.

Glucose diacetone, when methylated by the modified method described in the case of fructose diacetone was converted into *monomethyl glucose diacetone* (b.p. 139° to 140°/12 mm., $[\alpha]_D\ 20^\circ - 32{\cdot}2^\circ$ in alcoholic solution) (*Trans.*, 1909, xcv., 1223). When heated in aqueous alcohol containing 0·4 per cent of hydrogen chloride the two acetone residues were removed simultaneously, and, on working up the product in the usual way, *monomethyl glucose* was obtained in good yield. Both the α- and β-forms of the sugar were isolated, the former being deposited spontaneously from methyl alcoholic solutions, while the latter was precipitated from concentrated solutions in methyl alcohol by the addition of acetone.

α-Form: Rectangular plates; m.p. 157° to 158°. Mutarotation in aqueous solution :—

$$[\alpha]_D\ 20^\circ\ +96{\cdot}7^\circ \longrightarrow 55{\cdot}5^\circ.$$

β-Form: Acicular prisms; m.p. 130° to 132°. Mutarotation in aqueous solution :—

$$[\alpha]_D\ 20^\circ\ +31{\cdot}9 \longrightarrow 55{\cdot}1^\circ.$$

The sugar was shown to possess the structure—

$$CH_2OCH_3{\cdot}CHOH{\cdot}\underbrace{CH{\cdot}CHOH{\cdot}CHOH{\cdot}CHOH}_{O}$$

from the fact that it gave the same monomethyl glucosazone as that obtained from monomethyl fructose (*loc. cit.*).

Monomethyl methylglucoside, prepared by Fischer's method, failed to crystallise, the specific rotation of the mixed α- and β-forms in alcoholic solution being $+99{\cdot}3^\circ$.

Dimethyl Glucose.

Methylation of benzylidene α-methylglucoside gave an excellent yield of *benzylidene dimethyl α-methylglucoside* (m.p. 122° to 123°, $[\alpha]_D\ 20^\circ\ +97{\cdot}0^\circ$ in acetone solution). By carefully regulated hydrolysis a molecule of benzaldehyde was eliminated and *dimethyl α-methylglucoside* was formed (m.p. 80° to 82°, $[\alpha]_D\ 20^\circ\ +142{\cdot}6^\circ$ in aqueous solution). On complete hydrolysis the glucoside was converted into *dimethyl glucose*, which was isolated in α- and β-forms. The β-modification melted at 108° to 110° and separated in delicate needles from dilute solutions of the sugar in ethyl acetate, while the α-variety (m.p. 85° to 87°) was obtained by the addition of dry ether to a concentrated solution in ethyl alcohol. The mutarotation of each was determined in pure acetone :—

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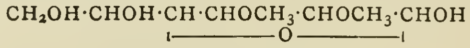
* A Paper read before the British Association (Section B), Dundee Meeting 1912.

* A Paper read before the British Association (Section B), Dundee Meeting, 1912.

β-Form : $[\alpha]_{D}20°$ $+5\cdot9° \rightarrow +50\cdot90°$
α-Form : $[\alpha]_{D}20°$ $+81\cdot9 \rightarrow +48\cdot3°$.

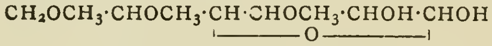
The sugar, under conditions favourable to ozazone formation, gave a *dimethylglucosephenylhydrazone* and has thus the probable structure :—



$$\mathrm{CH_2OH{\cdot}CHOH{\cdot}\underbrace{CH{\cdot}CHOCH_3{\cdot}CHOCH_3{\cdot}CHOH}_{O}}$$

Trimethyl Glucose.

Glucose monoacetone was converted into *trimethyl glucose monoacetone* (b.p. 138° to 139°/12 mm.), from which, on hydrolysis, *trimethyl glucose* was obtained. The sugar failed to crystallise, and thus the specific rotation could only be determined for the equilibrium mixture of α- and β-forms ($[\alpha]_D$ 20° $-8\cdot3°$ for both alcoholic and aqueous solutions). No solid glucoside, hydrazone, or other derivative could be obtained. The constitution, deduced from that of glucose monoacetone is expressed by the formula :—



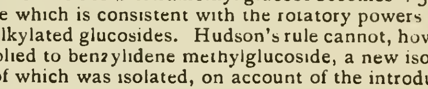
$$\mathrm{CH_2OCH_3{\cdot}CHOCH_3{\cdot}\underbrace{CH{\cdot}CHOCH_3{\cdot}CHOH{\cdot}CHOH}_{O}}$$

Discussion of the Optical Results.

Ten out of the possible thirty-one methylated glucoses are now available for comparison. We find that the rotatory powers of these substituted glucoses are only slightly affected by changes in concentration or by change of solvent. Further, in the case of mutarotatory forms, accurate initial values can be determined in acetone solution, as the optical change remains suspended until a catalyst is added. We are thus able to show that both monomethyl- and dimethylglucose conform to the generalisation established by C. S. Hudson regarding molecular rotation in the sugar group (*Journ. Am. Chem. Soc.*, 1909, xxxi., 66). As the two sugars are substituted respectively externally and internally to the γ-oxidic ring, it would appear that Hudson's rule is applicable to certain types of substituted sugars and can be used for calculating the activity of unknown β-forms or for the adjustment of approximate values determined experimentally. On this basis the specific rotation of β-tetramethyl glucose becomes +32·16°, a value which is consistent with the rotatory powers of the fully alkylated glucosides. Hudson's rule cannot, however, be applied to benzylidene methylglucoside, a new isomeric form of which was isolated, on account of the introduction of a new asymmetric system into the molecule.

Our results also show that the hydroxyl groups in glucose fall into two classes with respect to their influence on optical power, (*a*) those situated within the γ-oxidic ring, and (*b*) those external to the ring. In class (*a*) the asymmetric systems in which the hydrogen atom is above and the hydroxyl group below the plane of the ring, exert a dextro-rotatory effect. Those in which the reverse arrangement exists are lævorotatory. Definite configurations can thus be suggested for the α- and β-glucoses.

The effect of methylating the hydroxyl groups of class (*a*) is to greatly intensify the rotation of the system to which it belongs, while in class (*b*) the effect is relatively small. If the groups are numbered according to the scheme :—



$$\mathrm{\underset{(6)}{CH_2OH}{\cdot}\underset{(5)}{CHOH}{\cdot}\overbrace{\underset{(4)}{CH}{\cdot}\underset{(3)}{CHOH}{\cdot}\underset{(2)}{CHOH}{\cdot}\underset{(1)}{CHOH}}^{O}}$$

the deduction can also be made that the optical effect of methylating the hydroxyl group No. 2 is to raise the rotation of glucose by an unknown amount (*x*) which is probably over 100 per cent.

Methylation of No. 3 depresses the dextro-rotation to the extent $x + 20\cdot7$ per cent. On the other hand, methylation in positions 5 and 6 contributes a rise in the dextro sense to the extent of 48·9 and 8 per cent respectively. These numbers are arrived at by adopting as the standard of comparison in each case the value

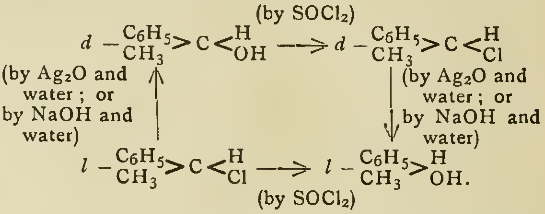
$$\frac{[M]_D\ \alpha\text{-Form} + [M]_D\ \beta\text{-form}}{2}.$$

The application of these quantitative results is now being tested in the case of partially alkylated mannoses and galactoses.

INTERCONVERSION OF THE ENANTIOMORPHOUS FORMS OF PHENYLMETHYLCARBINOL.*

By Dr. ALEX. McKENZIE and GEORGE W. CLOUGH.

Work on the Walden inversion has been hitherto confined practically entirely to changes undergone by carboxylic acids or their derivatives, esters, &c. In the present communication it is shown that an optically active alcohol can be transformed into its enantiomorphously-related isomeride by the aid of a Walden inversion. The following cycle can be effected :—



$$\begin{tikzcd}
d-\begin{smallmatrix}C_6H_5\\CH_3\end{smallmatrix}\!>C<\!\begin{smallmatrix}H\\OH\end{smallmatrix} \arrow[r, "\text{(by SOCl}_2\text{)}"] & d-\begin{smallmatrix}C_6H_5\\CH_3\end{smallmatrix}\!>C<\!\begin{smallmatrix}H\\Cl\end{smallmatrix} \arrow[d, "\text{(by Ag}_2\text{O and water; or by NaOH and water)}"] \\
l-\begin{smallmatrix}C_6H_5\\CH_3\end{smallmatrix}\!>C<\!\begin{smallmatrix}H\\Cl\end{smallmatrix} \arrow[u, "\text{(by Ag}_2\text{O and water; or by NaOH and water)}"] \arrow[r, "\text{(by SOCl}_2\text{)}"'] & l-\begin{smallmatrix}C_6H_5\\CH_3\end{smallmatrix}\!>\!\begin{smallmatrix}H\\OH.\end{smallmatrix}
\end{tikzcd}$$

On the other hand, the action of phosphorus trichloride on the *d*-carbinol is accompanied by a change of sign of rotation and the resulting *l*-α-chloroethylbenzene is considerably racemised.

Action of Thionyl Chloride on the Active Carbinols.—*d*-Phenylmethylcarbinol was prepared by the resolution of the hydrogen *dl*-succinic ester by means of brucine according to the method of Pickard and Kenyon (*Trans. Chem. Soc.*, 1911, xcix., 45). It boiled at 104°/23 mm. and had $[\alpha]_D$ 20 +43·36, a value in agreement with that quoted by Pickard and Kenyon.

The *d*-alcohol (4 grms.) was added gradually to thionyl chloride (10 grms.). The product was distilled under diminished pressure and the fraction boiling at 85°/20 mm. amounted to 4 grms. It had α_D 20 $+26\cdot90°$ ($l=0\cdot5$), d_4^{20} 1·0631, whence $[\alpha]_D$ 20 $+50\cdot6°$. Found Cl = 25·3; calc. 25·2 per cent.

The *l*-alcohol, obtained by decomposing the mother-liquors from the crystallisation of the brucine salt of the hydrogen succinic ester, had α_D $-26\cdot70°$ (l 1); 41 grms. were added as before to 56 grms. of thionyl chloride. The fraction boiling at 85°/20 mm. had $[\alpha]_D$ 20 $-30\cdot15°$. Found Cl = 25·3; calc. 25·2 per cent.

Action of Phosphorus Trichloride on d-*Phenylmethylcarbinol.*—The *d*-alcohol (5 grms.) was added drop by drop to phosphorus trichloride (20 grms.) cooled in ice. The product was fractionated. The portion boiling at 80° to 80·5°/15 mm. had α_D 18 $-4\cdot32°$ ($l=0\cdot5$), d_4^{18} 1·0638; whence $[\alpha]_D$ 18 $-8\cdot12°$. Found Cl = 25·1, calc. 25·2 per cent.

Action of Silver Oxide and Water on l-α-*Chloroethylbenzene.*—Six grms. of the partially racemised α-chloroethylbenzene with $[\alpha]_D$ 20 $-30\cdot15°$ were added to 60 cc. of water and the mixture shaken with silver oxide (6 grms.) for two hours and then heated on the water-bath for fifteen minutes. The alcohol was removed by distillation in steam, extracted with ether, and fractionated. The fraction boiling at 196° to 200 (2 grms.) had α_D $+3\cdot71°$ ($l=0\cdot5$).

Action of Sodium Hydroxide and Water on l-α-*Chloroethylbenzene.*—Six grms. of α-chloroethylbenzene with α_D 20 $-30\cdot15°$ were boiled for two hours with a solution of 6 grms. of sodium hydroxide in 60 cc. of water. The alcohol was obtained as in the preceding experiment.

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* A Paper read before the British Association (Section B), Dundee Meeting, 1912.

The fraction boiling at 196° to 200° (2 grms.) had α_D +0·65° ($l = 0{\cdot}5$).

The displacement of chlorine by the hydroxy-group is accordingly accompanied by more racemisation when sodium hydroxide is used in place of silver oxide.

This work is being continued.

REPORT ON DIFFUSION IN SOLIDS.*

By CECIL H. DESCH, D.Sc., Ph.D.

The occurrence or non-occurrence of diffusion in solid substances is of fundamental importance for the theory of solid solutions and isomorphous mixtures. In order that any mixture of substances in the solid state may be legitimately regarded as a solid solution it must be shown that diffusion is capable of taking place within it from regions of high to those of low concentration. The ambiguity which at present exists in respect to this question is due in part to ambiguity in the definition of the solid state, and in part to differences of opinion as to the facts. The popular distinction between fluids and solids is traversed by the more scientific classification into amorphous and crystalline substances. It is evident, however, that such substances as the glasses, although connected by all possible gradations with liquids on the one hand, and sharply separated from crystalline substances on the other, yet possess most of the properties commonly associated with solids, whilst the liquid crystals of *p*-azoxy-anisole, for example, although definitely crystalline, cannot be regarded as solid bodies in any sense of the word.

The following classification (modified from that given by G. Tammann, "Krystallisieren und Schmelzen," Leipzig, 1903, p. 5), then, represents the possible states that may be assumed by a substance, although any one substance is not necessarily capable of assuming all of these states:—

Isotropic.	*Anisotropic.*
Gaseous	Crystalline, including liquid crystals and one or more solid crystalline modifications.
Liquid	
Amorphous or glassy	

Diffusion takes place in liquid crystals in apparently the same manner as in isotropic liquids (O. Lehmann, "Flüssige Krystalle," Leipzig, 1904, p. 76), and they are therefore omitted from consideration in the present Report. On the other hand, both amorphous and crystalline solids are considered. The former class is restricted to the natural and artificial glasses, whilst the jellies, which are undoubtedly of a colloidal character, are treated briefly at the close on account of the importance of certain periodic phenomena observed in them for the general theory of diffusion. The materials in which diffusion has been either observed or suspected are treated in the following order:—Glasses, metals, minerals, salts, and organic crystalline substances; these sections being in some cases sub-divided for greater convenience. A short summary of the evidence concludes the Report.

Diffusion in Glasses, and Devitrification.

The production of coloured glass by the application of a layer of strongly coloured glass to a thicker colourless mass involves diffusion, but the temperature employed is so high that the glass is soft, and cannot be regarded as solid. The colouring matter does not appreciably diffuse at atmospheric temperatures. Thus, a sheet of fourteenth century ruby glass, 5 mm. thick, was found on microscopical examination to be built up of fifty-five coloured and eighty-eight colourless layers, the boundaries between which were yet distinct, although under a higher magnification zones of intermediate shade, which may have arisen during the process of manufacture, could be detected (J. Fowler, *Archæologia*, 1880. xlvi., 65). The observations on diffusion in glass at moderate temperatures are almost entirely limited to experiments depending on electrolysis, which are described in the following section. The process of devitrification, however, involves diffusion, although only through comparatively small distances, and the evidence on this point may be briefly reviewed.

The formation of crystals in a glassy material (devitrification) is strictly comparable with the process of crystallisation from a liquid, and its course depends on two factors—the number of centres appearing in a given time—and the linear velocity of crystallisation (G. Tammann, *Zeit. Elektrochem.*, 1904, x., 532; "Krystallisieren und Schmelzen," p. 148). Quantitative measurements have been made in the case of glassy borates (W. Guertler, *Zeit. Anorg. Chem.*, 1904, xl., 268), and numerous observations of the devitrification of amorphous organic compounds have been recorded (O. Lehmann, "Molekularphysik," Leipzig, 1888, i., 707). In silicate glasses the crystals formed are usually very minute. They may become so numerous, when the glass is maintained for a long time at a suitable temperature, as to result in complete opacity—Réaumur's porcelain (experiments conducted 1727-29). The formation of much larger crystals during the slow cooling of glass has been observed in a few cases. Thus, a quantity of 400 tons of glass having escaped from a furnace, the slow cooling of the mass led to the formation of spherulites (F. Fouqué, *Comptes Rendus*, 1899, cix., 1). In this case the glass was an almost pure mixture of silica, lime, and soda, and the crystals were entirely composed of wollastonite. In a similar accident, in which the glass also contained much magnesia, very large spherulites of diopside, up to 4 cm. in diameter, were formed, together with wollastonite (L. V. Pirsson, *Am. Journ. Sci.*, 1910, [4], xxx., 97). It is to be noted that the spherulitic mode of crystallisation is most liable to occur when the crystals separate at a temperature below the metastable limit (J. Chevalier, *Min. Mag.*, 1909, xv., 224).

Similar conditions are observable in blast-furnace slags, which may be of any texture from that of a pure glass to that of a stony, minutely crystalline mass. A large number of minerals have been identified in such slags (see, for instance, W. Mathesius, *Stahl. u. Eisen*, 1908, xxviii., 1121; M. Theusner, *Metallurgie*, 1908, v., 657), and minute crystallites, which from their form must have segregated from the mass after it became rigid, may often be detected (H. Vogelsang, "Die Krystalliten," Bonn, 1875). The early stages of devitrification are easily seen in slags which have been granulated by means of air or water (C. H. Desch, "The Chemistry and Testing of Cement," London, 1911, p. 98).

Natural glassy rocks offer a still better series of examples. Here, again, all stages of devitrification may be observed, the spherulitic mode of crystallisation being frequent, as in rhyolites. It is sometimes possible to show that the crystallisation must have taken place at a comparatively low temperature. Thus, in the pitchstones of Arran, the phenocrysts are of augite or enstatite, but the minute crystallites which are so characteristic of that rock, are of hornblende, a low-temperature mineral (A. Harker, "The Natural History of Igneous Rocks," London, 1909, p. 225). The great viscosity of the mass at the time of formation of the hornblende is shown by the clear areas, free from microliths, surrounding the crystallites. Similar crystallites are found in the lava of Mauna Loa (E. S. Dana, *Am. Journ. Sci.*, 1889, [3], xxxvii., 441), whilst the extreme slowness of devitrification is shown by their absence from some recent lavas, even with a high percentage of iron, as that of Kilauea. Remelting the dolerite of Rowley Regis also yields a clear glass. That the process of devitrification—that is, of passage into the stable condition—proceeds to completion if given sufficient time is shown by the fact, noticed by Harker, that glassy rocks of Palæozoic age are almost unknown, although many rocks of that period show, by the presence of perlitic

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* Read before the British Association (Section B), Dundee Meeting, 12.

and other structures, that they have previously been glassy. The effects of devitrification may be produced artificially by heating pitchstones and other glassy rocks (F. Rutley, *Proc. Roy. Soc.*, xl., 430).

The crystallites formed in all the above instances are of different composition from the glassy mass, and their formation therefore involves diffusion. The devitrification of such a substance as silica, however, is merely a process of molecular change, not necessarily accompanied by diffusion. Some geologists have attributed still greater importance to the growth of crystals in a glassy magma at low temperatures, and have explained a number of structures frequently observed in rocks to the growth of previously formed crystals at the expense of a small quantity of glassy ground-mass (J. W. Judd, *Quart. Journ. Geol. Soc.*, 1889, xlv., 175).

Porcelain is probably partly glassy and partly microcrystalline. The diffusion of solid carbon, either in the amorphous form or as graphite, into porcelain at 1000—1500° has been recorded on more than one occasion (R. S. Marsden, *Proc. Roy. Soc. Edin.*, 1880, x., 712; J. Violle, *Comptes Rendus*, 1882, xciv., 28). The mechanism of the process has not been studied, but the presence of the carbon at a considerable depth below the surface has been determined both microscopically and chemically.

The Electrolysis of Glass and Porcelain.

Very interesting results have been obtained in the course of studies of the electrolysis of glass. The electrical conductivity of heated glass, first observed by H. Cavendish ("Electrical Researches," London, 1879, p. 181), was measured and shown to be electrolytic in character by H. Buff (*Lieb. Annalen*, 1854, xc., 257), who was followed by many other workers. It was even found possible (W. Thomson, *Proc. Roy. Soc.*, 1875, xxiii., 463) to construct a copper zinc cell with an intervening plate of glass as the electrolyte, a measurable e.m.f. being obtained at temperatures of from 50° to 120°. If two concentric glass bulbs are used, of which the inner contains a solution of copper sulphate and the outer one of zinc sulphate, with platinum wires as electrodes, a Daniell cell of high resistance is obtained (H. Helmholtz, Faraday Lecture, *Trans. Chem. Soc.*, 1881, [1], xxxix., 277). A more detailed study revealed some remarkable facts (E. Warburg, *Ann. Physik.*, 1884, [3], xxi., 622; W. C. Roberts-Austen, "Third Report to Alloys Research Com., *Proc. Inst. Mech. Eng.*, 1895, 238). A stout plate or bulb of soda glass is used as a partition, separating mercury on the one side from sodium amalgam on the other, and a current is passed from the amalgam through the glass to the mercury, a temperature of from 200° to 350° being employed. After about thirty hours, an appreciable quantity of sodium is found to have been removed from the amalgam and transferred to the mercury, the glass meanwhile remaining clear. When lithium amalgam is substituted for sodium amalgam, the current passes, and sodium appears in the mercury cathode, followed after a time by lithium. At the same time an opaque layer of silica appears at the anode surface and gradually spreads through the glass. A glass originally containing 2·4 per cent of potassium and 13·4 per cent of sodium was found after an experiment to contain the same proportion of potassium, but only 5·3 per cent of sodium and 4·3 per cent of lithium. The transfer of sodium follows Ohm's law.

The atomic volume of lithium is less than that of sodium. When a metal of larger atomic volume than sodium, such as potassium, is used in the form of an amalgam, it is found to be impossible to cause it to enter the glass. Gold and copper enter the glass, but do not penetrate completely, and after a time coloured deposits of these metals appear below the surface. In a similar manner silver penetrates into lead glass, producing a characteristic structure which is made visible by the silver stain. In all these cases the metal entering the glass has a smaller atomic volume than that which is expelled from it, a fact which led Roberts-Austen to regard the process as one in which the atoms of the metal entering pass along tracks or galleries in the glass left by the atoms of the metal expelled. The transfer may undoubtedly be described as due to diffusion. Warburg's experiments have been recently repeated with certain additional precautions (M. Le Blanc and F. Kerschbaum, *Zeit. Phys. Chem.*, 1910, lxxii., 468).

Diffusion of Gases through Metals.

The permeability of certain heated metals to gases, especially of platinum and iron to hydrogen, was observed by H. Ste. Claire Deville and L. Troost (*Comptes Rendus*, 1863, lvii., 965; H. Ste. Claire Deville, *Ibid.*, 1864, lix., 102), and further studied by Thomas Graham in his celebrated memoir on diffusion (*Phil. Trans.*, 1866, clvi., 399). The question has been frequently investigated, the metals most commonly employed being platinum and palladium. The permeability of heated silver to oxygen was also determined by L. Troost (*Comptes Rendus*, 1884, xcviii., 1427). In all cases the rate of diffusion increases rapidly with the temperature. The metal exercises a selective action and behaves as a semi-permeable membrane, palladium and platinum allowing hydrogen to pass, but not most other gases, whilst silver transmits oxygen, but not hydrogen or nitrogen. The diffusion is not proportional to the pressure of the gas, but the figures obtained may be explained on the assumption that the molecules of hydrogen diffusing are dissociated into single atoms, and that the diffusion is proportional to the pressure of the dissociated gas (W. Ramsay, *Phil. Mag.*, 1894, [5], xxxviii., 206; A. Winkelmann, *Ann. Phys.*, 1901, [4], vi., 104; O. W. Richardson, J. Nicol, and T. Parnell, *Phil. Mag.*, 1904, [6], viii., 1; O. W. Richardson, *Ibid.*, vii., 266; *Proc. Camb. Phil. Soc.*, 1905, xiii., 27). This view has, however, been disputed (G. N. St. Schmidt, *Ann. Phys.*, 1904, [4], xiii., 747; see reply by A. Winkelmann, *Ibid.*, 1905, [4], xvi., 773), adsorption being invoked to explain the anomalies.

The diffusion of nascent hydrogen through metals has also been studied. Thus, when iron is made the cathode in an electrolytic cell, hydrogen rapidly diffuses through the metal, and pressures of many atmospheres are obtained (M. Bellati and S. Lussana, *Atti R. Ist. Ven.*, 1890, [7], i., 1173; 1891, [7], ii., 987). Platinum, palladium, and nickel show the same effect in a much smaller degree. The diffusion increases very rapidly with the temperature, the increase being of the order of T^5 (A. Winkelmann, *Ann. Phys.*, 1905, [4], xvii., 590).

There is a close relation between the diffusivity of a gas through a metal and the absorptive power of the metal for that gas. The semi-permeable character is extremely well marked, gases other than hydrogen not diffusing through platinum at a white heat, even in sufficient quantity to be detected by means of the spectroscope (W. W. Randall, *Am. Chem. Journ.*, 1897, xix., 682). The diffusion of gases through colloidal membranes, such as caoutchouc, is of a simpler character, as is shown by the simple proportionality of the diffusion to the pressure and to the temperature (see, for instance, Graham, *loc. cit.*, and S. von Wroblewski, *Ann. Phys.*, 1876, clviii., 539). Its discussion does not fall within the range of this Report.

The Passage of Liquids through Metals.

The only liquid which has been observed to pass through metals without destroying their structure is mercury. It was observed in 1713 that a complex mixture (Homberg, *Mém. Acad. Roy. Soc.*, 1713, p. 306, not actually published until 1739), consisting essentially of an amalgam of silver and mercury, was able to pass through a plate of silver without rendering it brittle. At a much later date it was shown that mercury would also pass through other metals, including lead, tin, zinc, and gold (J. F. Daniell, *Journ. Roy. Inst.*, 1831, [2], i., 1). The experiment was devised of causing mercury to flow from one vessel to another at a lower level, using as a syphon a rod of cast lead, bent so as to form two arms of unequal length (J. Henry, *Proc. Am. Phil. Soc.*, 1841, iv., 56, 84). Tin may be used in the same way (E. N. Horsford, *Am. Journ. Sci.*, 1852

[2], xiii., 305). Copper and brass were subsequently added to the metals exhibiting this behaviour (J. Nicklés, *Comptes Rendus*, 1853, xxxvi., 154).

It is unlikely that true diffusion in the solid state plays any important part in the process of penetration of mercury in such cases. Mercury dissolves lead or tin, forming a liquid amalgam at the ordinary temperature, and this amalgam probably makes its way through the intercrystalline spaces. It was observed by Henry that the transfer of mercury takes place much more readily through cast lead than through hammered or rolled metal, the intercrystalline spaces of the latter having been closed by the mechanical treatment. The metal also becomes exceedingly brittle during the process, owing to the loosening of the crystalline texture by the action of the liquid amalgam.

(To be continued)

NEW THERMOMETERS FOR MELTING-POINT DETERMINATIONS.

By ALVIN S. WHEELER.

UNIFORMITY in practice in making melting-point determinations would be very desirable, for even to-day there are far too many cases where different observers disagree. The failure to agree is not always due to the quality of the material if we may have confidence in the analytical data given. Many forms of apparatus are in use, as well as various kinds of thermometers. Other factors also enter in. The practice of reporting the corrected reading is a step in the right direction, and its extension should be constantly urged.

In order to avoid the necessity of making corrections for the exposure of the mercury column, I have devised a thermometer with a short scale, so that it may be completely immersed in the bath. The method of construction may be readily seen from the accompanying sketch. Owing to the compact form of the scale it was necessary to construct a set of seven thermometers, each with a milk glass scale of 50° with divisions in degrees. The length of the scale is 35 mm. The thermometer jacket is lengthened so that the total length is 20 cm. This permits of its suspension by means of a cork, as in the Thiele apparatus, which is a particularly good form of apparatus to be used with this thermometer. The mercury bulb is small and compact, and above it is a constriction to enable one to attach the capillary tube if that is desired.

For the protection of the manufacture of the thermometers, Patent No. 507320 has been entered in the German Patent Office.

University of North Carolina,
Chapel Hill, N.C., U.S.A.

Molecular Weight of Selenium in Solution.—F. Olivari.—Selenium does not form crystallisable compounds with fused mercuric bromide, and hence the latter may be used as a solvent in cryoscopic experiments. The results of such experiments seem to show that the selenium molecule undergoes a progressive dissociation from a more complex to a less complex state (Se_8 ?).—*Atti della Reale Accademia dei Lincei*, xxi., No. 11.

THE PROBLEM OF BENZENE STRUCTURE REVIEWED FROM THERMOCHEMICAL STANDPOINT.

By WILLEBRORD TOMBROCK.

IN comparing the amounts of heat which are developed in the subsequent hydrogen additions to benzene, two facts may be drawn attention to:—

1. These heat developments are not the same, but differ considerably.
2. They are less than the heat of addition in open-chain compounds.

$$\underset{\text{Benzene.}}{C_6H_6} + H_2 = \underset{\text{Dihydrobenzene.}}{C_6H_8} + 0{\cdot}8 \text{ cal.}$$

$$\underset{\text{Dihydrobenzene.}}{C_6H_8} + H_2 = \underset{\text{Tetrahydrobenzene.}}{C_6H_{10}} + 25 \text{ cals.}$$

$$\underset{\text{Tetrahydrobenzene.}}{C_6H_{10}} + H_2 = \underset{\text{Hexahydrobenzene.}}{C_6H_{12}} + 27{\cdot}8 \text{ cals.}$$

$$\underset{\text{Hexahydrobenzene.}}{C_6H_{12}} + H_2 = \underset{\text{Hexane.}}{C_6H_{14}} + 11 \text{ cals.}$$

(See Stohmann and Langbein, *Journ. f. Prakt. Chem.*, 1893, xlviii., 453).

As open-chain additions may be mentioned:—

$$\underset{\text{Ethylene.}}{C_2H_4} + H_2 = \underset{\text{Ethane.}}{C_4H_6} + 31{\cdot}9 \text{ cals.}$$

$$\underset{\text{Propylene.}}{C_3H_6} + H_2 = \underset{\text{Propane.}}{C_3H_8} + 32{\cdot}5 \text{ cals.}$$

$$\underset{\text{Fumaric acid.}}{C_4H_4O_4} + H_2 = \underset{\text{Succinic acid.}}{C_4H_6O_4} + 32{\cdot}5 \text{ cals.}$$

(See Henrich, "Neuere Theoretische Anschauungen," 1908, s. 28—29).

It seems to me a matter of course to ascribe the diminution of the ordinary addition heat development to the absorption of energy in the molecule, part of the true addition energy being then retained. And equally natural it may be to assume that this retained energy serves to cause a kind of tension or strain which is possible by a closed chain structure.

Now, if—

a = true addition heat for all cases;

e', e'', and e''' = amounts of energy retained in the first, second, and third additions;

we get—

$$1.\ a + e' = 0{\cdot}8 \text{ cal.}$$
$$2.\ a + e'' = 25 \text{ cals.}$$
$$3.\ a + e''' = 27{\cdot}8 \text{ cals.}$$

In the fourth addition the ring structure is broken. Therefore no energy can be retained to cause chain-tension, or for this case—

$$e'''' = 0.$$

On the other hand, energy must be required to open the ring, and it is obvious that the energy retained in the molecule in the former additions and stored by means of the ring tension, must now be set at liberty.

So if—

r = energy required for ring breaking in benzene,

we get—

$$a + e'''' + r - (e' + e'' + e''') = 11 \text{ cals.},$$

and from 1, 2, and 3—

$$e' + e'' + e''' = 53{\cdot}6 \text{ cals.} - 3a.$$
$$e'''' = 0.$$
$$a + r - (53{\cdot}6 \quad 3a) = 11 \text{ cals.}$$
$$4.\ 4a = 64{\cdot}6 - r \text{ cals.}$$

Now, from Equation 4 it is evident that the true addition heat (*a*) may be obtained when the amount of energy necessary to open the benzene ring (*r*) is determined independently. And this may be done by subtracting the calculated heat of combustion of benzene from that which is experimentally found.

For if—

S = extra energy necessary to the ring opening.
C_{exp} = heat of combustion of benzene experimentally determined.
$C_{calc.}$ = calculated heat of combustion special energy for ring breaking *not* being accounted for.

we have—

$$S = C_{exp} - C_{calc.};$$

and whereas r = whole energy required to ring opening.

$$5.\ r = S + v_1.$$

Wherein—

v_1 = energy necessary to the breaking of an ordinary single carbon union.

Now,—

$$v_1 = -14{\cdot}71$$

(See Thomsen, "Thermo-chemistry," Ramsay Series, 1908, p. 391),

And so from 4 and 5 :—

$$4a = 64{\cdot}6 - r \text{ cals.}$$
$$4a = 64{\cdot}6 - S - v_1.$$
$$4a = 64{\cdot}6 + 14{\cdot}71 - (C_{exp} - C_{calc.}).$$

6. $4a = 79{\cdot}31 - (C_{exp} - C_{calc.})$[*]

This final equation by which the true addition heat for benzene may be calculated is in a sense a touchstone to the structure of benzene. For the calculated heat of combustion depends on the structure which we assume for the benzene nucleus.

Let us first consider v. Baeyer's centric structure with nine single carbon bonds. In this case :—

$$C_{calc.} = 792{\cdot}72 \text{ (from Thomsen, p. 494).}$$

Taking for C_{exp} Thomsen's value,—

$$C_{exp} = 799{\cdot}35,$$

we get—

$$4a = 79{\cdot}31 - (799{\cdot}35 - 792{\cdot}72).$$
$$4a = 72{\cdot}68 \text{ cals.}$$
$$a = 18{\cdot}17 \text{ cals.}$$

This result I think very unfavourable to the centric formula. For it means that though the influence of the ring structure on the addition heat has been duly accounted for, this value must yet differ very considerably from that found for addition to open chain structures (± 32 cals.).

On the contrary, taking Kekulé's formula, we find—

$$C_{calc.} = 841{\cdot}17 \text{ (Thomsen).}$$
$$4a = 79{\cdot}31 - (799{\cdot}35 - 841{\cdot}17).$$
$$4a = 121{\cdot}13.$$

$a = 30{\cdot}2$ cals.[†]

In this case the true addition heat for benzene is therefore in close agreement with the ordinary value. And this in my eyes not only establishes the superiority of Kekulé's formula but also the soundness of our premises and reasoning, which we may briefly resume.

1. In addition of hydrogen to closed chain compounds part of the addition heat is retained in the molecule.
2. This retained energy is set at liberty when the chain is opened.
3. For the ring opening extra energy is necessary.

P.S.—Returning to our initial experimental values, it becomes evident, as has already been observed by Stohmann (Stohmann and Langbein, *loc. cit.*), that the transition from benzene into dihydrobenzene requires a comparatively great amount of energy. Now, on further investigation in this matter this has become plausible to me if besides the angular tension of von Baeyer also the possibility of a distance tension is accepted. I take the distance between two single bonded carbon atoms to be less than that between two double united ones. The study of this subject being, however, not yet finished, I must needs refrain from going from our close-to-fact conclusions into far more hypothetical speculation.

University of Utrecht, April-July, 1912.

SILOXIDE, AN UNRIVALLED SUBSTITUTE FOR QUARTZ GLASS.[†]

By Dr. Ing. FELIX THOMAS.

(Concluded from p. 119).

I. *Titanium Oxide-Silicic Acid* (*T Siloxide, Titan Glass*).

THE objects experimented upon were the same as in the case of zircon glass (tubes, cubes, rods, &c.) and of similar dimensions. This product also was handed to me by the manufacturer, Dr. Franz Wolf-Burkhardt, of the Elektrothermal Works, Seebach-Zurich, per the Zirkonglas-Gesellschaft m.b.H., Frankfort-on-the-Maine.

1. *Surface Properties, Colour, Finish.*—Since in the melting of titanic acid with silicic acid in a reducing atmosphere the former is reduced to a lower stage of oxidation, the resulting product has a bluish colour, varying from light to dark according to the quantity of titanium added. In the case of a smaller percentage of titanium the glass, if in thinnish flakes, compares quite favourably with quartz glass in point of transparency; in the case of a greater percentage of titanium the glass is of course far less transparent, a circumstance which, however, is of no consequence for most purposes.

2. *Resistance* (*a*) *to Bending.*—What has already been said in the case of zircon glass applies here also. The values obtained are summarised in Table IV.

TABLE IV.

Description.	Breaking strength in kgs./sq. cm.			Wall-thickness of tubes in mm.		
	(*a*.)	(*b*).	(*c*).	(*a*).	(*b*).	(*c*).
V	110	86		3	2·8	
Q	150	350 (?)	148	2·1	2·9	2·0
TS 0·1 ..	471	471		3·5	3·4	
TS 0·5 ..	386	376		3·1	3·0	
TS 1·0 ..	152	199		2·7	3·5*	
TS 2·0 ..	481	427		4·3	3·9*	
TS 2·5 ..	278	302		3·6	3·8	

* Material porous.

Since the walls of the tubes differ considerably the curve of the breaking strength as a function of the thickness may be given for the purpose of clearer explanation. Taking the loads "p" as abscissæ and the thickness "S" as ordinates we obtain theoretically a curve like *a* in Diagram II. The most favourable material will be that whose p/S curve at first runs evenly and then quickly ascends; moreover, the maximum resistance should of course lie as high as possible; that means, starting with the smallest thicknesses, the material must attain very nearly its maximum of relative resistance. In the case of metals these conditions will be almost fulfilled; in a certain degree with glass, transparent quartz glass and similar bodies. Not, however, with opaque quartz glass, and just as little with opaque siloxide, since in the two latter cases we have to deal with materials which are far from homogeneous. Here we have together with increased thickness a more or less increasing relative breaking strength.

But here also the best material will be that whose p/S curve fulfils the above-mentioned conditions, and as quickly as possible attains its highest maximum value. If we draw, so far as the few figures of the table permit it, the

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[*] It must be reminded that in calculating $C_{calc.}$ combustion heat of benzene, special energy for ring break ought *not* to be accounted for.

[†] Taking for C_{exp} Stohmann's value we get—
$a = 33{\cdot}2$ cals. ($C_{exp} = 787{\cdot}48$).

[*] From the *Chemiker Zeitung* 1912, No. 4.

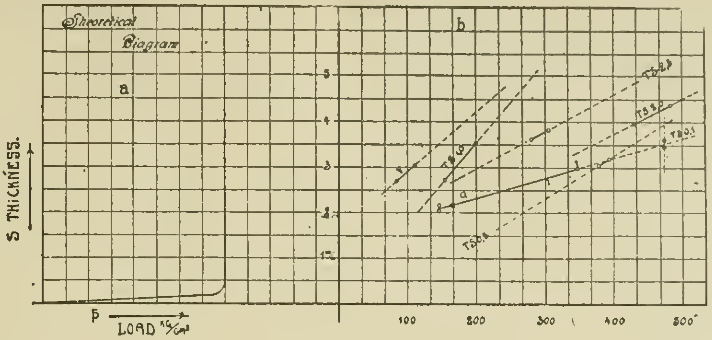

Diagram II.

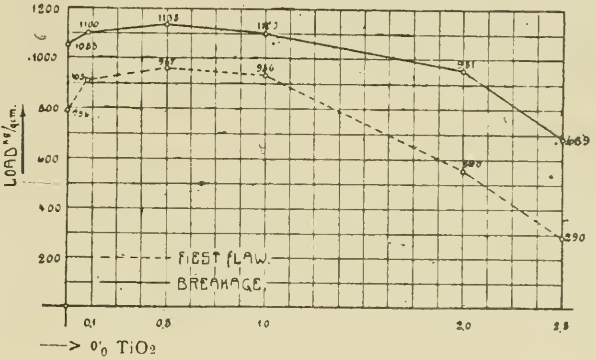

Diagram III.—Curve of Breaking Strengths of Titanium Glass.

different curves, we obtain the diagram *b* (Diagram II.). TS 0·5 has apparently the steepest course and the greatest maximum; even steeper is perhaps TS 0·1 with the highest maximum value, though this cannot be positively asserted owing to the slight difference in the thicknesses of the two experimental tubes. TS 2·0 has also a good course and a high maximum, so that all the glasses from 0·1 to 2·0 per cent would appear to be suitable for use.

(*b*) The experiments for pressure resistance carried out with the same material (vitreosil excepted) had the results given in Table V.

Table V.

Description,	Resistance in kgs./sq.cm.					
	Appearance of first fracture.				Actual breaking.	
	a.	*b.*	*c.*	*d.*	*a.*	*b.*
*Q . ..	189	470	—	1140	667	921
(Cube of 1 sq. cm. pressure surface).						
†TS 0·1 .	352 (?)	856	955		1020	1190
TS 0·5 .	961	—			1140	1130
‡TS 1·0 .	(111)	(114)			—	—
§TS 1·0 .	—	843			1030	1170
TS 2·0 .	793	326 (?)			932	970
TS 2·5 .	272	308			600	778

* In (*a*) load irregularly (by pushes) applied.
† In (*c*) load irregularly applied.
‡ Material porous.
§ In (*b*) load irregularly applied.

The material Q is apparently the strongest but at the same time the most inelastic, being quite unable to stand loads jerkily applied, whereas the TS material, since it appears to be in general somewhat more elastic, endures this unfavourable kind of test quite well; its relative resistance to pressure is, it is true, somewhat behind that of the Q material but comes very close to it in the case of the 0·1 and especially 0·5 per cent. In Curve III. the values of the above table are repeated graphically for better inspection.

3. *Devitrification.*—As in the case of the ZS material, this was definitely determined. Table VI. shows the observed results:—

Table VI.—*Here also the Work was invariably carried out in CO Atmosphere.*

Description.	Temp. °C.	Duration, hours.	Degree of devitrification, ring, &c.
V ..	1500	1	Flake ½ mm. thick; crystallisation within. Inferior ring. Melted at the edges.
Q ..	1500	1	Moderately devitrified. Inferior ring.
Q ..	1500	2	Completely devitrified. No ring. Could be crushed between the fingers.
TS 0·1	1500	2	Flake quite thin. Good ring. Still very firm.
TS 0·1	1500	1	Tinge of devitrification. Well preserved ring.
TS 0·5	1500	1	Tinge of devitrification. Well preserved ring.
TS 0·5	1500	1½	Tinge of devitrification. Well preserved ring.
ZS 1·0	1500	1	Very thin flake. Preserved ring.
ZS 1·0	1500	2	Not perceptibly more devitrified than after 1 hour. Preserved ring.
TS 2·0	1500	1	Very slightly devitrified. Good ring.
TS 2·0	1400	2	Tinge of devitrification. Fully preserved ring.
TS 2·5	1500	1	Tinge of devitrification. Good ring. Appearance that of unused tube.

The TS material has therefore even a greater power of resistance against high temperatures than zircon glass, and that for all the percentages so far experimented with. The troublesome tendency to crystallisation on the part of pure quartz glass when subjected to continued heat at a high temperature is here greatly reduced, so that in titanium glass we see a product both mechanically and thermally superior to quartz glass.

The experiments concerning softening points, chemical resistance of titanium glass to alkalis (against acids, zircon and titanium siloxides are at least as proof as quartz glass) and some other problems are not yet concluded, and will be published in a later treatise, also the properties of glasses obtained by the addition of other metallic oxides, whose examination is now in hand. The properties of the xircon oxide-titanium oxide-silicic acid group have no special interest; in general they combine in each other the properties of the individual glasses, but have been tested only up to an addition of 1 per cent of the oxide mixture.

The above experiments were carried out with the co-operation of Privy Councillor Prof. Dr. W. Borchers in the course of 1911 in the Metallurgical and Electrometallurgical Institute of the Technical College at Aachen.

A LARGE BOOKSTORE.

To have built up one of the largest businesses of its kind in the world, employing over sixty people, with branches throughout London, all this accomplished in the small space of about seven years, is an achievement which any man would be proud of, and it is doubtful whether such an achievement has ever before been accomplished in the business world. This is the record of Messrs. W. and G Foyle, of 135, Charing Cross Road, who have recently opened what will doubtless be the largest and most unique bookshop in the United Kingdom.

All letters and enquiries are answered the same day, and all books despatched as far as possible within twenty-four hours of order. So minute is the system of classification adopted, that any book or letter can be found within a few minutes. A printed list of abbreviations running into several hundred items is in use throughout the offices and for the convenience of the staff.

They also have a system whereby any books asked for and not in stock can be obtained within a few days. They issue their own periodical, fortnightly, containing thousands of books wanted by customers; and, at the same time, have on record the saleable books of almost every second-hand bookseller, so that when a book is enquired for, they know where to place their hands on same, from outside sources.

The twenty-two catalogues issued are very comprehensive and simple.

Messrs. Foyle owe their success to working from the commencement upon a thoroughly systematic basis right throughout their business, to judicious advertising, and to the loyalty of their staff. They have imported originality into their methods, they have been always amenable to suggestions, whether from customers or from their own staff, and they believe in making use of all the time they have at their disposal.

Solubility of Thorium Sulphate in Sulphuric Acid and in Solutions of Lithium Sulphate.—M. Barre.—The solubility of thorium sulphate in solutions of lithium sulphate increases as the proportion of the latter in the solution is raised. The evaporation of the solution gives crystals of the two constituents, but in view of the enormous increase of solubility it seems almost certain that a complex salt exists in solution. In sulphuric acid the solubility of thorium sulphate increases up to 34 per cent of sulphuric acid, and then diminishes regularly.—*Bull. Soc. Chim. de France*, xi.—xii., No. 13.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

Annual General Meeting, New York, 1912.

Report of Council.

The number of members on the register is now 4273 as compared with 4300 at the last Annual Meeting. During the year 225 new members have been elected as compared with 245 last year; and the losses have been 253 as compared with 244 last year.

The Council regrets that the losses by death amount to forty-nine as compared with twenty-nine last year, viz.:—E. E. Babb, J. W. Baird, E. Beanes, H. vom Berge, H. Court, R. Burns Cuming, Dr. E. Divers, C. A. Drake, B. Dukes, Dr. H. V. Frost, W. K. Gaylord, Read Gordon, R. Graesser, T. Griffiths, Dr. G. Grottanelli, Wm. Gutcher, D. Harris, A. Harrison, Dr. A. Hess, J. A. Hicks, Dr. P. L. Hobbs, A. Huntzinger, J. Jekyll, H. A. Kittle, R. J. Levy, Dr. J. Muter, B. E. R. Newlands, Jas. Oddie, John Pattinson, Thos. Pears, W. J. Peet, S. V. Peppel, F. G. Perkins, C. E. Pickett, H. Rogers, Sir Samuel Sadler, P. G. Sanford, Dr. M. Shimosé, Hermann Spies, C. E. Stuart, S. J. Studer, J. Pimm Strangman, W. B. Syme, Dr. J. H. Wainwright, L. Weeple, W. Whitehouse, W. A. Wilson, S. M. Winkler, and Wm. Wood. Dr. Divers was President of the Society in 1905-6, and both he, Mr. Newlands, and Mr. Pattinson worked for many years on the Publication Committee with devotion and zeal. Dr. Shimosé was the inventor of the Japanese explosive identified with his name. Messrs. Levy and Pears were among the victims of the *Titanic* disaster.

Four ordinary members retire from the Council and four nominations have been made to the vacancies. No ballot is required.

The following Chairmen of Local Sections retire:—Dr. A. McGill (Canada), Mr. Arthur Carey (Liverpool), Mr. E. Grant Hooper (London), Mr. E. F. Hooper (Newcastle), Prof. T. Gray (Scotland), Mr. Thos. Steel (Sydney), and Mr. E. A. Brotherton (Yorkshire). The following have been elected to succeed them:—Mr. W. P. Cohoe, Prof. F. G. Donnan, Mr. G. T. Holloway, Mr. T. W. Lovibond, Dr. Thos. Ewan, Mr. Loxley Meggitt, and Mr. George Ward. The Council desires to express its thanks to the retiring Chairmen for their services.

The Journal in 1911 numbered 1478 pages of text besides supplement and advertisements, as against 1482 pages in 1910. On the recommendation of the Publication Committee, the list of British patent applications has been placed in the Supplement in such a way that it can be bound with the Journal if desired.

The tenancy in Palace Chambers, Westminster, having expired, offices have been taken at Broadway Chambers, Westminster, at about the same rental.

The Balance Sheet and Annual Statement of Account, which has already appeared in the June 29th issue of the Journal, will be laid before the meeting.

The Council has appointed the President, Dr. Messel, F.R.S., to represent the Society on the Governing Body of the Imperial College of Science and Technology in the place of the late Dr. Divers, F.R.S. The Councill will be glad to receive suggestions in connection with the establishment of an efficient system of education in Chemical Technology.

Mr. Thos. Tyrer has been elected a representative of the Society on the Board of the National Physical Laboratory. A special Committee of the Laboratory has just commenced an investigation into the properties of glass for optical and other scientific purposes.

The first volume of International Annual Tables of Constants, to which attention has been called recently in the Journal, has now appeared and justifies the support given by the Council, as mentioned in last year's report.

The cost having been greater than was anticipated, a second donation has been given.

The Society is taking part with other institutions in several inquiries of common interest; with the Textile Institute as to the dyeing of textiles with indigo, with the Chemical Society into the possibility of so preparing abstracts as to avoid duplication, and with the Institute of Metals in considering the nomenclature of non-ferrous alloys. It has also taken part in a recent conference on the International Interchange of Students.

The Royal Commissioners for the Exhibition of 1851, who have recently established a system of Industrial Bursaries, and are subsidising young graduates in science who propose to take up industrial positions, have invited the Society to express its opinion thereon. Great diversity of opinion on the subject was expressed by the Sections, and the Council sent to the Commissioners a synopsis of the various views expressed. The Royal Commissioners have expressed their indebtedness to the Society for its assistance.

The Society's medal, founded in 1896, and awarded once in every two years for conspicuous service rendered to Applied Chemistry by research, discovery, invention, or improvements in processes, has this year been awarded to Sir William Crookes, O.M., F.R.S., for his epoch-making discoveries in physical chemistry and the rare metals.

At the celebration of the 250th Anniversary of the foundation of the Royal Society the Council was represented by the President of the Society, who presented an address. A copy of this address appeared in the Journal for July 31st.

An International Exhibition will be held in San Francisco in 1915 to mark the opening of the Panama Canal, and the Board of Trade has expressed the opinion that Great Britain should take part in it. The Council of the Society is of the same opinion and trusts that the Exhibition will be supported by the Chemical Industry.

The Council has done its utmost to give publicity in Great Britain to the Eighth International Congress of Applied Chemistry, now about to commence its sittings.

ADDRESS OF THE PRESIDENT, DR. R. MESSEL, F.R.S.

At a time when the latest discovery of interest may be instantly flashed to the remotest part of the world by wireless telegraphy, and the technical press discusses every possible problem as it arises, a Presidential Address seems to me to be almost an anachronism. In very few cases is it possible to communicate anything not already known. Whatever issue a speaker may desire to consider is sure to have been dealt with till it is almost threadbare, and I fear that the topics I venture to bring before you must be enrolled in the latter category.

I propose to deal with some aspects of the remarkable progress made within my recollection. The ceaseless energy with which industry has availed itself of the achievements of pure science has made possible the manufacture, on a large scale, of products, either unknown but a few years ago, or seen as specimens in scientific collections, or produced only by nature. That I shall refer to relatively very few of these triumphs of chemical research and invention and mainly to inorganic products must be evident when I mention that the period covered embraces the discovery of the aniline dyes and that of artificial rubber, as well as the invention of the first electric telephone and of wireless telegraphy.

As my recollections unfortunately go back over so long a period, I feel tempted to drag in here one which may be of interest to some of my audience, though it has no connection with the matter I propose to deal with. In 1861, when I was at school at Friedrichdorf, in Germany, my master, Philip Reis, invented the first telephone. I was present at its birth, and assisted Reis in making the mechanical parts of some of his instruments and also repeatedly in his experiments, Reis being at one end of the circuit speaking or singing, I listening at the other, or *vice versâ*.

The introduction of synthetic processes may be said to be the keynote of progress of modern industrial chemistry.

One of the most fascinating compounds recently introduced into industry is calcium carbide, CaC_2. It had lain dormant since its discovery in 1862 by Wöhler, until your countryman Wilson and Moissan made use of the electric furnace to produce it; now its manufacture constitutes a mighty industry, close on 300,000 tons being produced annually. Serving as it does as raw material for the manufacture of calcium cyanamide, it is now the parent of numerous other products of great importance. Among these may be mentioned acetylene, C_2H_2, so largely used as an illuminant, and for welding and cutting metals, and I may remind you that the possibility is foreshadowed that this gas will be of use as the starting point in making other chemicals. Calcium cyanamide, apart from its undoubted great value as a fertiliser, is coming to the fore as a source of cyanides, now so largely used in extracting gold. What may be of far greater importance, it is convertible by the action of superheated water into ammonia, which in turn may be converted into nitric acid and nitrate of ammonia by oxidation with air under the catalytic influence of platinum.

I have recently noticed alarming reports in the press that the impossibility of procuring supplies of nitrate of soda from Chili in time of war may prove a serious handicap to any country in the production of explosives and powder. Considering that the quantity of nitrate of soda used for the purpose is but a fraction of that required in agriculture and that large stocks are held for this purpose almost everywhere, I cannot share the writers' fear. But in view of the fact that ammonia salts are produced by all gas works and of the many attempts to produce it synthetically, the catalytic method of producing nitric acid from ammonia may deserve more attention than it has received up to now, especially if ammonia, no matter how produced, should become a sufficiently cheap raw material.

The most interesting feature in the production of calcium cyanamide is the use of pure nitrogen. Of the various methods of preparing the gas, that which involves fractional distillation of liquefied air seems to be preferred. We are becoming familiar in industry with the impossible, but who *could have expected* such a possibility only a few short years ago? Think of the excitement caused in the scientific world when, in 1877, Pictet and Cailletet first succeeded in liquefying oxygen. Pictet's work was then described as the most brilliant achievement in modern science. The barrier between condensible and permanent gases was broken down, and the latter term was deprived of its significance; but how much work remained to be done, what ingenuity had yet to be exercised, to translate this scientific discovery into a process for the industrial preparation of nitrogen. Success has been achieved by the exertions and ingenuity of several of our greatest authorities in physical and chemical science; nowadays, every gas that is required is readily procurable in the liquefied form (Cl_2, SO_2, N_2O, CO_2, NH_3, &c.) in the well known steel cylinders capable of withstanding enormous pressures.

If I have laid stress on the conversion of ammonia into nitric acid, the reason is that ammonia is obtainable locally everywhere, either as a by-product of the manufacture of illuminating gas or Mond gas and from coke-ovens, and that the installation for converting it into the acid is a relatively cheap one. The numerous attempts to produce ammonia synthetically from its elements, nitrogen and hydrogen, or from various nitrides, such as those of titanium, boron, magnesium, aluminium, and calcium, can moreover only be of benefit in solving the problem. True, the direct production of nitric acid by means of *the electric arc* from atmospheric air may appear to be a more rational process, but so long as this industry is tied to water power, and the difficulties of transporting nitric acid as such in aluminium or iron packages be not overcome, the case seems different in my judgment, particularly in countries where water power is not available and other power as yet too expensive. It is to be remembered that to carry nitric acid safely in iron packages, about 10 per cent of concentrated sulphuric acid has to be added, and that if one or the other of the ammonia processes under trial should make it possible to transport it as nitrate of ammonia, from which it can readily be liberated at the place of consumption, the difficulty of carriage in the event of war would still remain.

My reason for referring at such length to the production of these compounds of nitrogen is their importance in agriculture. Food the nations must have, and it seems that to this end they will require the services of the chemist more and more as population grows. The great stimulus our medallist, Sir William Crookes, has given to the production of nitric acid by calling attention to the near approach of the exhaustion of the deposits of nitrate of soda is well known. His suggestion to utilise Cavendish's discovery of the direct interaction of the constituents of the atmospheric air and the success, so far achieved, have often been referred to; the work done by Birkeland and Eyde, by Schoenherr, Pauling, and others, is also well known, but it gives me particular pleasure to point out that here again America was the first to attempt the realisation of this great problem. The realisation of that other great problem, *i.e.*, the production of *ammonia from its elements*, appears likewise on the eve of accomplishment, and I hope it will not be long before we shall have details of the manner in which it has been solved in practice, and how the great technical difficulties have been overcome. It will likewise be interesting to learn something about the relative efficiency of the various uranium and iron catalytics used, &c. If the published particulars as to temperature (about 650°) and pressure (about 150 atmospheres) be correct, the task to be solved was one of no mean order. Meanwhile, we can only offer our best wishes to the ever-enterprising Badische Aniline und Soda Fabrik.

Two of the other processes mentioned before, namely, that of the production of ammonia from calcium nitride, and from aluminium nitride, are likewise most interesting, the former for chemical reasons, *i.e.*, the conversion of metallic calcium first into calcium nitride, Ca_3N_2, then by the action of hydrogen on this compound into calcium hydride and ammonia, the calcium hydride being subsequently re-converted by means of nitrogen into calcium nitride and ammonia—so that a relatively small quantity of calcium is theoretically sufficient to produce an infinite quantity of ammonia. Numerous processes have been devised for producing hydrogen; one of the latest is Pictet's, who splits up hydrocarbons either directly into hydrogen and carbon, or by means of steam, at the melting-point of iron, into hydrogen and carbon monoxide, thus materially increasing the yield.

Inasmuch as aluminium nitride yields on hydrolysis, together with ammonia, a particularly pure form of aluminium hydrate, starting from an impure raw material, it may become of great importance to the aluminium industry. I well remember aluminium and more often magnesium being made by Bunsen by the electric arc on a diminutive scale as a lecture experiment. We students used to cough violently when the white fumes which were given off began to fill the lecture-room, until Bunsen, smiling pleasantly, mentioned that the white fumes were due to the ammonium chloride he had added to keep the surface of the metal bright, and that ammonium chloride was an excellent remedy for a cough. The coughing then stopped. As a curiosity, bars of the metal about 3 in. by 1 in. by ½ in. were handed round, and weighed by every one in his hand; the metal was doubtless produced by Ste. Claire Deville's sodium process. The annual output of aluminium in 1909 was over 24,000 tons, produced electrically. Now that the problem of autogenous welding of the metal, which so long defied all efforts, has been solved, the use of aluminium for chemical apparatus has become practical; apart from its utility in handling nitric acid, the metal has proved to be of the greatest value in breweries, in the food industry, and in varnish works.

The application of aluminium as a fuel by Goldschmidt has further led to the production, by his alumino-thermite process, of many metals in a relatively pure form otherwise only producible by the agency of the electric current. Chromium, manganese, and molybdenum prepared by this method, besides various alloys of nickel, iron, and copper with these metals, or with titanium and vanadium, have found a use mainly in the iron industry. The ingenious process of welding rails and repairing castings by means of the thermite process is of course known to all, as well as the use of tungsten and tantalum as filaments in electric incandescent lamps. The fact that tantalum filaments, of vastly greater strength than those formerly produced by compression of the metal in powder form, can now be obtained by drawing the metal through diamond dyes, will doubtless give an increased stimulus to the use of the element. The mention of tantalum may call to your mind the fact that the expression rare is fallen into disuse, as the earths once known as rare are in everyday use, and, owing to the scientific acumen displayed by Auer von Welsbach, the gas industry is now well able to hold its own against the electrical. But electricity is in evidence everywhere in our industry. It threatens to displace the furnace in the alkali works, it provides us with chlorine, and the time may not be distant when muriatic acid is made electrically. We are indebted to the electric furnace for the sodium industry (with its application to the cyanide, sodium amide, and other manufactures) and to the production of ferrosilicon, carborundum, and graphite, for which, in the form of electrodes and lubricants, America, thanks to Mr. Acheson, remains as yet unsurpassed. The manufacture of nickel by the remarkable Mond carbonyl process should not be forgotten. This metal would appear to have some future in the elimination of carbon bisulphide from coal-gas and possibly as a catalytic in other industries. We do not, however, always want to get rid of sulphur. A most original idea, successfully carried into practice by Frasch, in Louisiana, is no doubt that of liquefying sulphur in the bowels of the earth and then pumping it up.

After thus rambling through the highways and byways of inorganic chemistry, we now arrive at a different class of industries. There is no need to go into any detail, but suffice it to say that their influence has been of momentous importance industrially, and in turn has acted and reacted greatly on science. Merely to mention them is sufficient. I refer, of course, to dyestuffs and synthetic organic products, including drugs.

(Amongst synthetic drugs there figures now the famous indicator phenolphthaleine. Being colourless and tasteless itself whilst turning pink on the addition of soda, it had been added by Government to earmark certain kinds of hock. The quite unexpected result is that the indicator is now sold as a splendid aperient under the name of "Purgene").

(To be continued)

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Australian Meeting, 1914.

Preliminary Notice.

As misapprehension has been found to exist as to the date of this Meeting, it is desired to remind Members that the invitation to visit Australia was accepted by the General Committee for the year 1914, not 1913. The Meeting in 1913 will be in Birmingham.

The following programme is issued for no other purpose than to give a general indication of the probable course of the Meeting. It is based upon existing travelling arrangements, which are liable to alteration, and it is to be regarded as strictly provisional in every respect.

Full details will be announced in due course, and the usual inquiry will be made of Members as to their intention to attend the Meeting.

Outward Journey, 1914.

I. Main Party. Leave London, by direct steamer (*via* Suez), Friday, July 3, or overland to join steamer at a Mediterranean port, about July 10. Arrive Fremantle (for Perth), Western Australia, August 4.

II. Advance Party, to visit Western Australia for one week. Leave London by steamer, June 26, or overland about July 3. Arrive Perth, W.A., July 28.

The above parties, united on August 4, proceed to Adelaide.

III. Members travelling by New York or Montreal, Vancouver, trans-Pacific steamer, and Sydney; or by Cape Town, South Africa, to join united party (above) at Adelaide, leaving England about June 22—26.

United Party :—

Adelaide.—Saturday, August 8—Wednesday, August 12. Lectures—Receptions—Excursions. August 12-13, Adelaide to Melbourne (train).

Melbourne.—Thursday, August 13—Wednesday, August 19. Presidential Address (first part)—Meetings of the Sections—Lectures—Receptions—Excursions. August 19-20, Melbourne to Sydney (train).

Sydney.—Thursday, August 20—Wednesday, August 26. Presidential Address (second part)—Meetings of the Sections—Lectures—Receptions—Excursions. August 26-27, Sydney to Brisbane (train).

Brisbane.—Friday, August 28—Monday, August 31. Lectures—Receptions—Excursions.

Homeward Journey.

Members requiring to return home by the earliest possible date will proceed from Brisbane (September 1) by train to Adelaide (September 4) and there join direct steamer (*via* Suez), arriving London by steamer October 11, or overland from a Mediterranean port, about October 3.

Returning by steamer *via* Thursday Island, Port Darwin (Northern Territory), Java, Singapore, and Colombo, and joining the direct steamer (*via* Suez) at the last-named port, Members should reach England about October 10-18.

A party proceeding *via* Sydney to New Zealand for one week's visit should reach England towards the end of October, according to homeward route.

The journey from Eastern Australian ports to Yokohama (*via* Hong-Kong) occupies about a month; the return to Englahd may be made thence by trans-Pacific or trans-Siberian routes.

NOTICES OF BOOKS.

Lubrication and Lubricants. By Leonard Archbutt, F.I.C., F.C.S., and R. Mountford Deeley, M.Inst.C.E., M.I.Mech.E., F.G.S. Third Edition. London: Charles Griffin and Co., Ltd. 1912.

It has been a matter for regret that this valuable compendium on Lubrication and Lubricants should have been unavoidably out of print for some time, and engineers and chemists will welcome the appearance of the third edition, enriched with full accounts of the latest work which has been done on the subject. It will be useful to both classes of men, and analysts will find that it contains much matter relating to the testing of lubricants by physical, chemical, and mechanical means, which is of special value to them, and is not otherwise easily accessible. Space is fairly evenly divided between practice and theory, and in the third edition Pétroff's work on the friction of lubricated bearings is discussed for the first time, and the large amount of work which has been done on the connection between chemical constitution and lubricating value is given adequate notice, while methods of lubricating motor vehicles are fully treated.

General Foundry Practice. By Andrew McWilliam, A.R.S.M., M.Met., and Percy Longmuir, B.Met. Second Edition. London: Charles Griffin and Co., Ltd. 1912.

This book has obtained for itself a fully recognised position as a somewhat condensed text-book of general foundry practice, intended chiefly though not exclusively for the use of foundry managers and foremen. It is thoroughly practical in character, and chapters are devoted to the causes and prevention of the production of wasters in casting, either from faults due to mould and pattern or faults due to the metal. Micrographic analysis is briefly treated, but the author warns the student not to pay overmuch attention to the vast amount of hastily collected material which is being published in this sphere. The theoretical aspects of the subject are not discussed. In the second edition some new matter and illustrations have been added, and an effort has been made to bring the book thoroughly up to date.

The Dynamics of Particles and of Rigid, Elastic, and Fluid Bodies. By Arthur Gordon Webster, A.B.(Harv.), Ph.D. (Berol.). Second Edition. Leipzig: B. G. Teubner. New York: G. E. Stechert and Co. London: Williams and Norgate. 1912.

The second edition of this book of lectures on dynamics is practically a reprint of the first, which met with an immediate success both in England and America. Although not written to cover the syllabus of any particular examination the book will be very useful to the student who is attending a course of lectures on physics or applied mathematics at our universities. Given a fair knowledge of the calculus he should be able to follow the text easily, and it contains a sufficiently full treatment of dynamics for the average physical student's first year course.

Poems, Mathematical and Miscellaneous. By Henry Daw Ellis, M.A. London: The Chiswick Press. 1912.

Those who want a little light reading for their idler moments of relaxation will find it in this small volume of poems on subjects mathematical, humorous, and serious. They will meet, and perhaps laugh with, many of their acquaintances of more strenuous times—ions and electrons, even the calculus and Bergson's philosophy—in holiday guise, and will no doubt enjoy the author's light touch on serious subjects and his keen appreciation of their humorous side.

Die Electrolytische Alkalichloridzerlegung mit starren Metallkathoden. ("The Electrolytic Decomposition of Alkali Chlorides with Solid Metallic Kathodes"). By Dr. Jean Billiter. Part I. Halle-a.-S.: Wilhelm Knapp. 1912. (16.50 Mk.).

In this book the author restricts himself to the consideration of processes, patented in Germany, England, and the United States, for the decomposition of alkaline chlorides, in which solid kathodes are employed, those in which liquid (mercury) kathodes are used having already been treated in a monograph by Lucion. The numbers of patents included amounts to roughly 450. In the case of all German patents relating to methods and apparatus the claims are reproduced word for word, and an illustrated description is often given, while discussions of the usefulness and probable success of the methods advocated follow. These discussions reveal the acumen and technical knowledge of the author, but it seems to be carrying a desire for completeness rather too far to give some space to the reproduction of the patent claims, and to a short description of the proposed apparatus, &c., and then dismiss the process as "quite useless." In a short introduction the theoretical principles underlying the most important practical methods are explained. Details of the application of the methods on a large scale will follow in a second volume which is to appear during the year.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 4, July 22, 1912.

Catalytic Preparation of Phenolic and Diphenylenic Oxides. — Paul Sabatier and Alph. Mailhe. — Mixed phenolic oxides may be prepared by the catalytic dehydration of mixtures of two phenols in presence of thoria. A certain amount of each simple oxide is always obtained as well, and sometimes simple or mixed diphenylic oxides are produced in addition, hydrogen being eliminated. Thus a mixture of paracresol and α naphthol at 450° gives paracresyl oxide, diparacresylene oxide, and a considerable amount of the oxide of paracresylene—α-naphthylene.

Chemical Equilibrium of the System : Ammonia Gas and Ethylene-diamine Hydrochloride.—Félix Bidet.—From the study of the action of gaseous ammonia upon solid anhydrous-diamine hydrochloride and the inverse reaction between liquid ethylene-diamine and solid ammonium chloride it is found that at the same temperature (at 0° and below) there are two distinct values of the limiting pressure. This may be explained by supposing that in a first phase the monohydrochloride $C_2H_4(NH_2)_2HCl$ is formed, and that in a second phase the base is displaced and partially unites with its hydrochloride. Apparently certain compounds, which are stable at 0° and below, are totally decomposed at about 10°.

Hydrogen Derivatives of Apoharmine.—V. Hasenfratz.—When hydriodic acid is used as reducing agent two hydrogenated derivatives can be obtained from apoharmine ; one of these, tetrahydroapoharmine, $C_8H_{12}N_2+H_2O$, has not been prepared before. The existence of methylapoharmine, $C_8H_7N_2CH_3$, and of the nitroso derivative of dihydroapoharmine, $C_8H_9N_2(NO)$, shows the presence of an NH group in apoharmine and in dihydroapoharmine. If methyl iodide, in combining with these two bases, attached itself fo the NH group the two products obtained would be decomposed by potash, giving the corresponding methylated derivatives. This is the case with apoharmine, but not with dihydroapoharmine, hence in the latter iodomethylate the methyl iodide must be attached to a tertiary atom of nitrogen. Thus dihydroapoharmine is both a secondary and tertiary base.

Catalytic Hydrogenation of Ketones.—G. Vavon.—The author has applied the platinum black catalytic method to a great number of ketones (aliphatic, cyclic, aromatic, ethylenic, terpenic, ether-salt, diketonic), and has found that it constitutes a very general method of transforming them into secondary alcohols.

Action of Sodamide on 1-4-Dibenzoylbutane.—Edouard Bauer.—The action of sodamide on 1-4-dibenzoylbutane is somewhat complex. The final products are two isomeric compounds of formula $C_{18}H_{16}O$. Apparently 1-benzoyl-2-phenyl-2-cyclopentanol is first formed, but being unstable it loses water and yields benzoylphenylcyclopentene. If the action of the sodamide is prolonged for three or four hours the results are different. Small quantities of benzoic acid, the two phenylbenzoylcyclopentenes, benzamide, a product $C_{12}H_{13}ON$, and an unsaturated hydrocarbon, $C_{11}H_{12}$, are formed.

Bulletin de la Société Chimique de France.
Vol. xi.—xii., No. 13, 1912.

Contributions to the Study of Nickel as Catalyser.—J. B. Senderens and J. Aboulenc.—The authors have investigated the catalysing action of anhydrous oxides of nickel, obtained by calcination, of hydrates of nickel, and of oxidised pyrophoric nickel, and have found that no definite temperature, at which reduction takes place, can be given. The temperature of reduction varies considerably with different specimens, and in the case of the anhydrous oxides this may be explained as being due to different degrees of calcination. It is possible that the hydrates are reduced to a series of suboxides which become more and more difficult to reduce. Apparently it is impossible to arrive at the complete reduction of the oxide, but the mixture of reduced metal and oxide obtained is more active than the reduced metal alone.

Ether Oxides of Cinnamic Alcohol.—Henri Beaufour.—The methyl ether of cinnamic alcohol readily yields the iodohydrazine when treated with iodine and yellow oxide of mercury. This can then be transformed into methyltropic aldehyde by silver nitrate, and then into the corresponding acid and alcohol, $C_6H_5—CH<\begin{matrix}CH_2OCH_3\\CH_2OH\end{matrix}$. The author hopes that the dehydration of this alcohol will yield the ethylenic derivative, $C_6H_5—C\begin{matrix}=CHOCH_3\\<CH_3\end{matrix}$.

N-Methyl and N-Dimethyl-2-3-Dioxybenzylamine. — René Douetteau. — 2-Oxy-3-methoxybenzylic aldehyde (orthovanilline) when subjected to Cannizaro's reaction gives the corresponding alcohol, the hydrochloric ether of which when treated with dimethylamine and monomethylamine gives dimethyl ethers of the two bases, N-methyl and N-dimethyl-2-3-dioxybenzylamine. The bases themselves may be obtained by demethylation.

Atti della Reale Accademia dei Lincei.
Vol. xxi., No. 11.

Analysis of a Molybdenite from Calabria.—R. Nasini and Enrico Baschieri.—The authors have analysed a specimen of molydenite from Calabria, and have found that it contains no elements except molybdenum and sulphur. They searched especially for Masataka Ogawa's supposed new element, nippon, allied to molybdenum, but found no trace of it.

MISCELLANEOUS.

Chemical Laboratory Fresenius, Wiesbaden, Germany.—During the Summer Term, 1912, there were forty-nine students on the books, including five ladies. The nationality of the students was as follows :—Thirty-two were from Germany, four from Russia, three from Holland, two from Belgium, two from Austria, one from Luxemberg, one from England, one from Switzerland, one from France, one from Spain, and one from Brazil. The Directors of the Institute, Geh. Regierungsrat Prof. Dr. H. Fresenius and Prof. Dr. W. Fresenius, are assisted by four duly qualified lecturers and heads of departments. Besides these there is a staff of twenty-nine assistant Chemists including eight ladies. The next Winter Term will commence on October 15th. During the Summer Term, 1912, a number of scientific treatises originated from the Laboratory Fresenius ; they were published in different chemical journals, especially in the *Zeitschrift für Analytische Chemie*, edited by the Directors. As special print appeared "Chemische Untersuchung der Drei-Lilien-Quelle zu Wiesbaden, sowie Untersuchung derselben auf Radioaktivität," by Geh. Regierungsrat Prof. Dr. H. Fresenius (Wiesbaden, C. W. Kreidel's Verlag). Besides the scientific work, a great number of chemical analyses were executed during the Summer half year, 1912, for commercial, mining, industrial, and agricultural purposes, also in the interest of sanitary boards, criminal, and other states departments.

THE CHEMICAL NEWS.

Vol. CVI., No. 2758.

PHOTOTROPY.*

By Professor SENIER.

About three years ago, in conjunction with Mr. F. G. Shepheard, while trying to obtain certain acridines and acridones by the condensation of salicylideneamines we noticed that one of these compounds, salicylidene-*m*-toluidine, which was yellow when freshly prepared and kept in the dark, changed to orange when exposed to sunlight, and that on removal from the light it gradually returned to the original colour. This photo-reaction was found to be reversible at will, but the change from yellow to orange was very much quicker than the reverse change from orange to yellow. On consulting the chemistry journals we found that four observers had preceded us in the discovery and study of this phenomenon, and that it had been named *phototropy* by Marckwald in 1899. His phototropic compounds were two: anhydrous quinoquinoline hydrochloride and β-tetrahydro-α-ketonaphthalene. Biltz in the same year extended the field of phototropy to the arylaldehyde hydrazones and osazones, and Pabst in 1902 added dibenzylaminobenzil. In 1908 Stobbe contributed an important addition to the subject in a detailed study of various fulgides, in which measurements of the wave-lengths of the light employed were made. In 1909 our first communication was made to the Chemical Society, and it has been followed by several others in which we have had the advantage of the co-operation of Miss Rosalind Clarke. We have sought to discover further instances of phototropy in the hope that by their study we might be able to throw more light on this interesting phenomenon. Soon afterwards Padoa commenced an extended study of hydrazones, which, in his hands, have proved a rich source of phototropic substances.

Of the numerous analogues of salicylidene-*m*-toluidine we have examined, mostly new compounds, but including some already well known, we have found fourteen which exhibit phototropy distinctly. They are (specimens shown):—Salicylidene-*m*-toluidine, salicylidene-*o*-4 xylidine, salicylidene-*o*-chloroaniline, salicylidene-*p*-aminobenzoic acid, salicylidene-β-naphthylamine, salicylidene-*o*-anisidine, disalicylidene-*m*-phenylenediamine (needles), disalicylidene-*m*-phenylenediamine (plates), 2-hydroxy-3-methoxybenzylidene-*p*-xylidine, salicylideneaniline (two polymorphous forms), salicylidene-*o*-bromoaniline, salicylidene-*p*-bromoaniline, and salicylidene-*p*-anisidine.

The following diagram indicates generally the behaviour of a phototropic substance under the successive influence of light and darkness, or more precisely of light waves towards the violet and light waves towards the red of the solar spectrum.

$$\begin{tikzcd}\text{Lighter coloured phototrope} \arrow[r, shift left, "\text{Waves towards violet}"] & \text{Darker coloured phototrope.} \arrow[l, shift left, "\text{Waves towards red}"]\end{tikzcd}$$

Phototropy is a phenomenon confined to solids, it is not exhibited when the compounds are fused or when in solution. In the case of the salicylideneamines the colour changes are from various shades of yellow to orange or red. The lighter phototrope exists only in the absence of light or in presence of light towards the red end of the solar spectrum, and the darker phototrope correspondingly only exists when light is falling on the substance, or more precisely the light towards the violet end of the solar spectrum. The particular portion of the spectrum which effects these changes varies with each compound, but, as Stobbe has shown, the relation between that which effects the first change and that producing the reverse change is always the same. At the ordinary temperature the first change from the lighter to the darker phototrope is rapid —requires only a few minutes—while the reverse change is usually slow, and though sometimes a matter of minutes it may take hours or days, or even weeks. At a higher temperature which is different for each compound, we find that the reverse change also may be affected almost instantaneously. Padoa in a recent investigation has made the interesting announcement that by mixing certain other compounds in very small proportion with the phototropic compound, both of these changes may be made much more rapid—the added substance acting as a catalytic sensitiser.

Another point we have observed is that there is a temperature limit for each compound above which phototropy does not take place. In some cases it corresponds to the melting-point, but in others it is much below that temperature. It then seemed to us probable that many substances which had not hitherto shown phototropy might do so at temperatures below the ordinary temperature, the only temperature at which hitherto they had been examined. Our search for such instances was rewarded by the discovery of two:—Salicylidene-*p*-anisidine and 2-hydroxy-3-methoxy-benzylidene-*p*-xylidine, both of which are active at −20°.

Three hypothetical explanations of phototropy have been considered by investigators of this phenomenon. First, ordinary intramolecular rearrangement, metastasis; second, stereo rearrangement; third, change of crystalline form, polymorphism. Most inquirers have abandoned all three as at least unlikely. As I have already discussed this question (Presidential Address to the Chemistry Section), I will merely add here as bearing upon the third hypothesis, that two of the compounds above mentioned, disalicylidene-*m*-phenylenediamine and salicylideneaniline, exist in two polymorphic forms, each of which gives phototropes.

Another question, which is at present engaging our attention, is the kind of energy evolved when the darker phototrope, in the absence of solar energy, or possibly also when under solar influence, returns to the lighter form. A comparison with the analogous phenomenon of phosphorescence, as shown by Stobbe, will make this clear:—

$$\begin{tikzcd}\text{Non-luminous photogene} \arrow[r, shift left, "\text{Solar energy}"] & \text{Luminous photogene.} \arrow[l, shift left, "\text{Absence of solar energy}"]\end{tikzcd}$$

In this case the energy accumulated from sunlight in the first change is evolved as luminosity, phosphorescence, in the reverse change. It remains for future investigation to discover the corresponding form in which the solar energy stored in the darker phototrope is evolved when it returns to the lighter variety.

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* A Paper read before the British Association (Section B), Dundee Meeting, 1912.

THE DECOMPOSITION OF AMYGDALIN AND VICIANIN BY ENZYME ACTION.*

By ARTHUR COMPTON, B.A., M.B.,
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In 1830 Robiquet and Boutron (*Ann. de Chim. et de Phys.*, 1830, [2], xliv., 352) isolated from the seeds of bitter almonds, *Amygdalus communis*, a substance crystallising in colourless rhombic prisms, to which they gave the name *Amygdalin*. This substance they considered to be the source of the essence of bitter almonds yielded by the latter under the influence of humidity.

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* A Paper read before the British Association (Section B), Dundee Meeting, 1912.

Seven years later, Liebig and Wöhler (*Ann. d. Pharm.*, 1837, xxii., 1) separated from almonds an albuminous substance, *emulsin*, which, in presence of water, decomposes amygdalin with the production of benzaldehyde, hydrocyanic acid, and glucose:—

$$C_{20}H_{27}O_{11}N + 2H_2O = C_6H_5.CHO + HCN + 2C_6H_{12}O_6.$$

Amygdalin. Benzaldehyde. Hydrocyanic acid. Glucose.

The decomposition does not appear to take place in the plant because the glucoside and the emulsin are localised as shown by Johansen (*Ann. Sci. Nat. Bot.*, 1887, 7 Série, vi., 118), and Guignard (*Comptes Rendus*, 1890, cx., 477) in separate cells. It is only when the cells are altered by some mechanical or other agency and their contents mix that the reaction takes place.

Later, many other plants were discovered which contain cyanogenetic substances analogous to amygdalin. A useful list of such plants may be found in a communication made by Greshoff at the York Meeting of this Association (*Brit. Assoc. Report*, 1906, p. 138; *Bull. Sci. Pharm.*, 1906, xiv., 589). To-day the cyanogenetic glucosides of many of these plants have been isolated in a definite crystalline state; for instance, the *lotusin* of *Lotus arabicus* (Kuther) isolated by Dunstan and Henry from a plant growing on the banks of the Nile; the *linamarin* of Jorissen and Hairs obtained from *Linum usitatissimum* (Flax), and recognised later as identical with the *phaseolunatin* isolated by Dunstan, Henry, and Auld from *Phaseolus lunatus* (Java beans); the *dhurrin* of *Sorghum vulgare* (the Great Millet or Guinea Corn) isolated by Dunstan and Henry; the *sambunigrin* of Bourquelot and Danjou present in *Sambucus nigra* (Elder tree); the *vicianin* of Gabriel Bertrand isolated from *Vicia angustifolia* (Wild Vetch); the *mandelonitrile glucoside* of Emil Fischer, isolated by Hérissey from *Cerasus padus* (the Bird Cherry), by Power and Moore from *Prunus serotina* (the Wild Black Cherry), and recently again by Hérissey from *Photinia serrulata*).

Few of these glucosides in their relation to the amygdalin of Robiquet and Boutron present a greater interest to-day than the *vicianin* of Bertrand. The masterly study of its constitution and diastatic decomposition by this investigator in collaboration with Weisweiller has thrown a new light on the hydrolysis of amygdalin by enzyme action.

The presence of the glucoside was first pointed out in 1899 by Brunying and Van Haarst (*Recueil de Travaux Chim. de Pays-Bas*, xviii., 468) as a constituent of the seeds of the Wild Vetch, *Vicia angustifolia*. These enquirers observed the production of hydrocyanic acid when the powdered seeds were distilled with water containing tartaric acid, and they assumed in consequence the existence in the seeds of amygdalin or an analogous substance. Seven years lates the cyanogenetic glucoside present was isolated by Bertrand (*Comptes Rendus*, 1906, cxliii., 832) in a definite crystalline form. It forms tufts of brilliant colourless needles, easily distinguishable in physical properties from amygdalin.

Under the influence of an aqueous extract of *Vicia angustifolia* the glucoside is transformed into equal molecular proportions of hydrocyanic acid, benzaldehyde, and a biose crystallising in spherulitic aggregates of small needles, to which Bertrand and Weisweiller (*Comptes Rendus*, 1910, cl., 180) gave the name of *vicianose*:—

$$C_{19}H_{25}O_{10}N + H_2O = C_6H_5.CHO + HCN + C_{11}H_{20}O_{10}.$$

Vicianin. Benzaldehyde. Hydrocyanic acid. Vicianose.

This biose presents a peculiar interest in the fact that it is the first disaccharide isolated from a glucoside.

If instead of submitting the glucoside to the action of an extract of *Vicia angustifolia* it be submitted to that of an extract of almonds (bitter or sweet), the hydrolysis takes place differently with the production of the simple sugars, arabinose and glucose, instead of the biose vicianose. It was in utilising this observation that Bertrand and Weisweiller (*Comptes Rendus*, 1910, cli., pp. 325, 884) succeeded in obtaining in a state of purity the two constituents of the disaccharide and establishing its constitution. They found that under the influence of almond emulsin vicianose yielded *d*-glucose and *l*-arabinose:—

$$C_{11}H_{20}O_{10} + H_2O = C_6H_{12}O_6 + C_5H_{10}O_5.$$

Vicianose. *d*-Glucose. *l*-Arabinose.

Hence in the diastatic decomposition of vicianin we must admit the existence of two distinct enzymes:—First, *Vicianinase*, present in the extract of *Vicia angustfolia*, which attacks the glucoside with the production of vicianose and mandelonitrile, the latter being immediately decomposed in presence of water into its constituents, benzaldehyde and hydrocyanic acid,[*] and second, *Vicianase*, present in the extract of *Amygdalus communis*, which exerts its influence on the vicianose, resolving it into *d*-glucose and *l*-arabinose. Thus we see that, whether the glucoside be attacked, first by the vetch extract followed by the almond extract, or simply by the extract of almonds alone, the end products of the decomposition are the same in either case. (See Scheme A.)

If we compare this decomposition of vicianin by enzyme action with what we know regarding the behaviour of amygdalin—glucoside so closely related to vicianin, indeed only differing from it by the substitution of a molecule of *d*-glucose for a molecule of *l*-arabinose—a striking contrast at once becomes evident.

Amygdalin, as we have seen, under the influence of almond emulsin undergoes a complete hydrolysis, resulting in the production of equal molecular proportions of benzaldehyde and hydrocyanic acid, and two molecular proportions of *d* glucose. On the other hand, as shown by Emil Fischer (*Ber.*, 1894, Bd. xxvii., 2989), the glucoside, when submitted to the action of an extract of a bottom yeast of the Frohberg type, is only partially hydrolysed, half the sugar residue being split off as glucose without the nitrogenous portion of the molecule being attacked. It was thus that Fischer (*loc. cit.*) prepared his well known mandelonitrile glucoside, a substance crystallising in colourless needles, easily distinguishable by its physical characters from amygdalin and vicianin:—

$$C_{20}H_{27}O_{11}N + H_2O = C_{14}H_{17}O_6N + C_6H_{12}O_6.$$

Amygdalin. Mandelonitrile glucoside. Glucose.

Under the influence of almond emulsin the glucoside of Fischer is hydrolysed in its turn into benzaldehyde, hydrocyanic acid, and glucose:—

$$C_{14}H_{17}O_6N + H_2O = C_6H_5.CHO + HCN + C_6H_{12}O_6.$$

Mandelonitrile glucoside. Benzaldehyde. Hydrocyanic acid. Glucose.

Adopting the name *amygdalose* for the biose in the molecule of amygdalin and conforming to the usual nomenclature of enzymes, we must admit that the yeast extract contains *amygdalase*, a name which has already been proposed by Caldwell and Courtauld (*Roy. Soc. Proc.*, 1907, B, lxxix., 350). This enzyme only attacks the disaccharide, just as *vicianase* only attacks *vicianose*, whilst almond emulsin contains in addition the enzyme, which Gabriel Bertrand and the author (*Comptes Rendus*, 1911, clii., 1518) have named *amygdalinase*, capable of separating the nitrile residue from the sugar residue exactly as *vicianinase* liberates the nitrile from *vicianose* in the molecule of vicianin.

In the light of Emil Fischer's work the diastatic decomposition of amygdalin by the enzymes of emulsin is

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[*] The decomposition of the nitrile which takes place spontaneously in the presence of water is, according to Rosenthaler (*Biochem. Zeit.*, 1908, Bd. xiv., 328; 1909, Bd. xvii., 257; 1910, Bd. xxvi., pp. 1, 7, and 9), accelerated by a special enzyme. See also K. Feist (*Archiv. d. Pharm.*, 1909, ccxlii., 226, and 1910, ccxlviii., 101).

$$C_{19}H_{25}O_{10}N \xrightarrow[\text{(present in the \textit{vetch} and in \textit{almond}-emulsin)}]{\text{Vicianinase}} \begin{cases} C_6H_6.CHO \\ HCN \\ C_{11}H_{20}O_{10} \end{cases} \xrightarrow[\text{(present in \textit{almond}-emulsin)}]{\text{Vicianase}} \begin{cases} C_6H_{12}O_6 \\ C_6H_{10}O_5 \end{cases} \quad \ldots\ldots\ldots \quad (A).$$

$$C_{20}H_{27}O_{11}N \xrightarrow[\text{(present in Frohberg \textit{yeast} and \textit{almond}-emulsin)}]{\text{Amygdalase}} \begin{cases} C_6H_{12}O_6 \\ C_{14}H_{17}O_6N \end{cases} \xrightarrow[\text{(present in \textit{almond}-emulsin)}]{\text{Amygdalinase}} \begin{cases} C_6H_5.CHO \\ HCN \\ C_6H_{12}O_6 \end{cases} \quad \ldots\ldots\ldots \quad (B).$$

$$C_{20}H_{27}O_{11}N \xrightarrow[\text{(present in \textit{almond}-emulsin)}]{\text{Amygdalinase}} \begin{cases} C_6H_5.CHO \\ HCN \\ C_{12}H_{22}O_{11}\ (?) \end{cases} \xrightarrow[\text{(present in \textit{almond}-emulsin)}]{\text{Amygdalase}} \begin{cases} C_6H_{12}O_6 \\ C_6H_{12}O_6 \end{cases} \quad \ldots\ldots\ldots \quad (C).$$

usually considered to take place as shown in Scheme B, a scheme which presents a marked contrast with that representing the decomposition of vicianin (A). However, on account of the similarity of constitution of amygdalin and vicianin—the two glucosides being considered as formed by a central molecule of *d*-glucose united by its aldehyde extremity to a molecule of *l*-mandelonitrile and by its primary alcohol extremity to a special sugar molecule, the special sugar being *d*-glucose in the case of amygdalin and *l*-arabinose in the case of vicianin—there is reason to ask if the decomposition of amygdalin by almond emulsin does not sometimes, by analogy with that of vicianin, take place as shown in Scheme C.

With the discovery of a source of *amygdalinase* free from *amygdalase* a new light will doubtless be thrown on this interesting question. There is nothing, however, incongruous in the idea that the attack of the glucoside should take place according to one or other scheme according to the relative richness of the preparation of emulsin in *amygdalinase* and in *amygdalase*. In the event of the former enzyme predominating in the preparation, it is reasonable to suppose that the hydrolysis would take place according to scheme (C), while should the *amygdalase* predominate scheme (B) doubtless would indicate more exactly the stages of the hydrolysis. Support of this point of view is to be found in the researches of the author in collaboration with Gabriel Bertrand (*Ann. Inst. Past.*, 1910, xxiv., 931) on the individuality of the enzymes *cellase* and *amygdalinase* present in emulsin. It was found that the relative proportions of the two enzymes in question varied with the source of the preparation. Thus, apricot emulsin was found to be eighty-five times richer in *amygdalinase* than in *cellase*, while wheat bran emulsin was about one and a-half times as rich in *cellase* as in *amygdalinase*.

Interesting as is this question of how the cyanogenetic glucosides amygdalin and vicianin are decomposed *in vitro* by their attendant and other enzymes, there is no reason to think that the mechanism of the decomposition is less varied in the living cells. One wonders how exactly such hydrolyses take place *in vivo*, resulting as they do in the simultaneous formation of benzaldehyde and simple sugars assimilable by the plant, on the one hand, and the violent poison hydrocyanic acid on the other. If the glucosides are hydrolysed in the plant as *in vitro*, it is not unlikely, as Hérissey (*Thèse*, Paris, 1899, p. 82) conceives, that the toxic products formed are taken up immediately to form synthetically more complex products harmless to the plants.

ACETYL HALOGEN SUGAR COMPOUNDS AND OTHER SUGAR DERIVATIVES.*

By W. SLOAN MILLS, M.A., D.Sc., B.E.,
Lecturer on Chemistry, Woolwich Polytechnic.

The synthesis of sugar and sugar derivatives is a subject which has for a long time engaged the attention of chemists.

By the action of hydrochloric acid on a mixture of sugar and alcohol or mercaptan, Emil Fischer prepared a large number of glucosides of the alcohols and mercaptans (*Ber.*, 1893, xxvi., 2400; 1894, xxvii., pp. 674, 2483, 2985; 1895, xxviii., 1145). Combinations of glucose with dihydric and trihydric phenols were also obtained in this way (*Ber.*, 1890, xxiii., 1358), but the method was not found applicable to the preparation of glucosides of the monohydric phenols (*Ber.*, 1894, xxvii., 1358). Glucosides of monohydric phenols were prepared by Michael (*Comptes Rendus*, lxxxix., 355) by the action of the alkali salts of the phenol on acetochloroglucose, a substance prepared by Colley (*Ann. Chim. Phys.*, 1870, xxi., 363) as an impure syrup by the action of acetyl chloride on glucose. A similar syrupy chloro-derivative of galactose was prepared by Ryan, and applied by Ryan and myself to the preparation of α-naphthyl-galactoside (*Journ. Chem. Soc.*, 1901, lxxix., 704).

The yield of glucoside obtained from these impure acetyl-halogen sugar compounds was small, and so those working in this field welcomed the discovery of pure crystalline compounds which could be used as starting materials for the synthesis of other glucosides and sugar compounds. Only two such crystalline derivatives were obtained by Colley's method, namely, acetylchloroarabinose prepared by Ryan and myself, and acetylbromoglucose described by Koenigs and Knorr. A general method of preparing these crystalline derivatives was discovered by Fischer and Armstrong, who obtained a beautiful series of well-defined crystalline compounds by the action of anhydrous liquid hydrochloric or hydrobromic acid on acetyl-sugar derivatives in sealed tubes at the ordinary temperature. They converted these into alcoholic and phenolic glucosides, and the synthesis of a number of disaccharides has also been successfully accomplished by means of these compounds (*Ber.*, 1902, xxxv., 3144; 1909, xlii., 2776).

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* A Paper read before the British Association (Section B), Dundee Meeting, 1912.

Early in 1903, under the guidance of Professor Fischer, I began the investigation of triacetyldibromoglucose, a compound which was prepared by the action of an excess of anhydrous liquid hydrobromic acid on β-pentacetylglucose (*Ber.*, 1902, xxxv., 836).

I had occasion to leave Berlin before the work had developed, and wishing to further the investigation early in 1906 at Queen's College, Galway, where a plentiful supply of liquid air, which is necessary for the preparation of these halogen compounds, was not readily available, I decided to endeavour to obtain the corresponding iodine compound.

My experiments resulted in finding a very simple and convenient method of preparing monoiodoacetyl sugar derivatives at ordinary temperature. The method does not require the use of liquid air, and quantitative yields of these compounds can easily be obtained in a beautifully crystalline form. They were found to be well suited to the preparation of alkyl and phenol glucosides.

Acetyliodoglucose and acetyliodogalactose were prepared by me at Queen's College, Galway, and formed part of a thesis presented to the Royal University of Ireland for a Doctor of Science Degree in 1906. Meanwhile, Fischer has described the former compound (*Ber.*, 1910, xliii., 2521), which, however, he obtained by a more indirect method. The other compounds described were prepared at Woolwich Polytechnic.

β-Acetyliodoglucose, $C_6H_7O(OAc)_4I$.

Hyriodic acid gas was generated by the action of water on iodide of phosphorus, and dried by means of calcium chloride and phosphorus pentoxide. A slow stream of gas was passed into β-pentacetylglucose (5 grms.) dissolved in dry methylene chloride (8 cc.) until the solution was saturated. The side tube of the distilling flask in which the experiment was made was directly connected with a vacuum pump, and the methylene chloride and excess of hydriodic acid distilled off. The thick syrup remaining solidified on being rubbed with a glass rod moistened with alcohol.

When quickly re-crystallised from alcohol an 85 per cent yield of what theory required was obtained. It is readily decomposed by alcohol when allowed to remain in contact with it for some time or when heated with it.

It melts at 108° to 109°, and reduces hot Fehling's solution. It readily yields acetyl alcoholic and acetyl phenolic glucosides.

Various attempts were made to prepare α-acetyliodoglucose from α-pentacetylglucose, but in all cases the "β"-compound was isolated. The melting-point of the product obtained from the α-pentacetylglucose agreed with the melting-point of the product obtained from the β-pentacetylglucose. Both products yielded the same acetylmethylglucoside when treated with silver carbonate and methyl alcohol. The product obtained from α-pentacetylglucose with hydriodic acid when dissolved in methylalcohol, and treated with silver acetate instead of silver carbonate, yielded tetracetyl-β-methyl glucoside. This indicates that under these circumstances an alkyl group enters the acetyl sugar rest in preference to an acetyl group. Otherwise, pentacetylglucose would have been formed instead of tetracetylmethylglucose.

Other experiments with α-pentacetylglucose with the object of obtaining, if possible, α-acetyliodoglucose included the saturation with hydriodic acid of, first, a solution of α-pentacetylglucose in methylene chloride below 0° C.; second, a solution of α-pentacetylglucose in acetic anhydride; third, a solution of α-pentacetylglucose in methylene chloride in presence of zinc chloride. The "β"-iodo compound was isolated in each case. Fischer has also been unsuccesful in obtaining the "α"-iodo derivative.

Corresponding Derivatives of Galactose, Maltose, Lactose, and Raffinose.

β-Acetyliodogalactose may be prepared from β-pentacetylgalactose in the same manner as the glucose compound. It melts at 93° to 94°, and is much more difficult to obtain crystalline and more readily decomposed by alcohol. It was most readily obtained crystalline by the spontaneous evaporation of a solution in carbon disulphide.

Octaacetyl maltose yields acetyliodomaltose, a sample of which when crystallised from a mixture of ligroin and chloroform melted at 62° to 66°.

Acetyliodolactose was readily obtained even from impure acetyllactose by the action of dry hydriodic acid on a solution of the acetyl compound dissolved in benzene. When re-crystallised from a mixture of acetone and ether it melts at 142°.

Acetylraffinose also yields an iodo derivative.

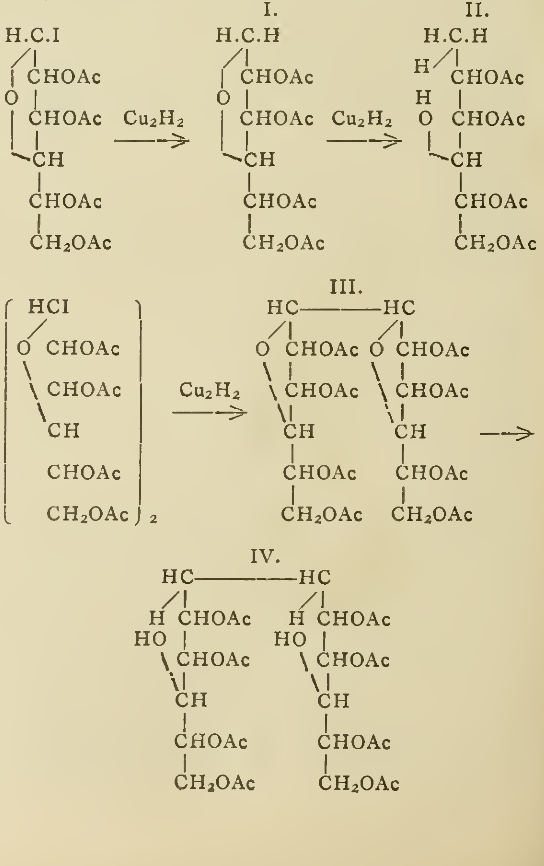
For the preparation of these iodine derivatives methylene chloride and chloroform seemed to be the most suitable solvents. A convenient method of testing the syrup obtained for iodine is to touch a small portion with a glass rod moistened with concentrated nitric acid, when a dark precipitate of iodine is produced.

In two or three different experiments I failed to obtain any change in β-pentacetylglucose dissolved in methylene chloride when acted on by dry hydriodic acid generated by the action of iodine on resin.

The Interaction of Acetyliodoglucose with Cuprous Hydride.

Freshly prepared acetyliodoglucose was mixed with excess of copper hydride, which had been dried by being washed with absolute alcohol and with absolute ether. The plastic mass obtained was allowed to stand for three days, and the syrup obtained from the chloroform extract yielded a readily crystalline substance when dissolved in hot dilute alcohol. When purified by re-crystallising from alcohol it melted at 104° to 105°. It does not reduce Fehling's solution after hydrolysis.

It was thought that one of the following reactions might take place:—



On analysis, 0·1730 grm. gave 0·3118 CO_2 and 0·1010 H_2O. C = 49·16, H = 6·49.
$C_{28}H_{44}O_{19}$ requires C = 49·10, H = 6·47.

The numbers agree with those required by the fourth formula if the compound may be considered to be combined with one molecule of water of crystallisation.

It is intended to obtain further evidence for Formula IV. by a cryoscopic determination of the molecular weight, and an estimation of the water of crystallisation supposed to be present.

I am at present engaged with a study of the interaction of finely divided copper on the above mentioned acetyl-iodo sugar derivatives.

THE
CONSTITUTION OF MANNITOL TRIACETONE.*

By J. C. IRVINE and BINA MARY PATERSON, B.Sc.

The condensation of sugars or polyhydric alcohols with acetone involves the loss of the elements of water from the ketonic group and two hydroxyl groups, and is influenced in a marked fashion by the configuration of the hydroxy-compound. Fischer, on the basis of experiments carried out with glycerol, ethylene glycol, and trimethylene glycol, came to the conclusion that the reaction involved hydroxyl groups attaehed to β-carbon atoms, but, for several reasons, this view cannot be applied generally. In the case of reducing sugars especially, the reaction is complicated by several factors, including the fact that part of the molecule is a ring structure and thus presents the possibility of *cis* and *trans* condensation with the ketone. The simplest conditions for a study of the reaction are thus available in the case of an active polyhydric alcohol, and we have, in the meantime, confined our attention to mannitol.

Although it is impossible to arrest the condensation of mannitol with acetone at intermediate stages, we find that by carefully regulated hydrolysis three molecules of the ketone can be removed successively from mannitol triacetone. The reaction thus gives an index of the varying stability of the ketonic residues and proceeds according to the scheme:—

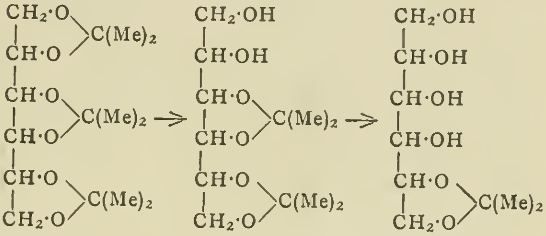
Mannitol triacetone → Mannitol diacetone → Mannitol monoacetone → Mannitol.

In view of the extreme instability of the intermediate compounds, indirect methods had to be employed to determine their constitution. This was effected in each case by methylation and subsequent hydrolysis. The resulting compounds were thus alkylated in the positions from which the acetone residues had been removed, and the position of the methyl groups was finally determined by standard methods. The results are summarised below:—

Mannitol diacetone was prepared by heating a solution of mannitol triacetone in 68 per cent alcohol containing 0·1 per cent of hydrogen chloride. The hydrolysis was continued at 40° for 150 minutes. The compound melted at 37° to 39° and showed $[\alpha]_D$ 20° +15·7° in alcoholic solution ($c = 2·7$). When methylated by the silver-oxide reaction it was converted into *dimethyl mannitol diacetone*, a colourless mobile liquid boiling at 140° to 141°/13 mm. and showing $[\alpha]_D$ 20° +21·9° in alcohol. This compound, when hydrolysed, was converted into a *dimethyl mannitol* (m.p. 93°, $[\alpha]_D$ 20° −8·8 in alcohol) giving, on oxidation, a *dimethyl mannonic acid* which was identified by analyses of the calcium salt.

On the other hand, when the hydrolysis of mannitol triacetone, under the conditions described above, was continued for four hours, the main product was *mannitol monoacetone* (m.p. 85°, $[\alpha]_D$ 20° +23·2°). This was converted into *tetramethyl mannitol monoacetone* (b.p. 137° to 140°/11 mm., $[\alpha]_D$ 20° +32·2°), and finally into *tetramethyl mannitol* (b.p. 167° to 169°/13 mm., $[\alpha]_D$ 20° −12·5). The latter, on oxidatfon with nitric acid, gave a *tetramethyl mannonic acid* (b.p. 180° to 182°/12 mm., $[\alpha]_D$ 20° +10·1°), which failed to give a lactone on repeated distillation. For the purposes of comparison, the isomeric *tetramethyl mannonic acid* was prepared from methylmannoside and found to be entirely different, as, on distillation, it was completely converted into *tetramethyl mannono-lactone* (b.p. 174°/11 mm. $[\alpha]_D$ 20° in dilute alcohol $+78·8° \rightarrow 27·5°$).

A review of all the above results shows that in dimethyl and tetramethylmannitol the alkyl groups are present in positions 5 : 6 and 3 : 4 : 5 : 6 respectively, so that the structure of mannitol triacetone and its partial hydrolysis may be expressed by the scheme:—



The linkage of each of the condensed groups is thus in the α-position throughout, but the order in which the acetone residues are removed is quite unexpected and involves complex stereochemical considerations.

Our results are supported by experiments recently made by Mr. J. L. A. Macdonald, who, in similar work, converted glycerol acetone into a *monomethyl glycerol* (b.p. 109°/12 mm.) which was identical with the compound obtained on decomposition of $\alpha : \beta$-dibromo—α-methoxy—propane with silver acetate, and hydrolysis of the product.

It should, however, be mentioned that evidence was obtained that mannitol triacetone is either a mixture, or is capable of reacting in more than one form. When tetramethyl mannitol was oxidised by Fenton's reagent, the bulk of the material remained unaltered, but a small quantity of 2 : 3 : 5 : 6-tetramethyl mannose was formed which was identified by conversion into the anilide. A small quantity of material in which at least one acetone residue connected γ-carbon atoms must therefore have been present in the original specimen of the triacetone compound.

THE ENZYMES OF *LINACEÆ*.*

By J. VARGAS EYRE.

Recent work of Armstrong and Horton has shown that the enzyme and accompanying glucoside—*linamarin*—occurring in the wild Java bean (*Phaseolus lunatus*) belong to the β-series, and that the enzymic extract from these beans is practically without action on amygdalin but readily hydrolyses prunasin and linamarin. Continuing this work it is now shown that this dual activity of *linase*—as deduced from a study of the active extract of the Java bean—is not due to the activity of a single enzyme.

Study of the *Linaceæ* has revealed distinct evidence of the presence of a variety of enzymes in the leaf and seed of this species of plant; also, that the proportion in which they occur is subject to considerable variation. From the results found it is not possible to regard *linase* as being equally active towards *linamarin* and *prunasin*; consequently it must be that the extract from the Java bean contains *prunase* as well as *linase*.

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* A Paper read before the Briiish Association (Section B), Dundee Meeting 1912.

* A Paper read before the British Association (Section B), Dundee Meeting 1912.

It may well be that *linase per se* is without action on *prunasin*.

During the period of plant growth slight changes in the hydrolytic activity of the flax enzymes towards various glucosides has been observed; a decreased activity towards *linamarin*, and an increased activity towards *prunasin* and *amygdalin* taking place as the season advances. Enzymic activity is found to be correlated with the presence of a cyanophoric glucoside; those species of flax which resemble *Linum usitatissimum* or *L. perenne* in general habit of growth, and which carry blue, white, or red flowers, are more or less richly cyanophoric, whilst the yellow-flowered species, *L. flavum*, *L. arboreum*, *L. maritimum*, &c., which differ in habit from common flax, contain neither enzyme nor glucoside.

The amount of cyanophoric glucoside present in different species is different, and is subject to variation throughout the period of growth. White flowering perennial flaxes invariably contain prussic acid long after its disappearance from the blue-flowered varieties of the same species.

The development of glucoside and of active enzyme in the seed is found to be slow, and the process of ripening, although apparently without much influence on the enzymic activity, occasions a steady decrease in the amount of cyanophoric glucoside present in the seed. Ripe seed are found to contain no cyanophoric glucoside.

REPORT ON DIFFUSION IN SOLIDS.*

By CECIL H. DESCH, D.Sc., Ph.D.

(Continued from p. 155).

Solid Diffusion in Metals.

It is in metals and metallic alloys that the most complete and satisfactory experiments in solid diffusion have been made. The existence of diffusion in solid metals has been fully established, and although doubts may be raised as to the crystalline character of the material through which diffusion takes place, the range of temperature covered by the experiments is so great that it is difficult to conceive of the persistence of amorphous metal throughout.

Leaving the cementation of iron for separate consideration, the earliest scientific record of the production of an alloy by union in the solid state appears to be the observation of M. Faraday and Stodart (*Quart. Journ. Sci.*, 1820, ix., 319; "Exp. Researches in Chemistry," 1859, p. 57) that iron and platinum could be alloyed by welding at a temperature below that at which fusion could take place. A solid solution is formed in this case.

Several early metallurgical processes have been quoted by W. C. Roberts-Austen as depending on solid diffusion (*Phil. Trans.*, 1896, clxxxvii., A, 383). One of these is the ancient process of extraction of silver from gold by cementation, described by Pliny and others (a full account is given by J. Percy, "Metallurgy of Silver and Gold," London, 1880, i., 379), in which the alloy is packed in a mixture of salts and heated for a long time at a temperature well below the melting-point. The silver is gradually extracted, leaving a residue of solid gold. Another process is that of "kernel roasting," in which cupriferous iron pyrites are slowly roasted in air, the final product being a central "kernel" of cuprous sulphide, enclosed in a shell of ferric oxide, whilst the silver originally present wanders outwards, and appears in the free state as a lace-like coating on the surface (W. C. Roberts-Austen, *loc. cit.*).

In both of these processes, however, gases intervene in the reaction, and a porous mass remains, so that it would be rash to attribute the extraction of the metal to solid diffusion without further evidence.

The diffusion of one metal into another has an important influence on the technical process of electroplating. For instance, it was found that when a thick layer of copper was deposited electrolytically on a sheet of platinum (G. Gore, "The Art of Electro-metallurgy," London, 1877, p. 47), and the compound sheet was heated to dull redness, the copper oxidised and peeled off, leaving a surface which could be cleaned by nitric acid and then presented the appearance of the original platinum. On again heating to redness, however, a fresh layer of copper oxide was formed, and this process could be repeated more than once. The diffusion of an electrolytically deposited layer may even take place at the ordinary temperature. Thus a thin layer of copper or brass deposited on zinc slowly disappears, the zinc resuming its greyish white appearance, and this occurs even when the outer surface is protected from atmospheric action by a layer of lacquer (G. Langbein and W. T. Brannt, "The Electro-Deposition of Metals," Philadelphia, 1891, p. 133).

A platinum wire coated electrolytically with silver and drawn to a smaller diameter through a draw-plate becomes completely soluble in nitric acid, showing that alloying has taken place ("Observation of Rouma," quoted by W. Spring, *Ber.*, 1882, xv., 595).

A layer of silver, deposited on copper, may be absorbed in course of time if sufficiently thin. As copper is capable of dissolving about 5 per cent of silver in the solid state, absorption will cease when this concentration has been reached. It has been suggested by W. Guertler ("Metallographie," Berlin, 1910, i., 183) that the absorption might be hindered by the interposition of a thin layer of electrolytic iron, in which silver is not soluble to a measurable extent. On the other hand, the interposition of a layer of gold would facilitate diffusion, as this metal forms solid solutions in all proportions with silver and with copper, and also increases the mutual solubility of those metals. Copper will diffuse into iron through an intervening layer of nickel (W. C. Roberts-Austen, *Journ. Iron and Steel Inst.*, 1887, i., 73).

A few minor instances of diffusion into metals at the ordinary temperature may be noticed. The penetration of sulphur into silver, blackening it to a considerable depth, has been recorded (Homberg, *Mém. Acad. Roy. Sci.*, 1713, 306), as well as the gradual diffusion of iron into silver in the course of several years (J. H. Howell, *Nature*, 1906, lxxiii., 464).

The earliest systematic investigation of diffusion in the solid state is due to W. Spring, whose experiments have suggested those of most subsequent workers in the subject. It has been observed by Spring that various powdered solids could be formed into a compact mass by the application of high pressure (*Bull. Acad. Roy. Belg.*, 1878, [2], xlv., 746), and further experiments showed that the compression of mixtures of metals with arsenic (*Ibid.*, 1883, [3], v., 229) or with sulphur (*Ibid.*, 492) brought about the formation of arsenides or sulphides without rise of temperature. Alloys were also formed by compressing their components (*Ber.*, 1882, xv., 595). Of these, the most interesting case is the formation of brass by compressing a mixture of copper and zinc filings. The union is very incomplete, and it is necessary to reduce the conglomerate to filings and to repeat the compression five or six times. The same memoir describes the formation of fusible alloys by pressure, but the study of the constitution of these alloys was unknown at the time, and in the light of more recent knowlege it is obvious that the production of a readily fusible mass is no proof of chemical union, as the eutectic is merely a conglomerate. It was in fact soon shown that fusible alloys could be produced by merely mixing filings of their component metals (W. Hallock, *Zeit. Phys. Chem.*, 1888, ii., 378). The temperature at which such a mixture melts is above the true eutectic temperature by an amount which depends on the coarseness of the powders used (C. Benedicks and R. Arpi, *Metallurgie*, 1907, iv., 416). Other experiments (C. Drewitz, *Verh. Ver. Beförd. Gewerbefl.*, 1902, lxxxi., 325), in which the formation of fusible alloys by pressure was assumed from the compact appearance and low melting-point of the product, are inconclusive for the same reason.

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* Read before the British Association (Section B), Dundee Meeting, 1912.

These objections do not apply to the later experiments of Spring, in which true interpenetration was shown to occur (*Zeit. Phys. Chem.*, 1894, xv., 73; *Bull. Acad. Roy. Belg.*, 1894, [3], xxviii., 23). Two cylinders of the same metal, accurately faced and freed from grease, were found to adhere firmly at ordinary temperatures and to become fully united on heating. Union occurred with all the metals examined with the exception of antimony, and was usually so intimate that when the two cylinders were subsequently separated by force the fracture passed through the metal on one side or the other of the plane of junction. Quite similar results were obtained when the two cylinders were of different metals. Thus, when zinc and copper were placed in contact and heated to 400° for six to eight hours, the two cylinders became united by a layer of brass 0·8 mm. in thickness, whilst copper and antimony similarly formed a layer of the purple alloy. Vapour undoubtedly played a part in some of the reactions recorded, as it was found that a thin layer of brass was formed at 400° even when the zinc and copper were separated by a distance of 0·8 mm., and cadmium also volatilised to a small extent. The intervention of vapour had been previously suggested in explanation of some of Spring's earlier welding experiments (W. Hallock, *Am. Journ. Sci.*, 1889, [3], xxxvii., 402), and similar conclusions have been reached by a study of reactions between solid salts in closed vessels (E. P. Perman, *Proc. Roy. Soc.*, 1907, lxxix., A, 310).

When mixtures of copper and silver filings are compressed into cylinders by the application of a pressure of 8000 atmospheres, the pressure being maintained for a month at the ordinary temperature, apparently homogeneous masses are obtained which, however, prove on microscopical examination to consist merely of unaltered filings united by adhesion, no interpenetration having taken place (G. Spezia, *Atti R. Accad. Sci. Torino*, 1910, xlv., [2], 525). It is quite possible that in these experiments traces of grease or of oxide hindered perfect contact, as negative results were equally obtained when all the filings were of copper or of silver respectively, whereas Spring's experiments with carefully polished and cleaned surfaces showed that union was sufficiently intimate to tear the metal when an attempt was made to separate it, showing that molecular interpenetration must have occurred to some extent. Spezia supports his views by reference to the native copper of Keweenau Point, Lake Superior, which frequently contains inclusions of native silver which have not diffused into the surrounding copper in the course of geological ages (C. T. Jackson, *Am. Journ. Sci.*, 1845, [1], xlix., 81; *Comptes Rendus*, 1845, xx., 593). This author also points out the importance of distinguishing between uniform (hydrostatic) pressure and differential pressure causing flow. The latter may be expected to have the greater influence. Many experiments show that great hydrostatic pressure, even when long continued, is without influence on the properties of metals (see also O. Faust and G. Tammann, *Zeit. Phys. Chem.*, 1910, lxxv., 108).

It was an important contention of Spring that only those reactions were favoured by the application of pressure which proceeded with diminution of volume. This principle, so important in relation to systems containing a gaseous phase, has received less consideration in respect to solid systems.

The investigation of Roberts-Austen, recorded in the Bakerian lecture for 1896 (*Phil. Trans.*, 1896, clxxxvii., A, 383), has become classical, owing to the well-designed character of the experiments and to the accuracy of the quantitative method employed. The case selected for special study was that of the diffusion of gold into lead. Discs of an alloy of lead with 5 per cent of gold were accurately faced and pressed into contact with cylinders of pure lead. The specimens were then kept at constant temperature for several weeks, and the diffusion was measured by cutting the lead cylinder into discs and estimating the proportion of gold in each disc by the usual method of dry assay. The gold alloy being placed at the base of the cylinder, diffusion had to take place upward against gravity. The following results were obtained after heating at 165° for thirty days:—

No. of section from base.	Weight of section in grms.	Au per cent.	Diffusivity.
1.	0·64	0·039	
2.	2·33	0·030	0·005
3.	2·02	0·015	

Further experiments at different temperatures gave the following values for the diffusity (expressed in sq. cm. per day) (A. Fick, *Pogg. Ann.*, 1855, [2], xciv., 59).

100°	0·00002
165°	0·005
200°	0·008
251°	0·030
550° (in liquid lead)	3·19

As an illustration of the extent of the diffusion, it may be mentioned that at 251° the gold had risen against gravity to a height of 7 cm. in less than a month. Further experiments, continued for four years at 18°, showed that at that temperature the gold had risen 7·5 mm., the quantity diffusing in a thousand years being calculated as being nearly equal to that which would diffuse in molten lead in one day (*Proc. Roy. Soc.*, 1900, lxvii., 101).

The conditions of these experiments may be examined a little more fully. The equilibrium of alloys of lead and gold has been investigated (R. Vogel, *Zeit. Anorg. Chem.*, 1905, xlv., 11). Gold forms two compounds with lead, Au_2Pb and $AuPb_2$. Only the second of these could play any part in the diffusion, owing to the large excess of lead present. There is a eutectic point at 215°, so that in the experiment conducted at 251° the transport may have taken place by means of capillary ascent of the liquid eutectic, but the other experiments recorded are at temperatures well below the eutectic point. Another experiment recorded in the Bakerian lecture showed that the rate of diffusion of gold in solid silver at 800° is of the same order as that of gold in lead at 200°. In this case a compound is not formed, and diffusion can only take place by the formation of a solid solution.

Further experiments on the same lines as those of Spring have been carried out by G. Masing (*Zeit. Anorg. Chem.*, 1909, lxii., 265; see also G. Tammann, *Zeit. Elektrochem.*, 1909, xv., 447), who prepared conglomerates of various pairs of metals by compressing mixtures of the filings in a steel cylinder under 1000 to 5000 atmospheres. The extent to which union had taken place after heating to different temperatures and for different times was estimated by taking heating curves and comparing them with the curves obtained under similar conditions from alloys prepared by fusion. In certain cases the results were confirmed by microscopical examination and by determinations of the electrical conductivity. The results show that pressure alone is without influence on diffusion or combination, and serves merely to bring the fragments of the two metals into intimate contact. Intimate mixtures of very finely ground zinc and cadmium, or copper and silver, melt at the eutectic point of the corresponding series, but the mass is at once distinguishable under the microscope from one obtained by fusion, by the absence of the eutectic structure. Only traces of a compound are formed when the two metals combine without an appreciable formation of solid solutions, as in the pairs Mg-Pb, Mg-Sn, Mg-Zn, and Mg-Sb. (These mixtures were not examined microscopically). Diffusion is perceptible in the case of cadmium and magnesium, which form a continuous series of solid solutions containing a compound MgCd, and of aluminium and magnesium, in which series the compound Al_3Mg_4 forms solid solutions with an excess of aluminium.

The alloys most fully studied by Masing were those of bismuth and thallium. Heating the mixture of filings, previously rendered compact by pressure, to 120° for five and a-half hours brings about the formation of a coloured layer surrounding the particles of thallium. This layer consists of a saturated solid solution, rich in thallium, whilst more prolonged heating causes the appearance of a second layer, composed mainly of the compound Bi_5Tl_3. The thickness of these two layers increases at higher temperatures at the expense of the original metals. The diffusion in this case is recognisable by means of the microscope after a year at atmospheric temperature. Lead and thallium behave similarly, as far as the evidence of heating curves goes, but a microscopical examination was not carried out. A determination of the electrical conductivity at different intervals shows that in this case also diffusion proceeds at a measurable rate at the ordinary temperature. The diffusion of tin into copper at 200°, and of zinc into copper at 400°, was also observed by more than one method.

The last-mentioned process, the diffusion of zinc into copper, lends itself well to microscopical observation on account of the formation of compounds differing in colour from the original metals. The superficial conversion of copper into brass by the action of zinc vapour has been known since the experiments of Spring, or even longer, and has been made the basis of a technical process (S. Cowper-Coles, *Electrochem. and Metall.*, 1904, iii., 828). The object to be coated is packed in zinc dust, mixed with zinc oxide or carbon to prevent caking, and heated at 250° to 300° in a rotating drum. The process has found a more extensive application in the coating of iron with zinc as a substitute for wet galvanising, and is known as "Sherardising." The zinc vapour unites with the metal (iron or copper) to form a superficial alloy, but the subsequent penetration of zinc into the interior takes place by true diffusion.

The manner in which diffusion takes place in such complex cases is conveniently studied by immersing a rod of copper in molten zinc and withdrawing it after a short time. An adherent layer of a white brittle alloy is formed, and microscopical examination of a transverse section shows that this is separated from the copper by an intermediate layer which is readily identified as the β-constituent (C. H. Desch, "Metallography," London, 1910, p. 221). There is a sharp boundary between this layer and the unaltered copper. If the metal is heated for several hours at 700° and slowly cooled, it is found that zinc has diffused inwards, the white outer layer disappearing, whilst the zone of the β-constituent has greatly increased in breadth, and has formed a new layer, composed of the α-constituent, between it and the unchanged copper core.

The most recent, and in some respects the most satisfactory, experiments are those of G. Bruni and D. Meneghini (*Atti R. Accad. Lincei*, 1911, [5], xx., 671, 927; *Intern. Zeit. Metallographie*, 1912, ii., 26). These authors employed metals of high melting-point, which form solid solutions without chemical combination, and they followed the progress of the diffusion by means of the change in the electrical conductivity. A nickel wire, 0·5 mm. diameter, was coated electrolytically with copper until the increase of weight corresponded with 59 per cent copper and 41 per cent nickel. The compound wire was then heated to 1000° in hydrogen, and the conductivity was determined from time to time. A slight increase of conductivity was noticed in the first hour, owing to the conversion of electrolytic copper into the better-conducting annealed form, but after this a continuous decrease of conductivity was observed, the minimum being practically reached after 140 hours, when the value attained was exactly that of a homogeneous alloy of the same composition. Exactly similar results were obtained when gold wires were coated with silver or copper. In a further experiment the area of contact of the two metals was greatly increased by coating a copper wire, 0·075 mm. diameter, with nickel and copper alternately, until thirty layers of each metal had been deposited. The thickness of the layers gradually diminished towards the outside, ultimately reaching a value of about 2·5 μ. Such a wire became homogeneous, as shown by microscopical examination as well as by the determination of the conductivity, after less than two hours at 1000°, whilst diffusion proceeded at an appreciable rate at 500°. These authors are now engaged on experiments with still finer layers of the two metals, with the object of studying diffusion at still lower temperatures.

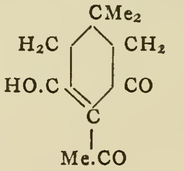
The attempt has been made to draw a distinction between diffusion in metals and that in fluids on the ground that the penetration of oxygen into iron or steel in the ordinary process of tempering does not proceed indefinitely, but ceases at a certain finite depth, dependent only on the temperature (C. Barus and V. Strouhal, *Bull. U.S. Geol. Surv.*, 1886, xxvii., 51; C. Barus, *Nature*, 1889, xli., 369). This is, however, inconsistent with the facts, as it is now known that the tempering colours, by which the thickness of the oxidised film is judged, are dependent on time as well as on temperature, and that although the diffusion of oxygen in such cases is slow, the process continues to greater and greater depths if given sufficient time.

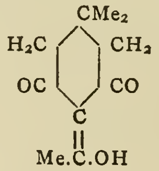
(To be continued)

THE STUDY OF HYDRO-AROMATIC SUBSTANCES.*

1. *The Behaviour of* c-*Acetyldimethyl- and* c-*Acetyltrimethyldihydroresorcins towards Hydroxylamine and Phenylhydrazine.*—It has been pointed out (*Journ. Chem. Soc.*, 1911, xcix., 1101) that trimethyldihydroresorcin does not behave towards many reagents in a similar manner to dimethyldihydroresorcin, for it exhibits tautomeric forms, and also its molecule is not symmetrical. In order to clear up several points of interest the *c*-acetyl derivatives of these two dihydroresorcins are being investigated.

c-Acetyldimethyldihydroresorcin behaves as a monobasic acid, and may be represented by one or other of the following formulæ, probably the second:—





When acted on by hydroxylamine it gives an acid oxime (I.), an isoxazole (II.), and an oxime of the isoxazole (III.), and with phenylhydrazine it behaves in a similar manner giving an acid phenylhydrazone, a phenylpyrazole, and a phenylhydrazone of the phenylpyrazole.

The behaviour of *c*-acetyltrimethyldihydroresorcin towards hydroxylamine has not been investigated owing to the fact that the isoxazole is a liquid or very low melting solid; but with phenylhydrazine it gives an acid phenylhydrazone and a phenylpyrazole, though all attempts to prepare a phenylhydrazone of the phenylpyrazole have so far failed. It is presumed that *c*-acetyltrimethyldihydroresorcin is similarly constituted to the corresponding derivative of dimethyldihydroresorcin, but the results will be discussed at length in another publication.

2. *The Action of Phosphorus Pentabromide on Dimethyldihydroresorcin.*—In 1903 it was shown (*Journ. Chem. Soc.*, lxxxiii., 110) that phosphorus pentabromide acts on dimethyldihydroresorcin to give several bromodimethylcyclohexanones, and also certain bromoxylenols. One of the latter substances (melting-point, 96—97°) was thought to be a derivative of 1 : 2-xylenol-3, and this has now been

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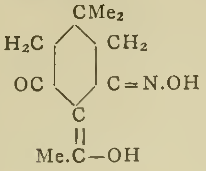
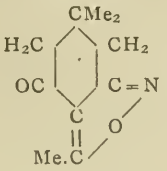
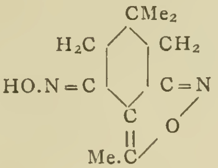
* Report of the Committee, consisting of Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), Dundee Meeting, 1912.



I.



II.



III.

definitely shown by synthesis which proves it to be 4 : 5-dibromo-1 : 2-xylenol-3. The formation of this substance necessitates the wandering of a methyl group into an ortho-position, and several instances of similar reactions have already been recorded. A closer investigation of the reaction shows that apparently derivatives of 1 : 3-xylenol-4 are also formed, and at first sight this would appear to mean that a methyl group had wandered into a meta-position. There is, however, another possibility. If one methyl group can wander into an ortho position why, under certain conditions, should not both methyl groups wander into ortho-positions, thus giving rise to a 1 : 3-xylenol?

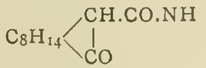
The reaction is very complicated and not easy to work out, owing to the difficulty of separating the mixture of bromoxylenols produced. At the present time attention is being particularly directed to the synthetic formation of those bromoxylenols which appear likely to be produced in the reaction, as very few of these substances are described in the literature.

DYNAMIC ISOMERISM.[*]

Camphorcarboxamide and Camphorcarboxypiperidide. — During the past year an investigation has been completed of the isomeric changes taking place in solutions of two crystalline derivatives of camphorcarboxylic acid (the amide and piperidide), which were first prepared and examined about four years ago by Dr. Glover. The changes of rotatory power which take place in the freshly prepared solutions are extremely complex. In solutions of the piperidide in benzene, a period of induction is followed by two periods of acceleration and two periods of retardation in the rate of change of rotatory power; the changes can only be explained by assuming that three distinct isomeric changes take place, and that a condition of equilibrium is ultimately established between four distinct isomerides.

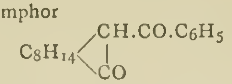
Measurements of solubility have shown that in the case of each substance a proportion amounting to about one-third persists in the original form when a condition of equilibrium is finally attained to.

In purifying the two substances it was found to be almost impossible to secure homogeneous material until they were separated in the form of measurable crystals from solutions in ethylic acetate. A remarkable morphotropic relationship was detected between the amide—



$$C_8H_{14}\left<\begin{array}{l}CH.CO.NH\\ \,|\\ CO\end{array}\right.$$

and α-benzol camphor



$$C_8H_{14}\left<\begin{array}{l}CH.CO.C_6H_5\\ \,|\\ CO\end{array}\right.$$

An investigation of the equations for two consecutive unimolecular changes has already been published (*Trans. Chem. Soc.*, 1910, xcvii., 2634—2645); and a detailed account of the experiments now referred to above will be published at an early date.

The Committee ask for reappointment, and for a grant of £30 as in the preceding year.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

Annual General Meeting, New York, 1912.

(Concluded from p. 160).

President's Address (*continued*).

I will not weary you by repeating what has been related so often and so fully. It is, however, noteworthy how, from the outset, the establishment of new industries, based on the discovery of aniline dyes, and of methods of producing alizarin and indigo artificially, has in turn given rise to many others, as the organic and inorganic chemicals they required, which were little if at all known to commerce at the time, had to be produced on a large scale. Benzol, nitrobenzol, aniline, to mention only a few, were among the newcomers, later on came anthracene.

(It is interesting to note that in the early days of aniline dyes, certain chemicals were smuggled into the works under a wrong name to hide their identity. I was at the time in the employ of Dr. Eugen Lucius, later a member of the firm Meister, Lucius, und Co., hence this recollection. Great difficulties were experienced in recovering arsenic or disposing of the residues. A story is told with reference to these difficulties, amusing perhaps to all except those concerned in it. All troubles seemed to be over when some stranger appeared who undertook to dispose of these residues and was richly paid for his services. Ostensibly he had interested some capitalist in a "perfect process" for the recovery of the arsenic, and had been advanced considerable sums for the alleged purchase of the residues which were warehoused as a security. As may be imagined, the *chevalier d'industrie* presently disappeared, and the illegal storage and the strict regulations as to the disposal of arsenical material entailed a further considerable expenditure on the enterprising capitalist).

The coal-tar industry is now the largest consumer of inorganic products, and was the cause of the invention of the catalytic process of manufacturing sulphuric anhydride. May I be allowed to relate how I came to be connected with this industry? I was a pupil of Professor Strecker at Tübingen in the later 'sixties. When some few years later I again met him and his brother—who was a chemist at Hoechst—and Dr. Brüning, one of his pupils, he spoke of the importance of fuming sulphuric acid in the alizarin industry. The process of sulphonating anthraquinone had been introduced or was about to replace Perkin's dichlor-anthracene process, the use of ordinary concentrated oil of vitriol having proved to be very destructive to the anthraquinone at the elevated temperature that had to be employed. To my question how this fuming acid could best be made, he replied "that is a problem for you to solve." A few experiments convinced me that, given pure gases, the catalytic action of platinum was the rational solution of the problem; I had to wait, however, for an opportunity of carrying my idea into practice. This came when, in April, 1875, a telegram reached me from my then principal, Mr. W. S. Squire, asking me to read up that night about

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[*] Report of the Committee, consisting of Prof. H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Prof. Sydney Young, Dr. C. H. Desch, Dr. J. J. Dobbie, Dr. M. O. Forster, and Dr. A. Lapworth. (Drawn up by the Secretary). Read before the British Association (Section B), Dundee Meeting, 1912.

Nordhausen acid as it was required by an alizarin works, I showed Squire how simple a matter it was to bring about the combination of sulphur dioxide and oxygen by means of platinum and other catalytics, but it was not until at his request I had carried out a number of experiments with bisulphates, &c., which were not very successful, that he asked me "to try my dodge"; henceforward we worked conjointly on the production of the anhydride by catalytic action. Though the process was patented in Squire's name, September, 1875, as others were afterwards or in the name of Neal (a clerk in a Patent Agent's office), they are the joint work of Squire and myself. Soon after, in the 2nd October Heft of *Dingler's Polytechnischen Journal*, Winkler published an account of his process which was practically identical with ours. Both of us erred at that time in believing that stoichiometrical proportions of the gases were the best to use, and the various similarities gave rise to unpleasant comment. In letters, however, which I possess, Winkler freely acknowledges the independence of our work, and only regrets that he had deprived himself of the benefit of the invention by his publication, but he was anxious to work with us.

I cannot leave this chapter without paying my tribute to the work done by others in developing the catalytic process, and foremost, to the late Dr. Knietsch and his co-workers in the Badische Aniline and Soda Fabrik. At the same time, I will let you into one or two secrets. The one is that so far I have not been successful in working with the spent oxide of gasworks. It has the advantage of relative freedom from arsenic, but the drawback of producing an acid which is not so bright and colourless as that made from pyrites. The colour is due to the organic matter in the raw material and to the formation of nitric oxide from its nitrogenous constituents. Nitric oxide can be traced in the burner gases, and it is not eliminated in the washing process to which the gases are submitted. Another point is that there is a loss of platinum amounting to about 1 grain per ton of monohydrated acid produced; the loss must be of a mechanical nature, and can be detected in the drips, although platinum is not discoverable in the gases at this enormous dilution. I believe I can find confirmation of the assumption that the platinum is carried forward owing to the rapidity of the current, because in none of the processes I have worked at a relatively low velocity have I found any loss of platinum, except such as is unavoidable in extracting the asbestos.

Fuming sulphuric acid has found its chief use in the coal-tar colour industry, in refining certain petroleum oils—mainly the Russian oils—and vaseline, and in the explosives industry. As nitro-cotton forms the basis of the celluloid industry, which has been so greatly developed of late, I must mention it and the rivals which it has found in acetyl and cuprammonium cellulose, and last, but not least, in the viscose discovered by Cross and Bevan. These materials are used in large quantities for the production of artificial silk, photographic films, and artificial hair; nor must I omit to mention the important wood-pulp industries depending on chemical processes.

Sufficient examples have been given to illustrate my case: to show that science and industry are working hand in hand, and the importance of the result which such co-operation has produced.

In fact, no branch of industry has been left untouched by the ceaseless and irresistible advance of chemical science and technology.

And now when we look back on this long list of chemical industries which I have brought before you and their great variety, we have to ask ourselves:—Can a chemist be so trained that on entering into any kind of works he will at once be of use and efficient, apart from the expectation that, as a matter of fact, he is supposed to be a proficient analyst? My answer is in the affirmative, provided that the employer himself knows something about the industry in which he is engaged; in that case he will be patient and not expect too much from a beginner.

My illustrations must serve to show that if the student is but to know the chemical and physical principles which underlie so wide a range of activity as any one of the industries I have pictured provides, his time will be more than occupied; to expect him to be conversant also with the technical and economical aspect of industrial problems and to be able to apply his knowledge forthwith is going too far. Technical training can only be of real value after a sound foundation in the principles and practice of pure science has been acquired. Again do I ask:—Can such technical knowledge be acquired by the student before entering into practice as well as the scientific knowledge that will be of use to him and his employers in all or the majority of the industries I have enumerated? It is evident it cannot; and if it cannot be done, is it worth the student's while to sacrifice much time at the most important and critical part in his life, as far as learning is concerned, in acquiring technical knowledge which may be of no assistance to him in after life?

(To a father's request to lay stress on his son obtaining particular knowledge about his own (the father's) industry, one of my professors replied:—"You do not teach your son gymnastics in order that he shall be efficient when a man in turning somersaults in competition with others").

Too early concentration on special subjects must have a bad effect on the development of the power and habit of thinking independently and on the development of the faculty of imagination in the student. If he can find time, apart from his bread and butter education, it is much better for him to turn his mind to subjects of general culture, such as history, art, and literature. Experience teaches me that technique is very readily acquired in practice by one who has been scientifically trained. The most important task of the employer in industry, as in every other walk in life, is to find the right man; and the right man with scientific knowledge, who has imagination and power of observation and can select and command competent subordinates, is immeasurably more useful than the otherwise right man without scientific knowledge. Before all things, it is necessary to find the right man; experience and inventive faculty must do the rest. It is not that we do not possess sufficient knowledge when we leave our colleges as students! what we lack is experience and the power of applying our knowledge. Our great chemical industries have been originated and developed by scientifically trained men; to name only a few, men such as Perkin, Caro, Brunck, Solvay and Mond, Young, the Siemens's, Duisburg, have never found any difficulty in securing the co-operation of engineers or electricians competent to construct any kind of plant they have required to carry out their problems.

In fine, Carlyle has well said:—"He who has learned how to learn can learn anything"; the best system of education is the system which teaches each man how to educate himself.

Our education really begins when we leave college and the storm of life forms our character. We have to study, as nothing in this world is given to us for nothing; books, our scientific and technical societies, must assist us.

(These societies, the intercourse with professional friends engaged in the same pursuit as ourselves or in kindred industries, are invaluable to our education and so are their papers and periodicals. Unfortunately, most of us have to keep not one but quite a number of scientific periodicals, and here we are faced with the fact that they all contain abstracts and that the same matter is abstracted in most of them, yet we cannot find this out till we have waded through them. Prof. Noyes made an attempt to prevent this overlapping about ten years ago, and the International Association of Chemical Societies, which held its first meeting in Paris in 1910 and met again in Berlin this year, will consider this problem amongst others in London in 1913. In the case of purely scientific chemistry, there should not be much difficulty in succeeding; as regards applied chemistry, objections have been raised, which our Council is now considering. Were it possible to rid ourselves of the incubus of overlapping abstracts, it would doubtless be a great saving of time to all of us and its realisation should not be lightly set aside).

Had time permitted much might have been said of industries which are almost specifically American and of developments that are now taking place in connection with the manufacture of food supplies. My difficulty has been merely to indicate the vast number of directions in which the chemist is now rendering service to Society. Each one of my hearers will be able to enlarge upon one or the other of the topics to which I have referred. I can only ask you now to reflect how much lies behind my story. The progress witnessed in my time is inconceivable. It is impossible for one in my position to do justice to such a theme, but of its infinite importance to our civilisation there can be no question.

NOTICES OF BOOKS.

The Physiology of Protein Metabolism. By E. P. Cathcart, M.D., D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

In this valuable monograph, which is one of the series of monographs on biochemistry edited by Dr. Plimmer and Dr. Hopkins, the author discusses the most important results which have been obtained recently by the great army of workers on protein metabolism. Very little is said of the actual details of experimental work, but the results which have been obtained are shortly and clearly stated. Possibly the average physiologist would have welcomed some discussion of these results, when, as frequently happens, their accuracy and completeness are open to doubt, but the references to literature are very full, and the advanced student will find that the monograph gives an excellent summary of the subject.

Inorganic Chemistry for Beginners. By the Rt. Hon. Sir Henry Roscoe, F.R.S., D.C.L., LL.D., and Joseph Lunt, D.Sc. (Vict.), F.I.C. Second Edition. London: Macmillan and Co., Ltd. 1912.

This small book on inorganic chemistry still holds its own among its numerous rivals, and for the use of beginners it is hardly to be surpassed. Besides giving clear and concise accounts of experimental work, it contains a very satisfactory outline of elementary theoretical conceptions, and useful little summaries emphasise the salient points of each chapter in a form which will make them of great value to the young student. Short sets of questions are also included. In selecting their subject matter the authors have followed the suggestions of the Department of Science and Art, and thus the most important non-metallic elements only are treated. Some revision has been done, and a few alterations made, mostly of minor importance, in the second edition, and all the calculations are based on the system of atomic weights in which O = 16.

Uber Lichtsummen bei Phosphoren. ("On the Light Aggregates of Phosphorus"). By P. Lenard. Heidelberg: Carl Winter. 1912.

This paper, which has been reprinted from the *Sitzungsberichte der Heidelberger Akademie der Wissenschaften*, contains an account of the author's investigations of what he calls the light-aggregate of phosphorus. The light energy given out by a specimen of phosphorus in the course of its luminescence is given by the time integral of the emitted light intensity, taken over the whole duration of the luminescence. To this energy the author has given the name light-aggregate. In the article he describes the apparatus used to determine it experimentally, and discusses its constancy in varying conditions and the excitation of phosphorus by light and by the cathode rays.

Les Rayons Ultra-violets et leurs Applications. ("The Ultra-violet Rays and their Applications"). Paris: Le Mois Scientifique et Industriel. 1912. (2 fr. 75).

In this pamphlet the physical, chemical, and biological properties of the ultra-violet rays are first discussed, and the construction of the chief types of mercury vapour-lamps is then fully described. The different systems of lighting are explained, and also processes employed to modify the coloration of lamps with glass bulbs. The application of the rays for sterilisation is treated in detail, and short accounts are given of the employment of them in medicine and for miscellaneous purposes.

CORRESPONDENCE.

THE THERMOCHEMISTRY OF BENZENE.

To the Editor of the Chemical News.

Sir,—I have read Mr. Willebrord Tombrock's paper on "The Problem of Benzene Structure Reviewed from Thermochemical Standpoint," appearing in the Chemical News for September 27th (vol. cvi., p. 155), with considerable interest. The following points occur to me in connection with it:—

1. When H_2 is added to an unsaturated (ethene) body, such as ethylene, propylene, or fumaric acid (to take Mr. Tombrock's examples), what happens is not merely the formation of two C.H links, but a C:C link is replaced by a C.C link. We must not assume, however, that this is the case with the addition of H_2 to benzene; since it is only the case if Kekulé's formula be true. Hence, Mr. Tombrock is not justified in using the value of a derived from unsaturated (ethene) bodies in dealing with the addition of H_2 to benzene; or, if he does use this value of a, he must not only allow for the energy due to the tension of the benzene ring, but *also* for the energy due to the tension of the C:C linking.

2. When benzene is converted into hexane how many C.C links are severed? Mr. Tombrock assumes that only one is severed, for he writes $r = S + v_1$. But if, say, Ladenburg's or Claus's formula is correct, *four* such links are severed, since, according to these formulæ, the benzene molecule contains nine C.C links, whilst the hexane molecule contains only five. In fact, Mr. Tombrock's assumption is only justified if Kekulé's formula be true.

Naturally, if Mr. Tombrock bases his calculations on assumptions which are only justified if Kekulé's formula be true, his conclusion can hardly be otherwise than that Kekulé's formula is true.

I would also call Mr. Tombrock's attention to the following facts:—

3. Thomsen's value for v_1 (= 14·71) is exceedingly hypothetical; since, as I have so often pointed out, the thermochemical values of the various carbon and other links are not obtainable in the present state of knowledge, the data relative to such reducing to a set of indeterminate equations. All that can be obtained are certain derived constants, involving two or more links. (See my "On the Calculation of Thermochemical Constants," 1909, and various papers in the Chemical News).

4. As I have pointed out in the work referred to above, the low heat of combustion of benzene is incompatible with any such formula as Kekulé's which makes it an unsaturated body. The actual value of the energy of the tension in the benzene ring I have calculated from Thomsen's experimental results to be only 5·6 cals. This is much less than that due to one C:C link (= 16·0 cals.), and Kekulé's formula ascribes three of these links to the benzene ring! Since, moreover, both Ladenburg's and Claus's formulæ involve tension due to the configuration of the molecule, Armstrong and Baeyer's centric formula seems on the whole to be most preferable.—I am, &c.,

H. Stanley Redgrove, B.Sc.

The Polytechnic, Regent Street, London, W,

THE PREVENTION OF CORRUPTION.

To the Editor of the Chemical News.

SIR,—It seems from inquiries which have reached me that the provisions of the Prevention of Corruption Act, which forbids under heavy penalties of fine or imprisonment the asking for, or receiving, the offering, or giving, of bribes or secret commissions, are still unfamiliar.

Many persons in the chemical industry appear to be equally unaware of the existence of the Secret Commissions and Bribery Prevention League, Incorporated (President, the Right Hon. Sir Edward Fry, G.C.B.), which was formed to enforce the Act, to advise, warn, and, if necessary, to prosecute, and has a large and influential membership. Several of the leading chemical manufacturers are already members of the League.

If any of your readers desire any information which it is within my power to give, I shall be glad if they will communicate with me.—I am, &c.,

THE SECRETARY,
Secret Commissions and Bribery Prevention League,
Incorporated.

3, Oxford Court,
Cannon Street, London, E.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 3, July 29, 1912.

Equilibrium of Lithium Sulphate and Alkaline Sulphates in presence of their Solutions.—C. Spielrein.—Lithium sulphate forms double salts with the sulphates of the alkalis. Potassium and ammonium sulphates yield salts of formulæ $Li_2SO_4.K_2SO_4$ and $Li_2SO_4.(NH_4)_2SO_4$ respectively. Sodium yields the double salt $Li_2SO_4.3Na_2SO_4.12H_2O$. This salt rapidly effloresces in air, and after three days in presence of quicklime it loses all its water.

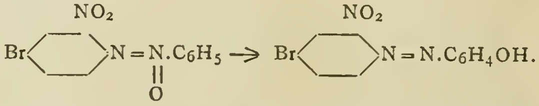
Formula of Organo-magnesium Derivative.—Pierre Jolibois.—The reasons given by Grignard for adopting the formula $Mg{<}^{I}_{C_2H_5}$ for ethyl magnesium iodide do not seem to be conclusive, whereas the formula $Mg{<}^{C_2H_5}_{C_2H_5}.MgI_2$ does not conflict with any experimental facts, and provides an explanation of the syntheses which can be performed with this substance. Moreover, it explains the formation of a mixture of magnesium iodide and hydride, MgH_2, when the derivative is heated.

Atti della Reale Accademia dei Lincei. Vol. xxi. (i.), No. 12.

Aromatic Azoxy-compounds.—A. Angeli and Bruno Valori.—Paraoxyethylazobenzene, when oxidised with hydrogen peroxide in acetic solution, yields two isomeric azoxy-compounds, the α-form $C_6H_5.N{=}\underset{\underset{O}{\|}}{N}.C_6H_4(OC_2H_5)$, and the β-form $C_6H_5.\underset{\underset{O}{\|}}{N}{=}N.C_6H_4(OC_2H_5)$. Similarly, two bromoazoxyorthotoluenes may be obtained. The two corresponding paranitroazoxybenzenes, when subjected to Wallach's reaction, both give paranitroparaoxyazobenzene. The α-compound remains unaltered when treated with nitric acid, while the β-derivative gives a mixture of *p*-*p*-dinitroazoxybenzene, and the new compound paraorthonitroazoxybenzene. Chromic acid has no action on the α-derivative, while it converts β into the α-form.

Action of Sulphuric Acid on Acenaphthene.—E. Oliveri-Mandala.—By the action of concentrated sulphuric acid on acenaphthene only one monosulphonic derivative is obtained. No variations in the experimental conditions lead to the introduction of more than one sulphoxyl group into the nucleus, and in this respect acenaphthene differs from anthracene, fluorene, &c., which give polysulphonic acids. The author has prepared and investigated the monosulphonic acid, the formula of which is $C_{12}H_{10}SO_3.2H_2O$, and also its potassium and barium salts, its methyl and ethyl ethers, and other derivatives.

Constitution of Bromonitroazoxybenzene.—Bruno Valori.—When nitric acid acts on parabromoazoxybenzene the NO_2 group takes up the ortho-position with reference to the azo-group in the bromonitroazoxybenzene thus produced. If the bromonitro compound is heated with concentrated sulphuric acid the isomeric oxyazo-derivative is obtained, an oxygen atom migrating, according to the equation—



This is proved by the fact that it is possible to obtain the same compound by the reaction of the chloride of *o*-nitro-*p*-bromophenyldiazone with phenol.

MISCELLANEOUS.

Armstrong College, Newcastle-upon-Tyne.—Special Evening Lectures.—The Newcastle Section of the Society of Chemical Industry and the Armstrong College are this winter arranging courses of Evening Lectures on special subjects in Applied Chemistry, which, it is anticipated, will prove specially interesting to those chemists and engineers already engaged in the industries. To inaugurate the scheme a special fund is being raised, which has already received liberal support from the principal manufacturers in the district. Two courses of five lectures each have been arranged for this winter, for which the Committee has secured the services of well-known specialists. The first course is on "Coal Gas Manufacture and the Carbonisation of Coal," by Dr. Harold C. Colman, of London, and the second on "Metallography," by Dr. Desch, of Glasgow University. The first course will commence on October 16th, and be continued at fortnightly intervals. The second course is to commence on January 28th, 1913.

Cambridge Manuals of Science and Literature.—Mr. A. C. Chapman (the President of the Institute of Brewing) contributes a volume to the Cambridge Manuals (one of the eight to be published on October 1st). It is fitting that a volume on Brewing should find a place in the series. Every man knows that beer and fermented drinks of a similar nature have been made almost from time immemorial, but probably does not know—and it is this that the author explains so clearly—that the principles underlying the apparently simple process of brewing are of great importance and intense interest. These principles have only been understood since the time of Pasteur, and their investigation has enriched the chemical and biological sciences with some of their most valued intellectual achievements. This book is confined as far as possible to an explanation of the principles underlying the various parts of the brewing process, and the author has endeavoured in describing these to employ language intelligible to the well-educated layman for whom the book is primarily intended.

THE CHEMICAL NEWS.
Vol. CVI., No. 2759.

THE CAUSES OF THE INDUCTION PERIOD.[*]

By R. de J. FLEMING STRUTHERS.

The mode of decomposition, on gradually heating, of the vapour of nitrogen chloride diluted with an indifferent gas differs from the progressive and regular decomposition that occurs on exposure to the action of light. In the former case no change is perceptible till the temperature reaches a certain value, then sudden decomposition begins and appears always to culminate in an explosion.

When vapour of nitrogen chloride is heated gradually in an atmosphere of hydrogen an explosion likewise occurs; but here interaction results and ammonium chloride is precipitated. Precipitation of ammonium chloride also results quantitatively when hydrogen chloride interacts with vapour of nitrogen chloride.

When a mixture of nitrogen chloride vapour and hydrogen is exposed to the action of light only a very small proportion of nitrogen chloride is converted into ammonium chloride. This shows that practically all the nitrogen chloride is decomposed by light before any hydrogen chloride can be formed; and that for this reason nitrogen chloride must be an inhibitor of combination between chlorine and hydrogen on exposure to light, and be capable of producing a period of inaction comparable to Bunsen and Roscoe's "induction period."

THE TRANSFORMATION OF AROMATIC NITROAMINES AND ALLIED SUBSTANCES, AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.[†]

I. *The Conversion of Chloro-, Bromo-, and Nitro-aminobenzenes into Substituted Anilines.*

In the recent reports of this Committee, the results of work on the transformation of chloro- and bromo-aminobenzenes into halogen-anilides, and of nitroaminobenzenes into nitroanilines has been communicated. In the case of the former compounds, it has been shown that the transformation is not an intramolecular change, but consists of a primary reaction of the chloroamine and hydrogen chloride, the presence of which is essential, thus:—

$$Ar.NClAc + HCl \rightleftarrows Ar.NHAc + Cl_2 \rightarrow ClAr.NHAc + HCl.$$

Whether a true intramolecular change is possible under certain conditions has not yet been discovered, but it must not be supposed that the possibility is excluded.

The conversion of the nitroaminobenzenes into the isomeric nitroanilines offers a very marked contrast.

(i.) All acids, and not one specific substance, bring about the transformation. The relative effectiveness of different acids is generally proportional to their activities in other processes. Moreover, when no side-reactions occur, the speed for a monobasic acid is proportional to the second power of the concentration, at least in aqueous and dilute acetic acid solution.

(ii.) Although there is evidence, but of no certain kind, that the nitration of another substance by a nitroamine can occur (for example, of acetanilide or 2:4-dichloroaniline by *s*-tribromonitroaminobenzene), under certain narrowly defined conditions, there is nothing corresponding to the remarkable chlorination of one anilide by the chloroamine of another, which has been described. No radicle (ion) or substance which is a powerful nitrating agent appears to be free in the system.

(iii.) The solid crystalline nitroamine changes into the nitroaniline, the crystals of the latter apparently growing out of the former in the presence of gaseous hydrogen chloride in a P_2O_5-dry atmosphere.

(iv.) Although nitrous acid appears during the transformation, and diazonium salts are produced, the presence of urea in the system does not affect in any way the speed or the products of the change.

(v.) The nature of the nitroamine and of the catalyst has a very marked effect on the extent of the side-reaction in which the diazonium salt is produced. The maximum amount of diazonium salt is found with 2:4-dichloronitroaminobenzene, much less with the corresponding 2:4-dibromo compound, and none with 1-methyl-3-bromo-4-nitroaminobenzene.

The nature of the catalyst has a similar influence. When nitric acid is the catalyst no appreciable quantity of diazonium salt can be found. In the presence of perchloric acid, the maximum amount of diazo compound is produced; hydrogen chloride yields less and sulphuric acid still less. The ratio of diazonium salt to nitroaniline for a given catalyst appears to be independent of the concentration of the catalyst or the composition of the medium; thus in the case of hydrogen chloride and 2:4-dichloroaniline in various mixtures of acetic acid and water, the ratio, nitroaniline/diazonium salt = 3·7/1.

Conclusion.—So far as the evidence goes, the provisional conclusion may be drawn that the conversion of nitroaminobenzenes into nitroanilines differs from the conversion of chloroamines, and may probably be regarded as an intramolecular change. But the possibility that under certain conditions a cleavage into aniline and a nitrating substance occurs, at least partly, cannot be excluded. Thus as an instance *s*-trichloronitroaminobenzene in an environment when transformation is generally rapid yields largely *s*-trichloroaniline.

In the substances which we have closely investigated, one ortho-position only is vacant, into which the nitro group can migrate. The migration of the nitro group into the para-position is observed in the conversion of 2:6-dibromonitroaminobenzene into 2:6-dibromo-4-nitroaniline; this change is, however, accompanied by the formation of about an equal amount of the isomeric 2:4-dibromo-6-nitroaniline, the bromine atom in the ortho-position being displayed (Orton and Pearson, *Trans. Chem. Soc.*, 1908, xciii., 725). From a consideration of the relative proportions of *o*- and *p*-nitro-anilines and -anilides produced under various conditions, in the transformation of nitroamines, nitration by acetyl nitrate, &c., Hollemannn (*Ber.*, 1911, xliv., 704) has concluded that the ortho-compound is generally formed by way of the nitroamine, whilst the para-compound is formed by some other process. In the case above cited, however, the *p*-nitroaniline is undoubtedly obtained from the nitroamine, although perhaps not by a simple intramolecular rearrangement. Comparison of the two changes shows at least that the conversion to the *o*-nitroaniline is a far more rapid and easy process.

Formation of Nitroaminobenzenes.—Owing to the difficulties of following further the conversion of nitroamines into nitroanilines, we have been led to study the conditions and mechanism of the formation of nitroamines. An excellent way of converting anilines into nitroamines is by treatment in acetic acid solution with a mixture of nitric acid and acetic anhydride (Orton, *Trans. Chem. Soc.*, 1902, lxxxi., 806, and Orton and Edwards, *Reports*, 1911). The behaviour of nitric acid offers in this respect a marked contrast to that of other strong acids; they are powerful accelerators of the direct reaction between the anhydride

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[*] A Paper read before the British Association (Section B), Dundee Meeting, 1012.

[†] Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P Orton (Secretary), Dr. S. Ruhemann, Dr. A. Lapworth, and Dr. J. T. Hewitt. Read before the British Association (Section B), Dundee Meeting, 1912.

and anilines (Orton and Smith, *Trans. Chem. Soc.*, 1908, xciii., 1242; 1909, xcv., 1060). In order to investigate these highly distinctive reactions more closely a means of determining acetic anhydride in such systems was required. A good method was finally devised (Edwards and Orton, *Trans. Chem. Soc.*, 1911, xcix., 1181) which is based on the following reactions; certain anilines, for example, 2 : 4-di-chloroaniline, react with acetic anhydride in acetic acid solution, even containing a certain proportion of water, very rapidly and quantitatively; the anilide is extracted from the diluted medium with chloroform, and the excess of aniline removed by treatment with an acid; finally the anilide is converted into a chloroamine which can be estimated by titration. In this manner very small quantities of acetic anhydride can be estimated in the presence of acetic acid.

With the aid of this method of analysis, the hydrolysis of acetic anhydride has been studied, and remarkable differences between nitric and other acids, in their effect on this process, discovered.

II. *Hydrolysis of Acetic Anhydride.* (With Marian Jones, B.Sc.)

So far the hydrolysis of acetic anhydride has only been investigated in aqueous solution by Menschutkin and Vasilieff, Lumière and Barbier (these investigators used a titrimetric process), and Rivett and Sidgwick (*Trans. Chem. Soc.*, 1910, xcvii., pp. 733, 1677), using the change of electric conductivity. With the aid of the method above described, it is possible to follow this reaction in various media, and in presence of catalysts.

(i.) *Hydrolysis in Aqueous Solution.*—Table I. shows typical results of experiments when three different methods of measurements are used.

Table I.

	A.	k_1 15°	k_1 25°.
Lumière and Barbier ..	0·491	0·0735	—
	0·491	k_1 0° = 0·03	—
Rivett and Sidgwick ..	0·487	0·074	0·1383
	0·265	0·0793	0·1484
	0·058	0·0835	0·1561
Orton and Jones	0·486	0·074	—
	0·269	0·084	—
	0·495	k_1 0° = 0·028	—

On the supposition that the reaction is represented by the equation $Ac_2O + H_2O = 2CH_3.CO_2H$, the velocity factor, k_1 = the product of the velocity coefficient, k_{11}, of this reaction of the second order, and the concentration of the water, which is perceptibly constant,—

$$= \frac{1}{t} \cdot \log \frac{A}{A-x},$$

where A is the initial concentration of the anhydride in molecules, and x the amount changed in time t (minutes).

(ii.) *Effect of Medium.*—Table II. shows the effect of the composition of the medium on the rate of hydrolysis.

Table II.

Medium.	Temperature.	Concentration of acetic anhydride.	Velocity-coefficient or velocity-factor.
Glacial acetic acid ..	16	0·0804 ($[H_2O]$ = 0·18)	k = 0·00042
95 p.c. acetic acid ..	16	0·0782	k_1 = 0·001
90 p.c. acetic acid ..	16	0·0815	0·0028
80 p.c. acetic acid ..	16	0·0813	0·0056
50 p.c. acetic acid ..	16	0·083	0·016
Water	15	0·473	0·074
95 p.c. aqueous acetone	15	0·087	6 p.c. hydrolysed in 118 hours.
50 p.c. aqueous solution	15	0·088	k_1 = 0·006
Acetic anhydride	15	10·3 ($[H_2O]$ = 1·8)	k_{11} = 0·000071

As the acetic acid is diluted, the rate of hydrolysis increases roughly proportionally to the amount of water in the medium. It is remarkable that pure acetic anhydride should be such a curiously unfavourable medium for its own reaction with water.

(iii.) *Effect of Catalysts.*—In aqueous solution alkalis are very powerful catalysts of the hydrolysis. Acids have, on the other hand, but a very feeble effect. Such slightly hydrolysed salts as sodium acetate occupy an intermediate position.

In anhydrous media acids produce a great acceleration of the reaction, but the effect diminishes as the proportion of water in the medium decreases.

Table III.

Medium.	Concentration of H_2SO_4.	Concentration of Ac_2O.	Temperature.	Speed of hydrolysis.
Glacial acetic acid	—	0·0804	16°	12 p.c. in 24 hours k_{11} = 0·0042
	0·002M	0·077	16°	52 p.c. in 10 mins.
90 p.c. acetic acid	—	0·0815	16°	k_1 = 0·0028
	0·0166M	0·0807	16°	0·016
	0·1M	0·091	15°	0·076
50 p.c. acetic acid	—	0·083	15°	0·016
	0·034M	0·0835	15°	0·03

With regard to the nature and concentration of the acid, it is to be noted that:—

(i.) In 90 and 95 per cent acetic acid molecular quantities of acids are equivalent in accelerating effect.

(ii.) In 50 per cent acetic acid equivalent quantities of acids produce equal effects.

(iii.) At intermediate compositions of the medium there is no simple relation.

(iv.) When the effect can be measured as in 90 per cent acetic acid, the rate of hydrolysis is found to be proportional to the concentration of the catalyst.

These relations indicate that the unionised acid is the effective catalyst in media containing 90 per cent acetic acid and upwards, but that the ionised acid is the catalyst in media containing 50 per cent acetic acid.

Nitric Acid as Catalyst.—In its relation to the hydrolysis of acetic anhydride, nitric acid occupies a unique position. Whilst in 50 per cent acetic acid its effectiveness is identical with that of other acids; as the proportion of water in the medium decreases, its relative activity steadily falls off, until in glacial acetic acid it is, compared with sulphuric acid, infinitesimal.

Table IV.

Medium—acetic acid.	Catalyst.	Concentration of Ac_2O.	Speed of hydrolysis.
50 p.c. ..	—	0·083	k_1 = 0·016
	0·034 M H_2SO_4	0·084	0·021
	0·07 M HCl	0·083	0·022
	0·071 M HNO_3	0·087	0·022
99 p.c. ..	—	0·0815	0·0028
	0·033 M HCl	0·081	0·023
	0·0165 M HNO_3	0·083	0·0065
	0·033 M HNO_3	0·0805	0·008
	0·066 M HNO_3	0·079	0·012
Glacial ..	—	0·0804	12 p.c. in 24 hrs.
	0·002 M H_2SO_4	0·077	52 p.c. in 10 mins.
	0·05 M HNO_3	0·08	32 p.c. in 24 hrs.

Nitric acid only acts as other acids when ionised; the abnormality appears when the acid is partially or wholly unionised. On diluting a solution of glacial acid containing nitric acid to 50 per cent acetic acid, hydrolysis follows at the same rate as if nitric acid had been added to acetic anhydride dissolved in a 50 per cent acetic acid. This result does not suggest that the formation of such compounds as acetyl nitrate, $CH_3.CO.O.NO_2$, or diacetylorthonitric acid, $(CH_3.CO)_2N(OH)_3$, which have been described by Pictet and others, is the immediate cause of the peculiarity. For it would then be necessary to assume that these compounds yield acetic anhydride and nitric acid on diluting the medium with water. Moreover, the fact that the addition of a trace of sulphuric acid to the system containing nitric acid in glacial acetic acid is followed by the usual very rapid hydrolysis, indicates that the condition of the nitric acid only, and not that of the acetic anhydride, is the cause of the peculiarity.

Discussion of Results.—The suggestion, in a discussion of Rivett and Sidgwick's results in the Annual Reports of the Chemical Society, 1910, that the mechanism of the hydrolysis of acetic and other anhydrides was not different from that of amides, esters, &c., as these authors had supposed, has been verified by our experiments. Since the reaction of acetic anhydride with hydroxy compounds (Franchimont, Skraup, and others), and with amino compounds, weak bases (Orton and Smith), is enormously accelerated by strong acids, it was to be expected that its reaction with water would be similarly influenced.

In recent years the mechanism of such reactions has received much attention, and has been shown, more especially in the case of esterification (Lapworth, Goldschmidt, and others), that the reaction may proceed in various ways, depending on the medium, presence, or absence of other substances (acids and other catalysts). Following the suggestion of these researches the hydrolysis of acetic anhydride may be represented by one or other of the equations :—

$$\text{(i.)}\quad Ac_2O + H_2O + = 2AcOH\ ;$$
$$\text{(ii.)}\quad Ac_2O + H_2O + H^{\cdot} = 2AcOH + H^{\cdot}\ ;$$
$$\text{(iii.)}\quad Ac_2O + H_2O = HX = 2AcOH + HX\ ;$$
$$\text{(iv.)}\quad Ac_2O + H_2O + (OH)' = 2AcOH + (OH)'.$$

The third component, $H^{\cdot}$, OH', or HX, may exert its influence by forming a reacting ionic or non-ionised complex with one or other of the two reagents.

In aqueous solution the choice lies between (i.), (ii.), or (iv.). Strong acids have a feeble, whilst bases and even such a slightly hydrolysed salt as sodium acetate have a powerful catalytic effect. These relations suggest that in aqueous solutions hydroxyl ions play the predominant part. In that case traces of acids by decreasing the concentration of the hydroxyl ion should have a great retarding influence. It is true that acetic acid does slightly retard the hydrolysis, but we have not found any such effect with sulphuric. Hence, although hydroxyl ions are powerful catalysts, it may be concluded that in pure water the hydrolysis mainly follows equation (i.), and is noncatalytic.

In relatively anhydrous media, reaction (iii.) obviously predominates. The reaction is very slow in the absence of acids ; molecular quantities of acids are equally effective, and the speed is a linear function of the concentration of the acid.

In media such as 50 per cent acetic acid or acetone, the catalytic effect is now due to the hydrogen ions (equation ii.) for equivalent quantities of acids are now of equal influence ; but inasmuch as the rate of hydrolysis is considerable in the absence of an acid catalyst, the reaction also follows equation (i.).

In media with less than 50 per cent of water the catalytic effect of acids follows both equations (ii.) and (iii.).

It is worthy of note that the velocity factor of the reaction is not independent of the initial concentration of the acetic anhydride, the value falling as the initial concentration increases. This fact was observed and commented on by Rivett and Sidgwick, and is deducible from Lumière and Barbier's results for aqueous solution. In our measurements the same fact is obvious both in aqueous and in 80 per cent acetic acid. Thus for the initial concentration 0·486 and 0·269 molecule the value of k_1 15° is 0·074 and 0·084 respectively, in aqueous solution ; in 80 per cent acetic acid, k_1 15° is 0·0047 and 0·0056 for the initial concentrations 0·1625 and 0·0813 molecule respectively. When log k is plotted against log c (the concentration) for a series of values of c (between 0·1169 and 0·3947), selected from Rivett and Sidgwick's measurements, approximately a straight line is obtained. Burke and Donnan (*Trans. Chem. Soc.*, 1904, lxxxv., 555) have observed a similar phenomenon in the reaction of silver nitrate and alkyl iodides, except that that value of k increases with increase of the concentration (of the silver nitrate). Here also log k and log c are linearly related, and hence the variation is expressed by the exponential law, $k = Kc^n$.

III. *Some Properties of Acetic Anhydride.* (With MARIAN JONES, B.Sc.).

Both our own experience and a study of the literature show that the complete separation of acetic acid and acetic anhydride, and hence the preparation of pure acetic anhydride, is no simple matter. Fractionation without a still-head of a mixture containing only 10 per cent of acetic acid will give but some 8 to 10 per cent of pure anhydride. By use of Young's "pear" still-head the pure substance, amounting to 50 to 60 per cent of the original material, can be readily obtained. Its physical constants differ materially from those usually given ; Landolt's values alone agree with ours. The boiling-point is 139·55 under 760 mm. pressure, and the density 1·0876 at 15°/4°, and 1·082 at 20°/4°. The refractive index for H*c* at 15° is 1·39069. At 15° about 2·7 grms. of water dissolve in 100 grms. of acetic anhydride, and 12 grms. of anhydride in 100 grms. of water.

Action of Halogens on Acetic Anhydride.—When light is excluded solutions of chlorine and bromine in acetic anhydride are quite stable. But in the presence of strong acids, iodine, ferric chloride, &c., a very rapid reaction follows :—

TABLE V.

Time (mins.).	Titre of 5 cc. in N/50 thiosulphate. Cc.
H_2SO_4 = N/3000.	
0	12·4
36	7·35
75	4·1
112	2·5
I = N/300.	
0	9·4
5	9·1
45	2·05
$FeCl_3$ = M/535.	
0	10·7
8	8·7
12·5	7·2
34	0·1

The catalysts are effective as the first power of their concentration ; when acids can be compared—for example, sulphuric and perchloric—it is found that molecular and not equivalent quantities are equally effective.

The fall in titre of the bromine is independent of the initial concentration of the solution, and hence bears a linear relation to the time ; that is, the graph of dx/dt is a straight line. Lapworth accounted for an exactly similar relation in the attack of bromine on acetone by supposing that the bromine only reacts with a tautomeride of acetone, the production of which from the acetone is far slower than its reaction with bromine. The rate of disappearance of the bromine is dependent, therefore, only on the formation of the tautomeride, and independent of the concentration of the bromine. In the case of acetic anhydride the reactive material is only formed in the presence of the catalyst. Hence the speed of the bromination, which is proportional to the concentration of the former, must obviously also be proportional to that of the catalyst. There is no such detectable acceleration of the action of bromine on acetic acid by acids (except possibly when their concentration is very high); hence, it may be deduced, a similar reactive substance is not produced, at least to a proportionate extent, from acetic acid under the influence of acids.

The Committee ask to be reappointed for the coming year, with a grant of £15.

REPORT ON DIFFUSION IN SOLIDS.*

By CECIL H. DESCH, D Sc., Ph.D.

(Continued from p. 170).

Cementation and Decarburisation of Iron.

The process of converting iron into steel by heating in contact with solid carbon has undoubtedly been practised from ancient times, although it is not described by ancient authors (J. Percy, "Metallurgy of Iron and Steel," London, 1864, p. 110). The examination of early implements sometimes shows that the iron has been superficially hardened by this means. For example, a Sinhalese chisel of the fifth century showed carburisation at the edge, the mass of the chisel being soft iron made by the direct process (Sir R. Hadfield, *Proc. Roy. Soc.*, 1912, lxxxvi., A, 94; *Journ. Iron and Steel Inst.*, 1912, i.). It is suggested that the process is of Indian origin. An accurate description of cementation, as well as of the converse process of decarburising iron by heating in hæmatite, is given by R. A. F. de Réaumur ("L'Art de convertir le fer forgé en acier, et l'art d'adoucir le fer fondu," Paris, 1722). As regards a theoretical explanation, the fact of reaction between solid substances was felt to be a difficulty, and an hypothesis was proposed, according to which the active cementing substance was not carbon, but gaseous hydrocarbons derived from impurities in the charcoal, or oxides of carbon (F. Le Play, *Ann. Chim. Phys.*, 1836, [2], lxii., 291; F. Le Play and A. Laurent, *Ibid.*, 1837, [2], lxv., 403). As, however, contact with a block of graphite was found to suffice when the iron was heated in a porcelain tube, the further assumption was made that carbon vapour was formed under such conditions (A. Laurent, *Ibid.*, 417). This was the beginning of a controversy that has been renewed at intervals down to the present day. The views of Le Play and Laurent were opposed by Gay-Lussac, who, whilst admitting that much in the process of cementation is obscure, closes his vigorously written memoir with the words (*Ann. Chim. Phys.*, 1846, [3], xvii., 221):—

"Il n'est plus permis aujourd'hui d'avoir une foi aveugle au principe si banalement répété des anciens chimistes, *corpora non agunt nisi soluta*. Il est certain, au contraire, que tous les corps, solides, liquides ou aériformes, agissent les uns sur les autres, mais que, des trois états des corps, l'état solide est le moins favorable à l'exercice de l'affinité."

The adoption of van 't Hoff's view of the nature of solid solutions would reconcile Gay-Lussac's conclusion with the principle of the older chemists.

The view that cementation is a process of true diffusion in the solid state was distinctly advanced by experiments which showed that the curve of distribution of carbon with depth at any given temperature had the form of a diffusion curve (R. Mannesmann, *Verh. Ver. Beförd. Gewerbefl.*, 1879, lviii., 31; A. Colson, *Comptes Rendus*, 1881, xciii., 1074). The memoir of Mannesmann is particularly valuable for its mass of experimental evidence. The form of the curve has since been re-determined with greater exactness, confirming previous conclusions (W. C. Roberts-Austen, *Journ. Iron and Steel Inst.*, 1896., i., 139). Mannesmann's experiments showed that under suitable conditions cementation only took place where the iron was actually in contact with solid carbon, whereas, if the active agent had been traces of gaseous compounds, the action should have been general and not localised. Charcoal always contains absorbed gases, which are removed only with difficulty, and special interest therefore attaches to experiments in which graphite or diamond is used in place of the amorphous modification. As far back as 1865 it had been shown that iron was carburised by direct contact with either graphite or diamond in an atmosphere of hydrogen (F. Margueritte, *Ann. Chim. Phys.*, 1865, [4], vi., 55). In such early investigations, however, no account was taken of oxides of carbon occluded in the iron, and the experiments have been repeated on many occasions by other observers, with contradictory results. Thus it was found that diamond would carburise iron at 1160° in an atmosphere of nitrogen (W. Hempel, *Ber.*, 1885, xviii., 998), and that the cementation was actually more rapid than when other modifications of carbon were used. Similarly, the direct contact of diamond with iron in a vacuum, the degree of which is not stated, was found to bring about cementation (W. C. Roberts-Austen, *Journ. Iron and Steel Inst.*, 1890, i., 91). On the other hand, it has been stated that the presence of gaseous compounds is necessary before any penetration takes place (L. Guillet, (*Rev. de Métallurgie*, 1906, iii., 227). Certain precautions have to be taken to avoid errors in the interpretation of the results. Thus, an experiment may fail from the absence of a satisfactory contact between the carbon and iron. This may be ensured by the application of pressure, which accordingly favours cementation (L. Guillet and C. Griffiths, *Comptes Rendus*, 1909, cxlix., 125). On the other hand, in the course of experiments in which negative results were obtained from solid carbon and iron in a high vacuum, both materials being previously freed from gas, it was observed that a small reduction in the degree of the vacuum, caused by the admission of gas, led to carburisation (G. Charpy and S. Bonnerot, *Comptes Rendus*, 1910, cl., 173).

A careful investigation, in which these conditions are taken into account, is due to F. Weyl (*Metallurgie*, 1910, vii., 440). The materials used were sugar charcoal, purified by heating in chlorine and in hydrogen; natural graphite, the ash of which had been reduced to 0·22 per cent by treatment with sulphuric and hydrofluoric acids; "kish," or graphite obtained by stirring molten iron saturated with carbon, the ash being reduced to 0·82 per cent by successive treatment with nitric acid, chlorine, and hydrofluoric acid; and diamond. Iron prepared in an electric furnace was used on account of its freedom from slag. The polished cube of iron rested by one of its faces on the surface of the carbon. A good vacuum was maintained, the pressure being always below 0·05 mm., and frequently as low as 0·001—0·002 mm. throughout an experiment. Positive results were obtained in all cases, whilst the supposition that gases played any important part in the transport of carbon was negatived by the observation that a layer of kaolin, 0·25 mm. thick, interposed between the carbon and the iron, sufficed to prevent all cementation. The influence of contact was shown by the fact that very little cementation was obtained with fragments of diamond when the iron rested upon them, whereas when the diamond dust was placed on the upper surface of the iron cementation occurred quite readily. In the latter case the finer particles of diamond came into contact with the iron, whilst in the former they were separated. In view of these results it is not easy to understand the failure of Charpy and Bonnerot to obtain carburisation under similar conditions, unless the contact between the two substances in their experiments was insufficiently good.

Graphite which is already present in the interior of a mass of iron is undoubtedly absorbed to a considerable extent on heating. Thus, when grey iron is heated to different temperatures above 700° and quenched, the proportion of combined carbon is increased, the quantity increasing rapidly with the temperature (G. Charpy, *Comptes Rendus*, 1907, cxlv., 1277). A similar observation has been made in respect to temper carbon, which is finely divided graphite (H. Le Chatelier, *Rev. de Métallurgie*).

Mention must now be made of a class of experiments in

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which the carbon is not used in the free state, but in the form of a steel rich in carbon. If the process be one of true diffusion, carbon should tend to pass from places of high to those of low concentration. This is found to be the case. When two pieces of steel, containing respectively 0·90 per cent and 0·15 per cent of carbon, are placed in immediate contact and heated, air being excluded, carbon passes from the high into the low carbon steel, the gain of weight of the one being almost exactly equal to the loss of weight of the other (G. P. Royston, *Journ. Iron and Steel Inst.*, 1897, i., 166). Experiments on this point have been made with great care, a cylinder of nearly pure iron being bored through longitudinally, and fitted over a core of steel containing a much larger proportion of carbon (J. O. Arnold and A. McWilliam, *Journ. Iron and Steel Inst.*, 1899, i., 85). After heating for ten hours *in vacuo* at 950° to 1050° the outer jacket was turned off, and the layer immediately adjoining the core was analysed. The diffusion of carbon was clearly proved in this manner.

The fact that the materials used in the practical cementation of iron are commonly not pure carbon, but contain combined nitrogen, has led on several occasions to the supposition that the carbon diffuses in the form of a compound of nitrogen, such as cyanogen, or that a nitride of iron takes part in the process, as well as the carbide. The cyanogen theory is due to W. Stein (*Polyt. Centr.*, 1851, 897), but need not be further considered here, as there is no reason to suppose that nitrogen is responsible for the transport of carbon within the metal, whatever may be the case in regard to the formation of the external layer of highly carburised iron. It is certain that the presence of cyanides and of gaseous carbon compounds greatly accelerates diffusion, but it does not follow that the process of diffusion into the interior differs in any respect from that which occurs when elementary carbon is the cementing agent (A. Ledebur, *Stahl und Eisen*, 1906, xxvi., 72). Very rapid cementation is brought about by the action of mixtures of the oxides of carbon on iron (F. Giolitti, *Journ. Iron and Steel Inst.*, 1911, ii., 307; summarising a series of papers contained in *Gazzetta*, 1910-1911), especially when the mixture in equilibrium with solid carbon at the required temperature is used. It is not necessary to assume that the gases penetrate to the interior of the metal and so convey the carbon; on the contrary, the experiments support the view that the function of the gas is merely that of reacting with the iron to form a superficial layer rich in carbon, from which diffusion inwards can then proceed. The investigations of Arnold and McWilliam and of others have clearly established the fact that the carbon does not diffuse in the free state, but as a carbide, Fe_3C, although the further assumption by the above-named authors, that an intermediate carbide, $Fe_{24}C$, is formed, has not met with general acceptance.

As the carbide is not appreciably soluble in α-iron it is to be expected that cementation should not take place below 690°, the lowest temperature at which austenite, the solid solution of carbide in γ-iron, can exist in a stable state, and this appears to be generally true, although cementation to a very slight extent at so low a temperature as 250° has been recorded (A. Colson, *Comptes Rendus*, 1881, xciii., 1074).

The diffusion of silicon into iron has often been observed (A. Colson, *C. R.*, 1882, xciv., 26). At 1200° it is possible to convert iron completely into a silicide by heating in contact with solid silicon, although in this instance the vapour of silicon has been considered to play a part in the reaction (H. Moissan, *C. R.*, 1895, cxxi., 621; P. Lebeau, *Bull. Soc. Chim.*, 1902, [3], xxvii., 44). The difficulty of observations of this kind is illustrated by the case of sulphur. An attempt to measure the diffusion of sulphides through steel led at first to very inconclusive results (E. D. Campbell, *Journ. Iron and Steel Inst.*, 1897, ii., 80), owing to the escape of fusible sulphides, but further experiments showed that true diffusion took place, and that when cuprous sulphide was used a part of the copper was also transported into the metal (Campbell, *Journ. Iron and Steel Inst.*, 1898, ii., 256; S. A. Grayson, *Ibid.*, 1910, 287).

When iron was placed in contact with alloys of iron containing other elements and heated at about 1000° *in vacuo*, diffusion was observed when the element studied was sulphur, phosphorus, or nickel, but not when it was manganese, silicon, chromium, aluminium, tungsten, arsenic, or copper (J. O. Arnold and A. McWilliam, *loc. cit.*).

The case-hardening of iron and steel is a process of superficial cementation, and what has been said as to the latter process applies also to the former. Many important details as to the velocity of carburisation and diffusion are to be found in Giolitti's memoirs.

The decarburisation of iron-carbon alloys by heating in an oxidising medium is the reverse of cementation. Oxides of iron are commonly employed as the medium. The process was described in detail by Réaumur (*Op. cit.*). It is known that the removal of the carbon is preceded or accompanied by the decomposition of the carbide into iron and temper carbon, and the reaction has been explained as one of oxidation of this free carbon by carbon dioxide, formed by reactions between the oxidising material and the carbide in the superficial layer of iron (F. Wüst, *Metallurgie*, 1908, v., 7; H. Becker, *Ibid.*, 1910, vii., 41). The explanation is, however, imperfect, and it is certainly possible for carbon to be removed without previous precipitation as temper carbon (W. H. Hatfield, *Journ. Iron and Steel Inst.*, 1909, i.). It is therefore most probable that removal of carbon by true diffusion actually takes place, in accordance with the theory formerly held, and that decarburisation by gas, although taking the principal share in some forms of the technical process, is not absolutely essential.

Segregation and Re-crystallisation.

Diffusion in solid metallic alloys is well illustrated by the segregation of constituents. A new phase commonly makes its first appearance in a finely divided form, and although chemical equilibrium may have been attained, physical equilibrium is not reached until the small particles have united to form larger aggregates. Steel offers a good example of this. The carbide separating from solid solution during cooling is at first in a state of ultramicroscopic division, and troostite has been described as a solid colloidal solution of carbide in iron (C. Benedicks, *Journ. Iron and Steel Inst.*, 1905, ii., 352; 1908, ii., 217). If more slowly cooled, finely granular sorbite and laminated pearlite are successively obtained. Pearlite has been commonly regarded as the normal form of the eutechtoid, but it is found that further heating causes the laminæ to contract, producing beaded forms (C. Benedicks, *Metallurgie*, 1909, vi., 567), and ultimately the carbide aggregates into coarse masses (J. E. Stead, *Journ. Soc. Chem. Ind.*, 1903, xxii., 340), so that the steel presents the paradoxical condition of containing both structurally free iron and carbide (E. F. Lange, *Metallographist*, 1903, vi., 9).

The dispersion of a newly formed solid phase in an ultramicroscopic form through a crystalline mass of metal is not uncommon (C. Benedicks, *Zeit. Chem. Ind. Kolloide*, 1910, vii., 290). It is observed in alloys of nickel and iron, of cadmium and tin (W. Guertler, *Intern. Zeit. Metallographie*, 1912, ii., 172), and also in the β-solid solution of copper and zinc (H. C. H. Carpenter, *Journ. Inst. Metals*, 1912, vii., 123). This last case is of special interest. The β-solution is not stable below 475°, at which temperature it is resolved into a mixture of the α- and γ-phases, which at first remain in a state of ultramicroscopic division. Segregation is extremely slow, even at temperatures only slightly below the transformation point, but is accelerated by the presence of the α- or the γ-phase in excess, or by the presence of a third metal in solid solution, such as aluminium.

When crystals of a solid solution separate from a liquid, the composition of the crystals is only uniform if the rate of cooling is so slow that time is allowed for continual re-adjustment of equilibrium between the solid and liquid phases by diffusion within the solid. If this is not the case, the crystals have a zonal structure, the outer zones being relatively richer than the inner in that component which lowers the freezing-point. Such zonal or "cored" structures are usually present in solid solutions of metals cooled under ordinary conditions. Although it has been attempted to explain these structures as produced by purely mechanical causes (F. Osmond and G. Cartaud, *Comptes Rendus*, 1904, cxxxix., 404), there is no doubt that the difference between adjoining zones is a chemical one, as is shown by the behaviour of the crystals on etching. It can be shown in an effective manner by immersing a specimen of a tin bronze, for example, in a solution of copper sulphate, when metallic copper is deposited only on those zones which are richest in tin (F. Giolitti, *Gazzetta*, 1908, xxxviii., ii., 352).

When such an alloy is annealed at a temperature well below the melting-point diffusion takes place, and the composition of the crystals becomes uniform. This process is easily observed by means of the microscope. The cores in an α-solid solution of tin in copper disappear when the alloy is heated to 750° for three hours (A. Portevin, *Rev. de Métallurgie*, 1909, vi., 813), and the time required in other cases is very similar.

In alloys which contain two solid solutions in equilibrium with one another, such as the $\alpha\beta$-alloys of copper and zinc, the structure also becomes coarser when the alloys are heated at a temperature at which diffusion takes place.

The increase in size of crystals is equally pronounced when only a single constituent—a pure metal or a solid solution—is present. The growth of the ferrite grains in soft steel at 700—720° is extremely rapid (J. E. Stead, *Journ. Iron and Steel Inst.*, 1898, i., 145; A. Joisten, *Metallurgie*, 1910, vii., 456), and the process may be very conveniently studied in such a solid solution as 70 : 30 brass (G. Charpy, "Etude des Alliages, Paris, 1901, p. 1). The growth of crystals may be watched in lead even at 60° if the metal has been previously strained (J. C. W. Humfrey, *Phil. Trans.*, 1902, cc., A, 225). It is always the larger crystals that absorb the smaller.

Whether the metal in which such re-crystallisation takes place is homogeneous or heterogeneous, diffusion must occur in order that the re-arrangement may come about. The effect has been explained by the principle that small crystals have a greater solubility than large, so that if small and large crystals of the same substance are both in presence of a solvent, solution and re-deposition tend to go on until only crystals above a certain size are present (W. Ostwald, *Zeit. Phys. Chem.*, 1900, xxxiv., 495). This has been verified for the case of calcium sulphate in water (G. A. Hulett, *Zeit. Phys. Chem.*, 1901, xxxvii., 385). A thermo-dynamical explanation has also been given (J. Curie, *Bull. Soc. Franc. Min.*, 1885, viii., 145) of the principle that the bounding surface between a crystal and its saturated solution tends to become a minimum, so that equilibrium is only finally reached when all the small crystals have united to form a single crystal.

The principle of differing solubility is rejected as an explanation by G. Tammann, *Nachr. K. Ges. Wiss. Göttingen*, 1912, p. 1), who assumes that the surface tension, which is less than the forces producing rigidity in a crystal at the ordinary temperature, may become much more considerable with increase of temperature. When the surface tension exceeds the opposing forces, two crystals unite as two drops of fluid would do. The hypothesis is ingeniously applied to explain the re-crystallisation of strained metals.

The Influence of the Amorphous Modification in Metals.

The view has been taken (G. Bodländer, *N. Jahrb. Min. Beil. Bd.*, 1899, xii., 52) that the occurrence of diffusion in heated metals is not a proof that diffusion may occur in a crystalline medium, as Spring's experiments have rendered the presence of amorphous material in metals extremely probable. Since then the existence of an amorphous modification in worked metals has been proved by much experimental work (G. T. Beilby, *Phil. Mag.*, 1904, [6], viii., 258), but it has also been shown that complete re-crystallisation occurs at very moderate temperatures, such as 250° for copper and 300° for silver (G. T. Beilby, *Journ. Inst. Metals*, 1911, vi., 5).

Recently, on the grounds of the behaviour of worked and unworked metals when subjected to tensile stresses at high temperatures, the hypothesis has been proposed that a small quantity of the amorphous modification persists to much higher temperatures (G. D. Bengough, *Journ. Inst. Metals*, 1912, vii., 123), the "temperature of complete recuperation" being fixed at 650° for copper and 710° for an alloy of copper and nickel. Even this modified hypothesis, however, only assumes the presence of a small quantity of intercrystalline material in the amorphous state, and the phenomena observed are in no way to be explained by diffusion through these small masses. An argument against diffusion in crystals is not, therefore, to be based on the existence of amorphous modifications of metals.

The Electrolysis of Crystalline Solids.

The electrical conductivity of metallic sulphides has repeatedly been the object of study, and it was shown by W. Hittorf that the conductivity of silver and cuprous sulphides was electrolytic in character (*Pogg. Ann.*, 1851, [3], xxiv., 1). The conductivity of most sulphides is, however, metallic. The electrolysis of natural quartz crystals was observed by E. Warburg and F. Tegetmeier (*Ann. Phys.*, 1888, [2], xxxv., 455), and it was found that electrolysis was only obtained in the direction of the principal axis. The actual electrolyte is the alkali silicate always present in natural quartz. Further investigations show that the conductivity of sulphides is more electrolytic at high temperatures and metallic at low temperatures (R. von Hasslinger, *Monatsh.*, 1907, xxviii., 239), whilst pure oxides of most metals conduct almost exclusively metallically (F. Horton, *Phil. Mag.*, 1906, [6], xi., 505). Elaborate investigations of a large number of compounds show that whilst electrolysis undoubtedly occurs, it is the exception rather than the rule, and that solid electrolytes are usually of a saline character (J. Koenigsberger, *Zeit. Electrochem.*, 1909, xv., 97; C. Doelter, *Ibid.*, 1908, xiv., 552; *Monatsh.*, 1910, xxxi., 493).

Special attention has been given to the conductivity of the mixtures of rare earth oxides used in the Nernst filament. These are regarded as electrolytes conveying an unusually large residual current (W. Nernst, *Zeit. Electrochem.*, 1899, vi., 41; 1900, vii., 373). It is possible that these masses are not entirely crystalline.

Solid barium chloride is an electrolyte, obeying Faraday's law (F. Haber and S. Tolloczko, *Zeit. Anorg. Chem.*, 1904, xli., 407), whilst sodium hydroxide presents anomalies, indicating that at 230° traces of a liquid substance are present in the pores. Porcelain, which is only in part crystalline, is an electrolyte from 300° upwards, its behaviour being that of a solution of alkali silicates in aluminium silicate as a non-conducting solvent (F. Haber, *Zeit. Anorg. Chem.*, 1908, lvii., 154).

Special interest attaches to the crystallised silver halides. Their conductivity in the solid state was investigated by F. Kohlrausch (*Ann. Phys.*, 1882, [2], xvii., 642). It was then found that solid silver iodide is an electrolyte (O. Lehmann, *Ann. Phys.*, 1889, [2], xxxviii., 396), and that films and threads of metallic silver make their appearance when a current is passed through a crystal under the microscope. Great weight is to be attached to microscopical investigations of this kind. Thus, it was found that solid silver chloride remained unchanged in appearance, and no polarisation could be observed when a current was passed through it, although the resistance diminished in a remarkable manner (M. Le Blanc and F. Kerschbaum, *Zeit. Electrochem.*, 1910, xvi., 242), but subsequent examination proved that the increased conductivity was due to microscopic filaments of metallic silver (*Zeit. Electrochem.*, 1910, xvi., 680).

Metallic alloys do not conduct electrolytically. A series of experiments in which two cylinders in different metals were placed in close contact, a current being passed, showed that no transport of matter took place, even when considerable currents were used (J. Kinsky, *Zeit. Electrochem.*, 1908, iv., 406). This is entirely in accordance with older observations. An isolated result, that carbon could be caused to travel with the current in steel (J. Garnier, *Comptes Rendus*, 1893, cxvi., 1449), is probably susceptible of another explanation.

(To be continued)

NOTES ON PLANT CHEMISTRY.

By Dr. P. Q. KEEGAN.

The Monocotyledon Difficulty.

Those analysts who have worked on dicotyledonous plants exclusively and then suddenly devote their attention to the monocotyledons will soon encounter grave difficulties of a certain kind. Suppose that he tries the leaves of the common water flag, for instance, and prepares a hot aqueous extract thereof freed from mucilage by methyl alcohol, and the latter boiled off. He tests for tannic matters. Yes, there is a red-brown precipitate by acet. Ur, a deep green colour by $FeCl_3$, a precipitate by Br water, and on boiling with dil. HCl a fine red coloration and precipitate very like a phlobaphene, and also coloured green by slight excess of NH_3. Now for a tannoid; yes, on pouring a little of the extract on some moist hydrate of alumina a beautiful yellow lake is gradually formed, but on evaporating a portion of the extract and treating with H_2SO_4 a yellow solution is obtained, which, however, passed rather quickly to brown. Then Mg amalgam is tried on the acidified alcoholic solution, but instead of getting paracarthamin, a phenolic or quinonic sort of matter is obtained, which yields fine red solutions and precipitates with NH_3 and with baryta water in slight excess. As our young analyst has learned by previous experience that an iron-greening tannin without an accompanying tannoid is rather uncommon, his suspicions are aroused, and he falls back, so to speak, till he finds that the green coloration by $FeCl_3$ is not reddened by alkali, and the extract when boiled with very dilute H_2SO_4 gives a dirty brownish tint and precipitate not so like a phlobaphene as before. There is, therefore, something wrong in the calculation. At last, after repeated trials, perhaps he is reminded of the foxglove leaves with their extraordinary plethora of resinous glucosides, and finds, after all, that he has entered on what may be called Saponin territory, which includes such familiar plants as the bluebell, daffodil, cuckoo-pint, early purple orchis, bog asphodel, &c. Of these the bluebell or wild hyacinth gives the most distinctive reactions of the presence of saponin unaccompanied by any tannoid; in the other plants named there is evidence of an intermixture of a small quantity of a tannoid specially distinguished by giving a brilliant yellow lake with moist hydrate of alumina. The leaves of the garden tulip had no saponin, but had a tannoid like a galangin. A very small quantity of caffetannin was detected in the leaf of lily of the valley, but none in those of bluebell. There is no doubt, however, that this tannin occurs in numerous monocotyledons, although in many cases in too minute quantity to be readily detectable. Whoever it was that first discovered it in monocotyledons, the fact is extremely interesting from various points of view; for instance, it supplies an explanation of the splendid blues of sundry flowers in the *Liliaceæ*, &c., and it proves unshakeably that the organic perfection or otherwise or the systematic position of a plant is unconnected with the products of deassimilation thereof.

Lime and Potash.

It has been stated that "a relative predominance of CaO in plant ash is associated with the purely vegetative tendencies of growth, and that of K_2O with the maturing tendencies of growth." This means that a heavy proportion of $CaCO_3$ in the ash would be found in a plant with a relatively more continuous vegetative growth, *e.g.*, the clover. The fact, however, seems to be that the predominant presence of lime seems to be connected with the inherent tendency to produce acids rather than tannins as products of deassimilation. Thus, of all the wild plants analysed by myself the tufted vetch and the great valerian contained the greatest quantity of CaO in their ash, viz., 40·6 and 37·5 respectively. The former produces large amounts of oxalic acid, the latter malic acid almost exclusively. In the vetch mere traces of tannoid were found, and no tannin, whereas in valerian the quantity of caffetannin detected was inconsiderable, as in many other plants. According to Vuillemin, in the leguminous tribes *Genisteæ*, *Vicieæ*, *and Trifolieæ*, tannin is wanting or feebly developed. This marked tendency to deassimilate acids is frequently shown in the amount of soluble carbonates in the ash, as in gorse and heather, *i.e.*, in cases where there is no vast amount of chlorides absorbed, and here also, as in dock, the percentage of lime may occasionally rise to 20, although this plant contains much tannin. Then, again, the oak leaf produces more tannin than that of any other of our native trees, and its brown autumn organ has 44 per cent CaO in its ash with 13 SiO_2, as against the acid-rich and tannin-poor autumn ash tree leaf with 45·8 and 3·6 respectively. In the oak, however, the proportion of tannin diminishes as the season advances, while that of the acids seems to increase—a circumstance rather universal in tree leaves at best; in fact, it would appear that the protoplasm while young and vigorous evolves aromatic compounds, and aliphatic products only when its vitality wanes. As regards the connection of potash with the maturing tendencies of growth, *i.e.*, production of fruit, it is clear that this constituent subserves the process of assimilation probably by keeping the protoplasm moist, and so prevents loss of vitality by dehydration.

Stray Notes.

Caffetannin was found by me in the leaves of foxglove, ash tree, and in the herb of water-cress. These are new records, and it is very remarkable that the two first have not been noted heretofore. In both cases the tannin occurs in small quantity, and is accompanied by a tannoid which is not gentisin nor quercitrin; it seems identical, at least in the ash leaf, with the peculiar tannoid present in ragwort, marigold, tansy, and some other compositæ, which is apparently not a glucoside and yields deep brown-black catechin-like products by oxidation or dehydration, due apparently to the production of quinone. The tannoid of the foxglove leaf is more like luteolin or scutellarin, the reactions with lead and tin being redder, also it has a phloroglucol nucleus. In the watercress the tannin appeared nearly pure, the aqueous extract turning a beautiful green in the air in a few hours, and this became pure red by dilute H_2SO_4, and green again by bicarbonate soda in slight excess. It is remarkable how tenaciously the ash and foxglove leaves retain their starch. Dried at 100° C. and finely powdered, and then boiled successively with benzene and alcohol, treated with hot water and dilute soda, and finally heated with very dilute HCl, a solution of starch is obtained yielding a deep pure blue coloration with iodine. Of the other leaves of trees examined by me in July or August those of holly, birch, wych elm, goat willow, wild cherry, and hawthorn retained their starch more or less under similar treatment, while in those of sycamore, alder, black poplar, rowan, Scots pine it had completely vanished.

The subject of chlorophyll presents great difficulty, but yet some scope for conjecture. There has been distinguished crystalline and amorphous chlorophylls, but without much effect. On one occasion I prepared as "pure" a solution of it as I was able, and then placing a few crystals of chlorate of potass therein, I applied a gentle heat and removed to a respectful distance. After the expected explosion had come off an odour was diffused in the room, and (this was the object of the experiment) the question was—What did this odour recall? It seemed to be more like that of burnt glycerin than anything else. This would imply that chlorophyll was related to fat-oil, but every plant analyst knows how tenaciously it clings to the wax extracted therewith from the leaf, and also that in many cases these waxes are esters of phytosterol. However, if we take a leaf and very carefully dry and powder it very fine, and then place some of the powder on a slide, mount in glycerin, and examine by a power of 300—400, we observe all the various forms of chloroplasts, flakes, granules, and masses of fine granulations so well described by D'Arbaumont. All these plastids contain something of deep green colour enclosed within their walls, for enclosures of some kind they certainly are, and there is no greenery seen anywhere else. This observation upsets our previously formed ideas as to chlorophyll. We now see that it is absolutely connected with the process of assimilation; its chromogen is born in the living protoplasm, and is never apparently cast out of it; it is associated not with carbohydrates or aleurone, but with some kind of oily matter, but at the same time it is produced only within the ambit, so to speak, of what may be regarded as an aleurone grain, *i.e.*, a cell by osmosis, as Jeffrin described it. It may be conjectured, and this is going as far as we can, that a powerful condensation of the protoplasm within this aleuric enclosure suffices to produce the green chlorophyll pigment, *i.e.*, a loss of water by exosmosis not sufficiently great to kill the protoplasm.

The saponarin detected by me (Chemical News, 1911, civ., 109) in the leaves of *Alliaria officinalis* was further examined. Special precautions were taken to exclude starch, saponin, or tannoid. The leaves were carefully dried and very finely powdered, and macerated for five days in a cold mixture of absolute ethyl and methyl alcohols, the solution filtered through asbestos, evaporated, the residue on cooling mashed up with powdered glass and cold water, filtered through asbestos, and tested with the same results as already described. Again, the leaves this time were coarsely cut, covered with water which was brought to the boiling-point, and then cooled, filtered, concentrated, the mucilage removed by methyl alcohol, &c., and tested with the same results so far as the iodine treatment was concerned, but the tannoid reactions were very feeble, and, moreover, the solution seemed to contain some kind of saponin. These results are very extraordinary, as in both cases the precipitate by IKI was absolutely identical, and behaved in exactly the same way as that got from a solution of starch, except only that it was red-violet and not blue. The result seems to be that this substance is either not identical with the saponarin found by Barger in soapwort leaves, or that the latter is really a kind of saponin, and not a tannoid.

Patterdale, Westmorland.

APOCYNUM OR INDIAN HEMP RUBBER.*

By CHARLES P. FOX.

Apocynum Hypercifolium (Nat. Order, Apocynaceæ) is an indigenous plant common to many sections of the United States. It is a strong rooted perennial with reddish stem, fibrous bark, long slender seed pods, seeds with long white cottony appendages, and a milky juice. The latex is white, viscous, neutral, or slightly alkaline, and has the strong acrid odour peculiar to the plant.

The usual coagulating reagents react with this latex in the following manner:—

Acids do not coagulate; latex becomes thin.

Alkalis do not coagulate; restore the viscosity; change the colour from white to brownish yellow.

Boiling coagulates slightly; action slow.

Acetone (one-tenth volume) coagulates immediately and completely; liquid is coloured chocolate-red.

Formaldehyde coagulates readily but is much slower in action than acetone.

Phenol coagulates the latex, but gives a soft product.

Salt solution coagulates slowly, giving a finely divided precipitate hard to coalesce. *Boiling* the same solution gives a soft product.

Of the above methods, the use of alcohol or acetone, and formaline are the only ones recommended. Of these two, acetone is preferred.

The latex of *Apocynum* differs slightly from that of *Asclepias* in that it coagulates spontaneously, even if it is kept in closed containers.

The naturally coagulated latex gives:—

Liquid portion	67·58 per cent
Cheese (wet)..	32·42 per cent

The *liquid* is white (not clear), slightly acid, and with the characteristic acrid odour. This liquid failed to coagulate after addition of more acid. Slight excess of alkali increased its viscosity, and changed its colour from white to brownish yellow, but did not precipitate or coagulate it. Boiling had no effect. Excess of acetone gave a finely divided precipitate, the particles of which were not cohesive. Evaporation of the mixture, after washing with water and treatment with boiling acetone, gave a small quantity of a black soft rubber destitute of strength.

The *cheese* was composed of:—

Water	33·46 per cent
Rubber	3·99 per cent
Resin	62·95 per cent

Working up this *cheese* with solvents, removing foreign matter by filtering through gauze, evaporating, with low heat, the excess of solvent, adding an excess of precipitant, removing the precipitating agent, washing and drying the precipitate, gave a good grade rubber.

The rubber obtained in this manner was black, firm, not tacky, odourless, and strong. In quantity, it is much better than the product obtained from its neighbour, milkweed.

Milkweed latex, however, is richer in rubber than that of Indian hemp. The amount of latex in the two plants are about the same. In both cases the amount of rubber present is too small to be of any economic importance.

Of the total rubber present in the latex, 96 per cent of it is won in the cheese formed in the natural coagulation of the latex. 96 per cent of the total rubber found ranks as good grade rubber.

The *resin* is mahogany-red, transparent, medium hard, tasteless, with slight characteristic odour.

The soil conditions under which the plant was grown exerted an influence upon the amount of rubber in the latex. Plants grown on dry sandy soil of West Akron gave a latex containing 2·27 per cent rubber and 20·69 per cent resin. Latex from plants grown in the wet swamps of South Akron contained only 1·12 per cent rubber and 15·04 per cent resin. Rubber from dry land plants appears to be of better quality than that obtained from wet grown plants.

Natural latex from dry grown plants, collected in August, during very dry weather, contained:—

Water	72·29 per cent
Solids	26·21 per cent
Ash..	1·59 per cent

Rubber in fresh latex was 2·36 per cent.

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* Presented before the Rubber Section, A.C.S,, at Forty-fifth Meeting, Washington, December, 1911. From the *Journal of Industrial and Engineering Chemistry*, iv., No. 5.

CONTAMINATION OF LABORATORY SAMPLES BY IRON DERIVED FROM CRUSHING MACHINERY.

By VICTOR LENHER.

The article by George A. James on the "Contamination of Laboratory Samples by Iron Derived from Crushing Machinery" in the *Chemical Engineer* (Sept., 1911, xiv., 380), calls attention to the too often neglected fact that in the preparation of samples for analysis the crushing or grinding apparatus employed may introduce material in such kind and quantity as would render the analysis worthless. Dr. Hillebrand, in *Bull.* 422, U.S. Geol. Survey, p. 50, lays stress on this point. Too much emphasis cannot be laid on the choice of grinding apparatus used in the preparation of samples for analysis. Recently a series of samples of quartzite were collected by the writer for analysis. Inasmuch as the quartzite beds, from which the samples were taken, were being valued for the purpose of being used in the manufacture of silica brick, it was desirable to obtain an accurate determination of the content of silica and particularly of iron.

Sample.	Metallic iron introduced from crusher (per cent).	Iron content of quartzite (per cent).
1.	2·92	0·49
2.	2·74	0·49
3.	2·73	0·23
4.	2·61	0·63
5.	2·82	0·25
6.	2·59	0·29
7.	1·86	0·55
8.	2·46	0·16
9.	2·65	0·75
10.	2·67	0·12
11.	2·81	0·16
12.	1·87	0·06
13.	1·98	0·20
14.	2·01	0·68
15.	2·62	0·11

The samples on being brought to the laboratory consisted of chips of the rocks, approximating in size ¾ inch square by ¼ inch thick. After being broken somewhat smaller by means of a hammer, they were reduced in a Braun crusher to pass a 120-mesh screen. The material in the original beds is of a light pinkish cast, while the powdered material was distinctly grey. Tests by the magnet revealed the presence of metallic iron in the powdered quartzite, but owing to the fine state of division of the powder, it was found to be impossible to satisfactorily remove the iron by means of the magnet.

Treatment of the powder with dilute sulphuric acid and subsequent analysis of the remaining quartzite is shown in the accompanying table.

The variation in the amount of metallic iron abraded from the crusher is, of course, dependent on the length of time of crushing.

It is interesting to note in connection with the above results that a similar set of samples were sent to one of the largest iron laboratories in the north-west, and reports were made showing an apparent iron content of the quartzite to be from 1·42 to 2·97 per cent iron.

It has been the frequent experience of the writer in the analysis ot igneous and metamorphic rocks to find the sample contaminated by iron from the bucking board, crusher, or such grinder as may have been used in reducing the sample. As a rule, this metallic iron can be removed and at the same time determined by treatment with dilute sulphuric acid, and subsequent titration with permanganate. As a matter of fact, the more common material which will materially abrade iron or steel in crushing is not appreciably attacked by dilute sulphuric acid during the few minutes contact that is requisite to dissolve the finely divided iron. On the other hand, the general type of ores and products, which will themselves lose part or all of their iron to dilute sulphuric, will not appreciably abrade steel from the types of grinding apparatus on he market.

It cannot be too strongly emphasised, however, that the chemist is called upon to report on the constituents sought for, and when the common danger of contamination in the preparation of his sample presents itself, great care must be exercised to eliminate such errors.—*Journal of Industrial and Engineering Chemistry*, iv., No. 6.

EVOLUTION OF CHEMICAL ELEMENTS AND OCCLUSION OF GASES BY METALS.

By C. T. KINGZETT.

The constitution of matter and the so-called elements are subjects that have always had a peculiar fascination for me, and in point of fact my first printed publication concerning chemical subjects was in respect of the "Oneness of Matter," and was contributed to the pages of the Chemical News in the year 1871 (see Chemical News, 1871, xxiv., 131; xxvi., 138 and 202; xxviii., 288). It is not surprising therefore that in thinking over the investigations of recent years which have brought to knowledge the existence of argon, neon, xenon, and krypton as constituents of the air, and the apparent emanation of helium from radium, it has occurred to me that some of the observations made by Graham and others in respect of the occlusion of gases by metals may be capable of another interpretation than that ordinarily accepted, and in any case it would appear to be very desirable that these observations and experiments should be repeated and extended.

At the time these experiments were made there was no suspicion of the presence of other substances in the air than oxygen and nitrogen, nor was it thought possible for an apparently elemental substance like radium to break up into helium. Hence it would be well to make sure that the hydrogen and nitrogen, &c., supposed to be occluded by metals, are really identical with the mass of the gases employed, or whether, on the other hand, the substances occluded are different in essence, and possibly new so-called elemental forms of matter either existing in previous admixture with the non-occluded parts, or emanating therefrom by reason of the processes employed in the experiments.

As my laboratory is not well equipped for such investigations, I offer these suggestions publicly in the hope that some young investigators will re-examine the whole subject as one of a very promising character. A rough and-ready experiment could be made by taking pure nitrogen and passing it at an appropriate temperature and pressure over prepared copper as contained in a spaced out series of successive vessels, and so arranged that the whole of the gas is passed through the body of the metal, as distinct from a mere surface of it exposed to the gas. Careful determination should be made (1) of the weight of the metal and occluded gas; (2) the character of the unabsorbed gas remaining after the experiment; and (3) the character of the gas occluded by each successive mass of metal, and afterwards liberated therefrom, as contrasted, of course, with the gas originally employed. A similar experiment could be made with hydrogen gas and spongy platinum or palladium.

Having regard to the manner in which argon was separated from atmospheric nitrogen and the properties of Prof. Strutt's chemically active nitrogen, it would also be of considerable interest to ascertain whether nitrogen, as obtained from various sources, always exhibits a common behaviour in these respects.

In looking through the papers of Graham and the other investigators it will be apparent that there is not sufficient evidence that the substances occluded by platinum, palladium, copper, &c., are absolutely identical with the original or residual gases. Hence I make these suggestions.

A careful re-investigation of the whole subject should yield confirmative evidence of the accuracy of the views ordinarily taken concerning these phenomena, or throw further light on the component parts of a dominant elemental substance and its transmutations.

USE OF COPPER SALTS IN THE GREENING OF FOODS.*

The question of the use of copper salts in the greening of foods was referred by the Secretary of Agriculture, on March 11, 1909, to the Referee Board of Consulting Scientific Experts. Exhaustive investigations have been conducted by that Board, and the Department of Agriculture has received the Report of the investigations. The questions which were referred to the Referee Board are as follows:—

" Are vegetables greened with copper salts adulterated under the Food and Drugs Act of June 30, 1906, because—

" (*a*) A substance has been mixed or packed with them so as to reduce or lower or injuriously affect their quality or strength;

" (*b*) They have been mixed, coloured, powdered, coated, or stained in a manner whereby damage or inferiority is concealed;

" (*c*) They contain any added poisonous or other added deleterious ingredient which may render such articles injurious to health?

" 1. In large quantities?

" 2. In small quantities?"

The main general conclusions reached by the Referee Board from a study of their experimental results and other considerations are as follows:—

" (*a*) Copper salts used in the colouring of vegetables as in commercial practice cannot be said to reduce or lower or injuriously affect the quality or strength of such vegetables as far as the food value is concerned;

" (*b*) Copper salts used in the greening of vegetables may have the effect of concealing inferiority, inasmuch as the bright green colour imparted to the vegetables simulates a state of freshness they may not have possessed before treatment;

" (*c*) In attempting to define a large daily quantity of copper regard must be had to the maximum amount of greened vegetables which might be consumed daily. A daily dose of 100 grms. of coppered peas or beans, which are the most highly coloured vegetables in the market, would not ordinarily contain more than 100 to 150 mgrms. of copper. Such a bulk of greened vegetables is so large, however, that it would hardly be chosen as a part of a diet for many days in succession. Any amount of copper above 150 mgrms. daily may therefore be considered excessive in practice. A small quantity is that amount which in the ordinary use of vegetables may be consumed over longer periods. From this point of view 10 to 12 mgrms. of copper may be regarded as the upper limit of a small quantity.

" It appears from our investigations that, in certain directions, even such small quantities of copper may have a deleterious action, and must be considered injurious to health."

The Food and Drugs Act of June 30, 1906, provides that a food is adulterated "if it contain any added poisonous or other added deleterious ingredient which may render such article injurious to health." The Act also provides that a food is adulterated "if it be . . . coloured . . . in a manner whereby damage or inferiority is concealed." It is apparent from the findings of the Referee Board that all foods greened with copper salts are positively adulterated under the first above quoted provision of the law, and that in certain cases foods may be adulterated under the second above quoted provision.

The Secretary of Agriculture therefore will regard as adulterated under the Food and Drugs Act foods greened with copper salts which, on and after January 1, 1913, are offered for entry into the United States, or are manufactured or offered for sale in the District of Columbia or the Territories, or are shipped in interstate commerce.

All previous food inspection decisions on the subject of greening of foods with copper salts are amended accordingly.

The complete report of the investigations and conclusions of the Referee Board on this subject will be published by the Department of Agriculture.

R. E. Doolittle,
F. L. Dunlap,
A. S. Mitchell.
Board of Food and Drug Inspection.

Washington, D.C., July 12, 1912.

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* From the Secretary of the United States Department of Agriculture.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

Annual General Meeting, New York, 1912.

Dr. Messel's Presidential Address (*conclusion*).

In the course of his Address the President announced the award of the Medal of the Society. Unfortunately, Sir William Crookes, who had been nominated as medallist, was unable to be present, but his name was a household word. Sir William was now eighty years of age, and he found it too much to undertake this journey. (The President then read Sir Wm. Crookes's letter appointing him as his proxy to receive the medal). When he said that the Council had unanimously elected to give Sir William the medal, it needed no apology. It was a great honour to the Society that he has accepted the greatest honour they could have conferred on him. They would like to have him as President, but he (Sir William) had declined on account of his advanced age. He would not read every title which Sir William possessed; they amounted to twenty-eight; his medals included the Royal Society's Medal, the Albert Medal, the Gold Medal of the French Academy, and quite a number of others, and of his titles he need only mention his Knighthood.

The President then gave a few details of Sir William Crookes's life, as follows:—

Sir William Crookes, O.M., For. Sec. R.S., LL.D., D.Sc., &c., was born in 1832, and became a student of Hofmann at the College of Chemistry in 1848. He discovered thallium, which he recognised by spectrum analysis in 1861, and received a medal in 1862 of the International Exhibition for this discovery and for the preparation of the metal from some sludge resulting from the production of sulphuric acid, the insoluble iodide serving as a method of separation. The name thallium is derived from "Thallos," green twig. Notwithstanding the minute quantities at his disposal he determined its equivalent. In those researches he was the first to use a vacuum balance so as to avoid correction for flotation of weighed matter and of weights by air.

He made use of the Sprengel pump to secure vacua, very high vacua, and observed phosphorescence. Before that stage was reached Crookes observed the action of light on small suspended objects; this resulted in a series of papers, termed "Repulsion by Radiation," published in the *Phil. Trans.* of the R.S. in 1873, in which the radiometer was described.

Describing some phenomena of phosphorescence he showed that phosphorescent "streams" were deflected by the magnet and also demonstrated the mutual repulsion of two "streams" from the cathode pole of a vacuum tube. He concluded that, inasmuch as the phenomena produced by "cathode streams" (viz., propagation at right angles to the cathodic surface; concentration to a point by an aluminium mirror of parabolic section; great heat effects in the focus; mechanical effects, such as the rotation of paddle wheels; radiometer effects, &c.), the effects were to be attributed to "a fourth state of matter"; the gas was supposed to exist in an ultra-gaseous state, the free paths of the gases being so enlarged that they behaved as minute projectiles. (This has subsequently been recognised as independent of the nature of the gas in the tube; the particles are now accepted as streams of electrons; fresh researches by Lenard, J. J. Thomson, and many others, have given the true interpretation of the phenomena first observed by Crookes).

Crookes also carried out long and very careful investigations on the rare earths; he was led to this by the presence of a "citron band" in the phosphorescent spectrum of these bodies and of many ordinary minerals, which he observed during an investigation of the action of cathode rays in inducing phosphorescence in various chemical compounds. The citron band was finally traced to yttrium. But Crookes carried out enormous numbers of fractionations of salts of the rare metals and effected numerous separations. He gave an account of some of these investigations in his Presidential Address to the Chemical Society in 1887, and pointed out that by systematic fractionation it was possible to separate yttrium into five portions, each of which could be characterised by a different spectrum. He evolved a hypothesis of the "evolution of the elements," in which a new solid model was proposed to represent the periodic classification of the elements. Later on he prepared in a pure state and analysed many compounds of scandium.

Crookes was the first to notice that purification of uranium salts by ammonium carbonate or by extraction with ether had for the effect the separation of a substance which he named uranium X. This was the first clue to the so-called X-bodies from radio-active matter, which has led to such important results in Rutherford's and Soddy's hands.

He also was the first to observe that radium rays (the "α-rays") when allowed to fall on a phosphorescent screen of zinc sulphide emitted scintillations; as a result in 1903 he introduced the "spinthariscope," which has since made it possible to determine the actual number of α-particles (proved by Ramsay and Soddy to consist of molecules of helium) emitted from a known weight of radium and so to determine the actual rate of change of radium and its products into helium.

Crookes has published numerous papers on other subjects. For many years he was one of the chemists who controlled the purity of the London water supply. He has owned and edited the Chemical News since 1859 (more than half a century). In spite of his advanced age he is still in full possession of mental and bodily vigour and lets no day pass without spending many hours in his private laboratory in 7, Kensington Park Gardens, London. He was President of the British Association in 1898 and gave an address in which he drew the attention of the whole world on the food supply of the world. He pointed out the necessity of combining the nitrogen of the air with oxygen by electrical means in order to furnish cereals with nitrogenous food which is essential to their existence. Here again Crookes was first in the field in demonstrating the possibility of a "nitrogenous flame" in which air could be made to "burn" by stimulation with a Tesla discharge.

It is thus seen that Crookes's great genius has placed him in the very highest rank as a pioneer of science. His astonishing power of insight is unequalled in this generation and he has contented himself in indicating the way in which science may be advanced, rather than in reaping the fruits of his labour in gaining a fortune by its industrial application.

The President then exhibited the Medal, and also a portrait of Sir William Crookes.

Prof. Bogert moved that a cable be sent to Sir Wm. Crookes, congratulating him on the award of this Medal, and expressing their respectful homage.

This was carried by acclamation.

NOTICES OF BOOKS.

Elementary Quantitative Analysis. By William Briggs, LL.D., M.A., B.Sc., F.R.A.S., and H. W. Bausor, M.A. London: W. B. Clive. 1912.

A good elementary course of work in quantitative analysis, such as is required by prospective candidates for the London University Intermediate examinations in Science and Art, is given in this book. Simple gravimetric and volumetric work are included, with experiments illustrating the laws of chemical combination by weight. The experimental directions are concise and clear, the theory of each process is adequately discussed, and equations are given, while care has been taken to explain fully methods of calculating results from the data obtained in the experiments. The book contains a good selection of typical problems, for which alone the examination candidate will find it worth procuring. Without being particularly difficult these problems will frequently make considerable demands upon the student's ingenuity and resource, and will give him plenty of practice in applying the general principles of volumetric and gravimetric analysis. In some cases the methods of solution are indicated, but others are left entirely to the student to devise.

Problems in Practical Chemistry. By G. F. Hood, M.A. (Oxon.), B.Sc. (Lond.). London: Mills and Boon, Ltd. 1912.

This book is intended for the use of fairly advanced students who have a good general knowledge of both inorganic and organic chemistry, and the experiments described in it would require a well-equipped laboratory and some degree of skill on the part of the worker. In the text problems are put before the student, who, in some cases, is left to devise the methods of solution entirely by himself, while in others he is given some hints to guide him, or even full experimental details. The time necessary to complete the experiment is generally stated, and a high ideal of speed combined with accuracy is set before the student. In an appendix details are given for those problems which were not explained in the text, and this arrangement makes the book particularly suitable for those who are working with little or no help from a teacher. The problems, most but not all of which are quantitative, will give abundant practice in manipulation. The first part of the book is devoted to some general methods, *e.g.*, the preparation of acid salts and double salts, the determination of equivalents, &c., while the second part contains exercises on all the common elements in turn, arranged according to the Periodic System.

Photochemische Versuchstechnik. ("Technics of Experimental Photochemistry"). By Dr. Johannes Plotnikow. Leipzig: Akademische Verlagsgesellschaft. 1912.

Photochemistry is a comparatively young branch of science, and although an enthusiastic band of workers is doing much valuable quantitative work there is as yet a great dearth of text-books dealing exclusively with the subject. For this reason this book should be doubly sure of the welcome which its excellence will undoubtedly win for it. The author has done much to further research in photochemistry, and can write authoritatively regarding experimental methods. Some of the apparatus, described here for the first time, has been devised by him, as for example, the light thermostats; on the other hand, familiar forms are not passed over, and the book is complete in every sense of the word, although a careful selection has been made of really practically useful apparatus. Optical measuring instruments are fully described, and many mathematical tables are included. Apparatus for lecture experiments is particularly well treated. A certain amount of theory is introduced into the text, but only as much as is indispensable for the understanding of the processes and methods described.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 6, August 5, 1912.

Preparation of Four Dicyclohexylpropanes.—Paul Sabatier and M. Murat.—The catalytic hydrogenation over nickel of dibenzylketone yields 1 . 3-dicyclohexylpropane, $C_6H_{11}CH_2CH_2CH_2C_6H_{11}$. The 1 . 2-compound can be made by two hydrogenations over very active nickel of 1 . 2-diphenylpropane. Similarly 1 . 1-dicyclohexylpropane, $(C_6H_{11})_2.CH.CH_2.CH_3$, may be obtained from 1 . 1-diphenylpropane and the 2 . 2-compound, $(C_6H_{11})_2C.(CH_3)_2$, from 2 . 2-diphenylpropane.

Photolysis of Ketonic Sugars by Solar Light and Ultra-violet Light. — Daniel Berthelot and Henry Gaudechon.—The action of solar light on ketoses containing C_3, C_4, C_6, and C_7 gives carbon monoxide and an alcohol containing one atom of carbon less than the sugar. The photolysis of a series of homologous substances is slower the longer the chain. The ultra-violet rays produce the same effect, but secondary reactions are also produced. Thus the primary products undergo photolysis; water yields H_2 and O_2, formic aldehyde is formed, and oxidations occur. These complications are accompanied by an increase in the amount of CO_2, the appearance of the gases H_2 and CH_4, the acidification and darkening of the solutions.

Application of Luminous Energy in Chemical Analysis.—Marc Landau.—Ultra-violet light can be used for chemical analysis. Thus a mixture of C_2H_4, C_2H_6, and H_2 can be analysed by exposing it to the ultra-violet rays. The photopolymerisation of the unsaturated hydrocarbon first occurs, and when this is complete the contraction of volume is measured, oxygen is added, and photocombustion is allowed to proceed.

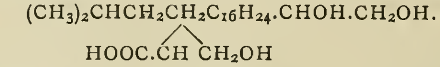
Bulletin de la Société Chimique de France. Vol. xi.—xii., No. 14, 1912.

Rotatory Dispersion of some Derivatives of Camphor.—L. Tchougaeff.—The author has pointed out that among the active substances of the terpene series it is the ketones particularly which possess a high coefficient of rotatory dispersion, its value being approximately equal to that of quartz for most colourless inactive substances. In the case of the derivatives of camphor the values are decidedly higher than the corresponding values of quartz and of most active colourless substances. Comparing the values with those of camphor it is found that they are greater for the $\alpha\alpha_1$-disubstituted derivatives, and less for the derivatives which are substituted only in the α-position. The dispersion of the α-halogen derivatives is practically constant and independent of the nature of the halogen in question. The dispersion of lævo-β-camphor is very nearly the same as that of natural camphor. Apparently the anomalous exaltation of the rotatory dispersion is a general property of all the members of the camphoric series containing the ketonic grouping C—CO—C, and is intimately connected with the selective absorption in the ultra-violet part of their spectrum.

Use of Camphor as Cryoscopic Solvent. — M. Jouniaux.—The cryoscopic constant of camphor is approximately 500, and is thus the highest of all solvents suggested for use in the determination of molecular weights. If the graphic method of determining the temperature of solidification is employed very accurate results can be obtained when camphor is used.

Action of Hydrogen Peroxide on Glycerine.—J. Effront.—The action of hydrogen peroxide converts a molecule of glycerin into two molecules of formic acid. The decomposition is quantitative and may be employed for the estimation of glycerin. Glyceric and glycolic acids are formed as intermediate products, and can easily be isolated. The author has noticed that the solar rays considerably increase the activity of hydrogen peroxide.

Action of Perhydrol in Presence of Concentrated Sulphuric Acid on Cholesterine.—S. Minovici and E. Vlahutza.—When perhydrol acts on cholesterine in acid solution, the hydrogen peroxide first adds itself on to the vinylic group; the alicyclic residue is then oxidised to give a ketonic group, and the ketodiol thus obtained is transformed into the corresponding oxyacid. Finally, a methyl group is removed, and the product is a monobasic acid of formula—



$$(CH_3)_2CHCH_2CH_2C_{16}H_{24}.CHOH.CH_2OH.\quad HOOC.CH\;\; CH_2OH$$

Ambreine.—J. Riban.—A substance to which the name ambreine was given has been extracted from ambergris by Pelletier and Caventon in 1820, and the author has obtained the same substance from deposits formed on the walls of vessels containing tincture of amber. Ambreine when warm and dry is very readily electrified by friction. It has no rotatory power in alcoholic solution; it melts at 82°, and cannot be volatilised under ordinary pressure. Its formula is $C_{23}H_{40}O$ or some multiple. With bromine it appears to give an octobrom derivative, and with phosphorus pentachloride a pentachlor compound.

Condensation of Phenylglycolic Nitrile with Aromatic Aldehydes in Presence of Thionyl Chloride. — S. Minovici and T. Zenovici. —Thionyl chloride transforms phenylglycolic nitrile into phenylchloraceto nitrile, (C_6H_5—CHCl—CN), which under the prolonged action of hydrochloric acid yields phenylchloracetamide, ($C_6H_5.CHCl.CONH_2$). Finally, the latter in presence of an aromatic aldehyde is transformed into a substance of formula $\begin{matrix} C_6H_5\text{—CHCl—CONH} \\ C_6H_5\text{—CHCl—CONH} \end{matrix}\!\!>\!R$. R being the benzylidene radicle of the aromatic aldehyde. This condensation occurs with benzoic, anisic, and cuminic aldehydes.

Determination of Purity of Essences of Terebenthine.— R. Marcille.—The determination of the acetic solubility (volume of acetic acid necessary to dissolve one volume at 15°) of essences of terebenthine and of the products of their fractional distillation can be used to detect the presence of adulterants. Thus petrol raises the solubility of the fifth fraction whilst benzene diminishes that of the first fraction. The determination of the thermosulphuric index with Tortelli's thermoleometer also enables impurities to be detected, and essences of terebenthine combine practically totally with sulphuric acid, while the common adulterants do not.

MISCELLANEOUS.

Royal Microscopical Society.—The next meeting of the Society, to be held at King's College, Strand, on Wednesday, October 16, at 8 p.m. precisely, will take the form of a Conversazione.

Literary Intelligence.—Messrs. Churchills announce for publication :—"Fatty Foods, their Practical Examination," a Handbook for the use of Analytical and Technical Chemists, by E. R. Bolton and C. Revis, Chief Chemist and Bacteriologist to Welford and Sons; with 36 Illustrations in the Text and 25 Original Photo-micrographs, comprising 6 Plates. "The Preparation of Organic Compounds," by E. de Barry Barnett; with 50 Illustrations.

Ternary System Sb—As—I.—E. Quercigh.—The supposed penta-iodides of arsenic and antimony, described by Sloan and Pendleton, are in reality mixtures of iodine and the respective tri-iodides. AsI_3 and SbI_3 form an uninterrupted series of mixed crystals with a minimum of about 30 per cent of SbI_3. The presence of iodine does not interfere with the solubility in the solid state of the two tri-iodides.—*Atti della Reale Accademia dei Lincei*, xxi., No. 12.

THE CHEMICAL NEWS.

Vol. CVI., No. 2760

CONNECTION BETWEEN BOILING-POINT AND MOLECULAR WEIGHT OF BODIES.

I.

The boiling-points of most liquids are connected in a very simple manner with their vapour densities. The boiling-point of a liquid measured on the absolute scale divided by the square root of the vapour density is a simple multiple of a constant. This is readily seen in the case of the non-metallic elements (see Table I.).

If T represents the boiling-point of a liquid and ρ the vapour density of its vapour, then—

$$\frac{T}{\sqrt{\rho}} = n \times \text{constant.}$$

For non-metallic elements n is two, except in the case of chlorine, bromine, and iodine, when it becomes four.

For compounds n may be once, twice, or thrice 3 $\sqrt{2}$.

For elements and compounds the constant is 10. As ρ is a number without dimensions, the dimension of the constant is degrees centigrade. Thus the constant is 10° C.

The relationships between melting-points follow on similar lines to the relationships between boiling-points; hence the fundamental interval of temperature measurement (100° C.), which is itself the space between a melting-point and a boiling-point, might be expected to bear some relationship to the constant; that the constant is the numerical root of the fundamental should not then be accidental.

Before proceeding further it would be well to consider Table I. The numbers in the last column will be spoken of as the constants. Thus the constant for argon is 19·6, the constant for chlorine is 40·3.

Notes on Table I.

This table consists of all the mono and diatomic non-metallic elements except helium and neon. The figures in the last column all approximate either to 20 or 40.

The constant of bromine is low owing to the presence of monatomic molecules.

The densities are calculated from 1912 International Atomic Weights.

The boiling-point of oxygen is probably high owing to the nature of the oxygen atom, as the constant for ozone is 22·2.

The constant for helium is 3, for neon 6·3.

Notes on Table II.

In order to show the relationship between the constant for these compounds and the constant for the elements, the numbers in the last column are calculated as multiples of $\sqrt{2}$.

In this table the compounds are allied, and none of their deviations from the mean are great. That bodies so closely allied as chloral and chloroform, phosphorus trichloride, and arsenic trichloride should have exactly the same constant should be of assistance in determining the cause of deviation.

All the bodies considered in this table contain at least three atoms of halogen to the molecule. For nearly all inorganic bodies tested containing three atoms of chlorine the deviations have been very small, but the more complex of the organic bodies deviate considerably; thus trichloracetic gives a constant 36·7 × $\sqrt{2}$, and phenyl chloroform, 34·7 × $\sqrt{2}$.

Table I.—*Non metals (Mono- and Diatomic).*

Element.	Density.	B p. Abs.	B.p. ÷ Square root of density.	
Hydrogen ..	1	20	20 ÷ $\sqrt{1}$	= 20
Argon	19·78	87	87 ÷ $\sqrt{19·78}$	= 19·6
Krypton ..	41·1	122	122 ÷ $\sqrt{41}$	= 19 0
Xenon	64·6	164	164 ÷ $\sqrt{64·6}$	= 20·4
Nitrogen ..	13·95	77·5	77·5 ÷ $\sqrt{13·95}$	= 20 8
Oxygen . ..	15·9	90·5	90·5 ÷ $\sqrt{15·9}$	= 22·7
Fluorine ..	18·86	88	88 ÷ $\sqrt{18·86}$	= 20 3
Chlorine ..	35·2	239	239 ÷ $\sqrt{35·2}$	= 40 3
Bromine ..	79·3	332	332 ÷ $\sqrt{79·3}$	= 37·3
Iodine	125·9	448	448 ÷ $\sqrt{125·9}$	= 39·9

Table II.—*Compounds.*

Empirical formula.	Approx. density.	Boiling-point.	Boiling-point ÷ Square root of vapour density.		
NCl_3 ..	60·3	344	344 ÷ $\sqrt{60·3}$	= 31 3	× $\sqrt{2}$
PCl_3 ..	68·8	351	351 ÷ $\sqrt{68·8}$	= 29 9	,,
$AsCl_3$ ..	90·8	403	403 ÷ $\sqrt{90·8}$	= 29 9	,,
$SbCl_3$ ..	113·3	473	473 ÷ $\sqrt{113·3}$	= 31 4	,,
$CHCl_3$ ..	59·8	334	334 ÷ $\sqrt{59·8}$	= 30·55	,,
CCl_3CHO	73·8	371	371 ÷ $\sqrt{73·8}$	= 30·55	,,
$POCl_3$ ..	76·8	380	380 ÷ $\sqrt{76·8}$	= 30·8	,,
$P_2O_3Cl_4$.	126	483—488	B.p. ÷ $\sqrt{126}$	= 30·4	,,
$PSCl_3$ ..	84·8	398	398 ÷ $\sqrt{84·8}$	= 30·6	,,
AsF_3 ..	66	333·5	333·5 ÷ $\sqrt{66}$	= 29·0	,,

Table III.

	Substance.	Constant.	
1.	H_2O	88	× $\sqrt{2}$
2.	NH_3	58	,,
3.	$N_2H_4.H_2O$ . ..	55	,,
4.	HCN	56	,,
5.	H_2SO_4	63	,,
6.	N_2O_4	31	,,
7.	N_2O	28	,,
8.	NOCl	33	,,
9.	$COCl_2$	28	,,
10.	$Ni(CO)_4$	25	,,
11.	$Fe(CO)_5$	27	,,
12.	CO_2	29	,,
13.	CH_4	27	,,
14.	C_2H_6	33	,,
15.	P_4O_6	33	,,
16.	CCl_4	27	,,
17.	$SnCl_4$	24	,,
18.	$SiCl_4$	26	,,
19.	Si_2Cl_6	26	,,
20.	$CH_2=CH_2$ . ..	32	,,
21.	Cl_2O	27	,,
22.	S_2Cl_2	35	,,
23.	SO_2	33	,,
24.	SO_3	36	,,
25.	$SOCl_2$	32	,,
26.	SO_2Cl_2	30	,,
27.	$S_2O_5Cl_2$	28·5	,,
28.	$SO_2Cl(HO)$ . ..	39	,,
29.	$[SO_2Cl(HO)]_2$ ..	28	,,
30.	HN_3	47	,,
31.	CO	16	,,

Notes on Table III.

It will be noticed that the numbers in this table fall into three groups.

1. With a mean of 90 $\sqrt{2}$
2. " " 60 "
3. " " 30 "

All except a few bodies at the end of this table have their factor near to 30, 60, or 90. Organic bodies have not been included in this list, as the author finds their large deviations make it necessary to study them in a different manner. No general law has been found for organic bodies, but a few rules enable the boiling-points of some organic bodies to be foretold to the fraction of a degree; the boiling-points of organic bodies will be treated later.

No. 28, sulphuric chlorhydrate, has a factor $39\sqrt{2}$ which is a considerable variation from the mean. If, however, the formula be doubled as in No. 29, a constant very similar to No. 27, an allied body is obtained. As the body decomposes on boiling, vapour density determination is impossible. Other exceptions, or at least apparent exceptions, are hydrazoic acid and carbon monoxide.

In the case of hydrazoic acid, HN_3, it is just possible the correct formula should be written H_2N_6. The six nitrogen atoms would be arranged in a similar manner to the six carbon atoms of the benzene ring.

This arrangement is supported by the following :—

NH_3 is a strongly basic hydride.	—CH_3 is a slightly electro-positive group.
N_2H_4 is a less strongly basic hydride.	—C_2H_5 is a very slightly electro-positive group.
N_6H_2 a strongly acid hydride.	—C_6H_5 is a slightly electro-negative group.

The above table shows a close relationship between the hydrides of carbon and nitrogen.

The constant for N_6H_2 becomes $33\sqrt{2}$.

II.

It has been shown from inspection that—

$$\frac{T}{\sqrt{\rho}} = n \times \text{constant (approximately)},$$

and that for classes of bodies, *e.g.*, trichlor derivatives,—

$$\frac{T}{\sqrt{\rho}} = \text{constant.}$$

This relationship throws considerable light upon the nature of intermolecular forces of attraction. Some of the theories here explained will be new, and should be of interest as an explanation of the nature of boiling-point.

From the kinetic theory of gases, the density of any gas at any temperature varies directly as the molecular weight of the molecules of gas divided by the temperature at which the density is measured.

If ρ_g is density of a gas at its liquefying-point.

If T is the liquefying-point of the gas.

And m is the molecular weight of the molecules.

Then—

$$\rho_g \text{ varies as } \frac{m}{T}.$$

The kinetic energy possessed by any molecule at any temperature is the same for that temperature whether it exist in gaseous or other form ("Kinetic Theory of Gases," Burbury, § 124).

At the boiling-point of a liquid therefore:—

$$\frac{\text{Kinetic energy of unit volume of liquid}}{\text{Kinetic energy of unit volume of gas}}$$

$$= \frac{\text{number of molecules in liquid}}{\text{number of molecules in gas}}$$

$$= \frac{\rho_L}{\rho_g}$$

Where ρ_L is the density of the liquid, the density o both gas and liquid being measured in the same units.

The kinetic energy of the molecules is equal to $\frac{3}{2}$ of the pressure.

If p is the pressure exerted at the confines of the gas.

If P is the pressure exerted at the confines of the liquid.

Then—

$$\frac{\text{Kinetic energy of unit volume of liquid}}{\text{Kinetic energy of unit volume of gas}} = \frac{P}{p}.$$

That is—

$$\frac{\rho_L}{\rho_g} = \frac{P}{p},$$

Now, P consists of p, together with a pressure A, due to the attraction between the molecules,—

$$\therefore \frac{\rho_L}{\rho_g} = \frac{p + A}{p}$$

$$\frac{\rho_L - \rho_g}{\rho_g} + 1 = \frac{A}{p} + 1$$

$$\frac{\rho_L - \rho_g}{\rho_g} = \frac{A}{p}.$$

Since ρ_g is small compared with ρ_L,—

$$\frac{\rho_L}{\rho_g} = \frac{A}{p}.$$

At the boiling-points of all liquids p is equal to atmospheric pressure, and therefore becomes a constant.

$$\therefore \frac{\rho_L}{\rho_g} \text{ varies as A.}$$

But ρ_g has been shown to vary as $\frac{m}{T}$.

$$\therefore \frac{\rho_L T}{m} \text{ varies as A.}$$

$$\frac{\rho_L}{\sqrt{m}} \times \frac{T}{\sqrt{m}} \text{ varies as A.}$$

But—

$$\frac{T}{\sqrt{m}} = n \times \text{constant.}$$

$$\therefore n \frac{\rho_L}{\sqrt{m}} \text{ varies as A.}$$

Now,—

$$\rho_L = \frac{N m}{v}.$$

Where N is the number of molecules in unit volume v of the liquid.

$$\therefore n \frac{N \sqrt{m}}{v} \text{ varies as A.}$$

Since v is equal to unity—

$$n \times N \sqrt{m} \text{ varies as A.}$$

Now, A is the attractive pressure due to N molecules occupying a volume v. That is, the attraction pressure due to each molecule varies as $n \sqrt{m}$.

Here n is a number whose value can readily be determined.

J. C. T.

Society of Chemical Industry.—An informal Dinner of the Society will be held on Wednesday, October 23rd, at the Criterion Restaurant, Piccadilly, W., Dr. Messel presiding, when the Medal of the Society will be presented to Sir William Crookes, O.M., F.R.S., who was unable to receive it in person at the Annual General Meeting in New York. Also the Past-President, Dr. Rudolph Messel, F.R.S., will be presented with a Souvenir of his period of Presidency, on returning from his visit to the Transatlantic Sections.

THE BROWNIAN MOVEMENT AND THE SIZE OF THE MOLECULES.*

By Prof. JEAN PERRIN, D.Sc.,
Faculté des Sciences à la Sorbonne, Paris.

Every day we see liquids in equilibrium, and all parts of them seem to us to be motionless. If we put a denser object into them it falls, perfectly vertically if it is spherical. Finally, when it has reached the bottom of the vessel, we know that it will not rise of its own accord.

These are very familiar ideas, and yet they hold good only for the dimensions to which our organs are accustomed. It is only necessary to examine with the microscope little particles placed in water to see that each of them, instead of falling regularly, is animated by a quite irregular and very brisk motion. They come and go, wheel round, rise, fall, and again ascend without showing any tendency to come to rest. This is the *Brownian movement*, named after one of your fellow-countrymen, the botanist Brown, who discovered it in 1827.

This remarkable discovery attracted very little attention. The physicists who heard tell of this agitation compared it, I think, to the movement of dust which one sees with the naked eye in a ray of sunlight, the effect of air-currents caused by slight inequalities in the temperature or pressure. But in this case neighbouring particles move nearly in the same direction, and roughly indicate the form of these air-currents. You will see, on the contrary, that the Brownian movement of two particles is completely independent, even when the distance between them is less than their diameter.

I am going to try to show you this phenomenon, one of the most beautiful which has been revealed to us by the microscope, and one which we shall prove to be a faithful picture of the movement of the molecules, or rather we shall prove that *it is itself a molecular movement* (just as the infra-red radiations are actually light).

You see here on the screen a cinematograph reproduction of the movement in water of round grains of gamboge (diameter rather less than 1/1000 mm.). This film was prepared by MM. Victor Henri and Comandon (Pathé film), and was kindly lent me by them. I should prefer to shown you the emulsion directly, by projecting on the screen the animated view which the microscope gives of it, but the enlargement necessary would be so great that the luminosity of the projection would be too faint for this large amphitheatre.

You see that in this very irregular movement it is not possible to pick out any general current drawing along several particles simultaneously. The movement cannot therefore be due to shakings of the plate which carries the droplet which is being watched, for those trepidations, when they are intentionally caused, produce precisely such currents which one sees simply superposed on the irregular agitation of the granules. Moreover, the Brownian movement persists on a thoroughly rigid structure, by night in the country as decidedly as by day in the town, on a table ceaselessly shaken by the passing of heavy vehicles (Gouy). There is not even any necessity to trouble to make the temperature of the droplet uniform. All that is gained by so doing is the suppression of currents which are perfectly recognisable, and have no relation to the irregular agitation observed. Nothing is gained either by greatly diminishing the intensity of the illuminating light or by changing its colour (Gouy).

Of course the phenomenon is not peculiar to water, but occurs in all fluids, being more marked when the fluids are less viscous, and hence especially strong in gases. In a moment I will show you the film of granules of gamboge in water; here is another which I owe to the kindness of MM. Victor Henri and de Broglie, and which shows you the Brownian movement in air of the ultra-microscopic droplets which form tobacco smoke.

In a given fluid the magnitude of the granules makes a great difference, and the agitation is the more marked the smaller the granules. This property was mentioned by Brown when he first made his discovery. As to the nature of the granules, it appears to have little if any influence. In the same fluid two granules move in the same way when they are of the same size, whatever their substance and density (Jevons, 1869). And, incidentally, this absence of influence of the nature of the granules eliminates all analogy with the displacements which a morsel of camphor undergoes when thrown on water,

Finally—and perhaps this is the strangest and most truly novel property—the Brownian movement never stops. Inside a cell, closed so as to prevent evaporation, it can be watched for days, months, and years. It is exhibited by the liquids enclosed in quartz for thousands of years. *It is eternal and spontaneous.*

All these characteristics point to the conclusion that the granules only reveal an agitation peculiar to the fluid itself, which they do more readily the smaller they are (just as a small boat more readily feels the waves of the sea than a large one). Thus we arrive at an essential property of what is called a fluid in equilibrium; this apparent rest is only an illusion due to the imperfection of our senses, and in reality corresponds to a definite permanent *régime* of violent and spontaneous agitation.

I should like to tell you how this perpetual agitation derives from the second law of thermodynamics the rank of an absolute truth (Gouy, 1888), and reduces it to a law of statistics; *i.e.*, to the affirmation of probabilities which are feebler the smaller the system to which one applies them, but our time is too short, and I must at once pass to the discussion of the cause within the fluid by which the phenomenon can be explained.

To find this cause we must appeal to molecular hypotheses. You know how how ancient they are, for Democritus and Leucippus, more than twenty centuries ago, knew that matter is composed of indestructible granules in incessant movement, atoms which Chance or Destiny grouped in the course of ages into the forms and substances with which we are familiar. But only tradition tells us of these early theories, and in the beautiful poem, written long after, in which Lucretius describes the atomistic views of Epicurus, I see nothing to show how these Greek philosophers were led to attribute a granular structure to matter.

It seems to me that this hypothesis might have been suggested to them by the familiar properties of mixtures. In any case there is a really serious argument in these properties which I will first discuss. For example, we all say when we have dissolved sugar in water that the sugar and water exist in the mixture, although we cannot distinguish different parts in the sweetened water. Similarly we say that there is oxygen in the air, and, more generally, we often recognise without hesitation in the properties of a mixture those of its constituents.

This is easily understood if the substances which form the mixture subsist in it, as flowers of sulphur and iron filings exist side by side in this mixture which I am making before your eyes. You can no longer distinguish the yellow from the black grains, and the whole looks to you to have a homogeneous grey colour. You will recognise the iron, however, even from some distance if I bring a magnet near the vessel containing the mixture; and this does not surprise you, for you know that you need only come nearer in order to distinguish the grains of sulphur from those of iron, which are in juxtaposition but are unchanged. Similarly the persistence of the properties of sugar in sweetened water would easily be explained if in this solution there are present little particles, simply mixed in juxtaposition, which by themselves would make water, and other particles which alone would form sugar. These elementary particles, or *molecules*, would be found in all mixtures in which we could detect sugar and water, and only their extreme minuteness would prevent us from seeing them individually.

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* A Discourse delivered before the Royal Institution, February 24, 1911.

Moreover, the molecules of a pure substance like water, if they exist, must be identical, otherwise they would not behave similarly when subjected to different attempts at fractionation, by boiling, for example, and the fractions successively separated would not be identical, whereas as a matter of fact they are (Dalton).

If the molecules exist, in order to understand solution and diffusion, we are forced to admit that they are in ceaseless motion. Suppose we pour alcohol carefully on to water, or superpose carbon dioxide and hydrogen (Berthollet), and leave the system at a perfectly constant temperature. You know that the two fluids gradually interpenetrate one another although the lighter may be above, and this could not occur if their molecules were motionless. When we have thus seen that the molecules of carbon dioxide diffuse into hydrogen, into oxygen, into nitrogen, and so on, it seems probable to us that they would also diffuse into carbon dioxide itself, and this amounts to saying that the molecules of carbon dioxide are in incessant motion.

This movement of the molecules also explains the pressure exercised by fluids on the walls of containing vessels, the pressure being due to the bombardment of the molecules against the walls. This explanation, worked out in the eighteenth century by Euler and Bernouilli, leads to Boyle's law, and enables us to calculate the mean velocity of the molecules of different gases (in the air of this room, for example, the molecules would have a mean velocity of about 500 metres per second). This result signalises the first success, in modern physics, of the old hypothesis of Greek atomism.

But we are still far from a direct verification, and the supposed movements of the molecules escape us, just as the movement of the waves of the sea escape an observer who is too far away to see them. However, if a boat were in view the same observer might see a rocking which would reveal to him the agitation of which he had no suspicion. Might one not hope similarly that if microscopic particles were present in a fluid these particles or this dust, if they were large enough to be watched under the microscope, might also be small enough to be appreciably affected by the blows of the molecules?

Now, you will guess what explanation we are going to give to the Brownian movement. Every granule situated in a fluid is unceasingly struck by the molecules round it. There is no chance that these blows will exactly balance one another; our granule will thus be irregularly tossed about, and perhaps this is the Brownian movement.

This tempting explanation (Weiner, 1863) was long regarded as doubtful. In order that it may be accepted it is at least necessary that the theory should foretell the order of magnitude of the phenomenon, and as yet we do not know whether it is not immeasurably greater (or less) than our hypothesis permits.

We shall see that this quantitative verification is possible, but to arrive at it I must remind you how, some time ago, the measurement of the viscosity of gases enabled us to determine the probable size and weight of the molecules. I shall then show you that the Brownian movement, supposed to be due to the blows of the molecules, also gives a means of determining the size of the molecules. If the two results, obtained by such very different methods, agree the origin of the Brownian movement will be determined.

If we admit the existence of the molecules we are forced, in order to explain the chemical laws of discontinuity (Law of Definite Proportions, Law of Multiple Proportions, Law of Proportional Numbers), to admit with Dalton the existence of *atoms*, characteristic of the various simple substances. For then the composition of a molecule necessarily varies by discontinuous bounds, corresponding to the entrance (or departure) of at least one atom. Thus we could deduce with precision, from the phenomena of chemical *substitution*, not the absolute weights of the molecules and atoms, but the ratios of these weights.

When, for instance, calcium is dissolved in water only half the hydrogen of the water is displaced. This may be explained by assuming that the hydrogen of each molecule of water is composed of two equal parts. These parts must be indivisible by all chemical means, since no other substitution ever gives us reason for thinking that there are more than two; these parts are called "atoms" of hydrogen. Moreover, a molecule of water, like any mass of water, weighs nine times as much as the hydrogen it contains; thus it weighs eighteen times as much as a single atom of hydrogen. By similar reasoning it is found that a molecule of benzene weighs seventy-eight times as much as one atom of hydrogen. The weights of the molecules of benzene and of water and of the atom of hydrogen are thus in the proportion of 78 : 18 : 1. Similarly in many cases the ratios of the weights of different molecules and atoms may be found. (Strictly speaking, all these ratios are not yet known; for instance, there is no substitution which gives the molecular weight of a simple substance like oxygen. We shall see in a moment how Avogadro's law enables us to fill up this gap). It is very remarkable that all these determinations are concordant, so that, for example, we can mention thousands of substances from the study of which we can deduce that the atom of carbon is twelve times as heavy as the atom of hydrogen. This gives us confidence in the atomic theory, but tells us absolutely nothing about the scale of the sizes of the molecules whether near us or infinitely distant.

We see at least that in order to arrive at the absolute weights of the different atoms or molecules, it is only necessary to know one of them. At the same time, we should also get (as Helmholtz as shown) the elementary charge which one atom of hydrogen (or, more generally, one monovalent ion) transports in electrolysis. For if we knew the weight of one atom of hydrogen, we should know how many of these atoms 1 grm. of hydrogen contains, and hence how much each carries in electrolysis, for we know that 1 grm. of hydrogen transports about 100,000 coulombs.

Let us then try to find one of these elementary weights, that of the molecule of oxygen, for instance.

Kinetic Theory.—Suppose that a mass of oxygen occupying 1 litre (at ordinary temperature and pressure) if liquefied. The n molecules which are present in it will almost come into contact, for the liquid is nearly incompressible. Now, we know that the true volume of the granules of a heap of sand is approximately two-thirds of the apparent volume of the heap; it is therefore probable that the true volume of our n molecules is not much less than two-thirds of the volume of the liquid, and if this value is accepted there can be no very great error. A more exact theory, due to Van der Waals, leads us to assume a value twice as small and to write:—$n \times$ volume of 1 molecule $= \frac{1}{2}$ volume of the liquid.

On the other hand, in the gaseous state in a given volume a fixed number of molecules n collide more often the larger they are. Or, if you prefer it, the mean free path of the molecule L is smaller in proportion as the molecules are larger or have a larger surface. Clausius and Maxwell have calculated this relation (assuming that the molecules are spherical) and have found—

$$n \times \text{surface of 1 molecule} = 0{\cdot}7\,\frac{\text{volume of gas}}{\text{mean free path}}.$$

If we know the mean free path we should then have, by dividing the two equations by one another, the ratio of the volume $\frac{4}{3}\pi R^3$ to the surface, $4\pi R^2$; *i.e.*, the radius of the molecule, and hence its volume and surface. One of these two equations, the first for instance, would give us n, the number of molecules which form a known mass of oxygen. The mass of the molecule of oxygen will thus be obtained.

But for this we must know the free path of the molecule. Maxwell was able to deduce it from the force which is exerted by friction between two gaseous layers which slide one on the other with different velocities.

It is easy to show the existence of this "internal friction" or "viscosity." You see the jet of gas which I light at the end of this long capillary tube. If now I shorten the tube (by cutting it) the jet of gas coming from it gives a much longer flame. Thus the gas comes out more quickly from a tube of the same section. There was therefore a large amount of friction in the path which I have cut off, in the interior of which the cylindrical gaseous columns slide on one another.

The molecular hypothesis easily explains this friction. In order to understand it let us imagine two trains of passengers moving on parallel rails with almost equal velocities. The passengers could amuse themselves by jumping incessantly from one to the other, receiving a slight shock every time. Thanks to these shocks the passengers alighting on the slower train would slowly increase its velocity, while in the same way that of the quicker train would slowly decrease. The two velocities would thus be equalised as by friction if the constant difference were not maintained. The same argument applies to two gaseous layers sliding one on the other, since they bombard each other without ceasing by a transference of the molecules from one to the other.

The mathematical analysis of this simple conception, made by Maxwell, has shown that the force of friction per square cm. between two gaseous layers at a distance of 1 cm., having a relative velocity of 1 cm. per second (a force which explains viscosity), approximately satisfies the equation—

$$\text{Viscosity} = \tfrac{1}{3}\ \text{density} \times \text{free path} \times \text{molecular velocity}.$$

The density of the gas and the viscosity are measurable. If we can determine the molecular velocity (mean) we shall have the free path.

This last process is easy. The pressure of the gas, as we have already said, is explained by the continual bombardment of the molecules on the walls, and these shocks are the more effectual the heavier and more rapid each of them is. The exact expression, due to Bernouilli, gives—

$$\text{Pressure} = \tfrac{1}{3}\ \text{density} \times \text{square of molecular velocity}.$$

This gives the required velocity. Applied to oxygen we find about 500 metres per second at the ordinary temperature; the molecules we are breathing are moving as rapidly as bullets.

We have now only to proceed step by step; we shall have the mean free path (1/10,000 mm. for air in ordinary conditions), then the molecular diameter (a molecule of oxygen is to a man very nearly as a man to the sun), then the number of molecules n to a litre (about 30,000 million of billions), and finally the weight of the molecule of oxygen which will give us, as we have seen, all the other weights of molecules or atoms.

We find thus, the possible error being roughly 30 per cent, that the weight of one atom of hydrogen is only the billion-billionth part of 1·6 grm., or $1{\cdot}6$ grm. $\times 10^{-24}$. As to the elementary charge it will be about 5×10^{-10}, or about the thousand-millionth of the charge which can be detected by an ordinary electroscope.

I am now going to tell you how, thanks to the Brownian movement, I have been able to give other means of obtaining the sizes of the molecules.

(To be continued).

The Combustion of Ammonia.—M. Terni (*Revue des Sciences*, August 15, 1912) has shown a simple method of demonstrating the combustibility of ammonia. Into a thick walled glass tube 17 cm. long and 2 to 3 cm. diameter place 5 cc. of 30 per cent hydrogen peroxide, 10 cc. of a concentrated solution of ammonia, and 1 grm. of finely powdered manganese dioxide. Oxygen is evolved, and the temperature of the liquid rises considerably. The gaseous mixture composed of oxygen and ammonia is inflammable. At the beginning the combustion is accompanied by little explosions, but soon the gas burns with a fine yellow flame.—W. R. F.

AN IMPROVED ACTINOMETER.

By W. R. FORBES, B.Sc.

THE pendulum actinometer of Bunsen and Roscoe (*Phil. Mag.*, 1893, xxxvi., 459—463) was modified by Richardson and Quick (*Brit. Assoc.*, 1893) so as to eliminate the calculations due to pendulum motion which arose in the former type.

The form described below has, it is claimed, two advantages:—

1. The mechanism can be rendered constant over a long period.
2. The rate of action can be varied.

The apparatus consists of a shallow camera box fitted at the back with means for introducing the sensitised paper. In the front face a slit is cut, and across this a plate is moved. The shutter or plate is attached to an electric chronograph, being hinged to the arm of the chronograph to secure vertical movement.

REPORT ON DIFFUSION IN SOLIDS.*

By CECIL H. DESCH, D.Sc., Ph.D.

(Concluded from p. 181).

Diffusion in Minerals.

THE question whether true solid diffusion ever occurs in minerals is very difficult to answer. The term "diffusion" has sometimes been employed rather loosely in geological writings, so that a complex rock such as granite has been spoken of as diffusing into surrounding schists, a comparison being made with Roberts-Austen's experiments with metals (E. Greenly, *Geol. Mag.*, 1903, [4], x., 207). In such a case the action is evidently one of mechanical percolation. The most favourable instances might be expected to be the secondary replacement of minerals and the formation of pseudomorphs. Attention has been drawn to the fact that whilst certain alterations, such as the conversion of olivine into serpentine, obviously proceed along cracks in the original crystal, other changes are of a much finer character, and must be assumed to depend on a molecular porosity (C. A. Macmahon, *Brit. Assoc. Reports*, 1902, 589). The writer has not, however, been able to find, from the examination of photo-micrographs and of rock-sections, that any cases of alteration can be attributed unhesitatingly to diffusion, as even when cracks are absent the alteration very commonly proceeds along cleavage planes. It is possible, but by no means certain, that such reactions proceed by true diffusion.

It has been urged as a fatal objection to the occurrence of solid diffusion in crystalline substances that crystals of native minerals are found in which successive zones of minerals known to be isomorphous with one another are in intimate contact, and yet there is no indication of inter-diffusion having taken place, although geological ages have elapsed since the crystals have been deposited from a fluid magma. Augite and the triclinic felspars often exhibit zonal structures in great perfection. In the case of metals, as described above, zonal structures occur when the rate of cooling of a liquid depositing crystals of a solid solution is too great to allow of equalisation of the solid solution by diffusion in order to re-establish equilibrium. Annealing at a temperature below the solidus curve favours diffusion; and usually brings about equalisation in a short time, measurable in hours.

The best zonal structures are obtained when the two end-members of the series composing the crystal have nearly identical molecular volumes, as in the triclinic felspars, in which the variation is only from albite, 100·13, to anorthite, 101·49 (T. V. Barker, *Trans. Chem. Soc.*, 1906, lxxxix., 1120).

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* Read before the British Association (Section B), Dundee Meeting, 1912.

The most favourable instances for the view that reactions involving diffusion may take place within a crystalline mineral are those of schiller-inclusions, as of magnetite in the olivine from peridotite, Isle of Rum (A. Harker, "The Natural History of Igneous Rocks," p. 257), and in the hypersthene from norite, Labrador, and also of rutile in certain felspars and pyroxenes. Such structures may well be due to the change in concentration of a solid solution during cooling causing the separation of the constituent in excess. The microperthitic intergrowths of albite and orthoclase in alkali-granite (Rockport, Mass.) and of albite and microcline in nepheline-syenite (Miask, Ural) are also instanced by Harker as being very possibly formed in the solid state. These structures are strongly suggestive of the eutectoids of certain metallic alloys. "Pyroxene-perthite," an intergrowth of rhombic pyroxene and diopside, suggests a similar origin (J. H. L. Vogt, *Tscherm. Min. Mitt.*, 1905, [2], xxiv., 537).

Agate and chalcedony are to be classed among solid colloids rather than among crystalline minerals, but the suggestion that certain brecciated and banded structures observed in them are not of primary origin, but have arisen through segregation in the solid state, should not be overlooked (J. Ruskin, *Geol. Mag.*, 1867-1870, iv.—vii.; reprinted in "Collected Works," xxvi., 36).

Finally, in this connection, mention may be made of the "pleochroic halos" observed in certain minerals, notably biotite, and attributed to the α-radiation from minute enclosures of radio-active material. Each halo is made up of several concentric shells, each of which represents the range of some of the types of α-particle emitted (J. Joly, *Phil. Mag.*, 1907, [6], xiii., 381; J. Joly and A. L. Fletcher, *Ibid.*, 1910, [6], xix., 630). Halos in all stages of development have been observed. Artificial pleochroic halos have been obtained in glass (E. Rutherford, *Mem. Manchester Phil. Soc.*, 1909, liv., v., 1). The origin of the halo is of course not ordinary diffusion, as the α-particles are shot off at great speed from the centre, but the penetration of the crystalline material appears certain.

Diffusion in Artificial Crystals.

The process of diffusion in crystalline salts or organic substances has been little studied. From the fact that isomorphous crystals frequently resolve themselves into their components on cooling, and that other crystals unite under similar conditions, it is certain that diffusion must take place, but there is usually no record of direct observation of this kind. It has, however, been observed that mixtures of 80 to 93 per cent of ammonium nitrate and 20 to 7 per cent of potassium nitrate, which solidify to form a mixture of two saturated solid solutions, become turbid on cooling past 104°, and monoclinic crystals then appear, which gradually absorb both the original forms, the mass ultimately becoming homogeneous. In some cases the resulting crystals are optically perfect, whilst in others traces of heterogeneity remain (F. Wallerant, *Comptes Rendus*, 1906, cxlii., 100).

The other case is more frequent. An instance described in the above memoir is that of mixtures of 67 per cent of ammonium nitrate with 33 per cent of cæsium nitrate. These mixtures solidify to form homogeneous cubic crystals, which become rhombohedral at a lower temperature. On cooling still further, these crystals are resolved into two distinct kinds of crystals, respectively isomorphous with the two components.

It will be sufficient to cite one other example among salts. Mixtures of sodium sulphate and potassium sulphate solidify in the form of homogeneous crystals throughout the whole range of composition, but at lower temperatures separation into the double salt, Na_2SO_4,K_2SO_4, and the excess of one or the other constituent takes place (R. Nacken, *N. Jahr. Min. Beil. Bd.*, 1907, xxiv., 1).

An interesting case of dissociation in, and crystallisation from, a solid solution has been observed in the case of *o*-nitrobenzaldehyde, which is converted into *o*-nitrosobenzoic acid in sunlight. The green unimolecular modification of the nitroso-compound is produced as long as it remains in a state of solid solution, but when this becomes saturated the nitroso-compound formed subsequently separates in crystals of the white bimolecular modification (C. A. Lobry de Bruyn and C. L. Jungius, *Proc. k. Akad. Wetensch. Amsterdam*, 1903, v., 643).

It does not appear that diffusion has been observed in the case of zonal crystals of salts or organic compounds, although such crystals are readily prepared by allowing a salt to grow in a saturated solution of an isomorphous salt, and similar crystals have been frequently investigated on account of the optical anomalies that they present. Very remarkable results have been obtained, however, by the examination of crystals which have absorbed a colouring matter, not isomorphous with the substance examined, during crystallisation. These crystals commonly present optical anomalies, and the distribution of the colouring matter is frequently not uniform, but is confined to certain zones or sectors. In some cases the anomaly is undoubtedly due to mechanical strain caused by the interposition of a foreign material in the mass of the crystal, as the same effect is observed in crystals built up of isomorphous salts, but in other cases the disturbance goes further than this (a review of the subject to 1891 is given by R. Brauns, "Die optischen Anomalien der Krystalle," Leipzig, 1891). Without referring to the very voluminous literature of this subject, a few typical examples may be mentioned. Experiments with 33 inorganic salts and 26 colouring matters, mostly aniline dyes, only resulted in stained crystals in four instances (J. W. Retgers, *Zeit. Phys. Chem.*, 1894, xii., 583). The nitrates of the barium group may be stained with methylene blue, these being perhaps the most successful instances of the kind (P. Gaubert, *Bull. Soc. Franç. Min.*, 1901, xxiii., 211). Potassium iodide crystals absorb iodine vapour, and the salt separates in coloured crystals from solutions containing iodine, but microscopical examination shows that the distribution within the crystal is very far from uniform (E. Sommerfeld, *N. Jahrb. Min.*, 1902, ii., 43).

Somewhat more exhaustive experiments have been made with meconic acid. Crystals of this acid may be stained if allowed to crystallise from solutions containing "Fettfarben," but if the colourless crystals are placed in a solution of the dye the colour is not absorbed (O. Lehmann, *Ann. Phys.*, 1894, [3], li., 47). It was objected that the experiment was only conclusive if it were also shown that the same solvent (benzene or light petroleum) did not extract the dye from previously stained crystals (W. Ostwald, *Zeit. Phys. Chem.*, 1894, xiii., 758). This proved to be the case (S. Ruzicka, *Zeit. Phys. Chem.*, 1910, lxxii., 381), and the evidence therefore shows that in this instance diffusion of the colouring matter does not occur, even when the conditions are apparently favourable.

Diffusion in Colloidal Gels.

The diffusion of salts in gels, such as gelatin, agar-agar, and colloidal silica, differs little from the same process in water, the diffusion following the same laws, and the velocity being diminished to a comparatively small extent. This was studied by T. Graham (*Phil. Trans.*, 1866, clvi., 399), and confirmed in detail by F. Voigtländer, *Zeit. Phys. Chem.*, 1899, iii., 316). The velocity diminishes with increasing concentration of the colloid, and is also influenced by the presence of foreign substances (K. Meyer, *Beitr. Chem. Phys. Path.*, 1905, vii., 393; H. Bechhold and J. Ziegler, *Zeit. Phys. Chem.*, 1906, lvi., 105).

Liesegang's Phenomenon.

An interesting phenomenon, which is of importance for the theory of diffusion in many cases, was first observed by R. E. Liesegang ("Chemische Reaktionen in Gallerten," Düsseldorf, 1898; "Ueber die Schichtungen bei Diffusionen," Liepzig, 1907). In the most convenient manner of conducting the experiment, a thin layer of gelatin, spread on a glass plate, is impregnated with potassium dichromate and allowed to dry. A drop of silver nitrate solution is then placed on the gelatin surface. As the solution diffuses outwards silver chromate is precipitated, but instead of forming a ring round the original spot, diminishing steadily in intensity towards the circumference, the silver chromate is deposited intermittently, forming a series of concentric rings, which under favourable conditions are of very remarkable regularity. Many other salts behave in the same way as silver chromate. It is not even necessary that a precipitate be formed, as similar rings may be obtained by the diffusion of a single salt, such as sodium phosphate (R. E. Liesegang, *Zeit. Phys. Chem.*, 1910, lxxv., 371), or by the hydrolysis of a chromium salt (H. R. Procter and D. J. Law, *Journ. Soc. Chem. Ind.*, 1909, xxviii., 297). Each ring is formed suddenly, and the distances between successive rings follow a definite law. An explanation of the phenomenon was suggested by W. Ostwald (*Zeit. Phys. Chem.*, 1897, xxiii., 365), who attributed the formation of rings to supersaturation. On this view the silver chromate at first formed remains in the form of a supersaturated solution in the gelatin until the metastable limit of concentration is passed. A ring is then formed, and the chromate in the immediate neighbourhood is attracted to that already deposited. The silver solution continues to diffuse, passing over a space which is practically devoid of chromate, until a new formation takes place, and the process is repeated. This hypothesis leads to quantitative results in agreement with those observed, and it is possible to calculate the metastable concentration product, a quantity resembling the "solubility product" for compounds precipitated from solution (H. W. Morse and G. W. Pierce, *Zeit. Phys. Chem.*, 1903, xlv., 589). The fact that two systems of rings, formed at different times in the same film of gelatin, can cross one another without interference seemed opposed to the explanation (R. E. Liesegang, *Zeit. Phys. Chem.*, 1907, lix., 444), until it was shown that the two systems are not in the same plane, and therefore do not come into actual contact (*Zeit. Phys. Chem.*, 1910, lxxv., 371). A more serious objection is that if the gelatin be previously impregnated with lead iodide and potassium iodide, so that abundant minute crystals are formed, on the addition of a drop of lead nitrate solution Liesegang's rings may still be obtained in the film, although the formation of supersaturated solutions would seem to be impossible (E. Hatschek, *Zeit. Chem. Ind. Kolloide*, 1912, x., 124). Other explanations have been proposed, based on the influence of the excess of soluble salt present (H. Bechhold, *Zeit. Phys. Chem.*, 1905, lii., 185), or on the difference in velocity of the two diffusing salts (E. Hatschek, *Zeit. Chem. Ind. Kolloide*, 1911, ix., 97), but it does not appear that either hypothesis will account for the whole of the facts (see also, for many important experiments on this subject, J. Hausmann, *Zeit. Anorg. Chem.*, 1904, xl., 110).

Liesegang's phenomenon has been recently invoked to explain the structure of agates by the diffusion of an iron salt into a silica gel (R. E. Liesegang, *Centr. Min.*, 1910, 593; 1911, 505; *Zeit. Chem. Ind. Kolloide*, 1911, ix., 296), and it has been found possible to imitate very closely the banded structures of agates by impregnating masses of gelatin with salts and allowing other salts to diffuse inwards.

Conclusion.

The foregoing account does not pretend to anything like completeness. The number of investigations—physical, chemical, metallurgical, and geological—bearing on this subject is extraordinarily large, but the selection given may serve to show the lines of argument. The older view that solid solutions have no existence among crystalline substances, and that isomorphous crystals have a minutely heterogeneous or zonal structure (see the reviews of the subject by O. Lehmann, "Molekularphysik," 1888, and, from an altered standpoint, "Flüssige Krystalle, 1904), has been recently revived in respect to metallic alloys (C. A. Edwards, *Journ. Inst. Metals*, 1911, v., 150; vi., 259; P. P. von Weimarn, *Zeit. Chem. Ind. Kolloide*, 1911, ix.), a department in which the conception of crystalline solid solutions has proved most fruitful. A decision as to the conditions under which diffusion occurs in solids is of the highest importance in relation to this question. A review of the evidence leads to the conclusion that the occurrence of diffusion in metals is established beyond any doubt, but that experiments are still lacking to prove its occurrence in transparent crystals of minerals, salts, or organic substances, even under favourable conditions, although even here indirect evidence points to its possibility. The subject is complicated by the occurrence of adsorption, and it is sometimes difficult to separate the effects of adsorption from those of diffusion, but it seems an exaggeration to suggest that the passage of metals into one another (G. Bodländer, *N. Jahrb. Min. Beil. Bd.*, 1899, xii., 53), forming easily recognisable intermetallic compounds, should be ascribed to adsorption, although such an explanation may possibly suffice in such cases as the passage of gases through heated metals, and the staining of transparent crystals.

THE PRODUCTION OF ETHYL ALCOHOL FROM WASTE PRODUCTS.

By ALCAN HIRSCH.

The first synthesis of ethyl alcohol was made about 1826, by Hennel, utilising the reaction of ethylene and sulphuric acid to form sulphovinic acid, which, upon heating with an additional quantity of sulphuric acid, yields alcohol. Berthelot improved this process by synthesising ethylene from its elements via acetylene, and by making a more complete conversion of ethylene into sulphovinic acid.

The one source of the alcohol is the action of the zymase of yeast upon glucose and other fermentable sugars. The sources of the fermentable sugars may be grouped into two classes:—

1. The products of the hydrolysis of starch and allied substances by means of an amylase.
2. Solutions of sugars obtained directly from fruits and plants and from the non-crystallisable by-products of sugar works, such as molasses.

The most economical source of starch in our country is probably Indian corn, costing about 21.00 dols. per ton. One ton of corn gives about 90 gallons of 94 per cent alcohol. About 2 gallons of raw molasses produce one gallon of 94 per cent alcohol, and this raw material costs about 0·21 dol. per gallon of 94 per cent alcohol. The costs of the distillation of the mashes and the rectification and purification of alcohol cannot be entered into here, but the approximate cost of 95 per cent alcohol (190 proof) to the consumer may be taken as about 0·50 dol. per gallon, exclusive of taxation.

Within the last two or three years two new commercial processes for the production of alcohol have been put in operation on a comparatively large scale. The purpose of this article is to present and discuss briefly from a chemical engineering standpoint these two processes, namely, the production of alcohol from sulphite cellulose waste lyes, and the production of alcohol from sawdust.

1. *Alcohol from Sulphite Lyes.*

In the sulphite process for the production of pulp, for every ton of cellulose there are about ten tons of sulphite lyes (T. H. Norton, *U.S. Cons. Rep.*, Nov., 1911), which contain one-half the weight of the wood originally introduced into the boilers. Among the substances present are —Dextrose and other sugars, xylose, acetic acid, tannic acid, nitrogen compounds, methyl alcohol, resins, &c., and calcium-lignin sulphonate, the chief product of the reaction. Most of the sugars in these lyes are fermentable, and they constitute about 1 per cent of the lyes, the yield of alcohol being from 15 to 17½ gallons per ton of cellulose (C. G. Schwalbe, *Zeit. Angew. Chem.*, 1910, xxiii., 1537).

Recently in Sweden two industrial processes have been developed—that of P. G. Ekström (Eng. Patent 6741, March 17, 1910) at Skutskär, and that of Wallin at Forss. These processes are practically identical, differing only in the neutralisation of the acid. The former uses lime, chalk, &c., and the latter waste causticisation sludge. The general scheme is as follows:—The lyes are first neutralised in large vats, then cooled in towers and aerated. In a mill producing 10 tons of cellulose per twenty-four hours the volume of the lyes to be treated is about 9000 gallons per day. A yeast nutrient, malt extract, or dead yeast is added to the cool neutral liquid, which is transferred to the fermentation vats. After fermentation (which takes three days or more) the yeast is separated and the liquid distilled in a continuous still. The percentage of alcohol is very low, and considerably more steam is used in the distillation than is required with mash from molasses, which usually contains about 7 per cent alcohol by volume. The alcohol obtained is already denatured, as it contains considerable methyl alcohol (from the unfermented lyes), furfurol, aldehydes, and sometimes acetone, but is practically free from terpenes.

The above process with a few minor changes is being worked on a large scale at several places in Sweden. The experimental plant at Skutskär began operations on May 24, 1909, using waste lyes from a 5000-ton cellulose plant. In March, 1910, 560 gallons of "normal strength" alcohol were produced per twenty-four hours. The total for the month was about 13,000 gallons. The process yields about 6 gallons of absolute alcohol for 1000 gallons lye, and about 14 gallons for every ton of cellulose.

As the alcohol produced from waste lye is denatured, its chief uses will necessarily be for heating and other industrial purposes. The industrial prospects of this process depend on the cost of production, conditions of taxation, and capacity of the market. Estimates of the cost of production for a mill producing 340,000 gallons per annum place the cost at about 9·50 dols. per 100 gallons. In Sweden the tax per gallon increases with the output, so that for an annual production of 340,000 gallons the cost of production, including the tax, is about 15·50 dols. per 100 gallons. In Germany excise regulations penalise new distilleries, so that, in addition to the cost of production, sulphite spirit would be subject to a tax of about 17.00 dols. per 100 gallons. Regarding the capacity of the market, in Sweden during the fiscal year 1908—1909 the total production of alcohol was about 5,800,000 gallons (absolute) and the imports were about 310,000 gallons. The sulphite lye mill at Larkudden is reported as having produced spirit during the year 1910 at the rate of 157,000 gallons per annum, and the annual rate of production at the present time is estimated at 250,000 to 400,000 gallons. The pulp mills of Sweden can produce 6,500,000 gallons of absolute alcohol per annum. It must be remembered that the present method of production from grain is always intimately connected with the agricultural industries of the country, and therefore will not be easily displaced. Also, while under special conditions (especially low taxation) the sulphite process can be worked at a profit, yet it does not solve the problem of the disposal of the waste lyes, as only about 1 per cent of the total weight of lyes is converted into alcohol. In fact, on account of the presence of dead yeast, &c., the problem of the disposal of the lyes may be aggravated by the use of this process.

2. *Alcohol from Sawdust.*

The cost of raw material is always of great importance in any industry. While Indian corn costs about 21.00 dols. per ton, sawdust in the vicinity of a large mill, where it is a by-product, can be bought at a cost of 30 to 50 cents a ton, including handling and transportation (short distances). One ton of sawdust, calculated to the dry basis, can yield 20 gallons of 94 per cent alcohol, which makes the cost of this raw material 2 to 2½ cents per gallon 94 per cent alcohol, as against 24 cents for Indian corn.

For nearly one hundred years it has been known to chemists that fermentable sugars can be produced from sawdust. The reaction is usually spoken of as being very simple, all that is necessary being to add a molecule of water to the cellulose. This hydrolysis is probably as complex as it is baffling. The unknown composition of those polysaccharides which we call cellulose, and the very different results obtained on hydrolysis under slightly different conditions of catalyser, temperature, and pressure, indicate that somewhat intricate reactions occur, the complete chemistry of which is not known at the present time. A very large number of patents have been granted on this reaction, the main differences being in method of manipulation and the catalysing acid used. Sulphuric acid has been used in many cases, but the subsequent removal of this acid has proved a serious stumbling block. No process that was capable of commercial application had been devised until the year 1900 when Dr. Alexander Classen was granted his first patent. The more important English patents granted him are:—No. 258, Jan. 4, 1900; No. 4199, Feb. 27, 1901; No. 12,588, June 20, 1901. "Process claimed consists in boiling cellulose in a closed vessel at a temperature of 120—145° C. with a solution containing sulphurous and sulphuric acids, or sulphurous and hydrochloric acids. A solution of 2 per cent or more of sulphurous acid and 0·2 per cent sulphuric acid is mentioned. The sulphuric acid may be conveniently formed in the boiler by admission of air or other suitable oxidising agent. In this way concentrations of 10 per cent sugar may be obtained, 80 to 90 per cent of which is fermentable. Conversion is complete in fifteen minutes.

An experimental plant using this process was erected at Aachen, and a similar plant on a larger scale was built at Highland Park, near Chicago. The results were satisfactory so that it was decided to build a commercial scale plant at Hattiesburg, Miss. The capacity of the conversion cylinder was two tons. After the conversion the acid was neutralised, cleared by subsidence, pumped into large vats, and fermented by yeast, and then distilled. From a commercial viewpoint this plant was a complete failure. From a chemical engineering standpoint it is an excellent example of a process which fell just short of success. The reasons given for the failure are:—1. Length of time required for conversion, 1½ to two tons requiring four to six hours. 2. Prolonged action produces gums and caramels and makes extraction of the sugar tedious and expensive. 3. Large quantity of acid required. 4. Lining difficulties, especially with lead linings.

Two chemical engineers, Ewen and Tomlinson, studied and undertook to improve this process. Their patent, U.S. 938,308, 1909, describes their process. The converter used by Classen was about 30 feet in length, and had a diameter of 3 feet, whereas in the Ewen and Tomlinson process the digester is much shorter, usually being about 12 feet in length and 8 feet in diameter. The latter line their converter with fire-brick instead of using the troublesome lead lining. The operation seems to be fairly simple. Sulphur dioxide gas to the extent of 1 per cent of the weight of the wood is introduced into the cylinder, and live steam is turned on until a pressure of 100 lbs. is obtained. The steam is then turned off, and the cylinder slowly revolved for forty to forty-five minutes, the temperature and pressure being kept constant. The total time of conversion is about one hour as against four to six hours in the old process. In operating this process it is important to raise the temperature as quickly as possible to the "critical-point," which is defined as "that temperature above which the production of unfermentable substances and the destruction of the sugars become excessive, and lies between 135° and 160° C." After extraction, the converted lyes have a total acidity of 0·64 per cent (calculated to H_2SO_4) containing sulphuric, acetic acids, a small amount of sulphurous acid, and aromatic compounds of the type of pyrogallol. These liquors contain about 5½ per cent of reducible sugars calculated to dextrose. Polyphenols, tannin, and furfurol are usually present in small amounts. These liquors are fermented and distilled in the usual manner, some care being required in the fermentation to have present a proper food for the yeast. The distilled alcohol obtained is potable, free from the odour and taste of wood, and from methyl alcohol and fusel oils, but contains traces of furfurol and aldehydes. One and one-half tons of dry wood give about 61½ gallons of 94 per cent alcohol. From figures obtainable it appears that the efficiency of the process is from 75 to 80 per cent of the theoretical yield of alcohol.

The Dupont Powder Company is operating a plant at Georgetown, South Carolina, for the production of alcohol from waste woods. This plant is licensed under the Ewen and Tomlinson patents, and while no figures were obtainable, it is stated that experiments so far indicate the ultimate success of the process.

W. P. Cohoe is the inventor of a process for making fermentable glucose-like substances from cellulose and ligneous materials (U.S. Patents 985,725, 985,726, 1911). The conversion is done in two stages:—First, steam is used producing acetic acid which is collected, and then steam and HCl vapours are introduced into the converter. The raw material used is generally sawdust.

The cost of production of alcohol by the sawdust process (Ruttan, *Journ. Soc. Chem. Ind.*, 1909, p. 1290) is said to be about equal to that of grain, although there is such an enormous difference between the cost of the raw materials. One company, however, claims to be able to manufacture alcohol by the sawdust process at a cost of 0·07 dol. per gallon.

Without going into the details of the chemistry involved, it is striking that, although the patents claim a conversion of cellulose into sugar, the so-called true fibrous cellulose, absorbent cotton, does not yield to this treatment. Also the material left after treatment contains cellulose which upon re-treatment yields but traces of fermentable sugar. Although authorities differ, it is claimed by some that the acid acts as a catalyser hydrolysing the lignone complex and a proportion of the "easily attacked cellulose." The oxycellulose and the "true cellulose" are said not to be seriously altered chemically.

It would seem that there is a possibility that a process might be evolved where the alcohol conversion of the wood pulp might be made first, and then the residue subsequently utilised for the production of paper pulp.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

GAS ANALYSIS AS AN AID IN FIGHTING MINE FIRES.*

By GEORGE A. BURRELL and FRANK M. SEIBERT.

Introduction.

The Bureau of Mines is conducting, as an essential part of the mine accidents investigations intrusted to it, an investigation of the factors involved in the origin and spread of mine fires, and of the means by which such fires may be prevented, limited, or extinguished. The authors, in connection with their work on mine gases, have made gas analyses and recorded observations on the condition of the atmosphere in mines. Some conclusions from their work are presented in this paper in the hope that they will be of service to those who may have to fight mine fires; for, although analyses of the gases from such fires have been made in the past, the systematic analysis of samples of the atmosphere of a burning mine or section of a mine has not received the attention its usefulness warrants.

In the early stages of a mine fire effort is directed toward fighting it at close range by using water from buckets, hose, or portable extinguishers, or by loading out the hot coal. Frequently this effort is not successful, and the mine or a section of it is sealed in order to smother the fire. Some fires gain such headway that the entire mine has to be flooded. This expedient, though effective, requires the use of an enormous quantity of water, not always easily obtained, and a subsequent expenditure of much money and time in draining the mine and putting it in working order.

Reasons for Sampling the Air of Sealed Areas.

When an entire mine, or a section of it, has been sealed to exclude air, the sampling of the atmosphere within the sealed area becomes desirable in order to determine the effectiveness of the stoppings or dams in excluding air. If the stoppings are tight, the fact is shown by a depletion of oxygen in the atmosphere behind them. A period of anxiety always follows sealing, and any aid that tends to allay fears as to whether the fire is spreading or enables the mine officials to act promptly in case conditions get worse, is worthy of consideration.

Another reason for the systematic collection and analysis of samples of air from the sealed area is to obtain information regarding the advisability of removing stoppings. Disastrous consequences have sometimes followed the premature reopening of sealed areas; moreover, fires have burned vigorously after external air was thought to be entirely excluded. Hence, stoppings are sometimes left in place for many months, and when they are eventually removed much uncertainty is sometimes felt as to the result.

The burning of coal and wood in a mine fire differs in some respects from the ordinary combustion of coal or wood in a boiler furnace; yet, just as periodic analyses of the escaping gases will indicate combustion conditions in the furnace, so periodic analyses of the atmosphere within a burning mine or section of a mine will indicate combustion conditions there, although these indications are less clearly understood and will be until some features of mine fires have been studied more fully.

Changes in Mine Air during Fires.

When a burning section of a mine has been successfully sealed, the atmosphere within changes in composition. It loses oxygen, and cannot support combustion. Then the coal, or wood, cools until re-admission of air cannot cause a blaze, and finally the temperature of the fire zone becomes normal. The cooling requires considerable time, because in a mine the embers and the hot coal are so excellently insulated that they cool slowly.

The principal changes in the composition of the atmosphere in a coal mine during a fire are as follows:—Oxygen is consumed in the burning of coal, and is absorbed by coal that is not on fire; carbon dioxide is produced, methane accumulates, and carbon monoxide and hydrogen form when the oxygen supply becomes insufficient for complete combustion.

Loss of Oxygen.

The atmosphere in a burning section of a coal mine loses oxygen not only by the combustion of the coal but by oxygen being absorbed by the coal. This absorption, which takes place at normal temperatures, appears to be mainly a chemical combination between the oxygen and certain unsaturated hydrocarbon compounds in the coal, and the rapidity with which it takes place depends upon the nature of the coal. The action may be so rapid that the fire plays only a minor part in depleting the oxygen of the air in the burning section. This is particularly the case when the area on fire is very small in proportion to the area enclosed. That such absorption takes place is fortunate, because the removal of the oxygen in an enclosed section is hastened, and the atmosphere more rapidly becomes incapable of supporting combustion.

The rapidity with which coal absorbs oxygen is shown by experiments performed by Porter and Ovitz in the course of their work upon the spontaneous combustion and

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* *Technical Paper* 13, Bureau of Mines, Washington.

destructive distillation of coal (" The Escape of Gas from Coal," *Technical Paper* 2, Bureau of Mines, 1911), Ten kilogrms. (22 pounds) of coal from Connellsville, Pa., absorbed, during the first day after mining, nearly one-half the oxygen in 10 litres of air. Slightly more than one-tenth as much carbon dioxide was produced as would have been produced had all of the oxygen absorbed combined with carbon to form carbon dioxide.

Parr and Barker (" Occluded Gases in Coal," *Bull.* 32, University of Illinois, 1909) also have shown that the absorption of oxygen by coal occurs rapidly, especially with freshly mined coal, and that the absorption is very noticeable even in samples of coal that have been mined two years.

The fact that oxygen is absorbed by the coal in mines is confirmed by the authors' analyses of many samples of mine air.

Production of Carbon Dioxide.

A very large proportion of carbon dioxide, more than 4 or 5 per cent, in the atmosphere of a sealed section of a mine is unusual except near the fire. Even in places where the oxygen has been entirely consumed, no large quantity of carbon dioxide has been found by the authors. A fire in a coal mine increases, of course, the total quantity of carbon dioxide produced, but if the samples collected from a closed section represent fire gases diluted by the atmosphere of those parts of the section that are not on fire, the carbon dioxide found is by no means proportionate to the oxygen consumed in the fire. This deficiency of carbon dioxide results from the absorption of oxygen by the coal without (as is largely the case in the combustion of coal in a boiler furnace) the formation of a proportionate quantity of carbon dioxide.

Accumulation of Methane.

In some mines methane escapes from the coal in large quantities, and under extreme conditions the atmosphere in some places may contain 50 per cent or more of methane in a very short time after becoming stagnant. On the other hand, samples collected by the author from workings in which the air had been stagnant for several months did not contain methane enough to form an explosive mixture even if the proportion of oxygen had been sufficient.

In a mine fire methane is undoubtedly formed from the burning coal, and such methane is added to that escaping from pores and cracks in the coal not on fire; but because the area on fire may be small as compared with the total space enclosed, the proportion of methane produced by the fire may be small throughout the larger part of this space. In one instance, samples collected directly over a fire contained only about 1 per cent more methane than samples collected behind a stopping 2000 feet from the fire.

Production of Carbon Monoxide and Hydrogen.

Usually the oxygen supply in a burning section of a mine is quickly reduced; then incomplete combustion begins, and hydrogen and carbon monoxide form at the fire. Carbon monoxide is so poisonous that deadly proportions are liable to be present in all parts of the section.

Samples of gases collected by the authors near a fire, where the coal was intensely hot and the oxygen content of the mine atmosphere was only 2 per cent, contained 1·5 per cent of carbon monoxide. The part that carbon monoxide plays in gas explosions during mine fires has aroused considerable conjecture, but the data thus far accumulated by the Bureau of Mines indicate that the danger from the formation of explosive mixtures of carbon monoxide, or of hydrogen, is subordinate to the danger from methane, because in some mines methane accumulates rapidly in any place where the atmosphere becomes still, and enough is soon present to form an explosive mixture with an inrush of air.

The explosive limits of a mixture of carbon monoxide and air lie between about 14 per cent (low limit) and 75 per cent (high limit) of carbon monoxide. The limits for a mixture of methane and air lie between about 5·5 per cent (low limit) and about 13 per cent (high limit) of methane. These limits apply to ignition of the gas at ordinary temperatures and pressures by an electric spark. Other methods of ignition, changes in the shape of the containing chamber, differing pressures and temperatures, change them somewhat. For example, Clarence Hall, explosives engineer of the Bureau of Mines, found that mixtures of natural gas and air used by him in testing explosives could be ignited by the flash of a blown-out shot of black powder when as little as 4·07 per cent of gas was present (see Note), whereas the authors, using an electric spark and confining the gas-air mixture in a Hempel explosion pipette, could not ignite a mixture containing less than 4·8 per cent of gas, and with this percentage of gas obtained only a slight inflammation throughout the mixture. The explosion was not strong until the mixture contained 5 per cent of gas.

(Note.—The inflammation, which was not violent, was produced by a flame from 1000 grms. of black powder. The charge was placed unstemmed in the bore hole of the cannon, and fired in 630 cubic feet of an atmosphere that contained 4·07 per cent of natural gas).

As the necessary proportion of carbon monoxide has not been detected in the after-damp gases the authors have examined, they believe that the possibility of explosions from the formation of carbon monoxide and air mixtures is remote. Still a point would undoubtedly be reached at which the addition of less than an explosive proportion of carbon monoxide to a non-explosive proportion of methane would result in the formation of an explosive mixture. Experiments along this line have not been conducted.

The production of hydrogen in a fire area seems to be even less than that of carbon monoxide, hence the danger from the formation of explosive mixtures of hydrogen is still more remote.

Production of other Combustible Gases.

Other combustible gases, such as ethylene (C_2H_4), may be produced by a fire in a mine, but seemingly they are formed in such small proportions that their value in indicating the progress of the fire, as shown by gas analysis, or their importance as factors in explosions, need hardly be considered.

Extinction of Flame.

Experiment shows that the flame of a candle or of a miner's open lamp is extinguished when the oxygen content of the surrounding air falls to about 16 or 17 per cent. Clowes (F. Clowes and B. Redwood, " Detection and Measurement of Inflammable Gas and Vapour in Air," 1896, p. 149) in experiments with atmospheres that would not support flames found, by allowing a candle to burn out in a closed vessel containing ordinary air, that the composition of the atmosphere in which the candle flame was finally extinguished by lack of oxygen was as follows:—Oxygen, 16·05; carbon dioxide, 3·15; nitrogen, 80·80 per cent.

The composition of the residual atmospheres in which other flames were extinguished was as follows (*Idem*, p. 165):—

Composition of Residual Atmospheres that Extinguished Flames.

Flame.	Percentage composition of atmosphere.		
	O_2.	CO_2.	N_2.
Hydrogen	5·50	—	94·50
Carbon monoxide	13·35	12·25	74·40
Methane	15·60	2·30	82·10
Coal-gas (Nottingham) .	11·35	4·90	83·75

The authors obtained the following results by placing flames in a gas-tight bell-jar, and allowing them to burn out:—

Composition of Residual Atmospheres that Extinguished Flames.

Flame.	Percentage composition of atmosphere.		
	CO_2.	O_2.	N_2.
Wolfe lamp	3·00	16·50	80·50
Atetylene lamp	6·30	11·70	82·00
Natural gas (*a*)	3·25	13·90	82·85
Candle	2·95	16·24	80·81

(*a*) CH_4, 82; C_2H_6, 16·4; N_2, 1·5; CO_2, 0·1 per cent.

To determine the uniformity of composition of the residual air three samples were taken in each experiment. One sample was taken at about the height of the flame, as soon as the flame went out; a second at the top of the jar, immediately afterward; and a third, ten minutes later. In each experiment the analyses of the three samples agreed within 1 per cent. The figures given in the table are the average of the three determinations.

In experiments such as these a flame undoubtedly burns in atmospheres containing slightly less oxygen than would support it under mining conditions, because there is no chance for a slight gust of air or a jerk of the lamp to extinguish it prematurely.

Although a mine fire that is well under way when stoppings are built may continue to burn in an atmosphere containing less than 15 or 16 per cent of oxygen, yet the above results afford some basis for estimating the amount of inleaking oxygen required to keep a fire burning or to cause a smouldering fire to burn more strongly. The following information, collected by the Bureau of Mines, is instructive :—

A fire in a heavily timbered stope in a metal mine had been brought under control by sealing the section, but as air was slowly admitted to re-open the section, the fire blazed when the oxygen content of the atmosphere reached 17 per cent. A fire in a timbered airway of an anthracite mine burned more vigorously when the atmosphere of the airway contained approximately 17 per cent of oxygen. In each of these cases, of course, the fires had smouldered in an atmosphere containing a smaller percentage than this.

Conclusions as to the approximate length of time a sealed mine or section of a mine should remain closed after a fire has been brought under control are hard to reach, because conditions differ at different fires. However, it is certain that analysis of a sample of the atmosphere in the mine or section will show whether the fire is well sealed, and will enable more intelligent conclusions to be drawn regarding the length of time that stoppings should be kept up. When the oxygen in an area is almost or entirely consumed, combustion necessarily must cease, and the question then is how long the embers can retain heat sufficient to cause them to re-kindle on the admission of air.

(To be continued)

MEMORIAL TO DISCOVERER OF OXYGEN.

Sir Edward Thorpe Unveils Statue of Dr. Joseph Priestley.

The greatest scientist of the eighteenth century—Dr. Joseph Priestley—was honoured by his fellow townsmen at Birstall, near Leeds, on Saturday last, when Sir Edward Thorpe, one of the greatest present day scientists, unveiled a magnificent bronze statue, erected by public subscription at a cost of £700.

Dr. Priestley has been termed "the father of modern chemistry." Born at Fieldhead, Birstall, in 1733, he showed from his earliest days a strong bent towards the study of nature. He did not devote himself seriously to physical science until 1766, when, encouraged by his new-found friend, Benjamin Franklin, he wrote a "History of Electricity," which was published in the following year and met with considerable success. The first outcome of Priestley's chemical work published in 1772 was of a very practical character. He discovered the way of impregnating water with an excess of "fixed air" or carbonic acid, and thereby producing what is now known as soda-water. In the same year Priestley communicated the extensive series of observations, which his industry and ingenuity had accumulated in the course of four years, to the Royal Society, under the title of "Observations on Different Kinds of Air," which was regarded as of so much merit and importance that the Society at once conferred upon the author the highest distinction in their power by awarding him the Copley Medal. In 1772 Priestley accepted the nominal post of librarian to Lord Shelburne, with whom he remained seven years. During this time his patron assisted Priestley in his scientific researches, financially and otherwise. Priestley next went to Birmingham, where he was placed within the reach of the best makers of apparatus of the day. He became a member of that remarkable "lunar" Society, at whose meetings he exchanged thoughts with such men as Watt, Wedgwood, Darwin, and Boulton. Priestley had by this time become confirmed in Unitarian beliefs, and at the time of the French Revolution he and his friends were held up to public scorn. Priestley was regarded as an enemy to Church and King, and in 1791 the loyal and pious mob, who, unchecked, and to some extent encouraged by those who were responsible for order, had Birmingham at their mercy for three days. Chapels and houses of the leading dissenters were wrecked, and Priestley and his family had to fly for their lives, leaving library, apparatus, papers, and all their possessions a prey to the flames. Priestley emigrated to the United States (where his posterity still flourish), where he died on February 6th, 1804.

It was whilst living with Lord Shelburne at Calne, in Wilts, that Priestley made the great discovery of his life—the discovery of oxygen. He had prepared an unknown gas, and in a spirit of curiosity thrust a lighted candle into the phial containing the gas, when suddenly, to his amazement, the flame blazed up in great splendour. The unknown gas was oxygen. In the monument which was unveiled on Saturday last, Priestley is shown in the supreme moment of his life. In his right hand he holds a lighted candle, and in his left an inverted bell-jar, at which he is gazing with an expression of intentness. In other statues of the great scientist at Birmingham, Leeds, and Warrington, a sun-glass is held in one hand and a pestle and mortar in the other. Priestley's reputation as a man of science rests upon his numerous and important contributions to the chemistry of gaseous bodies. His achievements are truly wonderful, when the disadvantages under which he laboured are considered. Without the careful scientific training of Black, without the leisure and appliances secured by the wealth of Cavendish, Priestley scaled the walls of science, trusting to mother wit to supply the place of training and ingenuity to create apparatus. By using a lighted candle as his mode of heating, Priestley discovered more gases than all his predecessors had done. He laid the foundation of gas analysis; discovered the complementary actions of animal and vegetable life upon the constituents of the atmosphere; and finally crowned his work by the discovery of that "pure dephlogisticated air" to which French chemists subsequently gave the name of oxygen. For these brilliant discoveries the Royal Society elected Priestley a Fellow, and gave him their Medal, while the Academies of Paris and St. Petersburg conferred membership upon him. Edinburgh had made him an Honorary Doctor of Laws at an early period of his career, but he received no recognition from the Universities of his own country. That Priestley's contributions to the knowledge of chemical fact were of the greatest importance is unquestionable when it is considered that the labours of Laplace, Young, Davy, Faraday, Cuvier, Lamarck, Robert Brown, von Baer, Schwann, Smith, and Hutton have been carried on since Priestley discovered oxygen. Amongst Priestley's other discoveries and inventions were nitrous oxide, sulphurous acid, hydrofluoric acid, ammoniacal gas, nitric oxide, fluosilicic acid, light carburetted hydrogen, carbonic oxide, and the pneumatic trough, &c.

The unveiling ceremony was a distinct success, and amongst those who paid their tribute to Priestley the Unitarian Divine, the fearless defender of rational freedom in thought and in action, the philosophic thinker, and that Priestley who held a foremost place among "the swift runners who hand over the lamp of life," and transmit from one generation to another the fire kindled, in the childhood of the world, at the Promethean altar of Science, were Sir Edward Thorpe, Prof. Sadler, Vice-Chancellor of Leeds University, Prof. Smithells, head of the Science Department of Leeds University, and Mr. Walter Runciman, M.P., Minister of the Board of Agriculture.

NOTICES OF BOOKS.

The Energy System of Matter. By James Weir. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

Although this book is written with more restraint than is usual in works of its nature, the author states his conclusions in such a controversial way that he will inevitably awaken the strenuous opposition of the bulk of his readers, who will perhaps find it difficult to give him his due. He believes that each planet forms a perfect complete self-contained energy system, thus rejecting the theory of the transmission of energy through planetary space, and he endeavours to verify this conclusion by reference to terrestrial phenomena. It is difficult to understand his attitude towards hypotheses, and, in fact, it seems impossible to believe that he actually realises the import of his statement that it is impossible to get behind or beyond phenomena, "the inscrutable manifestations of Nature." He appears to believe firmly that eminent scientific men attempt to rule the results of experiments into line with accepted theories. But the book is worth reading for its discussions of the transformations of energy and transmission processes.

Problems in Physical Chemistry. By Edmund B. R. Prideaux, M.A., D.Sc. London: Constable and Co., Ltd. 1912.

This book contains a complete course of numerical examples illustrating the most important work which has been done in physical chemistry. The examples are arranged in sections, each of which is prefaced by a brief explanatory introduction. The answers to the examples are given, and some hints as to methods in cases of difficulty. Full references are given to the sources from which the examples have been drawn. The course, which contains some problems of moderate difficulty, has been worked through by a class of advanced students at Liverpool University, and the exercises are arranged approximately in order of difficulty. Practical men as well as students will find it worth their study, for it will give them a good insight into modern quantitative principles and methods in physical chemistry.

Experimental Science. II. *Chemistry.* By S. E. Brown, M.A. (Cantab.), B.A., B.Sc. (Lond.). Cambridge: University Press. 1912.

This book represents the experience of a thoroughly practical teacher who has weighed the advantages of the old and new methods of teaching the science, and has extracted the best from both and so worked out a really useful course. It is intended for boys from twelve to sixteen years of age, who should be able to work through it in two years, giving two hours a week to the subject. It opens with an introductory chapter on apparatus and general laboratory methods; then physical and chemical change, elements, and compounds and mixtures, are taken up in succession. The students are expected to perform the experiments and deduce the results for themselves, and their natural ingenuity and originality are never damped, as was so often the case in the old method, while at the same time at the end of the course they would really have gained some knowledge of the facts of chemistry of which the heuristically trained student is often surprisingly ignorant. The course possibly covers rather too wide a ground, and the explanations and experimental directions are occasionally somewhat condensed, and it would be advisable for the student, at any rate, towards the end of his course, to do some extra reading. The chapters are always short and there are many summaries and tables, which serve to make the main facts clear; the smaller type, in which a good deal of the book is printed, is too minute for a school book.

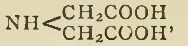
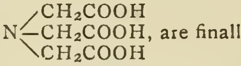
CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 7, August 12, 1912.

Syntheses of Glucosides of Alcohols by means of Emulsine.—Em. Bourquelot and M. Bridel.—The β-butyl, β-isobutyl, and β-allyl glucosides can all be prepared from the corresponding alcohols by means of emulsin. In the case of butyl and isobutyl alcohols it is necessary to use excess of glucose, so that the alcohols remain saturated, and thus good yields are obtained from small quantities of alcohol. β-Butyl glucoside crystallises in colourless needles; it is inodorous, has a bitter taste, and is hygroscopic. Its rotatory power is $-35{\cdot}4^\circ$. β-Isobutyl glucoside is not hygroscopic. Rotatory power $= -34{\cdot}96^\circ$. Melting-point, 99—100°. β-Allyl glucoside is colourless and hygroscopic; it melts at 96°, and its rotatory power is $-40^\circ\ 34'$.

Berichte der Deutschen Chemischen Gesellschaft, Vol. xlv., No. 10, 1912.

Action of Potassium Cyanide on Formaldehyde.—Karl Polstorff and Hermann Meyer.—When formaldehyde and potassium cyanide react the first product is the potassium compound of glycollic acid nitrile. This is hydrolysed to give glycollic acid and ammonia, and the latter reacts with the unchanged nitrile, giving aminoacetonitrile and water. From the two nitriles diglycollamide acid,  $NH{<}\begin{matrix}CH_2COOH\\CH_2COOH\end{matrix}$, and triglycollamide acid,  $N\begin{cases}CH_2COOH\\CH_2COOH\\CH_2COOH\end{cases}$, are finally formed.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Soluble Indigo.—Can any reader inform me if it is possible to obtain a soluble indigo which will not become reduced by the sugars; or if there is any process by which the colour of indigo may be rendered fast in the presence of sugars?—A. E. P.

MEETINGS FOR THE WEEK.

Friday, 25th.—Physical, 5. "Constitution of Mercury Lines Examined by an Echelon Grating and a Lummer-Gehrcke Plate," by H. Nagaoka and T. Takamine. "Mutual Inductance of two Coaxial Circular Currents," by H. Nagaoka. "Absorption of Gas in Vacuum Tubes," by S. E. Hill.

THE CHEMICAL NEWS.

Vol. CVI., No. 2761.

A NEW METHOD FOR THE DETECTION OF TRACES OF ARSENIC AND ANTIMONY.

By DONALD R. STADDON.

The following exceedingly delicate reaction affords a reliable test for traces of arsenic and antimony:—

From 0·5 to 2 grms. of the substance suspected to contain compounds of either of the above metals is dissolved in about 5 cc. water. From 0·5 to 2 grms. of sodium hydrosulphite, known in commerce as "blankit," is then added to the above solution, and the whole warmed. Rapid reduction takes place, and on allowing to stand for a few seconds precipitation of finely divided arsenic or antimony occurs. The precipitate varies in colour from light to dark brown in proportion to the amount of arsenic or antimony present in the original substance.

A solution of sodium hypochlorite dissolves the precipitate due to arsenic, the antimony remaining suspended.

Acids and acid salts are, of necessity, neutralised with arsenic and antimony free alkali before the application of the above test. Owing to its simplicity, in addition to its delicacy, for qualitative work the method might well be adopted as a substitute for the more tedious Marsh's test.

As 1 part sodium arsenite (containing 57·692 per cent arsenic) dissolved in 50,000 parts of water may be readily detected by the above method, the extreme sensitiveness of the reaction is evident.

CRYSTALLOCHEMICAL ANALYSIS.

By T. V. BARKER, B Sc., M.A.,
Demonstrator of Mineralogy, Oxford.

A method of identifying a substance without destroying it by a chemical analysis is of such supreme importance to chemistry that no apology is needed in laying a short description of it before chemists. This is all the more necessary since two articles on the subject which have recently appeared seem to be open to misapprehension in several directions. The writer is in a position to give first hand information, since he has not only had the privilege of working over a year with the discoverer of the method —Prof. Fedoroff—in St. Petersburg, but has also taken a minor part in perfecting the method.

In the literal sense of the term the method is not one of "analysis," but rather of "identification." Now several methods of identification are known, and in particular cases may be of such value as to make an ultimate chemical analysis unnecessary. Thus, the melting-point is a very useful property; its application, however, is quite restricted, since the presence of a small amount of impurity may lead to erroneous result. Again, even if the purity of the substance is beyond suspicion, the method is greatly circumscribed, inasmuch as there are scores of substances which have melting-points lying within the range of experimental error. On account of this, melting-point determinations are generally carried out, either as a test of purity or as a means of discriminating between one or two alternatives. It is obvious that a melting-point determination can never replace a quantitative analysis in cases where absolutely nothing is known concerning the origin and nature of the substance to be tested.

The real drawback to the use of a single property like that of the melting-point is that it is "scalar," *i.e.*, a property the characterisation of which does not involve *direction.* Other examples of scalar properties are the specific gravity, molecular weight, and boiling-point. Now it is clear that if two independent scalar properties, say, melting-point and specific gravity, were determined for every substance, they could be subsequently employed for identification purposes; and it is highly improbable that any two substances would exhibit the same values for both properties, so that identification might almost be regarded as absolutely certain. Needless to say, the two properties must be of a totally independent character; if, for example, the specific gravity were a linear function of the melting-point, the employment of both methods would possess but little advantage over the employment of but one of them. The addition of a third scalar property, say, the boiling point, would make identification absolutely sure. The drawback to the employment of a combination of scalar properties is that quite different operations demanding the use of different kinds of apparatus are necessary, which also usually involve the expenditure of a considerable amount of time.

In addition to the scalar properties there are others of a different nature, known as *vectorial.* The difference between the two classes of properties is that the former represent the nature of a substance in the mass, while the latter can only be defined with reference to a direction. Examples of vectorial properties are those which involve motion, *e.g.*, conduction of heat or velocity of light. Now the numerical values of such vectorial properties in crystalline material are generally found to vary with the direction investigated. Thus, two rays of light traversing a crystal along two mutually perpendicular directions have, as a rule, different velocities, or what amounts to the same thing, different refractive indices; nor is there any ascertainable relationship between the two. It is evident that if all crystalline substances were subjected to a thorough optical investigation and the results incorporated into two tables, then any given substance could be subsequently identified. Optical determinations, however, of a sufficient degree of accuracy demand such an expenditure of time and labour that an identification by such means is impracticable. It may be mentioned that optical methods are almost wholly used in the study of rocks, since the number of common minerals does not exceed twenty, which differ so greatly in optical behaviour that a simple examination of a thin slice in a polarising microscope is ample for identification.

There is, however, a vectorial property which is capable of easy determination; this is the geometrical form of the crystal. With certain reservations it may be stated that the crystalline form of a substance is characteristic of the chemical species; *i.e.*, not only are all crystals of a particular substance alike, but also the interfacial angles on a crystal of one substance are different from those on a crystal of any other substance. A complete measurement of all the angles on an average crystal may be effected by a skilled operator in an hour, provided the most recent labour-saving type of measuring instrument (goniometer) is used. It is seen that the crystalline form satisfies all reasonable conditions demanded of a suitable physical method of identification. When any substance has been carefully measured its geometrical form is known once for all. About ten thousand substances have been measured, and perhaps more than half of these date back some forty years. The question might well be asked—Why has a geometrical method of identification (crystallochemical analysis) not been previously developed by crystallographers and been placed at the disposal of chemists? The answer is that such great difficulties stood in the way of classifying the material—making up the identification table—that no one before Fedoroff had succeeded in turning the property to determinative purposes; nay more, it is questionable whether any one before him has even attempted the solution of the problem.

The reader is now asked to keep in his mind the general nature of a solid body bounded by plane faces; the polyhedra cut out of glass which are often used as paper weights will serve mentally as admirable models. In general when the model is held so that two faces are vertical, there will be a face on the top which is practically horizonal and the remainder of the faces will occupy sloping positions. Provided the model has not a simple symmetrical form like that of a cube, it is evident that there are many different ways of holding the model so that two faces shall be vertical; and it is practically certain that if such a model were handed successively to a number of students each would adopt a different way of setting it up. This is exactly the difficulty in describing many crystals, and is precisely the one which has to be cleared up before identification by means of the crystalline form becomes a practicable process. Since a crystal generally exhibits a considerable number of faces it will readily be understood that the possible number of settings is very great. Cases are frequent in which a chemical substance has been measured at different times by independent observers, with the result that settings have been adopted so greatly different as to hide identity.

The necessity for the discovery and application of definite principles enabling one to set up every crystal in a standard position will now be clear—if the crystalline form is to be used for purposes of identification and not merely as a property of subordinate interest. These principles have been discovered by Fedoroff: from the measured angular values he is able to indicate what pair of faces are the true vertical faces ("prism faces"), what face is the true top face ("basal plane"), and which one of the many sloping faces ("pyramid faces") is the most important. Having determined this correct setting, the rest is comparatively easy. The values of the following five angles are noted:—The angle between the two prism faces; the angles which the basal plane makes with each of the prism faces and also with the pyramid face; and finally, the angle which the pyramid face makes with either (it does not matter which) of the prism faces. When all these five angles, which may be termed the *characteristic angles*, are independent, it is seen that the possibility of two given substances exhibiting even approximately equal values for all five angles is out of the question.

In a certain number of crystals the five angles are really independent of each other; such crystals are said to belong to the triclinic system. In other cases the five angles are not wholly independent, for given three out of the five the remaining two can be calculated from them by simple trigonometrical methods; these crystals are "monoclinic," and the possibility of two substances exhibiting approximation in three independent values is highly remote. The next system is the "orthorhombic," in which all crystals are characterised by two independent angles, so that there is practically no possibility of any two substances having the same values for both. Then there are two systems, the hexagonal and tetragonal, in which there is only one characteristic independent angle. Consequently it might appear that the crystalline form loses all value for purposes of identification. But in practice it is found that the number of substances actually crystallising in these two systems is so small that no difficulty ever arises in distinguishing them from each other. The last system to be mentioned is the cubic; which is characterised by the fact that there is no difference in the angular values for the most diverse substances crystallising in that system. The method of identification, then, breaks down altogether for cubic substances. Fortunately their number is comparatively small, and what is still more fortunate is that compounds of complicated chemical composition, for which the new method is obviously most useful, generally crystallise in systems other than the cubic. Since the new method is one of identification by means of measurable properties, its application to any particular case presupposes that the substance has already been measured. The number of measured substances is rapidly increasing, and the applicability of the method is becoming thereby more and more general.

It is not without almost unthinkable labour that Fedoroff has been able to carry his method to a triumphant conclusion. It must be borne in mind that the correct setting has had to be determined by him for every one of the ten thousand substances which have been measured. Then methods have had to be thought out by means of which this vast mass of material can be arranged in catalogue form so as to permit of easy reference. A description of the methods of sub-classification adopted is beyond the scope of this article. It is sufficient to mention that the matter is arranged in order of the values of the five (or fewer) characteristic angles, so that the "Index" compiled by Fedoroff is one according to these angular values, and not according to chemical composition. Fedoroff has devised a system of symbols of an algebraic character in which the critical angles are introduced; the geometrical form of each substance is epitomised in its appropriate symbol.

The method of determination can now be indicated. Suppose one or possibly two crystals of an unknown substance, weighing a few centigrms. or perhaps less, be supplied for identification. The crystal is measured on the goniometer, and an inspection of the angles will prove what system the crystal belongs to. If it does not prove to be cubic, the method is applicable. By a study of the measured angles, the correct setting is determined. Then the values of the five (or fewer) characteristic angles are noted. The index is looked up, and as a rule the substance is at once recognised. If no substance in the index corresponding to the one measured is found, two alternative conclusions are possible; either the substance has never been previously described and consequently has not been incorporated into the index, or the method has failed. Cases in which the method fails are invariably those where the given crystal is so imperfectly developed that the angles are untrustworthy, or where the number of faces will not admit of the measurement of the five (or fewer) characteristic angles.

The time occupied by Prof. Fedoroff in identifying a substance is on the average about two hours.

With regard to the preliminary trials undertaken with the view of testing the trustworthiness of the method, it may be stated that Prof. Fedoroff has discovered the identity of certain crystalline specimens (the labels of which had been lost) belonging to the Museum of the Imperial School of Mines in St. Petersburg; he also requested the co-operation of three or four continental colleagues and of the writer, who endeavoured in his choice of material to test the new method as severely as possible. The writer asked for some specimens of Dr. Tutton, who courteously sent five. Six others were kindly remitted by Messrs. Colgate and Rodd, through Prof. H. E. Armstrong; the remainder were contributed by workers in the Chemical and Mineralogical Departments of the Oxford University Museum, and included many specimens which were kindly supplied by Messrs. Chattaway, Drugman, and Marsh. The total number of specimens thus collected was fifty, each specimen being designated by a number—and Fedoroff successfully identified forty-eight. The forty-ninth substance was proved by Fedoroff to be one which had not previously been measured. Crystals of the fiftieth substance were not sufficiently developed to admit of a successful determination. The success attained by Fedoroff was not so great with the specimens furnished by his Continental colleagues; the reason being that crystals with bright smooth faces were not specially chosen, and the angular readings were often untrustworthy. The majority of the fifty sent out from Oxford had been recrystallised by the writer, so that this material was more hopeful. It is seen that in Fedoroff's hands the new method is almost infallible with well crystallised specimens; when crystals of every degree of perfection are taken into account, successful results accrue in about eighty per cent of the cases.

The correctness of the settings suggested by Fedoroff for the ten thousand substances already measured is now being verified by certain methods of calculation. In very few cases indeed has a revision of the setting been necessary. In conjunction with MM. Artemieff and Sokoloff (who are also pupils of Prof. Fedoroff), the writer has taken part in revising some of the results; when the work is completed the Index will be published, after which it will be possible for any one acquainted with crystallography to carry out the identification. As no adequate description of the method of working has yet appeared except in Russian, the writer has undertaken the preparation of a full account in book form, which will appear in due course.

Enough has already been said to show that the method of identification as at present practised by Fedoroff is purely geometrical. It is true that he intends to avail himself of the optical properties, but only in those cases where the geometrical form is not well developed. The instrument used for measurement is the two-circle goniometer, the first type of which was devised by Fedoroff himself. The employment of the older forms of instrument, *i.e.*, the single-circle goniometer, is of course not excluded, but its use involves a greater expenditure of time and labour. In the determination of the optical properties Fedoroff will naturally use his new appliances, which were exhibited by the writer some four years ago before the Mineralogical and Geological Societies. These instruments may be said to mark an advance in the optical direction which is only equalled by the improvement he has made in the geometrical methods of investigating crystals.

It must now be mentioned that Fedoroff does not pretend to distinguish between isomorphous substances, since goniometrical measurements of such substances, no matter how carefully they be carried out, are with average material not sufficiently reliable for purposes of identification; the reason being that unless great care be taken to obtain good crystals, the small differences of angles can not be depended upon, and at any rate the evidence is greatly inferior to that obtained from a simple qualitative test, which soon decides which of the possible isomorphous compounds the substance really is. Fedoroff's identifications of some of the substances were therefore given in the form: —"Ammonium zinc sulphate or some substance isomorphous with it."

The success of the whole method obviously depends on the discrimination of the correct setting of the crystal; what are the principles underlying this discrimination? It might be thought that a purely empirical method if applied sufficiently intelligently would serve; but any one who has worked with crystals would speedily negative such a possibility, and as a matter of fact no one in the past has ever succeeded in devising a workable method of classifying crystals according to their angular values. The principles used are not arbitrary, but have been developed from the theory of crystal structure, and are in full consonance with the general physical properties of crystals. The genius of Fedoroff is of a many-sided character, but the geometrical faculty is perhaps most prominent; for looking back it is easy to trace the gradual development of this highly practical method of analysis from his first writings on pure geometry, which go back to the early eighties. His later work on the geometrical theory of crystal structure may be truly regarded as the immediate support on which the edifice of crystallochemical analysis rests. No researches which have been published since Fedoroff commenced his work have in the least contributed to the actual synthesis of the new method. It is true that contemporary publications of crystal measurements serve to extend the general applicability of the method; for no substance can be identified which has not already been measured and incorporated into the Index. It must be remembered that incorporation entails a previous determination of the correct setting; for it is the practice of all contemporary crystallographers without exception to describe their crystals on the usual lines, which are somewhat arbitrary and in some cases merely fortuitous; which haphazard and almost empirical procedure is now replaced by a rational, systematised, and almost infallible method.

The intermediate stages between Fedoroff's work and the fundamental beginnings of crystallography on which it ultimately rests, are represented by the mathematical studies of those investigators who helped to build up the structure theory during the first three-quarters of the nineteenth century. The fundamental laws of crystallography which were enunciated by Haüy in the latter part of the eighteenth century, and amended by Mitscherlich in about 1820, are of course the bed-rock on which everything in crystallography rests. Haüy proved, as far as his imperfect instrument allowed, that each substance has a characteristic crystalline form. The later invention of the reflecting goniometer by Wollaston in 1812 gave crystallographers an instrument of precision, and its employment by Wollaston and still more by Mitscherlich proved once for all:—First, that crystals of one and the same substance have always the same primitive form (*i.e.*, exhibit faces inclined at characteristic angles) except in those cases where a difference in form is the result of polymorphism; secondly, that the angles of isomorphous substances differ by measurable amounts, with the exception of those which crystallise in the cubic system. These results have always been tacitly accepted, and nothing that has been done since then has served to modify essentially the Mitscherlich-Haüy conclusions.

BENZENE STRUCTURE REVIEWED FROM THERMOCHEMICAL STANDPOINT.

II.

By W. TOMBROCK.

To give the long deduction previously developed (Chemical News, cvi., 155) a simplified and more comprehensive form, we may reduce the question into one equation (wherein combustion heats are represented by chemical symbols):—

$$\underset{\text{Hexane.}}{C_6H_{14}} \quad \underset{\text{Benzene.}}{C_6H_6} = 4H_2 \; . \; . \; . \; + r \text{ cals.}$$

If benzene might thermochemically be considered an aliphatic body the value of r should prove to be ± 0.

Now this is not the case, for we get—

$$r = 991{\cdot}2 - 784{\cdot}1 - 4 \times 37{\cdot}7 = 56{\cdot}3 \text{ cals.}$$

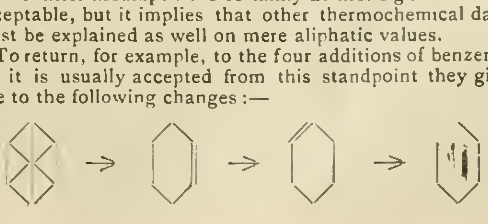
And this energetic difference must obviously be ascribed to the aromatic (closed ring) character of benzene.

Now, this energy ($r = 56{\cdot}3$ cals.) may be required for ring breaking—*i.e.*, for severing two carbon atoms in the benzene ring—and on this assumption Kekulé's formula turns out to be tenable. But I must agree here with Mr. Stanley Redgrove (Chemical News, cvi., 173) that this supposition implies already the assumption of Kekulé's structure. For supposing a ring closing to be the only difference between aliphatic and aromatic body means for this case to consider benzene merely a ring closed hexatriene.

On the other hand, explaining this energy ($r = 56{\cdot}3$ cals.) as to be necessary for four single bonds ($4 \times 14{\cdot}7 = 58{\cdot}8$) as it is done by Thomsen ("Thermochemistry," Ramsay Series, p. 394), implies the assumption that the thermical values found for aliphatic bodies are equally applicable to the aromatic series, or at least that the difference in character between aliphatic and aromatic bodies causes no appreciable difference in their thermochemical behaviour.

The latter assumption is certainly at first sight the more acceptable, but it implies that other thermochemical data must be explained as well on mere aliphatic values.

To return, for example, to the four additions of benzene. As it is usually accepted from this standpoint they give rise to the following changes:—



The first addition causes the loss of three single bonds, and the conversion of two C.C links into two C:C links.

The energy therefore required amounts to—

$$3 \times 14{\cdot}7 + 2(14{\cdot}7 - 13{\cdot}3) = 46{\cdot}9 \text{ cals.}$$

Even when taking the true addition heat to be as great as 32 cals. we get the thermical effect of—

$$-46{\cdot}9 + 32 = -14{\cdot}9 \text{ cals.}$$

whereas is found 0·8 cal.

Thus it is clear that the evidence given by this abnormal addition heat does not justify the assumption of the nine bonds and the use (without more) of aliphatic thermical values for benzene.

Also, the other additions calculated in this way give differences with the values found from about 4 to 7 cals.

So the influence of the aromatic character (closed ring structure) seems to be at least *not* inconsiderable for these cases.

Briefly resuming this discussion we write :—

1. The deduction made on p. 155–156 (Chemical News, vol. cvi.) has no argumentive value whatever for Kekulé's formula. It is, indeed, as Mr. Stanley Redgrove has observed, a vicious circle.

2. The combustion heat of benzene may be explained by Kekulé's formula when we ascribe to the influence of ring closing about—

$$56{\cdot}3 - 14{\cdot}7 = 41{\cdot}6 \text{ cals.}$$

Or, as we may put it more generally, when we assume the thermical influence of the aromatic character to be considerable.

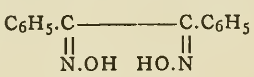
3. The combustion heat of benzene may be explained by Armstrong and Baeyer's formula on assumption that the energy necessary to the breaking of the ring is inconsiderable, or that the influence of aromatic nature on thermical processes may be neglected.

Utrecht, October 14, 1912.

THE DIOXIMES OF BENZIL.

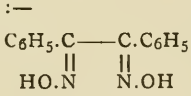
By W. E. GARNER.

The structural formulæ of the dioximes of benzil have been determined by the Beckmann transformation, and the α-, β-, and γ-forms are formulated as follows (Beckmann and Koester, *Ann.*, 1893, cclxxiv., 15) :—

(α) 

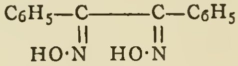
$$\begin{array}{ccc} C_6H_5.C & \text{———} & C.C_6H_5 \\ \| & & \| \\ N.OH & & HO.N \end{array}$$

M.p. 237° C.

(β) 

$$\begin{array}{ccc} C_6H_5.C & \text{——} & C.C_6H_5 \\ \| & & \| \\ HO.N & & N.OH \end{array}$$

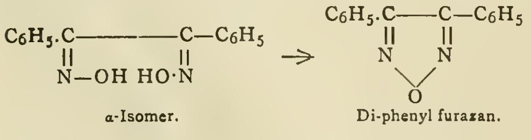
M.p. 206—207° C.

(γ) 

$$\begin{array}{ccc} C_6H_5{-}C & \text{——} & C{-}C_6H_5 \\ \| & & \| \\ HO{\cdot}N & & HO{\cdot}N \end{array}$$

M.p. 164—166° C.

Previously, it had been shown by V. Meyer and K. Auwers that these oximes gave diphenyl furazan by the elimination of water, aad that the reaction proceeded more readily with the γ-oxime than with the α-oxime, which behaviour could not be accounted for by the above formulæ.

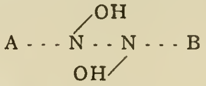


α-Isomer. Di-phenyl furazan.

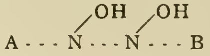
In these formulæ all of the atoms composing the molecule are depicted as lying in one plane, and this condition is difficult to represent by means of an ordinary space model. This is especially the case with the α-compound, for here, owing to the proximity of the nitrogen atoms, there is but little space for the hydroxyl groups.

But if these groups lie outside the molecular plane, then the above difficulties are removed, since formulæ can be proposed which are in agreement with the whole of the chemical evidence.

This is illustrated in the following diagrams, where A.B. represents the molecular plane :—



α-Oxime.



γ-Oxime.

In this method of formulation the two hydroxyl groups are nearer together in the γ-compound than in the α-compound. Thus the former the more readily yields di-phenyl furazan.

Chemical Department,
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VALENCY AND THE EVOLUTION OF THE ELEMENTS.

By M. d'A. ALBUQUERQUE.

For some time I have regarded certain facts in chemistry, such as similarity, affinity, instability, &c., as depending upon the internal constitution of the atoms, undoubtedly bearing some relation to the genetic formation of these atoms. I could, however, find no explanation of these facts until I heard of the phenomena of vacuum tubes, of radiant matter, of cathodic projections, and finally of radio-active substances bringing about "in vitro" the remarkable phenomenon of the generation of new elements. From the consideration of these phenomena, and in particular of the fact of the similarity of the products obtained from a number of elements, I deduced the conception and the proof of evolution in chemistry, and of the origin of the atoms. Spectroscopic researches and researches with the rare earths have confirmed my views, and have shown that evolution is the clue to the chemistry of the future. All my recent work has been in this direction. I began to look upon chemical affinity as the proof and explanation of atomic evolution, and saw in the similarity of the elements, or rather in the greater or less distance between the reacting atoms of a common ancestral type, the true cause of affinity and of the phenomena allied to it.

From the theory of a common origin of all the elements and especially of those belonging to the same family, and from the consideration of the resemblances existing between different atoms having the same valency, I have been led to look upon the elements of a certain valency as in some way representing the prototypes which are common to them with other atoms (with identical properties and the same valency charge). That is to say, an element with a given valency is quite a different atom from the same element with a different valency. Thus I am led to believe that the atomic properties vary when one passes from one valency to a different valency (in the same atom) as they vary with the valency as one passes from one family or group to another. I think I can foresee that all the properties in any way connected with the existence of "actual" or potential electric charges will follow the same variation.

Basing my conclusions on the differences observed in the atomic magnetic susceptibility of the diado-ferric (Fe″) salts and the ferric (Fe‴ ?) salts, diado-cobaltic (CO″) and cobaltic salts, I regard the ferric and cobaltic salts as salts of a hexavalent dimetallic radical, a possible type of the formation of at least some atoms. (Perhaps these researches on polymetallic radicles will be the subject of a future note. I have just heard that the forms of elements entering into combination change with the valency charge, Pope, *Journ. Chem. Soc.*, 1900, lxxix., 828).

In conclusion I wish to urge all who are interested in researches in physical chemistry to continue the investigation of elements like Sm, Ta, &c., which give salts of two different valencies, and to publish their results for the advancement of science and the establishment of a firm basis for the theories of evolution.

THE BROWNIAN MOVEMENT AND THE SIZE OF THE MOLECULES.*

By Prof. JEAN PERRIN, D.Sc.,
Faculté des Sciences à la Sorbonne, Paris.

(Continued from p. 191).

Law of Avogadro.—I have just shown you how the study of chemical substitutions gives, for example, the ratio of the masses of the molecules of benzene and water, which ought to be to one another as 78 : 18. Two masses of benzene and water which are in the ratio of 78 : 18 each contain the same number of molecules. Now, if we measure the volumes occupied in the gaseous state by these two masses, at the same temperature and pressure, we find that these two volumes are equal. This is not chance, and one invariably finds that two gaseous masses which contain the same number of molecules occupy the same volume when they have the same temperature and pressure. This is Avogadro's law, which may be stated as follows:—

> "In the gaseous state equal numbers of molecules of different substances, contained in equal volumes at the same temperature produce in it the same pressures."

(Note.—Avogadro's law, once well established, will give us by extrapolation molecular weights not obtained by the methods of chemical substitutions. For example, when we have found that 32 parts of oxygen or 2 parts of hydrogen produce in the same volume and at the same temperature the same pressure as 18 parts of water vapour, we know that the masses of these three kinds of molecules are to one another as 32 : 2 : 18).

You have learnt elsewhere (Boyle's law) that the pressure thus developed varies inversely as the volume occupied.

These gas laws have been extended by van 't Hoff to dilute solutions. We must, of course, in that case consider, not the total pressure exerted on the walls, but only the part of that pressure which is due to the blows of the dissolved molecules, the part called the osmotic pressure of the dissolved substance (which can be measured only by means of a "semi-permeable" wall, which stops the molecules of the solute but not those of the solvent). The laws of Avogadro and Boyle thus become:—

> "In the dilute state (gaseous or dissolved) equal numbers of any molecules whatever, contained in equal volumes at the same temperature, produce in them the same pressure. This pressure varies inversely as the volume occupied."

These laws are applicable equally to all molecules, large or small. The heavy molecules of sugar or of sulphate of quinine produce neither greater nor less effect than the molecule of hydrogen. Yet the molecule of sugar contains 45 atoms, and that of sulphate of quinine more than 100, and it would be easy to find other more complex molecules which obey the laws of van 't Hoff (or those of Raoult which follow from them).

> Is it not then conceivable that there is no limit of size for the assemblage of atoms which obeys these laws; is it not conceivable that even visible dust also obeys them exactly, so that a granule agitated by the Brownian movement has neither more nor less effect than a molecule of hydrogen, as regards the action of its bombardments on a wall which stops it? Or, more briefly, is it unreasonable to think that the laws of perfect gases may be applied also to emulsions composed of visible grains?

I have made this assumption, and it is in this direction that I have sought a crucial experiment which would decide the origin of the Brownian movement, and at the same time would either provide or preclude an experimental basis for the molecular theories.

The following appears to me to be the simplest:—

The Distribution of Equilibrium in a Vertical Column of Diluted Matter.—You know that the air is more rarefied on mountains than at sea-level, and that in a general way a column of gas is compressed under its own weight, the state of equilibrium resulting from the conflict between the force of gravity, which makes the molecules fall, and their movement which scatters them incessantly.

The law of rarefaction formulated by Laplace (to show how the altitude can be deduced from the barometer) follows of necessity from Boyle's law, and can be enunciated as follows.—

> Every time that one ascends a fixed distance, the density is divided by the same number. Or, more briefly, equal vertical elevations are accompanied by equal rarefactions.

For example, in air at the ordinary temperature the density diminishes by one-half each time one ascends 6 kilometres (it is immaterial from what level).

But the elevation which produces a double rarefaction would not be the same in hydrogen. A simple process of reasoning shows that the way in which the nature of the gas influences the result is a necessary consequence of Avogadro's law, and may be enunciated as follows:—

> The elevations which produce the same rarefaction for two different gases (at the same temperature) are inversely proportional to the weights of the molecules of these two gases.

For instance, if in oxygen at 0° it is necessary to rise 5 km. to make the density twice as small, it would be necessary to rise 80 km. in hydrogen at 0°, since the molecule of hydrogen is 16 times as light as the molecule of oxygen.

You see here (Fig. 1) a diagram showing three huge vertical cylinders (the largest is 300 km. high) into which the same number of molecules of hydrogen, helium, and oxygen have been placed. At a supposed uniform temperature, the molecules would distribute themselves as the diagram shows, collecting more towards the bottom the heavier they are.

Now we have been led to believe that the laws of perfect gases are possibly applicable to emulsions. If this is so, and if we make an emulsion in which the grains are equal, the distribution of matter in a vertical column of this emulsion ought to be the same as in a gas. In other words, once arrive at the distribution of equilibrium and then equal elevations will be accompanied by equal rarefactions. But if it is necessary to rise only 1/20 mm. *i.e.*, 100 million times less than in oxygen, for the concentration to become twice as small, then we must conclude that each grain of the emulsion weighs 100 million times more than one molecule of oxygen. This last weight could be ascertained if we could weigh the grain, which would be a stage between the molecular dimensions and those which are in our scale.

Of course the effectual weight of this grain would be the difference between its real weight and the thrust it would undergo in the liquid (according to Archimedes' principle). If the granules were lighter than the intergranular liquid, they would accumulate in the upper layers (equal depressions would produce equal rarefactions). They would distribute themselves uniformly if they had the same density as the liquid.

Practical Realisation.—To test these results I used the

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* A Discourse delivered before the Royal Institution, February 24, 1911.

emulsions which are obtained by precipitating alcoholic solutions of resins with water. Thus, as you see, we get with gamboge a beautiful yellow liquid, with mastic a white liquid like milk. The microscope reveals in these liquids the resin precipitated in the form of *solid* round granules, which do not agglutinate when the chances of the Brownian movement bring them into contact (which is what happens with other resins which give soft granules).

But the diameters of these granules are very varied, and I had to sort them so as to get emulsions in which all the grains were nearly the same size. The method I employed may be compared to the fractionation of a liquid mixture by distillation. Just as during distillation the parts first vaporised are relatively richer in volatile constituents, so during the centrifugation of an emulsion the portions first deposited are relatively richer in large granules. Thus you will see that it is easy to find a practical method of sorting the grains according to their size by fractional centrifugation. The operation is long (I spent some months over it), but it only requires patience).

Once get an emulsion with sufficiently uniform granules, and then the mean weight of the granules must be determined. Their density is measured like that of any other powder (the weight of resin in suspension in the flask used is determined by simply drying). The only difficulty is then to determine the diameter. The obvious way seems to be to measure it with a microscope by the clear chamber method by means of a micrometer objective. But the granules used are so small that errors of 20 per cent or more might easily be made. A method which is almost as direct consists in allowing a droplet of the emulsion to evaporate on the micrometer objective; it is found, as you can see here in a projection (Fig. 2), that the granules then arrange themselves in regular lines, the length of which could be measured with a fair degree of accuracy. Dividing this length by the number of granules gives the diameter.

Another longer but more accurate method consists in counting how many granules there are in a known volume of the standardised emulsion, which gives the mass of a granule, and hence its radius, since we know the density. For this method I used the fact, accidentally observed, that in a feebly acid medium the grains of gamboge adhere to the glass. At an appreciable distance from the walls the Brownian movement is not modified, but as soon as the chances of this movement bring a grain into contact with a wall the grain becomes motionless. The emulsion thus gets progressively weaker, and after some hours all the granules it contained are fixed. One can then count at one's leisure all those which come from a cylinder of arbitrary base (measured by the clear chamber).

Finally, a third method which I shall not explain to you in detail is based on the observation of the time necessary for the upper portion of a vertical column of emulsion (several centimetres high) to clarify to a given height. This time, required by the granules to descend on the average from this height, gives the diameter by applying the law of the fall of a sphere in a viscous fluid (Stokes).

These three processes agree, and this must be so to give us confidence in the accuracy of the measurements of a radius which is less than a thousandth of a millimetre.

Method of Observation.—We must now get an arrangement which will enable us to ascertain the distribution of equilibrium as a function of the height. For this purpose a drop of emulsion is placed in a shallow tank, the depth of which is 1/10 mm.; the drop is at once flattened out by a cover-slip which closes the tank and the edges of which are paraffined to prevent evaporation (see Fig. 3).

As the figure shows, the tank can be arranged vertically, the body of the microscope being horizontal, and thus the vertical column throughout which the emulsion can distribute itself may be made some millimetres high. It will be seen that the grains accumulate in the lower layers, and tend to give rise to a distribution of equilibrium (practically reached after one or two days), in which the progressive rarefaction as a function of the height is manifested as you can see in the projection, which plainly recalls the law of rarefaction of heavy gases.

But however small our granules are, they are so heavy that the rarefaction is very rapid, and the height over which measurements can usefully be made is less than 1/10 mm.

As the figure also shows, the tank can be made horizontal, the body of the microscope being vertical, in which case only about a quarter of an hour is necessary for equilibrium to be established. The objective of the microscope, of great enlarging power, has only a small depth of field, and we can only see clearly at the same instant the granules situated in a very thin horizontal layer, the thickness of which is only a little over 1/1000 mm. If the microscope is raised or lowered one sees the granules of another layer. The distance between these two layers may be deduced from the vertical displacement read on the screw of the microscope; the ratio of the number of granules perceived gives the rarefaction corresponding to a known elevation. It was with this apparatus that I made my first experiments.

I was not sure that there would be the least rarefaction, and, moreover, not even sure whether, on the contrary, all the granules would not group themselves quite against the bottom. But I saw that a permanent state of uniform rarefaction was established. This rarefaction is specially striking when, keeping the eye fixed on the preparation, the observer rapidly raises the microscope by means of its micrometer screw. The granules are then seen to be rapidly rarefied, like the atmosphere round an aerostat which is rising.

It now remains to make accurate measurements. When one sees in the field some hundreds of granules which are moving in all directions or which disappear while new ones make their appearance, one soon gives up trying to count them. Luckily we can take instantaneous photographs of the different layers, and then at our leisure count the number of granules in these layers on the plates.

It is thus easy to verify that equal elevations are accompanied by equal rarefactions. For instance, for granules of radius equal to 0·212 μ three successive rises of 30 μ practically lower the concentration to one-half, one-quarter, and one-eighth of its value. With other grains of radius equal to 0·367 μ an elevation of 6 μ is enough to make the density about twice as small. You see here a drawing obtained by placing one above the other five sections made at distances of 6 μ in this emulsion (Fig. 4).

To obtain the same rarefaction in air we have seen that it would be necessary to rise 6 km., a thousand million times as much. If our theory is correct the weight of a molecule of air would be the thousand-millionth part of the weight of one of our granules in water. The weight of the atom of hydrogen would be obtained in the same way, and now our interest centres on finding out if we shall thus obtain the same numbers as those given by the kinetic theory,

So I was much elated when I found at the first attempt numbers which were the same as those obtained by the kinetic theory; *i.e.*, by a fundamentally different method. I also varied the conditions of the experiment as much as I could. For instance, the mass of my granules had a series of values ranging between limits which were to one another as 1 : 40; I changed the nature of the granules, using different resins (especially mastic); by the addition of glycerin I increased the viscosity of the intergranular liquid in the ratio of 120 : 1, at the same time changing the nature of the liquid; finally, I made a considerable change in the apparent density of the granules, which in water varied from the same to five times as much, and which became negative for gamboge in glycerin with 10 per cent of water (in this last case the granules being lighter than the liquid accumulated in the upper layers).

(NOTE.—Quite recently under my direction M. Bruhat made the temperature vary from −10° to +58°, and still found the same weight).

I always obtained concordant results, giving for the

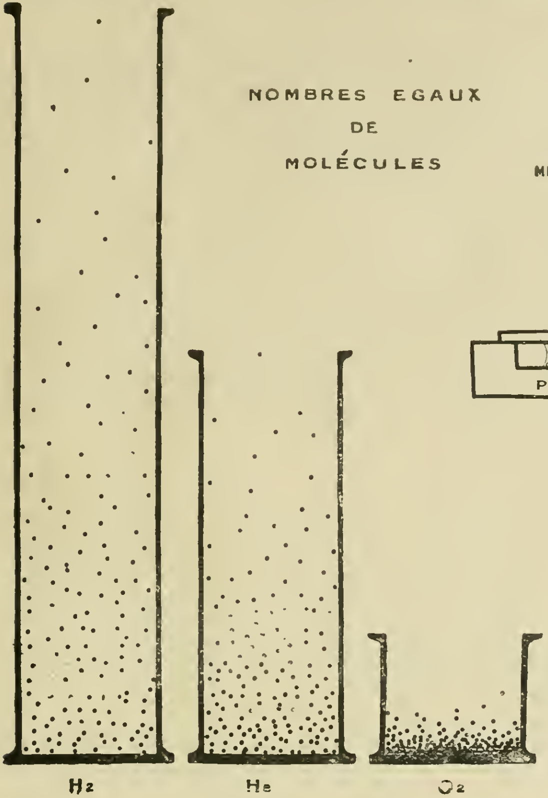

FIG. 1.

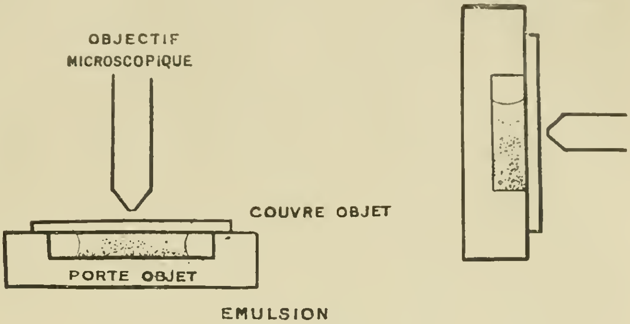

FIG. 3.

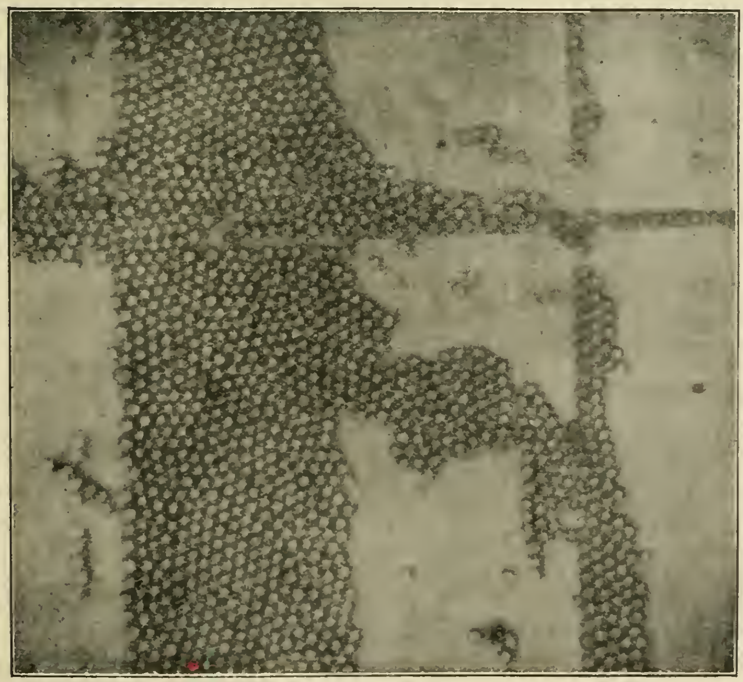

FIG. 2.

FIG. 4.

atom of hydrogen a weight very nearly equal to the value $1{\cdot}6 \times 10^{-24}$, given by the kinetic theory.

I do not think that this agreement can leave any doubt as to the origin of the Brownian movement. To understand how striking it is it must be remembered that before the experiment one could not have dared to affirm that the fall of concentration would not be negligible for such a small height as a few microns, or that all the granules would not collect in the immediate neighbourhood of the bottom of the tank. The first eventuality would give a zero value, and the second an infinite value for the weight of the hydrogen atom. That one should have hit exactly upon a value so close to that foretold, with *each* emulsion, in the *enormous* interval which seems *à priori* possible, could obviously not be a chance coincidence.

But there is more to be said. While the kinetic theory, because of the simplifications permissible in its calculations, gives results of an uncertain degree of approximation, even from perfect experiments, the numbers given by emulsions correspond to a true measure, such that there is no limit to its accuracy. By this method we can really weigh the atoms, and not only roughly estimate their weight.

The two series of experiments which I regard as the most accurate have thus given me for the weight of the atom of hydrogen (after the enumeration of about 30,000 granules) the value—

$$\frac{1{\cdot}47}{1{,}000{,}000{,}000{,}000{,}000{,}000{,}000{,}000},$$

or more briefly $1{\cdot}47 \times 10^{-24}$ grms.

The sizes of the other molecules can be derived from this. For example, you will easily see that there must be in each cc. of air (in normal conditions) thirty-one thousand millions of thousand millions of molecules, and that the elementary charge or electron must be $4{\cdot}2 \times 10^{-10}$ (C. G. S. electrostatic units).

(To be continued)

GAS ANALYSIS AS AN AID IN FIGHTING MINE FIRES.*

By GEORGE A. BURRELL and FRANK M. SEIBERT.

(Concluded from p. 197).

Relief Pipes at Stoppings.

In sealing any part of a mine certain precautions are observed, for it is a matter of common knowledge that a fire continues to burn for some time after stoppings are built, and the heated gases, unless they can escape readily, exert considerable pressure on stoppings. Moreover, an inrush of air after the cooling of the imprisoned atmosphere must likewise be guarded against or the fire may start afresh; again, dangerous explosione may result if the outflow of gases from a fire is checked too suddenly. At some fires the precaution has been adopted of having a pipe, with an elbow, placed in the upper part of the dam. This pipe dips into a vessel, an open barrel or keg, continuously supplied with water from a pipe fitted with a tap. The overflow from the barrel is allowed to run off. The tap is for shutting off the water when no longer needed. By this arrangement the outflow of gas is checked gradually, and is finally stopped when the pressure of the water over the outlet of the escape pipe equals that of the gas behind the stopping. The relief pipe also serves to indicate the pressure in the fire area. When the temperature rises the pressure is outward, and more gas escapes from the pipe; when the temperature falls the pressure is inward, and water is drawn into the pipe. After all combustion has ceased and the temperature has become normal, the atmosphere in the enclosed area may alternately expand and contract.

Collection of Samples—Significance of Data.

For the purpose of taking samples and determining the temperature and pressure of the imprisoned atmosphere a straight pipe provided with a valve should be placed in each stopping. Samples of gas can be collected with a small hand-pump, pressures can be read with a water-gauge, and temperatures can be taken with a thermometer inserted through the pipe.

Data obtained thus at regular intervals during the entire period that the fire is sealed are valuable, but their significance is governed more or less by the distance of the stopping from the fire. If this distance be great, changes in the condition of the fire will not be quickly indicated by the atmosphere behind the dam, and a change for the worse may occur before the fire fighters become aware of it. Clearly, however, in most cases the fire can burn more vigorously only by inleakage of air through the stoppings, consequently chemical analyses of the atmosphere just behind them show whether the inleakage of air is sufficient to keep the fire burning, and thus, perhaps, permit conditions to become worse.

Composition of the Atmosphere in Burning Mines.

Samples of gas were collected from behind stoppings that were built to seal off a fire in and close to the mouth of a drift mine working the Pittsburg bed. The first sample was taken through a hole in a concrete stopping, very near the fire, one day after the mine was sealed. The second and third samples were collected at the same place. Shortly after the third sample was taken water which had been forced in rose so high inside the dam that more samples could not be collected (see Table A).

The samples in Table B were collected from the same mine by inserting a tube in a small hole driven through the thin covering over the main heading near the mine mouth. The samples thus collected represent gases from a very hot part of the burning section.

These analyses are interesting because they show a rapid depletion of oxygen after sealing, and the formation of an atmosphere that would check the progress of the fire. In other words, they show that the dams were tight and the fire was being brought under control.

Samples were taken from behind another stopping, which was situated about 2000 feet away from the burning area, by boring a $\frac{3}{4}$-inch hole in the wooden brattice and drawing the gas into the sample container with a small air-pump. Later, by using helmets, entrance was made into the mine at this place, and three samples of air were obtained at points approximately 200, 600, and 800 feet inward from the stopping. Samples could not be collected farther in than 800 feet because of the heavy pall of smoke encountered there. The analyses of the samples are given in Table C.

The deficiency of oxygen in the samples was in part due to the absorption of oxygen by coal not affected by the fire. Except for the stagnant condition of the atmosphere and the heavy accumulation of black damp in the passages between this section and the burning section, the high oxygen content of the samples, especially of Nos. 1 and 2, would have caused apprehension as being sufficient to increase combustion. Because of the stagnation of the air, however, it was felt that little oxygen from outside was reaching the fire. Air was apparently leaking in to some extent at the place where these samples were taken, or a greater oxygen deficiency would undoubtedly have been found. On account of many small openings at different places on the surface, air could not be entirely excluded.

The mine was non-gaseous, and this fact accounts for the small amount of methane that accumulated directly at the fire area and at the brattice 2000 feet beyond. The knowledge that the accumulation of methane was slight was valuable, as it gave assurance that an explosion would not follow an accidental inrush of air.

The samples of gas given in Table D were obtained

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* *Technical Paper* 13, Bureau of Mines, Washington.

Table A.—*Composition of the Atmosphere in a Sealed Mine.*

No. of sample.	Date (1910).	Time.	Percentage of composition.					
			CO_2.	O_2.	CO.	CH_4	H_2.	N_2.
1.	May 22	7.30 a.m.	9·14	1·83	1·32	3·60	1·02	83·09
2.	May 23	2 p.m.	8·10	2·80	1·61	1·13	0·35	86·01
3.	May 24	8 a.m.	8·03	3·17	1·36	1·10	0·35	85·69

Table B.—*Composition of the Atmosphere in a Hot Part of a Sealed Mine.*

1.	May 22	7.35 p.m.	8·07	1·69	1·58	3·39	1·37	83·90
2.	May 23	1 p.m.	8·03	3·13	1·25	1·14	0·29	86·16
3.	May 24	8 a.m.	8·14	3·00	1·41	1·21	0·35	85·89

Table C.—*Composition of Atmosphere in a Sealed Area at a point remote from the Fire.*

No. of sampling.	Point of sampling.	Percentage composition.					
		CO_2.	O_2.	CO.	CH_4.	H_2.	N_2.
1.	Through stopping	3·47	13·65	0·60	1·01	0·18	81·09
2.	200 feet beyond	3·88	11·71	0·75	1·32	0·24	82·10
3.	600 ,,	4·81	9·47	0·80	1·78	0·20	82·94
4.	800 ,,	5·33	9·38	1·02	1·13	0·48	82·66

from behind one of several dams, which sealed a fire area in an anthracite mine. The dam was situated about 30 feet from the fire area. At the time the samples were collected, air was slowly leaking through another dam and some of the products of combustion were reaching the point of sampling. As some of these products of combustion were leaking out through the dam, compressed air was used in order to make the atmosphere outside the dam respirable while the samples were being taken.

Table D.—*Composition of the Atmosphere in a Fire Area in an Anthracite Mine.*

(In all the samples the proportion of hydrogen was less than 0·20 per cent).

No. of sample.	Date (1910).	Time.	Percentage of gases found.				
			CO_2.	O_2.	CO.	CH_4.	N_2.
1.	Oct. 27	5.00 p.m.	3·5	8·3	1·3	11·5	75·4
2.	,, 27	12.00 m.	3·8	9·6	0·7	13·1	72·8
3.	,, 28	9.45 a.m.	3·4	10·9	0·6	10·8	74·3
4.	,, 28	4.00 p.m.	3·4	11·3	0·6	10·3	74·4
5.	,, 28	4.30 p.m.	3·0	12·6	0·4	9·6	74·4
6.	,, 29	11.00 a.m.	3·3	14·1	0·6	9·0	73·0
7.	,, 29	3.30 p.m.	4·1	13·6	0·8	12·0	69·5
8.	,, 30	10.30 a.m.	4·8	10·1	1·2	14·1	69·8
9.	,, 30	5.00 p.m.	4·0	12·2	1·0	12·2	70·6
12.	,, 31	6.30 a.m.	12·2	6·6	0·4	6·6	74·2

When one of the writers arrived at the mine the fire had been temporarlly checked. It increased in strength afterwards, but was again checked. At the time of the collection of sample No. 1 the fire was seemingly under control. However, the increase of oxygen shown by samples 1 to 6 caused alarm, and efforts were directed toward tightening the old dams and building new ones a few feet in front of them. The coal bed at this place dipped rather steeply, and there was difficulty in building dams tight enough to hold water.

On the morning of October 29 the proportion of oxygen (shown by sample No. 6) in the atmosphere of the fire area was so much larger that the fire burst forth with renewed intensity. The chute in front of the dam had filled with smoke, and there were no doubts that the fire was gaining headway. Analysis of gas samples showed a dam sealing another chute leading to the fire area to be leaking air, and efforts were directed toward making it tight. When inleakage of air was prevented by tightening this dam and building new dams in front of the old ones, water was forced to the fire. The rise of the water inside the dams prevented the further collection of gas samples. The large proportion of carbon dioxide in sample No. 10 is due to the fact that carbon dioxide from a fire extinguisher had been forced into the area just prior to the taking of the samples.

As stated before, the samples of gas were obtained from behind a dam situated 30 feet from the burning area, while the products of combustion were slowly moving toward the point of sampling. External air was reaching the fire by leakage through another dam, and when sample No. 6 was collected the atmosphere behind the leaking dam contained about 20 per cent of oxygen. This dam was situated 90 feet from the fire and any air that reached the fire did so by slow diffusion. Just what percentage of oxygen in the atmosphere close to the fire caused the intensity of the latter to increase is difficult to state with exactness, but it certainly was between 14 and 20 per cent. The oxygen content was less than 20 per cent, because that was the content of the atmosphere just behind the leaky dam, but was more than 14·1 per cent, because that was the content after some oxygen had been consumed by the fire and absorbed by the unburned coal.

The bed of coal was gaseous. Table E gives analyses of samples collected behind a third dam, showing the accumulation of the methane evolved. This dam had been in place seven days when sample No. 1 was collected, but was not and had not been air-tight, as shown by samples taken before and after those reported. Except in its early stages the fire had no effect on the atmosphere at this place, because of the intervening roof falls. The analyses therefore show the changes in the atmosphere within a sealed area not influenced by fire in a gaseous bed of anthracite coal.

Table E.—*Changes in Composition of the Atmosphere of a Sealed Area of a Gaseous Mine.*

No.	Date (1910).	Time.	Determinations (per cent).				
			CO_2.	O_2.	CO.	CH_4.	N_2.
24.	Oct. 31	6.00 p.m.	2·2	15·0	0·0	14·0	68·8
25.	Nov. 1	6.30 a.m.	2·3	14·6	0·0	18·1	65·0
26.	,, 2	6.30 a.m.	2·6	6·2	0·0	24·2	67·0
27.	,, 2	9.45 a.m.	2·9	5·7	0·0	29·3	62·1
28.	,, 2	4.00 p.m.	2·4	6·2	0·0	30·1	61·3
29.	,, 3	6.30 a.m.	2·8	4·1	0·0	34·9	58·2
34.	,, 6	12.05 p.m.	2·6	3·0	0·0	53·0	41·4

The rapid oxygen decrease on November 2 (sample No. 26) resulted from tightening the dam.

The analyses in Table F show the composition of the atmosphere behind a tight stopping which had been built nine months prior to the collection of the samples to inclose a fire area in a bituminous coal mine working a bed that is considered non-gaseous. The accumulation of methane during several months' time amounted to about

5 per cent. The oxygen, it will be noticed, had been almost entirely consumed. Before the area was entered the samples were collected through the stoppings. When explorations were made by the use of breathing apparatus, samples were collected within the area. The fire had then been extinguished for a considerable time. The area inclosed was large.

TABLE F.—*Analyses of the Atmosphere of a Sealed Area in a Non-gaseous Mine.*

Determinations.	Sample No. 1. Per cent.	Sampls No. 2. Per cent.
CO_2	1·20	1·30
O_2	0·30	0·10
CO	0·00	0·00
CH_4	5·37	4·80
N_2	93·13	93·80

Table G gives the composition of samples of gases taken in November, 1911, from behind a stopping erected to seal a fire in a bituminous coal mine in Pennsylvania. The samples were collected four days after the sealing of the fire.

TABLE G.—*Composition of Gases from a Fire Area.*

Date (1911).	Time.	Percentage composition.				
		CO_2.	O_2.	CO.	CH_4.	N_2.
Nov. 20	1.30 p.m.	4·8	1·6	0·6	(*a*)	—
20	4.30 p.m.	4·8	1·6	0·6	(*a*)	—
21	7.45 a.m.	5·87	1·43	1·42	22·27	69·01
22	11.45 a.m.	5·84	1·02	1·03	24·45	67·66
23	3.20 p.m.	5·61	1·22	—	26·18	66·99
27	9.05 a.m.	5·22	0·97	1·17	30·86	61·72

(*a*) Not determined.

Table G shows that the percentage of oxygen in the atmosphere behind the dam decreased somewhat, thus demonstrating that there was no leakage of air through the dam, and also shows that the percentage of methane in the atmosphere increased.

AN IMPROVED GAS-ANALYSIS APPARATUS.

The authors have modified an Orsat gas-analysis apparatus to make a portable apparatus, as shown in Fig. 1, that is easy to manipulate and is sufficiently accurate for work at mine fires. With this apparatus carbon dioxide, carbon monoxide, and methane can be determined within about 0·2 per cent. Hydrogen, if present in the gas mixture, can be determined about as accurately by calculation from the combustion data.

The modified apparatus includes a burette of uniform diameter, graduated to 0·2 cc., and a slow combustion pipette, *d*, for burning methane and hydrogen. Pipettes *a*, *b*, and *c* contain glass tubes (not shown in the figure) to increase the absorption surface. The reagents used in these pipettes are:—(*a*) Potassium hydroxide solution; (*b*) alkaline pyrogallate solution; and (*c*) cuprous chloride solution. The gas sample is drawn in through the 3-way stopcock, *e*, and measured in the burette at atmospheric pressure. It is then passed successively into the potassium hydroxide, alkaline pyrogallate, and cuprous chloride solutions for the removal of carbon dioxide, oxygen, and carbon monoxide. The residual gas is diluted with air and passed into a slow-combustion pipette which contains a coil of No. 30 (B. & S.) platinum wire supported by two glass rods; this coil, when brought to a white heat by an electric current from a storage battery, ignites the combustible portion of the gas. After the combustible gases are burned the pipette is allowed to cool and the contraction in volume is measured. Finally, the carbon dioxide formed by the combustion is absorbed by potassium hydroxide and the contraction in volume is noted.

A calculation is then made for either methane, or methane and hydrogen combined. This depends upon the combustion data—that is, the contraction and the amount of carbon dioxide. Those samples that contain a percentage of methane which might cause an explosion if the residual gas were diluted with air and passed directly into the combustion pipette, are handled as follows:—

The residual gas is passed directly into the slow-combustion pipette, and the platinum coil therein is brought to a bright red heat. A quantity of air or oxygen sufficient to burn completely the combustible portion of the gas is then introduced from the burette at the rate of about 10 cc. per minute. In this manner quiet combustion takes place as the air or oxygen enters the pipette and comes in contact with the coil and the gas. An explosion from the formation of a mixture of oxygen and methane cannot follow. In order to simplify the apparatus as much as possible, water is used in the burette and in the combustion pipette. More accurate work can be performed if mercury is used, especially in the combustion pipette, but if distilled water slightly acidified with sulphuric acid is used, results of sufficient accuracy for the determination of conditions inside the fire area can be obtained. A more complicated apparatus has disadvantages when results are wanted quickly. This apparatus is so simple and portable that it can be carried from headquarters directly to a mine and set up there at any convenient place. The authors have taken it into mines and made determinations underground. A storage battery giving a current of 5 volts and 4 ampères can be used for heating the platinum coil.

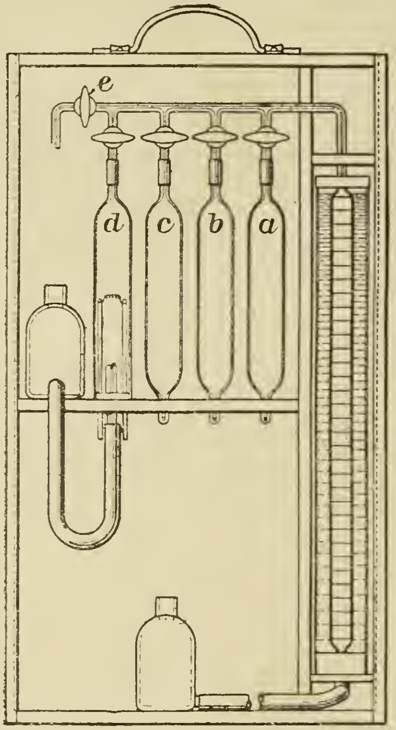

FIG. 1.—GAS ANALYSIS APPARATUS FOR USE AT MINE FIRES.

Descriptions of more accurate designs of apparatus for a wide range of gas analysis work, including portable and laboratory forms for the determination of the constituents in mine air, will be given in a forthcoming bulletin of the Bureau of Mines.

In conclusion, the authors again state that the purpose of this paper is to call the attention of mining men to the advisability of making more use of gas analysis at mine fires. Hence discussion of other expedients adopted in fighting such fires has not been attempted.

PROPOSED AVOGADRO PREMIUM.

The President of the Royal Academy of Science of Turin, Signor Paolo Boselli, announces that at the meeting on June 23rd, 1912, it was resolved that the residue of the money subscribed in memory of Amedeo Avogadro should be devoted to a premium for a chemical work, having some bearing on Avogadro's Law, to be published in the three years 1912—1914, and a special competition will be held for the purpose.

The rules of the competition will be as follows:—

A premium, entitled the Amedeo Avogadro Premium, of the value of 1500 L. (to take the form of a Gold Medal if desired), will be awarded to the candidate who in the three years 1912—1914 shall have published the best work on chemistry, either of an experimental or historical-critical nature, having some bearing on Avogadro's Law.

The works entered will not be returned, and must be written in one of the following four languages—Italian, French, German, or English, and at least three printed copies must be sent in by December 31st, 1914.

The competition will close on December 31st, 1914, and the premium will be awarded in the year 1915.

None of the national members, resident or non-resident, of the Royal Academy of Turin may compete for the premium.

NOTICES OF BOOKS.

Die Synthese des Kautschuks. ("The Synthesis of Caoutchouc"). By Dr. Rudolf Ditmar. Dresden and Leipzig: Theodor Steinkopff. 1912. (M. 3).

Although the author of this book recognised at the time of its publication that the problem of the synthesis of rubber was not by any means solved, he believed that a general review of the definite advances made would not be valueless, and was no doubt right in his contention. The book gives a short account of the work done up to March, 1912. Methods of preparing the initial materials used in the synthesis are treated in detail, and the most important German patent specifications are reproduced and fully discussed.

Notes sur la Physique et la Themodynamique. ("Notes on Physics and Thermodynamics"). By E. H. Amagat. Paris: Hermann et Fils. 1912.

The papers on physics and thermodynamics which the author has contributed to the *Comptes Rendus de l'Académie des Sciences* during the years 1873—1908 are collected in this book. They are arranged in order of publication, except when the necessity for grouping together those which deal with the same branch of the subject makes this impossible. Some few notes of explanation are occasionally inserted, but usually the text of the articles has been left unaltered. The papers, having been written during a period when the author was unable to prosecute experimental research in a laboratory, are entirely theoretical, and necessarily include many accounts of unfinished and incomplete investigations.

Buletinul Societatii Române de Stiinte. ("Bulletin of the Roumanian Scientific Society"). Vol. xxi., Nos. 1 and 2. Bucharest: Imprimeria Statului. 1912.

The minutes of the meetings of the Roumanian Scientific Society held from January to April, 1912, are contained in this number of the *Bulletins* of the Society, and it also includes papers giving the results of the research work, mostly in organic chemistry, performed by the members. Of these papers possibly the most important is one by M. Radulescu on the spiranes, or compounds containing a carbon atom common to two cyclic nuclei; the author has prepared many of these compounds, and studied their transformations. He also contributes an interesting article on the Periodic System and the theory of radicles. Both of these papers are printed in French.

Eloges Académiques et Discours. ("Academic Orations and Discourses"). Paris: A. Hermann et Fils. 1912.

This volume has been published by the Committee of French Geometers and those of other nationalities to celebrate the scientific jubilee of M. Gaston Darboux. It contains the addresses delivered by representatives of the Académie des Sciences and other learned Societies on the occasion of the presentation of the medallion to M. Darboux, as well as his reply. In addition all the orations and discourses pronounced by M. Darboux are reproduced. These deal with a great variety of subjects, but in all of them the same gifts of rare insight, sympathetic criticism, and lucid expression are clearly discernible.

OBITUARY.

Dr. MORRIS LOEB.

We much regret to have to announce the recent death of Dr. Morris Loeb, of typhoid fever and double pneumonia, in the fiftieth year of his age.

Dr. Loeb graduated at Harvard in 1883, and after graduation continued his scientific studiea at Berlin, Heidelberg, and Leipzig. He was assistant to Prof. Wolcott Gibbs at Harvard University from 1888 to 1889, when he was appointed Docent in Chemistry at Clark University. This post he relinquished to become Professor of Chemistry and Director of the Chemical Department at New York University. In 1906 he founded a private laboratory, where he devoted himself to research in inorganic and physical chemistry. He was a prominent member of the Chemists' Club, and a liberal donor to its funds, providing the entire equipment of the Meeting Room (Rumford Hall), the Library, and the Trustee Room (Priestley Room). He was also a munificent patron of Jewish Charitable Organisations in New York City, and contributed largely to the funds raised at Harvard for the Wolcott Gibbs Chemical Library. In 1906, and again in the present year, he was the President of the Chemists' Club. His most important research work included the study of the properties and preparation of the derivatives of phosgene, the determination of the electrical conductivity of solutions, and of the velocity of reactions, and the constitution of complex salts, and his early death has brought to a premature conclusion many important investigations which he was actively and successfully prosecuting.

CORRESPONDENCE.

SOPHISTICATED ALBUMEN.

To the Editor of the Chemical News.

Sir,—It may interest your readers to know that recently certain firms have been offering, at a low price, a so-called chicken albumen for genuine chicken albumen. We understand this albumen was falsified in Berlin.

We have tested the quality, and found it to be mainly duck albumen coloured, the object of which is obvious.

We estimate that 80 to 90 per cent of consumers would not find out the difference.

We are prepared, should any consumers be in doubt as to the genuineness of the quality they are now purchasing, to test same for them free of charge.

We enclose a sample of this sophisticated albumen.—We are, &c.,—

FELTON and CREPIN.

5, Savage Gardens, Tower, London, E.C.,
October 18, 1912.

SOUTH AFRICAN ASSOCIATION OF ANALYTICAL CHEMISTS.

To the Editor of the Chemical News.

SIR,—A society with the above name has recently been formed by analysts and chemists resident and practising in South Africa. The headquarters of the Association are in Johannesburg, but chemists resident within the Union of South Africa are eligible for membership.

The objects of the Association are to secure a high standard of professional conduct amongst analysts, and to uphold the status and interests of the profession of technical chemistry. In its constitution the Association has assumed power to undertake any measures which will encourage the study, or extend our knowledge, of technical chemistry.

The first Council of the Association is:—President—J. McCrae, Ph.D., F.I.C.; Vice-President—G. H. Stanley, A.R.S.M., F.I.C.; Honorary Treasurer—A. Whitby; Members—R. B. Denison, D.Sc., Ph.D.; J. Sprunt Jamieson, F.I.C.; C. F. Juritz, M.A., D.Sc., F.I.C.; R. Marloth, M.A., Ph.D.; James Moir, M.A., D.Sc.; Honorary Secretary—Jas. Gray, F.I.C., P.O. Box 5254, Johannesburg.—I am, &c.,

JAS. GRAY, Honorary Secretary.

Box 5254, Johannesburg,
September 30, 1912.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 8, August 19, 1912.

Quantitative Study of the Absorption of the Ultra-violet Rays by Alcohols, Acids, Ethers, Aldehydes, and Ketones of the Fatty Series.—Jean Bielecki and Victor Henri.—The absorption of the ultra-violet rays increases as the molecule becomes more complex. The acid function possesses a very great absorptive power; the aldehyde function is characterised by a band at 2800, and a very powerful absorption of the extreme ultra-violet; the ketone function is characterised by a band at 2680 and feeble absorption of the extreme ultra-violet.

Atomic Weight of Chlorine.—Georges Baume and F. Louis Perrot.—The authors have carried out a new series of determinations of the atomic weight of chlorine by bringing about the combination of a known weight of ammonia with gaseous hydrochloric acid. From the ratio $HCl:NH_3$ they have obtained the atomic weight $Cl = 35{\cdot}465$ ($N = 14{\cdot}009$, $H = 1{\cdot}0077$).

No. 9, August 26, 1912.

Benzylpyruvic Acid.—J. Bougault.—Benzylpyruvic acid can conveniently be prepared by the saponification of the amide of phenyl-α-oxycrotonic acid, $C_6H_5.CH=CH.CHOH.CONH_2$. At least two other acids are formed—a monobasic acid of formula $C_{20}H_{17}O_3N$ and a dibasic acid, probably of formula $(C_{10}H_{10}O_3)_2.1.5H_2O$. Benzylpyruvic acid readily condenses with itself, undergoing aldolisation, when treated with aqueous soda in the cold. It condenses even more readily with acetone, yielding either a compound containing equal numbers of molecules or else one containing 1 molecule of acetone to 2 of benzylpyruvic acid.

No. 10, September 2, 1912.

This number contains no chemical matter.

No. 11, September 9, 1912.

Synthesis of β-Benzylglucoside by means of Emulsin.—Em. Bourquelot and M. Bridel.—β-Benzylglucoside can be obtained by leaving a mixture of benzyl alcohol, glucose in excess, and emulsine for fifty days at a temperature of 18—24°. The glucoside is an odourless crystalline substance, with a very bitter taste. It is not hygroscopic. Melting-point 106°. It is lævo-rotatory, its rotatory power being −49·78°. It does not reduce cupro-potassium solutions.

Atti della Reale Accademia dei Lincei. Vol. xxi. (ii.), No. 1, 1912.

Thermic Analysis of Binary Mixtures of Chlorides of Monovalent Elements.—C. Sandonnini and G. Scarpa.—Cæsium chloride gives two compounds with cuprous chloride, $3CsCl.CuCl$, which decomposes when fused, and $CsCl.2CuCl$, which fuses without decomposition. Silver chloride gives a compound of formula $CsCl.AgCl$, decomposing when fused. Cæsium chloride gives with thallous chloride mixed crystals in almost all proportions.

Researches on Strychnine and Brucine.—R. Ciusa and G. Scagliarini.—Strychnine when heated with water to 160—180° yields the isomer isostrychnine, upon which bromine and alcohol act to give a substance of formula $C_{23}H_{28}O_2N_2Br_4$. This differs from isostrychnine in containing an extra C_2H_6 group (obtained from the alcohol), and also four atoms of bromine. It may be the hydrobromide of the ethyl ether of an acid, $C_{20}H_{21}NBr_3{<}^{COOH}_{NH}$, of formula $HBrC_{20}H_{21}NBr_3{<}^{COOC_2H_5}_{NH}$. Two atoms of bromine are attached at the double bond of isostrychnine, and the other replaces an OH group. The authors have prepared the pyridine salt of the acid $C_{20}H_{21}NBr.Br_2{<}^{COOH}_{NH}$.

Fixation of Unstable Nitrites by Organic Bases.—Gino Scagliarini.—The compound of magnesium nitrite and hexamethylene tetramine, $Mg(NO_2)_2.10H_2O+2C_6H_{12}N_4$, can be prepared by adding a solution of hexamethylenetetramine to a concentrated solution of magnesium acetate, in the proportion of about four molecules of the organic base to an atom of magnesium, and then adding an excess of concentrated sodium nitrite solution in the cold. A precipitate is formed, and may be filtered off and re-crystallised from water. The similar compound of manganese nitrite can be obtained by the same method.

Peroxide of Aluminium.—A. Terni.—When an excess of hydrogen peroxide is added to a concentrated solution of potassium aluminate a persistent precipitate is finally obtained. This precipitate, when filtered off and dried, forms a light amorphous white powder, behaving like a true peroxide. Thus it separates iodine from potassium iodide, and gives perchromic acid with an acidified chromate or chromic acid. Its formula appears to be $Al_2O_3.Al_2O_4.10H_2O$, although the results of its analysis are not very exact. Other attempts to prepare the peroxide, *e.g.*, by the action of H_2O_2 on aluminium hydrate or by the electrolysis of a solution of potassium aluminate, were unsuccessful.

THE CHEMICAL NEWS.

Vol. CVI., No. 2762.

PREPARATION OF NITRO-CELLULOSE (FULMICOTTON).

By A. DUFAY.

Nitro-cellulose may be prepared by means of a mixture of nitric anhydride and monohydrated nitric acid, or a mixture of $16{\cdot}5N_2O_5$ and sufficient HNO_3 to immerse the mass of cotton in it.

The reaction would be—

$$C_{24}H_{40}O_{20} + 16{\cdot}5N_2O_5 + nNO_3H = \\ = C_{24}H_{29}(NO_3)_{11}O_9 + 11H_2O + 22HNO_3 + nHNO_3.$$

The final result would be $C_{24}H_{29}(NO_3)_{11}O_9$, and would be limited by the weight of N_2O_5 contained in the mixture.

$$C_{24}H_{40}O_{20} + 12N_2O_5 + nHNO_3 = \\ = C_{24}H_{32}(NO_3)8O_{12} + 8H_2O + 16HNO_3 + nHNO_3.$$

It would be the same in the second reaction as well as in the following :—

$$C_{24}H_{40}O_{20} + 7{\cdot}5N_2O_5 + nHNO_3 = \\ = C_{24}H_{35}(NO_3)_5O_{15} + 5H_2O + 10HNO_3 + nHNO_3.$$

(It may be well to quote from the work of L. Troost and L. D. Péchard the method of preparing nitric anhydride. "*Third Process.*—Weber has succeeded in preparing nitric anhydride by dehydrating the acid, $2HNO_3 = N_2O_5 + H_2O$. The process, rendered practicable by Berthelot, consists in adding to fuming nitric acid, cooled by a mixture of ice and salt, a slightly greater weight of phosphoric anhydride in small portions, not allowing the temperature to rise above 0° ($6HNO_3 + P_2O_5 = 2H_3PO_4 + 3N_2O_5$). The mass finally sets into a jelly, which is introduced by means of a spatulum through a funnel into a tubulated retort corked with emery. It is then distilled slowly, being cooled as soon as the mass begins to swell. The nitric anhydride condenses in crystals in emery ground flasks fitting on to the neck of the retort, and cooled by means of ice. *Properties.*—The density of nitric anhydride is 1·522 at 14°; it fuses at 30°, giving a liquid which boils at 47°, and is rapidly decomposed at 80°. It cannot be preserved, even in a closed vessel at a low temperature, for it undergoes slow decomposition giving oxygen and nitrogen peroxide").

The object of this method of preparation is to avoid the use of monohydrated sulphuric acid in the manufacture of nitro-cellulose, and to replace it by a known quantity of nitric anhydride, corresponding to the formula of the fulmicotton which is to be obtained. The reason for this substitution may be seen from the following equations :—

$2N + 5O + H_2O = 2HNO_3$ (dissolved) .. + 28·6 cal.
H_2SO_4 + water = H_2SO_4 (dissolved) .. + 17·9 cal.

Since the reaction takes place in a nitric medium there is no fear of secondary reactions.

As the weight of cotton in the dry state and the exact degree of acidity of the bath are known the reaction can be verified and followed. (i.) The cotton is weighed in the dry state before and after being steeped. (ii.) The acid bath is titrated before and after, the second titration being referred to the final volume or weight. (iii.) The final washing is performed in a known quantity of distilled water, so that the total amount of acid can be determined. (iv.) A known weight of gun-cotton in the dry state is taken, and the NO_3 is transformed into ammonia by boiling it with an excess of ferrous acetate in presence of water; then the liquid is made alkaline by a solution of caustic potash, and it is distilled to drive off the ammonia which is fixed as ammonium chloride by absorbing the vapours in an excess of hydrochloric acid. The ammonia is finally weighed as ammonium chloroplatinate. The vapours can also be received in a standard solution of sulphuric acid, and the excess of acid determined by means of a standard solution of caustic soda. (v.) A known weight of gun-cotton is decomposed by an excess of a solution of ferrous sulphate in water containing sulphuric acid, and the NO is measured in a graduated vessel.

Commercial Preparation of Nitric Anhydride.—This process can be carried out on a large scale, using a retort made of enamelled iron and capable of being taken to pieces, to distil the nitric anhydride. A freezing machine and a sufficiently large apparatus, which can also be made of enamelled iron, to prepare the phosphoric anhydride, are required. Nitroglycerin can be prepared by this mixture, as well as nitrobenzene. It is also an advantage in the commercial preparation of gun-cotton to be able to use the same acid bath by replenishing it after each soaking with a sufficient quantity of N_2O_5 and HNO_3, after having determined the strength.

The only by-product is phosphoric acid plus a little phosphoric anhydride, which can readily be transformed into phosphorus if it is thought worth while, to be again converted into the anhydride. (Phosphoric anhydride exists in three states in the snowy flakes obtained in the crystalline, amorphous, and vitreous states—Hautefeuille and A. Perrey). The crystalline form is much the best to use, for it dissolves better. The amorphous and vitreous anhydrides give the crystalline anhydride on sublimation. The latter dissolves rapidly in water ("Traité de Chimie," L. Troost and F. D. Péchard).

Weight of Cotton and Gun-cotton.—It is difficult to weigh a very porous substance without exposing it to a rapid increase of weight, which renders the result uncertain. We have devised the following apparatus which enables us to weigh the material in absence of air. In its appearance this apparatus recalls Magdebourg's hemispheres, used in physics to demonstrate the action of the pressure of the atmosphere. The apparatus consists of two hollow glass hemispheres of 20 cm. diameter. Their rims are furnished with a metallic ring, made perfectly air-tight so that a vacuum can be maintained, and the surfaces of the two rings are ground with the greatest care. On one of these hemispheres there is a metallic stopcock, which screws on to the air-pump, and on the other there is a ring to facilitate weighing. The whole is as light as possible.

Process.—After the two metallic surfaces have been greased with vaseline a rubber ring is placed in position, and a partial vacuum is created, always to the same degree. The sphere is attached to the beam of a good balance and weighed. Air is then allowed to pass in by gently opening the tap, the apparatus is opened, and the cotton or gun-cotton, the weight of which is to be determined, is placed in it directly it is taken from the drying oven. The two hemispheres are put together, and the vacuum is made in the same conditions as before. The excess over the first weight give the weight of the substance.

Verification of the Commercial Operation in the Preparation of Fulmicotton.—We shall describe a control operation, which is performed at the same time as the industrial preparation, in the same conditions as to time, temperature, and mass of the liquid, with this difference only, that the mass of the cotton used represents a small proportion of the total mass, and similarly with the acid liquid. The ratios of the weights are the same in both cases, and it is actually a preparation on a small scale which serves as a control for the manufacture. The molecular weight of the cellulose, expressed in grms., is taken, or a submultiple of the weight plus the proportionate quantity of acid liquid. The acid liquid is titrated, the steeping is allowed to proceed, and the first washing is performed in a known weight of distilled water. The washing is continued in running water. The substance is dried and weighed, and the acid liquid is titrated after steeping, as well as the distilled water used for the first washing. From the results obtained the formula may be verified.

THE ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF SALTS OF NEODYMIUM AND PRASEODYMIUM AS MEASURED BY MEANS OF THE RADIOMICROMETER.*

By HARRY C. JONES and J. SAM GUY.

The work on the absorption spectra of solutions was begun in this laboratory by Jones and Euler about seven years ago. This investigation was undertaken in connection with the solvate theory of solution which Jones had shortly before that time proposed.

A fairly comprehensive review of the results obtained up to 1910 has already been published (*Zeit. Phys. Chem.*, 1910, lxxiv., 356). Only a very few points brought out by the work of Jones and Euler will be referred to here. They studied the effect on absorption spectra, of changing the concentration of the solution, of the addition of dehydrating agents when added to aqueous solutions, and the effect of adding water to solutions of certain salts in non-aqueous solvents.

The work of Jones and Anderson was far more comprehensive. They studied a large number of salts from the standpoint of Beer's law, and traced the origin of certain absorption bands to molecules, of others to atoms, or the electrons contained within them; and still others were caused by hydrates.

The most important point established by the work of Jones and Anderson was that the combined solvent as well as the dissolved substance plays an important *rôle* in the absorption of light, even when the solvent by itself has no selective absorption in the visible spectrum. They found that neodymium chloride dissolved in water has a very different absorption spectrum than when dissolved in methyl alcohol. When small amounts of water were added to the alcoholic solution we had the bands of the aqueous solution; that is, the "water bands," existing simultaneously with the bands due to the alcoholic solution, that is, to the "alcoholic bands." It was found that one set of bands was not the other set shifted in position, but the "water bands" were entirely different in number, in structure, and in position from the "alcohol bands." This was interpreted as due to the combination of the neodymium chloride, on the one hand, with water, and on the other with methyl alcohol; the hydrate having very different resonance, and, therefore, very different absorption from the alcoholate. This was regarded as strong evidence for the solvate theory of solution.

A number of points were established by the work of Jones and Strong, which extended over three years. In this work alone between 4000 and 5000 solutions were studied. In addition to mapping the absorption spectra of a large number of comparatively rare substances, Jones and Strong studied the effect of rise in temperature on the absorption spectra of non-aqueous solutions of a number of salts. By means of a gold-plated steel tube closed by glass windows, they were able to study such solutions up nearly to 200°. The general result was that the absorption bands were found to widen with rise in temperature up to the highest temperature studied. This was all predicted in advance from the solvate theory of solution.

Another point investigated was the effect on the absorption spectra of adding one acid to the salt of another acid. According to the prevailing chemical views the salt of one acid would be partly transformed directly into the salt of the second acid; the amount of the transformation depending on the relative strengths of the two acids and the relative amounts of salt and of acid added to it. If this were true we should expect to have the two absorption spectra corresponding to the two salts co-existing upon the photographic plate. Instead of this being the case, when we add an acid to a salt we have neither the bands corresponding to the original salt nor to the salt of the acid added, but bands intermediate in position between these two sets of bands; and these bands can be made to occupy any intermediate position that we choose by adding the proper amount of acid to the salt.

This we interpret as showing the presence of chemical systems intermediate between the initial and final systems. These intermediate systems are not taken into account at all in our ordinary chemical equations, but their existence in solution is shown, we believe, by their spectra. These intermediate systems are too unstable to isolate by our present chemical methods; but these systems must be reckoned with in working out an exact science of chemistry.

One of the most important facts established by the work of Jones and Strong is the effect of the combined solvent on the absorption of light by the dissolved substance. A large number of examples were found illustrating this point. Indeed, this was one of the chief problems investigated at this stage of the work.

Thus, urinyl chloride was found to have different absorption bands in each of the following solvents:—Water, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, ether, methyl ester, glycerol, and formamide; and neodymium chloride showed different absorption in each of the following solvents: — Water, methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, and glycerol.

Perhaps the most striking fact was that we could detect the difference between the absorption spectrum of a given salt in an alcohol and in its isomer. This was interpreted as strong evidence in favour of the view that there is combination between salt and solvent, and that each solvate has its own characteristic resonance, which was more or less different from that of every other solvate. In a word, this was regarded as direct evidence for the solvate theory of solution as proposed by Jones somewhat more than a dozen years ago.

Our own work has had to deal with three problems:—The study of the absorption spectra of aqueous solutions at high temperatures; the investigation of the question as to whether ions and molecules have the same or different absorption, and the study of absorption spectra by means of the radiomicrometer.

The first two problems have now been satisfactorily solved. We have worked with aqueous solutions of a large number of salts up to 200° in a brass tube with glass windows, and find *a general widening* of the absorption bands with rise in temperature. These results with illustrative spectrograms will soon be published.

The problem as to whether ions and molecules have the same or different absorption spectra was attacked in this manner. A spectrogram was made of a concentrated solution of, say, neodymium chloride; the layer of solution through which the light passed being 1 cm. thick. This solution was then diluted fifty times and light passed through a layer 50 cm. thick. The second solution was then diluted five times and light passed through a layer 250 cm. thick. These spectrograms were photographed on the same plate, the one beneath the other. The three spectrograms were always different. The one corresponding to the more concentrated solution always contained broader absorption lines and bands. These results with the corresponding plates will also soon be published.

The object of using a radiomicrometer in this work is twofold. The best photographic plate is limited to the wave-lengths 2000 A.U. and 7600 A.U., while by means of the radiomicrometer it is possible to study absorption spectra to wave-lengths as great as 20,000 A.U. to 30,000 A.U., and, indeed, to even much greater wave-lengths if solvents are used which do not have broad absorption bands in the longer wave-length portions of the spectrum. One object in using the radiomicrometer was

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* This investigation has been carried out with the aid of a Grant generously awarded one of us (Dr. Jones) by the Carnegie Institution of Washington.

then *to extend the range* over which the absorption spectra of solutions could be studied.

The other object in using the radiomicrometer was to *measure the intensities* of the various absorption lines and bands and of the various parts of the same band. In a word to work *quantitatively*. That such has been done will be seen from the following results:—

The Radiomicrometer.

Since the radiomicrometer, if properly constructed, is independent of any outside magnetic or electrical influences, it is evident that its use in the average physical laboratory is to be preferred to a thermo-couple galvanometer system.

Theoretically, the instrument is simply a suspended coil galvanometer, having a single loop of small copper wire with a thermo-couple on one end. If we could secure perfectly pure copper wire for the loop, that is, wire free from all magnetic metals, almost any desired sensibility could be obtained with this instrument. This, however, was the most difficult problem which confronted us in the proper construction of the radiomicrometer. Through the kindness and generosity of Messrs. Leeds and Northrup, of Philadelphia, we were furnished with a very good sample of small copper wire, which was etched to the desired size by immersing it in dilute nitric acid. By thus removing the outside layer from the wire most of the magnetic impurities, due probably to the dies used in drawing it, were removed.

The most difficult problem experimentally was the construction of the thermo-junction. This consisted of two alloys, one 90 per cent tin and 10 per cent bismuth, and the other 97 per cent tin and 3 per cent antimony. By a simple device worked out in this laboratory by Prof. Pfund we were able to obtain small strips of these alloys of any desired dimensions. About 10 grms. of an alloy were melted in a non-magnetic ladle over a Bunsen flame, and thrown tangentially with considerable force upon a carefully cleaned and very smooth glass surface.

By such procedure the metal in question could be thrown into filaments of almost any size; some of which were, indeed, entirely too small to handle. The filaments used in the construction of the radiomicrometer were about 1 mm. wide, 0·1 mm. thick, and about 5 mm. long. A full account of the soldering of such small filaments to one another and to the ends of the loop of copper wire has recently been published by Pfund.

The copper wire was first stripped of its insulation, heated by means of the current to anneal it, bent into the desired loop form, and etched to the proper size with dilute nitric acid. To the ends of the loop is soldered the thermo-junction, which is made in the shape of a letter V of sufficient width to meet the ends of the loop without strain. The surface of the junction is blackened to prevent loss of energy by radiation. To the other end of the loop there is fastened rigidly a light glass rod carrying the mirror and suspended by the quartz fibre above.

A concave mirror of about 4 mm. square, chipped from a silver optical lens of the desired focal length, was used.

This entire system of loop, junction, and mirror, weighing not more than 20 grms., was suspended by means of a small quartz fibre in such a manner that the loop hung midway between the poles of a strong magnet. The entire system was suspended within a glass tube, provided at the top with a ground glass stopcock and suitable windows for exposing the junction and viewing the mirror. The glass tube was also provided with a side tube for evacuation, to which was attached a carbon evacuator as devised by Pfund. With such an attachment an exceedingly high vacuum could be kept for an almost indefinite length of time.

By means of the ground glass stopcock to which the suspension was fastened, any adjustment of the position of the loop could be made even after the whole system was evacuated. The entire apparatus was supported upon a levelling table and carefully packed in cotton to protect it from outside radiation, leaving only a small opening for the entering radiation.

The instrument used throughout this investigation had a whole period of about eight seconds, and gave a deflection of 15 cm. for a candle at 1 metre distance when the light was allowed to pass through a glass window. When the instrument was evacuated the deflection was decreased about three and a-half times; the radiomicrometer then giving a deflection of about 50 cm. for a candle at the distance of a metre. Since about 50 per cent of the energy from a candle is cut off by the glass window, our instrument was capable of giving a 100 cm. deflection for a candle at a metre distance for one-half period of four seconds, using a rock-salt window.

A table compiled by Coblentz enables us to compare our instrument with those of previous workers (Bureau of Standards, iv., No. 3, Reprint No. 85).

Observer and references.	Full period (secs.).	Deflections in cm./mm.^{2} with candle at 1 metre distance.
Boys (*Phil. Trans.*, 1889, clxxx., A, 159)	10	0·9
Paschen (*Wied. Ann.*, 1893, xlviii., 275)	40	3
Lewis (*Astrophys. Journ.*, 1895, ii., 1).	20	1·3
Coblentz (*Bull.* Bureau of Standards, Sept. 1, 1907)	40	3·6
Coblentz (*Ibid.*)..	25	6 (*a*)
Jones and Guy	8	8
Jones and Guy	7	25 (*a*)
Jones and Guy	7	50 (*b*)

(*a*) *In vacuo.*

(*b*) *In vacuo*, rock-salt window with 2 sq. mm. surface.

The magnetic control caused by the impurities in the copper wire used for the loop was considerable when the highest sensibility was attained, and for this reason the instrument was not used *in vacuo*. The size of the quartz fibre was so regulated as to give a half period of four seconds with a deflection of about 16 cm. with candle and scale at 1 metre distance. Such sensibility was found to be ample for the red and infra-red measurements, while fair deflections were obtained for wave-lengths as short as 4500 A.U. Measurements could be made rapidly, and at the same time the magnetic control was not seriously disturbing. The instrument would always return to the initial zero to within one-half of a millimetre. Before each reading the scale was made to read zero, and duplicate readings usually agreed with one another to within 1 per cent.

The source of light was a Nernst glower, through which was passed a current from storage cells of 1·2 ampères and 110 volts. The current was very steady, and successive readings always agreed well with one another.

The cells used were made of brass about 4 cm. in diameter, carefully turned to the desired thickness, and plated with gold to prevent them from being attacked by any of the solutions. The very best optical glass was used for the ends, and duplicate cells always gave the same deflection both when empty and when filled with water.

Method of Procedure.

The light from the glower was first rendered parallel by a lens, then passed through the cell containing the solution, and again focused on the slit of the spectroscope. By a simple device either the cell containing the solvent or the solution could be placed in the path of the beam of light without change in the adjustment of either the instrument or the spectroscope. A metal screen was interposed between the source of light and the cells, and raised only a few seconds during the exposure. In this way the light was not allowed to fall on the junction any longer time than was required to get the deflection.

The light passing through the solution and focused on the slit of the spectroscope fell on the prism and thence passed out through the second slit of the spectroscope which replaced the usual eye piece. The light was then focused on the junction of the radiomicrometer. By means of a carefully calibrated head the position of the prism in the Hilger spectroscope used could be changed so as to throw any particular wave-length of the spectrum on the slit and hence on the junction. The width of the slit was so regulated as to give a reasonable deflection when the light was focused on the junction of the radiomicrometer. In the visible part of the spectrum the slits were 0·4 mm. in width, while in the infra-red end the width of the slits was cut down to 0·22 mm.

The method of procedure in making a set of readings was as follows:—First, the cell containing the solvent was placed in the path of light, the screen raised, and the deflection noted; then the cell containing the solution was placed in the same position as the cell containing the solvent, the screen raised, and the deflection again read. The position of the prism was then changed by turning the calibrated head, and the above procedure repeated.

Denoting the deflection obtained with the solution by I, and the deflection obtained with the solvent by I_0, we get I divided by I_0 as the ratio expressing the percentage of light absorbed by the solution.

The accompanying table gives the observed transmission of a solution of neodymium chloride having a concentration of 0·875 normal, the depth of the layer being 10 mm.

In the appended table there is given a typical example of the results obtained with many of the salts investigated. A temporary run was made throughout the entire spectrum in taking up the study of any given salt and the position of the bands noted. Then, having located approximately the position of the bands, a more careful study was made of the solution, taking the readings very close together in those regions of the spectra where absorption lines and bands had been noted in the preliminary run. It may be stated that the work was much more tedious in the case of neodymium compounds than with salts of the other metals, on account of the very large number of fine absorption lines and bands. These lines and bands have sharp edges, and unless the position of the prism and the width of the slits were in identical positions it is easily seen that an error might be made. A very slight shift in the position of the prism or of the slits would make a large difference in the total energy falling on the radiomicrometer junction, especially if the width of the line or band was nearly the same as that of the slit, or if the position of the prism was such as to throw the line or band on the exit-slit of the spectroscope.

Let us consider such a band as the λ 4300 of neodymium salts. This is a very intense but narrow band. On either side of this band there is almost complete transmission. If under a given dispersion the width of the slit necessary for a reasonable deflection of the radiomicrometer were greater than the width of this band, the reading of the intensity would not be correct on account of the light around the edge of the band. It is easily seen that no such difficulty as the above would be encountered with salts of cobalt-copper, chromium-copper, &c.; in a word, that we have subjected our method to the most crucial test in selecting salts of neodymium at the outset.

Throughout the entire spectrum from λ 4000 to λ 20,000 readings were made at each division of the calibrated head of the spectroscope, except in those regions where the preliminary run showed that there were no absorption bands. These divisions corresponded to from 20 to 50 Angström units, depending upon the portion of the spectrum, the wave-lengths being crowded together in the infra-red.

A study of the above table will show the following:—Beginning at λ 4920 there is 80 per cent transmission which decreases rapidly, reaching the first maximum near λ 5050, where there is 7 per cent transmission, the amount of light transmitted then increases slightly and then decreases to 2 per cent at λ 5150, after which it increases rapidly, reaching almost complete transmission at λ 5350. There is therefore a double band with the greater absorption near the red end. Other more marked minima occur at λ 5720, λ 7300, λ 7860, and λ 8605. The last three of these bands are not shown on the photographic plates of Jones and his co-workers. This seems to be the first time that bands λ 7860 and λ 8605 have been noted.

Observed Transmission of $NdCl_3$ *Solution.*

10 mm. layer of 0·875 N.$NdCl_3$.

λ.	I/I_0.	λ.	I/I_0.
4860	80	6700	60
4820	82	6720	57
4950	61	6760	63
4990	40	6780	61
5010	29	6810	74
5030	13	6850	97
5050	7	6910	99
5060	11	6990	97
5090	13	7060	91
5130	10	7100	80
5150	2	7140	47
5160	4	7190	29
5180	13	7220	8
5200	31	7240	1
5220	45	7290	0
5250	62	7330	0
5300	92	7370	5
5350	94	7410	17
5440	91	7450	42
5500	80	7500	64
5560	69	7550	79
5590	50	7600	84
5630	26	7650	75
5650	9	7690	57
5670	1	7720	34
5720	0	7760	14
5770	1	7810	4
5790	3	7860	0
5830	11	7920	2
5850	23	7980	6
5870	42	8020	16
5890	63	8060	34
5920	79	8110	59
5950	90	8180	79
5970	92	8230	91
6000	95	8330	95
6090	94	8360	90
6110	92	8400	80
6140	93	8450	62
6220	91	8500	37
6290	94	8550	20
6380	98	8605	16
6430	98	8660	23
6500	99	8720	41
6570	99	8780	43
6600	95	8890	65
6620	91	9000	90
6660	75	9580	100

A detailed graphical representation of the data given in the table is shown in Fig. 2.

Measurements on this as well as other solutions were made down as far as λ 20,000, but since no characteristic bands occur beyond the region plotted in the curve, it was not necessary to give the results.

In a word, there seems to be complete transmission as far as salts of neodymium are concerned beyond 1 μ. In this region the absorption of the water is very large indeed; being nearly complete over a large portion of the spectrum from λ 12,000 to λ 20,000.

(To be continued)

THE REFORM OF CHEMICAL AND PHYSICAL CALCULATIONS.

By C. J. T. HANSSEN.

Since the writer of these lines, about twenty years ago, discovered that at the 41° 10′ geographical latitude, sea-level, mean atmospheric pressure and temperature of freezing water ($\pm 0°$ C. = 273° C. absolute) 1 cubic metre *pure* oxygen gas exactly weighs 10/7 kg. = 1·4285714285 kg., and upon this fact as a basis wrote "Reform in Chemical and Physical Calculations" (published in 1897 in English, German, and Danish editions, and in various articles in Chemical News, and in other scientific and technical papers), it has been my desire that, as I then proposed, the chemists and physicists of all nations should refer their observations and calculations on gravity to one circle of geographical latitude, in similar way as the astronomers of all nations refer their observations and calculations to the Meridian of Greenwich.

I proposed that the 41° 10′ northern latitude should be adopted as the international circle of gravity, and this proposal was strongly recommended by Professor of Physics G. Karsten, of Kiel, by Professor W. Foerster, Director of the Royal Observatory of Berlin, and many other scientific authorities, but opposed by the numerous adherents of Professor Stas, because I did not acknowledge the Stasian atomic weight determinations, which were proclaimed as absolutely correct, and almost ruled chemical science; but times have changed, and already in the report of the International Committee on Atomic Weights for 1906 Professor F. W. Clarke and his colleagues declared that all Stas's determinations are "indirect" and not to be depended upon, and every year several of the faulty atomic weights with decimal fractions have been replaced by atomic weights in round numbers. In the tables of atomic weights, published October 14th, 1898, and all tables published later by Professor F. W. Clarke, W. Ostwald, T. E. Thorpe, G. Urbain, H. Moissan, F. W. Richarda, G. Hinrichs, Landolt, Seubert, and by C. J. T. Hanssen's articles in Chemical News (vol. cxix., p. 229, and vol. civ., p. 232) are now found atomic weights in round numbers for 58 of the 74 elements, viz.:—

H	1	Co	59	Sa	150
He	4	Ga	70	Eu	152
Li	7	As	75	Gd	156
B	11	Se	79	Tb	160
C	12	Br	80	Er	166
N	14	Yt	89	Tm	171
O	16	Cb	94	Yb	173
F	19	Mo	96	Lu	174
Ne	20	Rh	103	Ta	181
Mg	24	Pd	107	Wo	184
Al	27	Ag	108	Os	191
P	31	Cd	112	Ir	193
S	32	Sn	119	Pt	195
Ca	40	Sb	120	Hg	200
Sc	44	Io	127	Tl	204
V	51	Xe	128	Pb	207
Cr	53	Cs	133	Bi	208
Mn	55	La	139	Rd	225
Fe	56	Ce	140	Th	233
				U	240

And no doubt the remaining 16 faulty weights will soon be corrected and incorporated in the new simplified table of atomic weights, and when one central station on the international circle of gravity, 41° 10′, on the west coast of Italy, near Rome, one on the east coast of America, close to New York, one on the west coast of California, and one on Japan, then the way is ready for reform and development of theoretical and practical chemistry.

Copenhagen, Valdemarsgade 3,
October 17, 1912.

A SUBSTITUTION FOR RUBBER CONNECTIONS IN CHEMICAL APPARATUS.

By W. R. FORBES, B.Sc.

In setting up apparatus occasions often arise where rubber tubing is objectionable, and fusion of the tubes inconvenient. The following will be found a convenient method of surmounting the difficulty:—

Take a short piece of glass tube of wider bore than the tubes to be joined and fill it with wax. Bore a tube through the wax, and slip the piece over the tubes to be joined. To mould the tubes place an iron rod in the middle of the short glass piece and fill up with wax. If the iron rod is long its end may be warmed, and the heat travelling by conduction it may easily be withdrawn, leaving the mould complete. A supply of these tubes can be quickly made and kept ready for use.

THE BROWNIAN MOVEMENT AND THE SIZE OF THE MOLECULES.[*]

By Prof. JEAN PERRIN, D.Sc.,
Faculté des Sciences à la Sorbonne, Paris.

(Concluded from p. 206).

The Sizes of the Molecules can be Deduced from the Degree of Agitation.—Thus we have extended the laws of gases to emulsions with much success, and at the same time obtained the absolute weights of the atoms. It is remarkable that in these measurements we have not had to concern ourselves about the activity of the Brownian movement. The laws of gases are verified by emulsions equally well in glycerin, in which the Brownian movement is hardly perceptible, and in water, in which it is very brisk, the only difference being that the distribution of equilibrium occurs much more quickly in water than in glycerin.

On the other hand, this Brownian movement, when studied by itself, will give us a new method of determining the size of the molecules, perhaps less intuitive than the preceding method, but just as accurate; it was suggested by Einstein in an admirable theoretical article (1905).

Without trying to follow the infinitely complicated path which a granule describes in a given time, Einstein considers only its displacement during that time; *i.e.*, the rectilineal segment which joins its starting-point to its final position, and shows that if certain fundamental hypotheses of the kinetic theory are correct, the knowledge of the *mean* value of this displacement enables us to determine the sizes of the molecules.

I cannot now give the details of this argument, and must confine myself to saying that the principal hypothesis used by Einstein consists in supposing not only, as has already been done, that at the same temperature all the molecules have the same mean energy of movement, but that even a perceptible granule has the same mean energy of movement. Then Einstein's formula gives this mean molecular energy, since we know the mean displacement in a given time, in a liquid having a known viscosity, of spherical granules of known radius. The molecular energy can be obtained thus, and at the same time the masses of the different molecules, for we have seen that we know what must have been their velocities in order that their bombardments on the walls might explain the pressures observed.

Einstein pointed out that the order of magnitude of the displacements observed agreed perfectly with the theory, and left to the experimenters the task of making a more precise comparison. Since I had round granules of known

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[*] A Discourse delivered before the Royal Institution, February 24, 1911.

diameter I was in a position to make this comparison, as M. Langevin pointed out to me when he told me of Einstein's theory, of which I was then ignorant. I first entrusted the measurements with gamboge to M. Chaudesaignes and with mastic to M. Dabrowski, and then I myself plotted the positions. The result was decisive, and showed the rigorous exactitude of Einstein's formula, the weight of the atom of hydrogen calculated by this method being $1{\cdot}45 \times 10^{-24}$ grms., practically identical with the number which the distribution in height of the emulsions gave me.

You see on the screen here, enlarged so that sixteen divisions represent 50 microns, three diagrams obtained by tracing the segments which join the consecutive positions of a single granule of mastic of radius $0{\cdot}52\ \mu$, marked at intervals of thirty seconds, with a clear chamber. It was by taking the mean of similar segments that Einstein's formula was verified.

These diagrams, however, give you only a very feeble idea of the enormous complexity of the actual trajectory. If, for instance, the positions were plotted at the end of each second, each of these rectilineal segments would be replaced by a polygon of thirty sides, relatively just as complicated as the diagram here reproduced, and so on.

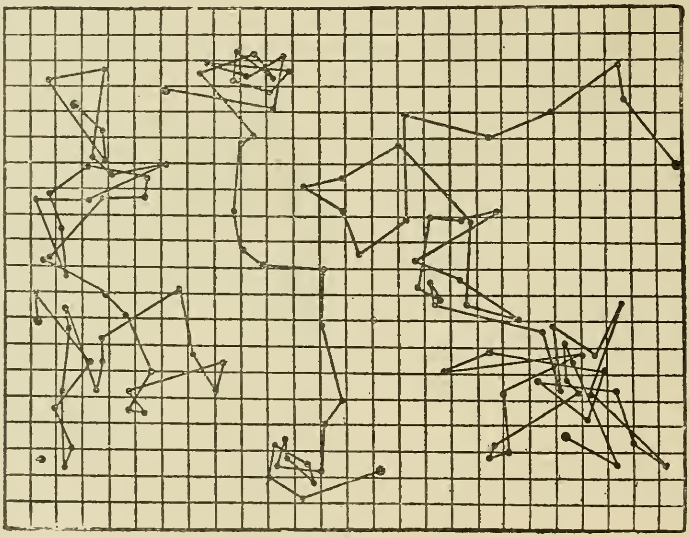

Fig. 5.

To vary these conditions I succeeded in preparing granules much larger than those which I had used up to the present. For that purpose I allowed water to fall slowly on an alcoholic solution of mastic, by a funnel with a drawn out tube. The granules which are formed in the zone of passage have usually a diameter of a dozen microns, a diameter which is measured directly in the clear chamber, and they are then about 100,000 times heavier than the smallest I used. In order that this weight should not keep them constantly in immediate contact with the bottom, I observed them in a solution of urea which has almost the same density as theirs. I have thus shown that Einstein's formula is still applicable. Finally, I proved another formula, also deduced by Einstein from the molecular hypotheses, which relates to the mean rotation of a granule in a given time. This formula foretelling about 100° of rotation per second for granules of the order of a micron would appear to be difficult to verify. But, luckily, I had large granules; owing to the size of these grains, and because some of them contained little enclosures which act as marks, *I have been able to demonstrate and measure their rotation.* The measurements, as yet not very accurate, gave me $1{\cdot}56 \times 10^{-24}$ as the weight of the atom of hydrogen, so that there is no doubt about the applicability of this new method of arriving at the size of the molecules.

I have nothing more to tell you about my researches, but you will at least allow me to mention other quite recent methods, which also enable us to determine the sizes of the molecules. One of them, due to Lord Rayleigh, gives the number of molecules contained in a column of air of calculable mass, from the diffraction which they cause in solar light, and which, favouring the most refrangible colours, is the origin of the *blue of the sky.*

To determine the size of the molecules it is thus only necessary to measure at the same time, for the same radiation, the light of the sun and in a known direction that of the sky. The measurements (Bauer and Moulin), which do not allow of great accuracy, because of the difficulty of calculating the part which the rays reflected from the ground take in the illumination of the sky, nevertheless give the order of magnitude very fairly, indicating within about 50 per cent $1{\cdot}6 \times 10^{-24}$ for the weight of the atom of hydrogen.

Another more accurate method is based upon the measurement of the electric charges transported by microscopic droplets, These charges are generally small, and are integral multiples of an atom of electricity, thus directly measurable, which is equal to that which an atom of hydrogen can transport in electrolysis. As the amount transported by 1 grm. of hydrogen is known, we have thus the weight of the atom. This method, suggested by Townsend and Sir J. J. Thomson, and perfected by H. A. Wilson, and especially by Millikan (who succeeded in proving very definitely the atomistic structure of electricity), actually gives numbers lying between $1{\cdot}4 \times 10^{-24}$ and $1{\cdot}7 \times 10^{-24}$.

Another group of measurements has its origin in the properties of radio-active substances. You know that some substances emit α-rays which make zinc sulphide phosphoresce. Sir William Crookes, examining this phosphorescence under the microscope, saw that it resolved itself into a swarm of scintillations extinguished as soon as they appeared. The rays which excite them are material, for wherever they penetrate the presence of helium may be proved (Rutherford); they are probably formed by atoms of helium positively charged. Sir William Crookes supposed that each scintillation marked the arrest of one of these atoms, which are hurled out with the enormous velocity of 20,000 km. per second. If then the number of scintillations due in a given time to a known mass of radio-active substance is counted, and if we measure the volume of the helium liberated in the same time, we know how many atoms this volume contains, and the size of the molecules follows from it. We can also (I do not lay stress on this point, simply for want of time) measure the positive charge radiated or the fraction of the radio-active substance destroyed. These wonderful experiments give for the weight of the atom of hydrogen numbers lying between $1{\cdot}4 \times 10^{-24}$ and $1{\cdot}6 \times 10^{-24}$.

I can only mention to you the existence of the beautiful theories by which Planck and Lorentz have connected the size of the molecules with the distribution of energy in the spectrum of an incandescent substance. The measurements, which may be made very accurate, now give for h the weight $1{\cdot}6 \times 10^{-24}$.

I think that you will be struck by the diversity of the ways which thus lead to the same result. If our hypotheses are false each of these phenomena could give any range of values lying between zero and infinity. For instance, as regards the Brownian movement the measurement of the mean displacement would give numbers differing for large and small granules. These values would, moreover, bear no relation to those, equally variable, given by the distributions in height. The facts that there is convergence, not only in each method, but in all the methods; that phenomena as fundamentally different as the viscosity of gases, the Brownian movement, the blueness of the sky, the electrification of droplets, radio-activity, the distribution of energy in the spectrum, all show the discontinuity of matter, and give the same magnitudes for the elements of matter, *these facts demonstrate the objective reality of the molecules*. Perhaps you will also find that this marvellous agreement gives you a good example of the satisfaction that the love of the beautiful finds in the study of the sciences.

DETERMINATION OF LITHIUM.

By LESLIE RUSSELL MILFORD.

In the work with the first samples of the Saratoga mineral waters, which the writer has been analysing, the determination of lithium was found to be difficult, and the results obtained were not satisfactory because of the fact that parallel determinations would not check and too small volumes of water had to be used.

The waters of these springs are highly mineralised, the chlorides ranging from 100 to 11,000 parts per million. Therefore, a great deal of trouble was experienced in volatilising the ammonium salts when working with large volumes of water. Mechanical loss, due to decrepitation and splitting apart of the crystals, was a constant source of error. On the other hand, if one took a small volume of water the chlorides could be dried and the ammonium salts driven off more easily, but the possibility of multiplying errors would be great because of the relative small amounts of lithium present.

The need of an improvement or change of the method given on page 29, *Bulletin* 91, of the Bureau of Chemistry ("Mineral Waters of the United States"), became apparent. By consulting the literature and various solubility tables (Atherton Seidell, "Solubilities of Inorganic and Organic Substances," 1907) and studying the methods of Gooch ("Mineral Waters of the United States," U.S. Dept. of Agriculture, Bureau of Chemistry, *Bull.* 91, 1906), Treadwell ("Analytical Chemistry," 1911), Kennicutt (Chamot-Redfield, "Analysis of Water for Household and Municipal Purposes," 1911), Frenkel ("Extract from the Records of Medical Hydrology and Climatology," Paris, December, 1903), and Rammelsberg (Treadwell-Hall, "Analytical Chemistry," 1911), the following procedure was adopted whereby a larger volume of water could be used and a residue obtained which would give, when treated, a lithium salt containing only a spectroscopic trace of sodium and potassium.

Method.—Two hundred to five hundred cc. of the water are evaporated to dryness in a large platinum dish with the occasional addition of small amounts of concentrated hydrochloric acid. After all of the water has been evaporated to dryness the dish and contents are heated at 120° C. for about thirty minutes to dehydrate the silica. The residue is then treated with a little dilute hydrochloric acid, just enough to moisten the contents of the dish. Then about 25 cc. of 95 per cent alcohol are added and the residue is rubbed up with a little pestle until all lumps and crystals are crushed. The alcoholic extract is then poured on an 11 cm. quantitative filter and the filtrate caught in another platinum dish. The residue is washed with 95 per cent alcohol until it shows no lithium line when examined in the spectroscope. The alcoholic filtrate and washings are united and evaporated on the water-bath. When all of the alcohol has evaporated some dilute hydrochloric acid is added to the contents of the dish, and the whole evaporated to dryness, and then the residue rubbed up with absolute instead of 95 per cent alcohol. The filtrate is caught as before in a platinum dish and the residue on the filtrate washed with absolute alcohol until no lithium line is seen when tested from time to time with the spectroscope. The alcohol is evaporated, and the dry residue taken up with a little dilute hydrochloric acid. Calcium hydrate is added until the solution is alkaline. The magnesium is precipitated as the hydrate and the solution is filtered. To the filtrate add ammonium hydrate and ammonium oxalate to precipitate the calcium. This is allowed to stand twelve hours or over night, when it is filtered off. The calcium oxalate precipitate must be thoroughly washed (usually about 100 cc. of water is sufficient) as lithium is held relatively fast by the precipitate, and does not wash out easily. When the residue no longer shows lithium, as verified by the spectroscope, the solution is evaporated to dryness and the excess of ammonium salts driven off by first heating the dish on a radiator, then over the free flame. The residue in the dish is taken up with a little dilute hydrochloric acid, heated, and ammonia and ammonium oxalate are again added to precipitate any calcium which might be present. In any case the solution is filtered from any calcium or magnesium that precipitates on concentrating the solution. The filtrate is evaporated to dryness, and all ammonium salts are driven off by heating in platinum to a little below redness. The residue is again taken up with water, filtered, and washed (using as little wash-water as possible), then evaporated to dryness and heated in platinum to a little below redness to drive off any ammonium salts. All of the calcium and practically all the magnesium have now been removed, and there is left a residue containing lithium chloride with traces of sodium and potassium chlorides. If we have iodides and bromides present, this residue will contain small amounts of these substances because they are more soluble than the chlorides. In order to insure a residue consisting of chlorides only we treat the contents of the dish with a little dilute hydrochloric acid and chlorine water, evaporate to dryness, and gently ignite. By this we have replaced the iodine and bromine with chlorine.

The residue is now taken up with a little water and treated with a few drops of dilute hydrochloric acid and transferred to a large platinum dish.

About 30 cc. of amyl alcohol are added, and the contents of the dish brought to boiling with constant rapid stirring when heating to minimise the bumping caused by the escape of the water. When all of the water has evaporated, the dish is placed on the steam-bath and a drop of dilute hydrochloric acid added to reconvert small amounts of lithium hydrate to the chloride. The evaporation is continued until the volume reaches about 15 cc.

The amyl alcohol is then filtered into a platinum dish and evaporated to dryness. Water and a few drops of dilute sulphuric acid are now added, and the contents of the dish again evaporated to dryness. The excess of sulphuric acid is removed by heating the dish over a radiator and then over the direct flame to dull redness. The dish is cooled, the contents dissolved in water, and a few drops of ammonium hydrate are added to precipitate the last trace of magnesium which is invariably present at this stage. Filter, wash with boiling water, evaporate to dryness, free from ammonium salts, and repeat previous process till no more magnesium precipitates on addition of ammonium hydrate. Finally filter into a weighed platinum dish, evaporate to dryness, burn, cool in a desiccator, and weigh as lithium sulphate. From this result we subtract 0·0017 grm. to correct for the solubility of the sodium and potassium chlorides in amyl alcohol, their presence having been verified by the spectroscope.

The contents of the filters containing the NaCl, KCl, &c., which were taken out by the 95 per cent alcohol and absolute alcohol together with the contents of the platinum dish and filter from which the amyl alcohol has been driven off, are all dissolved in water, united, freed from other salts, and made up to a definite volume. By using aliquot portions we can determine sodium and potassium by Gooch's method. Or the usual procedure, using a small portion of the silica filtrate, can be followed.

Advantages Given by this Modification.

1. Waters high in chlorides can be handled with ease with no danger of loss of lithium by decrepitation.
2. Large volumes of water can be used, thus reducing the error when computing to milligrms. per litre.
3. The results can be found to check and can be obtained much more quickly by having a residue free from an excess of sodium and potassium chlorides.
4. The method involves the use of calcium hydrate instead of barium hydrate for the precipitation of magnesium. This procedure does not introduce another substance which has to be removed by ammonia and ammonium oxalate, because we have our calcium in common and have a precipitate of calcium oxalate which is less soluble and more easily washed than barium oxalate.—*Journal of Industrial and Engineering Chemistry*, iv., No. 8.

INDUSTRY AND CHEMISTRY OF SUGAR.

The following are abstracts of most of the papers which were presented before Section V.*a* of the Industry and Chemistry of Sugar in the Eighth International Congress of Applied Chemistry which has just drawn to a close in New York:—

"*Contribution à l'Etude des Torteaux d'Ecumes en Sucrerie.*" By Lindet et Charpentier (Paris).

The scums contain no free lime when properly washed with ammoniacal water; the remaining sugar is not there as soluble sucrate but as free sugar. The cakes contain also some insoluble tricalcic sucrate, which CO_2 has not decomposed. Shown by difference between sugar extracted in presence of HA and in presence of water alone. No lime, precipitable by CO_2, can be washed out by water or sugar water. Phenol water removes from press cakes from 0·58 per cent to 1·48 per cent of lime, which had been combined with albumin, pectin, &c. It does not dissolve carbonate of lime.

"*Sur la Précipitation incomplète par le carbonate de soude de la chaux combinée dans les jus sucrés.*" By T. de Grobert (Paris).

The theoretical amount of Na_2CO_3 was added to filtered beet juice to precipitate the lime. Fifty-two per cent of it was taken up in precipitating 52 per cent of the lime as carbonate, 30 per cent of it was neutralised by organic non-sugars (asparagin, glutamine, and other amides), and 18 per cent remained free. When double the theoretical amount was used 40 per cent of it was taken up in precipitating 81 per cent of the lime, 22 per cent by organic substance, and 38 per cent remained free. It is best to use not more than the theoretical amount.

"*Sur les relations entre la richesse saccharine des racines et les caractères chimiques des descendants d'une betteravemere dans la premiere generation.*" (I.). By K. Andrlik and J. Urban (Prague).

But little relation exists between weight or root and sugary strength, but saccharine richness increases as the foliage weight is less, in individuals one generation removed from a common mother beet. Low sugar strength corresponds to low dry matter in root or foliage. High sugar corresponds to a slight increase in ash of roots and a larger increase of ash in foliage. Nitrogen in roots or foliage may vary greatly for the same sugar content, though high sugar is apt to be accompanied by a slight rise in nitrogen in both roots and foliage and *vice versâ*.

"*Variabilite de la composition chimique des descendants d'une betterave porte-graine dans la premiere generation.*" (II.). By K. Andrlik and J. Urban (Prague).

The amplitude of variability of the nitrogen in beet roots of the first generation coming from the same mother beet = 88·2 per cent of the mean value found in the descendants studied (0·248 per cent); in leaves, 67·1 per cent of the mean N (0·325 per cent).

	Per cent.			Per cent.
Dry material in roots ..	33·4	of that present		(23·56)
Dry material in leaves ..	71·9	,,	,,	(13·78)
Ash in roots	64·7	,,	,,	(0·692)
Ash in leaves	81·8	,,	,,	(3·25)
				Grms.
Weight of fully developed roots	193	,,	,,	(331)
Weight of fully developed leaves	189	,,	,,	(357)
				Per cent.
Richness in sugar in roots	28·5	,,	,,	(16·3)

All these values refer to the period of maximum development of the foliage.

"*Variabilite de la consommation de l'azote des descendants d'une betterave porte-graine dans la premiere generation.*" (III.). By K. Andrlik and J. Urban (Prague).

The amplitude of variability of the development of nitrogen in individuals of the same lineage amounts to 202·6 per cent of the average development, that is, 1·98 grms. per plant. Sugar varies also. The ratio of nitrogen to 100 parts of sugar varies in different individuals. This varies to the extent of 81·8 per cent of the mean amount of nitrogen, which was for this generation 3·67 per cent sugar in the plant. The plants richer in sugar contain less nitrogen and *vice versâ*. By polariscopic selection of the beets, those higher in nitrogen are probably eliminated.

"*Etude Chimique sur la carbonation.*" By K. Andrlik and V. Stanek (Prague).

1. During triple carbonation the initial polarisation of the juice diminishes from 0·04 per cent to 0·16 per cent, and appears to be affected proportionally to the lime used.
2. Increasing the lime from 1·5 per cent to 3·5 per cent on weight of juice produces noticeable effects only in juices under 88 purity, where purity is slightly raised and ash and nitrogen diminished.
3. This same increase in lime affects the colour, which decreases as lime increases.
4. About 0·25 per cent of organic matter, on weight of raw juice, is further removed when 1·5 per cent to 3·5 per cent of lime is used.
5. The presence of water of combination in scums was demonstrated in those obtained by carbonating the lime (*a*) suspended in water, (*b*) suspended in sugar solution, (*c*) in scums from carbonation of raw juice. Elementary analysis of the scums has shown that the usual analysis

makes the extent of purification in regard to organic matters produced by the increase of lime appear to be two or three times greater.

"*How the Netherland Sugar Fabricants are being kept Informed, during Campaign, about the Quality of the Raw Sugar Produced.*" By M. G. Hummelinck and J. A. van Loon, Ph.D. (Holland).

Each manufacturer sends 1 kilo. sample of his week's raw product to the General Technical Society, who mix 500 grms. of the sugar quickly with 50 grms. water and put into a 5½ inch centrifugal with 48 threads per inch to inner gauze and 34 in outer. Raised to full speed of 2000 R.P.M. in ten seconds, and run two minutes more, sprayed in 15 seconds through pipette having lateral openings with 50 cc. water, and spin stopped at end of four minutes from start. Colour compared with standard, lowest admissable called 1. More colour is penalised. Charts are kept showing each run by a curve.

"*Sugar Beet Seed Growing in the United States.*" By C. O. Townsend (Garden City, Kansas).

Beet seed growing in the United States is in its infancy, but is important, as the best results are had from seed adapted to environment. Soil, climate, and the individuality of the grower are the principal factors. Beets of the best size, shape, and general health are selected at harvest time, a sample bored out and tested for sugar (and purity in composite sample), and the satisfactory beets siloed in and under sand or earth. They are planted 2½ or 3 feet apart very early in the spring and well cultivated. The seed stalks are cut when ripe, dried, threshed, and cleaned. Curly top fields of beets should be discarded; so should rotten beets.

"*The Status of Sugar-cane Manufacture in the Hawaiian Islands.*" By Noel Deerr.

566,031 short tons of sugar produced in 1911. Crop lasts thirty weeks. Most factories produce under 10,000 tons, some produce up to 50,000 tons. Lahaina (Bourbon, or Otaheite) cane principally is raised and generally is irrigated. Sixteen to 18 per cent of sucrase in some of the cane; average = 15 per cent, with 90 purity. Yellow Caledonia-cane pulls average down to 14·5 per cent. Nine, 12, and one 18-roller mills are used. Ten to 50 per cent maceration water, average 30 per cent, 90 to 96·75 per cent of the sugar in cane is extracted, average 93 to 93·5 per cent. Defecation with lime raises purity less than 2 per cent. Filtered through mechanical filters or wood shavings. Quadruple submerged vertical tube evaporators are used. Some calandria pans with 45° tubes. Return of molasses and crystallisation in motion suppress low goods. Sugar polarise 96 to 97, water 1 per cent; molasses = 45 true purity. Dutch oven furnaces and multitubular fire tube boilers. Fibre in cane = 12·3 per cent. 12·7 sugar produced per cent cane.

"*Notes on Sugar Manufacture in Porto Rico.*" By G. W. Rolfe (Mass. Inst. of Tech., Boston, Mass., U.S.A).

Sugar production has increased sevenfold since the Spanish-American war, and there are over forty Centrals, nearly all having modern machinery. Drainage and irrigation will bring much more land under cultivation. Nine-roller mills are usual, and give good results. Continuous defecation is used largely and drip feed, film type evaporators are used in many places. Vacuum pans are often poorly designed, and are not economical of steam. Some electric driven centrifugals are in use. Crystallisers are universal. Java methods of boiling are generally used.

"*Production of Alcohol and Sugar from the Sap of the Nipa Palm.*" By H. D. Gibbs (Bur. of Science, Manila, P.I.).

This palm grows abundantly in swampy lands with brackish water. Sap oozes from a cut below the flower on the flower stalk. 17·5 per cent solids, 16·5 per cent sucrose, trace of acid and of glucose. Fifty-four per cent nitrogenous substances. Trees yield 43 litres of sap each year for fifty years. 90,000,000 L. sap now produced yearly. Distilled, giving 10 million L. alcohol, used in brandies and all the usual ways. Two thousand plants per hectare can be raised and sugar made from juice, which should amount to 12 per cent, or 10,750 kgs. per hectare yearly (180 day campaign). With initial liming sap keeps ten days.

"*Sour-cane in Louisiana.*" By William E. Cross.

Cane killed by a freeze is caused to ferment rapidly if warm weather follows the freeze, as is commonly the case. The cane is cut and windrowed immediately upon a freeze where possible. The fermentation may produce dextrin, acetic acid, or alcohol. Dextrin is the most melassagenic and prevents graining at once, but disappears during six or eight months in the hot room. Acid produced by fermentation is best neutralised by sodium carbonate. Cane giving juice below 65 purity is rejected, other damaged canes are bought on a sliding scale or on an arbitrary basis. Usually a cane 10 cc. of whose juice neutralise 3 cc. of N/10 NaOH is considered the limit, though dextrin should be given greater consideration than mere acidity.

"*Bestimmung des Zeinheits Quotienten des Rubensaftes in der Digestionslosung.*" By Franz Herles (Graben 27 N. (Bazar), Prag, Austria).

The composition and so the purity of beet sap from the press vary with conditions, so the purity is of little value. The fineness and the method of extraction with warm water affect the results. The refractometer gives the density better than spindling. Two normal weights of beet pulp obtained with the Herles press are mixed with 354 cc. water, filtered, and the specific gravity taken in filtrate. To this is added 1/10 volume of 25 per cent lead acetate solution for polarisation, from which and the density the purity is obtained as well as the sugar content of the pulp.

"*Le Sucre Clerget des Melasses normales de betteraves par double polarisation neutre.*" By Prof. E. Saillard (Ecole Nationale des Industries Agricole, Paris).

1. The usual salts in molasses diminish the R. rotation of sucrose more than the L. rotation of the corresponding invert sugar.

2. Hydrochloric acid increases the L. rotation of invert sugar, SO_2 is without effect on the same.

3. The usual salts tend to cause the rotation of the nitrogenous matter to pass from L. to R. Salts vary in power in this respect. If one added hydrochloric acid to the nitrogenous matter and salts the rotation to R. becomes about equal.

4. In equivalent quantities hydrochloric acid increases the right rotation of asparagine and glutamic acid more than SO_2 does.

5. Hydrochloric acid in direct polarisation of pure sugar always diminishes the observation, the same if it is mixed with urea and observed in two or three minutes. SO_2 does not cause inversion of sugar at 20° during the time necessary for polarisation, but one cannot say how much SO_2 will produce the same deviation to the R. as the hydrochloric acid used for inversion. This quantity varies in molasses, especially if they contain different quantities of invert sugar. SO_2 has no effect on the rotatory power of invert sugar.

6. Ogilvie's method of 1911 differs from Pellet's of 1891 and 1897 in the use of SO_2. Even the former's modification of 1911 cannot be recommended for molasses analysis.

7. Clerget's method of 1852 for removing the influence of nitrogenous materials by adding to the direct polarisation two-sevenths of the difference between the polarisation to the left of the neutral inverted solution and of the acid inverted solution cannot be recommended.

8. One may determine the Clerget of normal beet molasses either by Andrlik's urea method at 20° C., or Ogilvie's by invertase, or by the method of double neutral polarisation with the use of NaCl or KCl for the direct

polarisation (Saillard). These observations do not apply to molasses containing much raffinose.

9. The French Clerget method, like the Clerget-Herzfeld method, gives too low a sucrose, especially in presence of much nitrogenous material.

"*Objectionable Nitrogenous Compounds in Sugar-cane Juice.*" By Fritz Zerban (Expt. Stn., P.O. Box 238, Rio Pedras, P. Rico).

While knowledge of these materials is meagre asparagin, glutamin, glycocoll, and leucin have been reported in cane-juice. The author investigated the nitrogenous constituents in the precipitate produced by $Hg(NO_3)_2$ and by Hg_2 in the filtrate after treating cane-juice with lead acetate and filtering. The principal substance found was *l*-asparagin with usual quantities of *a*-glutamine and of tyrosin. Sugar-cane does not differ from other plants in regard to the intermediate substances between inorganic nitrogenous compounds and plant proteids. Asparagin and glutamine break up during manufacture and partly form aspartic and glutamic acids. About 0·1 per cent asparagin occurs in juices, and would tend to give polariscopic readings about 0·1 per cent high. Glutamine partly neutralises this.

"*Determination of Moisture in Molasses.*" By Chas. C. Roberts (75 W. Lacrosse Ave., Lansdown, Pa., U.S.A.).

Difficulties in drying molasses are due to action of air at high temperatures and occlusion of water by external film formed. Drying undiluted molasses on platinum dish gives low results. Drying diluted molasses on pumice is unsatisfactory and tedious. Best method found was to drop about 7 grms. of about 30 per cent molasses in water on Adams's paper strip, and drying about three hours in air-bath at 98° C. for total water, or at 70° C. for moisture.

"*An Electrolytic Apparatus for Use in Invert Sugar Determinations.*" By B. B. Ross (Alabama Polytechnic Institute, Auburn, Ala.).

The Cu_2O obtained in the gravimetric invert sugar determination is washed into a stopcock tube having a restricted portion below the shoulder for the asbestos, with a platinum wire coil fused through the glass. After washing the Cu_2O clean, the cock is closed and the large tube three-quarters filled with dilute HNO_3 (4 cc. of 1·42 sp. gr. acid per 100 cc.), the platinum cylindrical cathode immersed in the acid, and a current, giving not over 1 cc. electrolytic gas per minute, passed, using the wire coil as anode. After deposition the acid is washed out and the cathode dried and weighed.

"*Determination of Sucrose in Confectionery containing Cooked Starch and in Marsh Mallows.*" By Chas. C. Roberts (Appraisers Stores, Philadelphia, Pa.).

26·048 grms. of material are dissolved in alcohol (400 cc. commercial alcohol make up to 1000 cc.), transferred to a 200 cc. flask, clarified with sub-acetate of lead solution (sp. gr. 1·25) or alumina cream, or both, made up with dilute alcohol to mark, filtered (covered), and polarised. Fifty cc. of the filtrate is evaporated in a covered beaker until no odour of alcohol remains, inverted by any recognised method, and polarised. Sucrose is calculated by Clerget's formula.

"*A Revision of the Hundred Point of the Saccharimeter.*" By Frederick J. Bates and R. F. Jackson (Bureau of Standards, Washington, D.C., U.S.A.).

Prepared pure sugar by two re-crystallisations. Ten grms. reduced 37 mgrms. Cu, while 1 mgrm. added invert sugar precipitated 2·5 mgrms. Cu more. Thus 0·01 per cent × 37/25 = 0·15 per cent reducing substance. This was partly due to reducing action of sucrose itself. By using Striegler's alkaline carbonate solution in place of the caustic alkali (V. Lippmanns, *Die Ch. Zuckerarten*, i., 606) only 7 mgrms. Cu_2O fell, while 1 mgrm. added invert sugar precipitated 3·2 mgrms. Cu_2O. No increase in reducing substances occurred during concentrating the sugar solution from 40 per cent to the crystallising point *in vacuo* at 32° C. 0·01 per cent invert sugar added caused precipitation of 1·9 mgrm. Cu_2O. The purified sucrose contained 1·1/1·9 = 0·006 per cent reducing sugar. To show the difference in speed of reaction between the reduction of Cu_2O by sucrose and by invert sugar, tests were run on pure sugar varying boiling from two up to six minutes and other similar tests with addition of 0·01 per cent invert sugar. The action of sucrose is progressive and increases with time. Action of invert sugar is complete before two minutes.

Caramel is formed by heating pure sugar even at low temperatures. 0·01 per cent, as measured by alkaline copper solution in terms of invert sugar, is produced at 79·5° C. in 1·8 hour; at 66·6° C. in 10·9 hours; at 50° C. in 107 hours; at 39° C. in 478 hours. For drying the air dried sample was ground in a mortar, placed in desiccator over $CaCl_2$ or CaO, and heated at 50° C. in a receiver exhausted to 1 or 2 mm. of Hg, sometimes for four hours.

They established the sugar values of certain quartz plates by comparison with sugar solutions of known concentration, and subsequent determination of the absolute rotation in circular degrees of the plates for monochromatic light of wave-lengths 589·25 (Na) and 546·1 (Hg). In addition measurements were made on solutions for monochromatic light with the polarimeter. 78·385 was found to be the optical rotation with Hg vapour light. Plate I. had a rotation value of 34·5969 for wave-length 589·25 and 40·668 for wave-length 546·1. The sugar value of the plate was found to be 99·827, but it reads on the saccharimeter only 99·812, therefore 0·015 must be added to the scale of the instrument. This scale correction added to the mean rotation of normal solution found gives only 99·912 instead of 100·00. The authors conclude tentatively that the Herzfeld-Schonrock standard is in error. Consequently the rotation of the normal quartz plate becomes 34·626 for wave-length 589·26 and 40·703 for wave-length 546·1.

"*A Constant Temperature Laboratory for the Polarisation of Sugars.*" By C. A. Browne.

The constant temperature room of the New York Sugar Trade Laboratory is 24 × 18 feet and 10½ feet high, containing tables for making up and filtering solutions, and three polariscopes, with a capacity of 150 samples to be tested in duplicate daily. The ceiling and wooden partitions are insulated by half-inch hairfelt between heavy papers, overlaid with matched boards seven-eighth inch thick, tongued and grooved. Double windows are used, and a door of cold storage type. An 8 h.p. ammonia compressor, mounted on the outer wall, rated at 5 tons refrigerating capacity per twenty-four hours, is used, driven by a 7·5 h.p. field control electric motor. The hot ammonia gas is liquefied in a 6 pipe condenser 12 feet long, using 600 to 900 L. water per hour. The liquefied ammonia expands in 300 feet of piping surrounded by an insulated cooling box through which the air for the laboratory is circulated by an electric fan. 600 cubic feet of air per minute is the maximum used. The equipment and installation cost 3000 dols., the hourly cost of electricity and water is 0·289 dol. Moisture is removed by the refrigerating pipes from incoming air, which is automatically regulated by dampers in air ducts, regulating the temperature to within one degree of 20° C. The motor and compressor are in an insulated compartment to exclude their heat.

"*Action of Disinfectants on Sugar Solutions.*" By Geo. P. Meade (Gramercy, Louisiana, U.S.A.).

Experiments on raw juice and on raw sugar washings showed that formaldehyde, chloride of lime, ammonium fluoride, and a cresolic preparation all tended to hasten the deterioration of a sugar solution when present in about 1 part to 10,000 parts of sugar solution. This is evidently due to stimulating action on both yeasts and bacteria. No such action took place in sterile sugar solutions.

NOTICES OF BOOKS.

The Chemical Constitution of the Proteins. Part I. *Analysis.* By R. H. Aders Plimmer, D.Sc. Second Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

A vast amount of work has been done in biochemistry since the first appearance of this book three years ago, and the chemistry of the proteins especially has been the subject of a great number of investigations. But the quality of the work done is hardly comparable with its quantity, and the author has no very important results to chronicle. Many of the investigations are still incomplete, and very frequently the results so far obtained are not even of unimpeachable accuracy. However, the second edition has been thoroughly revised in accordance with recent work, and in particular more detailed accounts are given of methods of analysing the proteins.

The Life of the Plant. By C. A. Timiriazeff. Translated by Miss Anna Chéréméteff. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

The lectures which the text of this book reproduces were delivered in Moscow, as long ago as the winter of 1876, and the English translation has been made from the seventh Russian edition. It is interesting to notice that the author was led to consent to the translation of them into English when he read the Presidential Address delivered by Prof. Armstrong before the Association of Public School Science Masters in January, 1910. Curiously enough the lectures followed very closely the syllabus suggested for botanical work suited for schools—beginning with the analysis of flour and ending with an exposition of Darwin's theory. They were intended to give the general public a real understanding of the most important facts of plant physiology, and they fulfilled their aim admirably. In clear and graphic language the author described the life of the plant, the functions of its various parts, its growth, the origin of organic forms, and Darwinism, of which he is a firm adherent. The book is very well illustrated, and cannot fail to arouse interest, owing to the freshness of its style and the excellent choice of material that has been made in it.

Methods of Organic Analysis. By Henry C. Sherman, Ph.D. Second Edition. New York: The Macmillan Company. 1912.

This book gives concise directions for all the usual analytical work applied to food and similar substances, and is adapted for the use of both students and practising chemists. Full references are given to larger treatises for the less common or more difficult processes, but representatives of all the more ordinary methods of estimation are described in detail. In the second edition some parts, such as those on sugars, proteins, and food preservatives, have been very much enlarged, while a new chapter has been added on solid and liquid fuels, and sections on industrial alcohol, drying oils, and crude petroleum are now included, as well as one on quantitative work on enzymes.

Studies in Radio-activity. By W. H. Bragg, M.A., F.R.S. London: Macmillan and Co., Ltd. 1912.

The researches described in this book deal chiefly with the phenomena attending the passage of the α-, β-, γ-, and X-rays through matter; a subject to which the author has devoted his special attention. He has not confined himself in the book to the description and discussion of his own work, but has included that of other prominent investigators in his survey, and gives in outline the main features of all the important results which have been obtained in this region. His attitude towards hypotheses in which he does not place implicit faith is marked by a perfectly philosophical spirit, and the book is a model of a scientific monograph. The most important generalisation to be drawn from the anthor's work is perhaps that of the interchangeability of the X- and γ-rays and the moving electron, and he is a believer in the corpuscular theory of the X- and γ-rays, and would thus lay aside, provisionally at any rate, the ether pulse theory. The book is one which should be read by all students of radio-activity.

Catalogue of Books on Useful Arts, Engineering, Chemical Technology, Manufactures, Mechanic Trades, in the Bolton Central Lending and Reference Libraries. Bolton: Libraries Committee. 1912.

The Bolton Public Library Catalogue consists of three parts; a list of books classified according to subject, an author index, and a subject index; the Dewey decimal system of classification is adopted in it. The catalogue is well arranged, and a glance through it shows that the library contains a good representative selection of the most modern books on chemical technology, engineering, and allied subjects; it is also evidently kept well up to date as regards new editions of standard works in the English language.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xi.—xii., No. 15, 1912.

Colour Reaction of Ammonia.—Pierre Thomas.—The formation of a blue coloration when ammonia or an ammoniacal salt is added to an excess of phenol solution and a small quantity of alkaline hypochlorite is a reaction which may conveniently be employed to determine ammonia quantitatively, It has the advantage of occurring in a very slightly alkaline medium, and of possessing no great sensitiveness, except for ammonia and other fairly rare substances, such as monomethylamine and glycocoll. It may be used to determine ammonia in water, but not in the liquids of the organism.

Density of Uranous Oxide and its Solubility in Nitric Acid and Aqua Regia.—A. Raynaud. — The density of amorphous uranous oxide, prepared by the reduction of uranyl oxalate in a current of hydrogen, is 8·2. The substance is less soluble in aqua regia than in HNO_3 alone. In both cases the solubility increases slowly and regularly from 0 to 20°. It then increases more rapidly up to 50°, after which temperature the increase is very slight up to 100°.

Decomposition of Diphenyl-nitrosamine by Heat.—MM. Marqueyrol and Florentin.—Wieland has stated that the aromatic nitrosamines decompose at about 130°, but the authors have found that the decomposition occurs at a much lower temperature, both in boiling benzene in a current of CO_2, or *in vacuo* at 75°, 60°, or even at 40°, using the dry substance. Among the products are diphenylamine and diphenyldihydrophenazine. This decomposition provides a very convenient method of preparing pure NO.

Analysis of Complex Lipoids by Alcoholysis.—MM. Fourneau and Pieltre.—Alcoholysis can be applied o the ether-alcohol extracts of organs containing lipoids, phosphatides, cholesterine, and possibly active basic principles. Thus if yolk of egg is dried, the fat is removed by extraction in a Soxhlet apparatus and the extracts are alcoholysed by methyl alcohol and hydrochloric acid, it is found that 200 grms. of the dry substance contain 3·5 grms. of cholesterine, 38 grms. of lecithine, and 60 grms. of neutral fats.

Atti della Reale Accademia dei Lincei.
Vol. xxi. (ii.), No. 2, 1912.

Constitution of Trimethoxy-phthalic Acids.—G. Bargellini and Olimpia Molina.—The authors have prepared synthetically a compound which is undoubtedly 3-4-5-trimethoxy-ortho-phthalic acid, and is identical with Windaus' acid, obtained by oxidising cochinine with potassium permanganate. Hence cochinine must contain three OCH_3 groups in neighbouring positions. The steps of the synthesis are:—(i.) Preparation of trimethoxy-trichlor-methyl phthalide by the action of chloral hydrate on the methyl ether of trimethyl gallic acid in presence of concentrated sulphuric acid. (ii.) Conversion of this phthalide by the action of alkalis into tri-methoxy-phthalide carbonic acid, which, when heated to a temperature above its melting-point (180—200°), loses CO_2, and is transformed into the corresponding tri-methoxy-phthalide. (iii.) Finally, this compound is oxidised in alkaline solution with $KMnO_4$.

Unstable Nitrites Fixed by means of Organic Bases.—G. Scagliarini.—A nitrite of copper and pyridine can be prepared by adding an excess of a solution of sodium nitrite to a mixture of three or four molecules of pyridine and one of copper nitrate. On shaking the liquid minute crystals separate out, and may be re-crystallised from alcoholic pyridine. The formula of the compound is $Cu(NO_2)_2.2C_5H_5N$. The corresponding compounds of nickel and cobalt, $Ni(NO_2)_2.2C_5H_5N.2H_2O$ and $4Co(NO_2)_2.CoO.10C_5H_5N$, may be prepared similarly.

MEETINGS FOR THE WEEK.

Monday, 4th.—Society of Chemical Industry, 8. "Nitrogenous Constituent of Para Rubber, and its bearing on the Nature of Synthetic Rubber," by C Beadle and H. P. Stevens. "Corrosion of Metals and Alloys in various Solvents," by A. J. Hale. "Viscosity of Lubricating Oils," by A. E. Dunstan and J. F. Strevens.

—— Royal Institution, 5. General Meeting.

Wednesday, 6th.—Society of Public Analysts, 8. "Detection and Estimation of Arachis Oil," by Norman Evers. "Examination of Chinese and Japanese Wood Oil," by A. C. Chapman. "Estimation of Manganese by the Bismuthate Method," by H. F. V. Little. The President will exhibit an apparatus for testing the purity of water by measurement of its electrical conductivity.

Thursday, 7th.—Royal Society. "Radiation and Absorption of Light in Gaseous Media, with applications to the Intensity of Sky Radiation," by L. V. King. "Standard Measuring Machine," by P. E. Shaw. "A Spectrophotometric Comparison of the Emissivity of Solid and Liquid Gold at High Tempsratures with that of a Full Radiator," by E. M. Stubbs and E. B. R. Prideaux. "Optical Properties of Substances at the Critical Point," by C. Smith. "Absorption of Helium and other Gases under the Electric Discharge," by R. J. Strutt. "Discharge between Concentric Cylinders in Gases at Low Pressures" and "Influence of the Nature of the Cathode on the Length of the Crookes Dark Space," by F W. Aston. "Determination of the Absolute Unit of Resistance by Alternating Current Methods," by A. Campbell. "Some Unclassified Mechanical Properties of Solids and Liquids," by A. Mallock. "Trichromatic Theory of Colour Vision—The Measurement of Fatigue of the Retina," by Sir W. de W. Abney.

Thursday, 7th.—Chemical, 8.30. "Some Time Reactions suitable for Lecture Experiments," by W. G. Glendinning and A. W. Stewart. "Problem of Strong Electrolytes," by J. Kendall. "Action of Semicarbazide Hydrochloride upon the *p*-Quinones," by I. M. Heilbron and J. A. R. Henderson. "Aniline Black and Allied Compounds," by A. G. Green and S. Wolff. "Nitro hydrazo Compounds—Part III., Influence of Ortho-groups on their Formation and Condensation," and "Existence of Quinonoid Salts of Orthonitro Amines and their Conversion into Furazaneoxides," by A. G. Green and F. M. Rowe. "Interaction of Azoimide and Nitrous Acid," by E. A. Werner. "Methylbenzyl-, Ethylbenzyl-, and Allylammonium Nitrites," by P. C. Ray and R. L. Datta. "Action of Ethylene Oxide on Hydrazine Hydrate," by E. de B. Barnett. "Hydrolysis of Acetic Anhydride," by J. C. Philip. "Studies in Chemical Crystallography—Part I., Co-ordination, Isomorphism, and Valency," by T. V. Barker. "Condensation of Bromo-acylhalides with Glucosamine," by A. Hopwood and C. Weizmann. "Formation of Tetrachlorophthalyl Chloride by Chlorination of Tetrachlorophthalide," by W. H. Mills and W. H. Watson. "Preparation and Properties of Sulphonic Esters," by J. Ferns and A. Lapworth. "Electromotive Forces in Alcohol—Part III., Further Experiments with the Hydrogen Electrode in Dry and Moist Alcoholic Hydrogen Chloride," by R. T. Hardman and A. Lapworth. "Properties of α-Bromonaphthalene," by J. I. Crabtree and A. Lapworth. "Absorption Spectra of the Cobalto Derivatives of Primary Aliphatic Nitroamines," by A. P. N. Franchimont and H. J. Backer. "Oxidation of Aconitine," by F. H. Carr. "Constituents of *Cluytia similis*," by F. Tutin and H. W. B. Clewer. "Constitution and Reactions of Thiocarbamides," by A. E. Dixon and J. Taylor. "Effect of Heat on a Mixture of Benzaldehyde Cyanohydrin and Metachloroaniline and Metatoluidine," by C. W. Bailey end H. McCombie. "Pilosine, a New Alkaloid from *Pilocarpus microphyllus*," by F. L. Pyman. "Alkaloids of *Pilocarpus racemosus*," by H. A. D. Jowett and F. L. Pyman. "Ignition of Electrolytic Gas ($2H_2+O_2$) by the Electric Discharge," by H. F. Coward, C. Cooper, and C. H. Warburton. "Viscosity of Compounds containing Two Unsaturated Groups in Varying Positions in the Molecule—a Comparison of the Effects due to Spatially Proximate and to Chemically Adjacent Unsaturated Radicles," by A. E. Dunstan, T. P. Hilditch, and F. B. Thole. "Relation between Viscosity and Chemical Constitution—Part V., Viscosity of Homologous Series. Part VI., an Additive Relationship afforded by Viscosity," by A. E. Dunstan and F. B. Thole. "Contributions to the Chemistry of the Terpenes—Part XIV., Oxidation of Pinene with Hydrogen Peroxide," by G. G. Henderson and M. M. J. Sutherland.

MISCELLANEOUS.

The Late Dr. Loeb.—At a special meeting of the Board of Trustees of the Chemists' Club of New York City, held October 8th, the following resolutions offered by Committee, consisting of Mr. Ellwood Hendrick, Mr. Clifford Richardson, and Mr. Walter E. Rowley, were adopted:—

Whereas Morris Loeb, the President of the Club, has been taken from us by death, and

Whereas he was the leading spirit in bringing to fulfilment ambitions and plans that had long been ours, and

Whereas he was always ready to shoulder burdens and to give help, and

Whereas he was a man of order, and of integrity in mind and in heart, sincere in scholarship, living without malice or scorn, speaking no evil, and generous in judgment, and

Whereas we were drawn to him by ties of deep and abiding affection, now, therefore, be it

Resolved, That we make this minute of our poignant grief at his passing, and that we cherish his memory as another of his great gifts to science and humanity.

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THE BACTERIOLOGY OF AËRATED WATER.

By G. D. ELSDON, B.Sc., A.I.C.,
and
NORMAN EVERS, B.Sc., A.I.C.

During the past few years attention has been drawn to the bacteriological examination of commercial soda-water, and a number of results have been published by public analysts and others—*e.g.*, Klein, "Report of the Medical Officer of Health for the City of London" (*Analyst*, 1911, xxxvi., 16). Thirty-seven samples of commercial soda-water have recently been completely analysed in the City Analyst's Laboratory, Birmingham, with the following bacteriological results:—In no case has typical *B. coli* (flaginac) been found in 50 cc. In two cases fermentation was obtained in glucose taurocholate with 50 cc., in two cases with 10 cc., and in one case with 1 cc.; but in all these cases further examination showed that these were not typical *B. coli*. The number of organisms growing on jelly in three days, found in twenty-five samples stored in syphons, varied from 1 to 150 per cc.; whilst the number found in waters stored in bottles, all precautions being taken to prevent the access of bacteria during opening, was found to be in some cases 1000 to 3000 per cc.

It seemed desirable to find our how far these bacteriological results, obtained in many cases probably several days (and possibly weeks) after bottling, are of value as an indication of the purity or otherwise of the original water, for it seemed probable that the presence of carbon dioxide under pressure would have a deleterious action on the micro-organisms present in the water. For the purpose of carrying out these experiments, the apparatus known as the "Prana Sparklet" syphon was used. The syphons were thoroughly cleaned and steamed for one hour, with careful heating and cooling to prevent breakages, on each of two successive days, the syphon-head being plugged with wool. The water to be experimented upon was then run in by means of a sterile funnel, and carbonated in the usual manner. Small quantities were withdrawn from the syphon from time to time for the purpose of bacteriological examination, estimations being also carried out on the water itself as a control.

Such experiments were carried out on—(1) the number of organisms growing on jelly at 21° C., counting after three days; (2) the number of organisms growing on neutral-red lactose taurocholate agar (Rebipel agar) at 37° C., counting after two days; and (3) the power of fermenting glucose taurocholate broth.

1. *The Number of Organisms Growing on Jelly at 21° C.*

Various samples of water were taken and aërated as described above, and the number of organisms per cc. growing on jelly at 21° C. estimated after various lengths of time in both the carbonated and uncarbonated water. The results obtained are given in Table I.

These results, obtained from different types of water, show that the total number of organisms is rapidly reduced by carbonation, and in well-filtered waters, where the number of organisms is small originally, carbonation prevents these organisms from multiplying. In the case of the polluted water, it will be observed that the number of organisms was very rapidly reduced.

2. *Number of Bacteria growing on Rebipel Agar at 37° C. in Two Days.*

Sterile tap-water was in two cases inoculated with a small number of *B. coli* (flaginac) grown in peptone water for two days. Part of the water was aërated, and the effect of aëration observed as before (Table II.)

TABLE I.

Number of bacteria growing on jelly in three days at 21° C.

Source of water.	Original water.	After three days.		After seven days.	
		Control.	Carbonated.	Control.	Carbonated.
Filtered river ..	950	910	125	867	93
Filtered upland surface	19	845	15	4200	1
Unfiltered upland surface	391	Liq.	3	5500	1
	3400	7300	53	7400	44
	290	2650	63	1700	51
	10,000	36,800	397	33,900	142
Deep well	Liq.	240,000	950	—	—

TABLE II.

Original water		63	7000
After three days ..	Control.. ..	62	—
	Carbonated ..	58	—
After seven days ..	Control.. ..	57	6200
	Carbonated ..	25	38
After fourteen days	Control.. ..	46	6100
	Carbonated ..	5	5

TABLE III.

Number of bacteria growing on Rebipel agar at 37° C.

Source of water.	Original water.	After three days.		After seven days.	
		Control.	Carbonated.	Control.	Carbonated.
Deep well water	275	1820	66	—	—
	108	44	19	8	7
River water ..	347	714	23	905	2

Experiments were then undertaken on the number of organisms growing on Rebipel agar which are naturally present in waters. The method used was similar to the one under Section I. The results are given in Table III.

3. *Effect of the Addition of Sodium Bicarbonate on the Fermentation of Taurocholate.*

Fifty cc. of sterile carbonated water were added to taurocholate, and then inoculated with a little cultivated *B. coli* (flaginac) and incubated at 37° C. After twenty-four hours a vigorous acid and gas production was observed.

Fifty cc. of sterile carbonated water containing 10 grains per pint of sodium bicarbonate were added to taurocholate and inoculated as above. After twenty-four hours a vigorous growth was observed.

Fifty cc. of a well-water known to contain *B. coli* were taken, and sufficient sodium bicarbonate added to make the alkalinity equal to 10 grains per pint. The water was then added to taurocholate, and after incubating at 37° C. for twenty-four hours, a similar growth was obtained to that given by the original water.

Fifty cc. of carbonated water containing sodium bicarbonate equal to about 5 grains per pint were put into taurocholate; after twenty-four hours a vigorous growth was observed.

These results show that the growth of bacteria in glucose taurocholate is prevented neither by an alkalinity of 10 grains per pint of sodium bicarbonate, nor by carbonation, nor by both together.

4. *Organisms producing Acid and Gas in Glucose Taurocholate.*

The results given in Table IV. were obtained by growing natural waters in glucose taurocholate with and without carbonation. In the table, (*a*) signifies the carbonated water, whilst (*b*) signifies the uncarbonated or control water.

TABLE IV.

		50 cc.	10 cc.	1·0 cc.	0·1 cc.
Well-water A—					
Original		+	+	+	−
After four days ..	(*a*)	+	+	−	−
	(*b*)	+	+	−	−
After seven days ..	(*a*)	+	−		
	(*b*)	+	−		
Well-water B—					
Original		+	+	+	−
After four days ..	(*a*)		+	+	
	(*b*)		+	+	
After seven days ..	(*a*)	+	+	+	
	(*b*)	+	+	+	
After twelve days ..	(*a*)	−	−	−	
	(*b*)	+	+	+	
Well-water C—					
Original		+	+	+	+
After four days ..	(*a*)		+	+	+
	(*b*)		+	+	+
After seven days ..	(*a*)		+	+	+
	(*b*)		+	+	+
After twelve days ..	(*a*)		+	+	+
	(*b*)		+	+	+

It will be seen that except in the case of the well-water B the carbonation did not sensibly affect the organisms fermenting glucose taurocholate in the time given.

Conclusions.

The general conclusions to be drawn from these experiments seem to be the following:—

(*a*) The total number of organisms growing on jelly at 21° C. is considerably reduced by carbonation, and a water containing originally a large number of organisms may, after a week's standing under pressure, contain only a number such as would be found in a very good water.

(*b*) *B. coli* are not so rapidly reduced as other organisms, but die off rather more rapidly than in ordinary water.

(*c*) The number of organisms growing on Rebipel agar are much reduced by carbonation, especially those which do not produce the typical *B. coli* red appearance. This latter fact was shown by the appearance of the plates after incubation.

(*d*) Ten grains per pint of sodium bicarbonate does not affect the growth of organisms in glucose taurocholate; neither does excess of carbon dioxide, such as is found in carbonated waters.

It follows, therefore, that bacteriological results obtained on a water which has been carbonated for more than twenty-four hours are of little value as an indication of the source or purity of the original water, except in the case of growth in glucose taurocholate. In this latter case correct results may probably be obtained for a week after carbonation.—*Analyst*, September, 1912.

SOME REMARKS ON THE THERMOCHEMISTRY OF BENZENE.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

I WAS very interested to read Mr. W. Tombrock's further communication on the above subject (CHEMICAL NEWS, cvi., 201), and I am glad to note that he agrees with the views I expressed in a letter dealing with his former communication (CHEMICAL NEWS, cvi., 173). Mr. Tombrock, however, still seems to be under the impression that Kekulé's formula can be harmonised with the thermochemical behaviour of benzene; I therefore contribute the following remarks, which show, I think, the impossibility of this.

1. If the difference in character between aliphatic and aromatic bodies causes, as Mr. Tombrock suggests, an appreciable difference in their thermochemical behaviour, this difference must be represented as a difference in the structural formulæ of the two classes of bodies. But this is just what Kekulé's formula does not do.

2. I give below an analysis of the thermochemical behaviour of benzene when repeatedly hydrogenated, in which I employ the "fundamental constants" I devised for dealing with thermochemical problems, and whose values I calculated from Thomsen's experimental data. These constants are more reliable than Thomsen's, because their values were not obtained by means of unlikely hypotheses (see my "On the Calculation of Thermochemical Constants," 1909). The experimental values (E) are Stohmann and Langbein's, already quoted by Mr. Tombrock; the theoretical values marked "K" are calculated on the assumption that Kekulé's formula is correct; the theoretical values marked "S" are calculated on the assumption that the benzene molecule contains nine C.C links, in a condition free from strain.

(i.) C_6H_6 (*Benzene*) + H_2 = C_6H_8 (*Dihydrobenzene*) + *w Cals.*

(E) $w = 0·8$ cal.

(K) One C:C link is replaced by one C.C link and two H atoms are added. Therefore $w = 2H' + L'_1 - L'_2 = \gamma' - \beta' = 46·0$ cals. $- 15·0$ cals. $= 31·0$ cals.

(S) Five C.C links are replaced by two C:C links and two H atoms are added. Therefore $w = 2H' + 2L'_2 - 5L'_1 = 5\beta' - 2\gamma' = 75·0$ cals. $- 92·0$ cals. $= -17·0$ cals.

(ii.) C_6H_6 (*Benzene*) + $2H_2$ = C_6H_{10} (*Tetrahydrobenzene*) + *x Cals.*

(E) $x = 25·8$ cals.

(K) Two C:C links are replaced by two C.C links and four H atoms are added. Therefore $x = 4H' + 2L'_1 - 2L'_2 = 2\gamma' - 2\beta' = 92·0$ cals. $- 30·0$ cals. $= 62·0$ cals.

(S) Four C.C links are replaced by one C:C link and four H atoms are added. Therefore $x = 4H' + L'_2 - 4L'_1 = 4\beta' - \gamma' = 60·0$ cals. $- 46·0$ cals. $= 14·0$ cals.

(iii.) C_6H_6 (*Benzene*) + $3H_2$ = C_6H_{12} (*Hexahydrobenzene*) + *y Cals.*

(E) $y = 53·6$ cals.

(K) Three C:C links are replaced by three C.C links and six H atoms are added. Therefore $y = 6H' + 3L'_1 - 3L'_2 = 3\gamma' - 3\beta' = 138·0$ cals. $- 45·0$ cals. $= 93·0$ cals.

(S) Three C.C links are broken and six H atoms are added. Therefore $y = 6H' - 3L'_1 = 3\beta' = 45·0$ cals.

(iv.) C_8H_6 (*Benzene*) + $4H_2$ = C_6H_{14} (*Hexane*) + *z Cals.*

(E) $z = 64·6$ cals.

(K) Three C:C. links are replaced by two C.C links and eight H atoms are added. Therefore $z = 8H' + 2L'_1 - 3L'_2 = 3\gamma' - 2\beta' = 138·0$ cals. $- 30$ cals. $= 108·0$ cals.

(S) Four C.C links are broken and eight H atoms are added. Therefore $z = 8H' - 4L'_1 = 4\beta' = 60·0$ cals.

The enormous differences between the experimental values and those calculated on the assumption that Kekulé's formula is correct, render this formula quite untenable, I think. The fact, however, that somewhat more heat is obtained than would be the case, according to theory, if benzene were a perfectly saturated body, indicates that the benzene molecule is in a slightly strained condition. The average value of the heat effect of this strain is given by the above calculations as $\frac{1}{4}(17·8 + 11·8 + 8·6 + 4·6)$ cals. $= 10·7$ cals. But probably that given by Equation (iv.), namely, 4·6 cals. is the most reliable. This value agrees very well with that (namely, 5·6 cals.) which I obtained from a consideration of the M.H.C. of benzene as determined by Thomsen. But even supposing that 10·7 cals. is the more accurate value, on the assumption that this total is contributed equally by each of the nine C.C links, this only works out to 1·2 cals. per link. By interpolation on the graph I have obtained (which has already appeared in the CHEMICAL NEWS) showing the connection between the angle of deviation of the carbon valencies and the thermochemical effect of the strain thus produced, I find that this corresponds to an angle of deviation of less than 3°.

The difficulty is to arrange the six C atoms in space so that the angles between the valencies shall not differ from the normal value of 109° 28′ by more than ± 3°. In fact, it does not seem to be geometrically possible; and both Claus's and Ladenburg's formulæ entail much greater deviations than this. It seems to me, therefore, that Baeyer and Armstrong's centric formula, which assumes that a condition of things quite different from that which obtains in the case of aliphatic compounds holds good in the benzene ring, is the preferable formula. It may, indeed, be said that the centric formula is merely a confession of our ignorance as to the intramolecular condition of benzene, but it is better to confess our ignorance than to assert, as Kekulé's formula does, that benzene is a highly unsaturated body in a condition of great intermolecular strain, when all the evidence shows that it is nothing of the sort.

I append the definitions of the constants used above for the benefit of readers who may not be acquainted with them.

H' = heat of formation of one C.H link from molecular hydrogen.
L'_1 = heat of formation of one C.C link.
L'_2 = heat of formation of one C:C line.
$\beta = 2H' - L_1 = 15{\cdot}0$ cals.
$\gamma = 4H' - L_2 = 46{\cdot}0$ cals.

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GALVANIC DEPOSITION OF COPPER ON PLASTER.

By A. DUFAY.

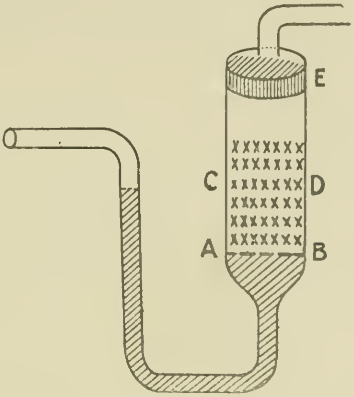
HEAT the plaster cast or object in a well ventilated oven at 50°, then introduce it into a paraffin-bath at 50° to 60°; remove it when no more gas is evolved, and allow it to cool. Cover the surface with a thin layer of photographic collodion, free from silver salts, diluted with 9 volumes of a mixture of alcohol and ether in convenient proportions. Allow it to dry. Coat with graphite, attach the conductors, coat with graphite a second time, and put the whole for a few minutes only into a 10 per cent solution of aluminium sulphate or alum. Connect the plaster cast with the negative pole of a source of electricity of E.M.F. of three volts, 1 ampère per square decimetre, and introduce into a bath of copper sulphate containing 5 to 8 per cent of sulphuric acid. Complete the circuit with a copper anode. A thin layer is very rapidly deposited, and the formation of it can readily be followed. Two reactions occur; firstly, reduction of the alumina to the metallic state, and secondly, combination of the aluminium and copper. In copper refining works this reaction could be used to produce cheaply, and even economising a small part of the current an alloy of aluminium and copper. For this purpose it would suffice to introduce into the bath a sufficient quantity of aluminium sulphate. The reaction can be used in analytical laboratories to determine alumina as aluminium by electrolysis. For by placing on the platinum anode made by a little grating in the form of a flat capsule a known weight of pure copper, and making the bath of aluminium sulphate to which a little nitric acid had been added, the aluminium could be determined by difference, for the increase of weight of the cathode would give the aluminium plus the copper, and the weight of the latter would be known.

A SIMPLE POTASH BULB.

By W. R. FORBES, B.Sc.

GEISSLER'S bulb was modified by Waters (*Journ. Am. Chem. Soc.*, 1910). The apparatus described below is a further modification. A good potash bulb should be light, easily cleaned, simple in form, and a good absorber.

A tube is drawn out in the form shown. At A and B internal glass projections are fused on which a perforated plate rests. Above this glass-wool is fairly loosely packed as far as C D, beyond which it is very loosely packed. The sube is closed at E by a ground glass stopper, which carries the exit tube. The tube is filled to C D with potash.



The layer of glass-wool beyond C D will retard evaporation and the carrying of much moisture by the issuing gas.

THE ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF SALTS OF NEODYMIUM AND PRASEODYMIUM AS MEASURED BY MEANS OF THE RADIOMICROMETER.

By HARRY C. JONES and J. SAM GUY.

(Concluded from p. 214).

Discussion of Results.

THE results for some of the solutions studied were plotted in the accompanying eleven curves. The percentage transmissions are the abscissæ, while the wave-lengths are the ordinates. These curves represent the transmissions of the solutions in question, and are termed transmission curves.

In Figures 1, 2, and 3 the transmissions of solutions of neodymium chloride are given in terms of Beer's Law. Here the product $n \times d = k$, where n is the concentration and d the thickness of the layer used. The concentrations beginning with Fig. 1 are:—3·43 normal, 0·875 normal, and 0·472 normal respectively; the corresponding depths of the solution being 2·5 mm., 10 mm., and 20 mm. The increase in the dilution from curve 1 to curve 2 is four times, while from curve 2 to curve 3 the dilution is double.

If the combined solvent plays no part in the absorption of a solution in that solvent, then these curves should be superposable, since we have kept the number of absorbers in the path of the beam of light in every case constant. In plotting the curves on such a small scale some of the details are lost, but a careful comparison of the curves will show that while there is, in general, *less transmission in the most concentrated solution and the absorption bands are somewhat wider, yet the intensity of the bands is greater* *in the most dilute solution.* This is especially true in the red and infra-red part of the spectrum, where the accuracy of measurement is greatest.

Photographic work done by the authors in this laboratory on the effect of dilution upon the absorption spectra of these same solutions (results soon to be published in full in a monograph of the Carnegie Institution of Washington), has shown that the absorption bands are always wider (more diffuse) in the most concentrated solutions. This does not, however, indicate that the intensity of the bands is really greater. It is probable that the width of any given band is partly a function of its diffuseness and not of its real intensity. It is evident that the photographic plate cannot give us any quantitative idea of the intensity of any band, since it is subject to changes due to times of exposure.

Let us consider the three absorption bands λ 7250, λ 7850, and λ 8600. In curve 1 the minima of transmission of these bands are about 4 per cent, 8 per cent, and 33 per cent respectively; while in curve 2 the minima of transmission are much lower; bands λ 7250 and λ 7850 reach zero, while band λ 8600 shows a still more marked decrease in transmission. These bands have been selected for discussion and not because the increase in intensity is peculiar to them alone. All the bands seem to show the same phenomenon. It is seen that the change in intensity of the band is greatest where the change in dilution is greatest, namely, from curves 1 to 2. Also the *position of the centre of the bands seems to be shifted slightly towards the longer wave-lengths* as the solution becomes more dilute.

Curves 4, 5, 6 show a similar test of Beer's Law for solutions of neodymium bromide. In these experiments the concentrations used were:—1·66 normal, 0·415 normal, and 0·207 normal respectively, while the corresponding depths of the solutions were: 2·5 mm., 10 mm., and 20 mm. In these solutions, as in those discussed above, we find the same general change in the intensity of the bands. They become more intense and slightly narrower as the solution is made more dilute; the product of depth of layer and concentration being kept constant.

Beginning with curve 4 there is a regular increase in the intensity of the bands, the increase being more marked where the change in dilution is greatest.

Curves 7, 8, and 9 represent the same test for solutions of neodymium nitrate. The concentrations were:—2·95 normal, 0·736 normal, and 0·368 normal; the corresponding depths of the solutions were the same as in the two previous experiments. The band λ 5700 of curve 7 seems to be an exception to the general relation pointed out above, but we think that this is due to an experimental error. This was the first solution studied by means of the radiomicrometer, and very small deflections were obtained in this portion of the spectrum. It is also seen that the change in intensity of the same band for the next dilution, as shown in curves 8 and 9, is in perfect harmony with the results obtained with the other salts of neodymium.

It is thus seen that we have three well defined cases; namely, solutions of neodymium chloride, neodymium bromide, and neodymium nitrate, *all of which show a well marked increase in intensity of the absorption bands with increase in dilution* when the requirements of Beer's Law are fulfilled. It is a well known physical principle that a resonator will vibrate more intensely when subjected to the vibrations from a single sympathetic resonator than when it is subjected to the vibrations from a large number of resonators, one of which has the same period as the original resonator and the others a pitch nearly its own. In a word, when several vibrators are near one another each seems to exert some influence upon those near it, and as a result none of them respond accurately to the pitch of the initial resonator.

The presence of an additional vibrator has a damping effect upon the other, and at the same time causes it to respond partially to vibrations slightly different from its own pitch, thus making the resonance less perfect.

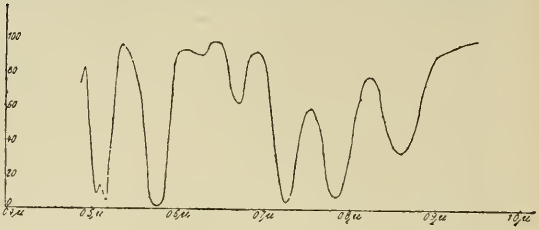


Fig. 1

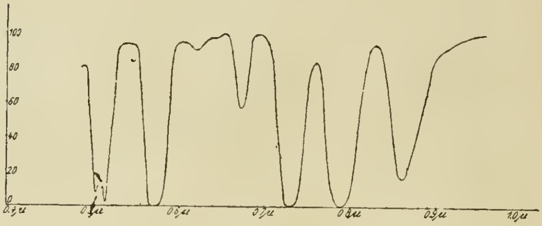


Fig. 2.

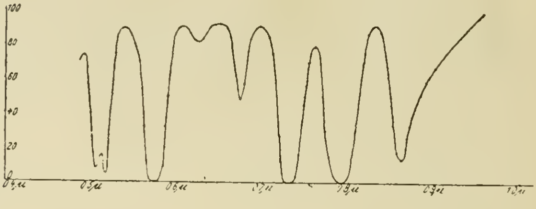


Fig. 3.

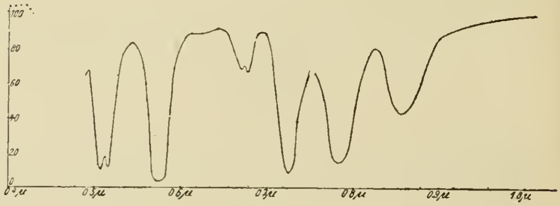


Fig. 4.

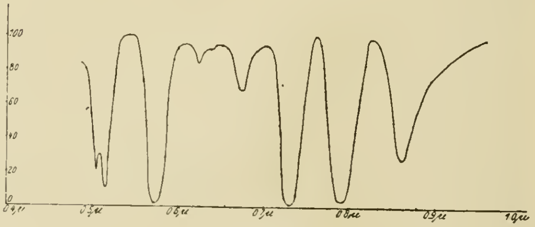


Fig. 5.

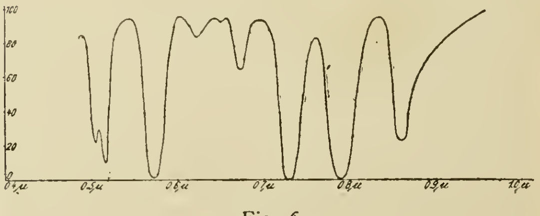


Fig. 6.

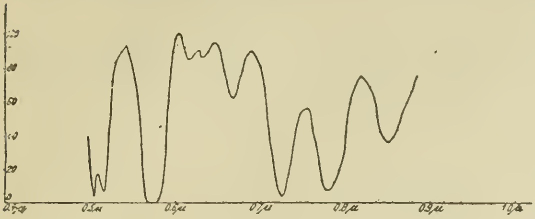


Fig. 7.

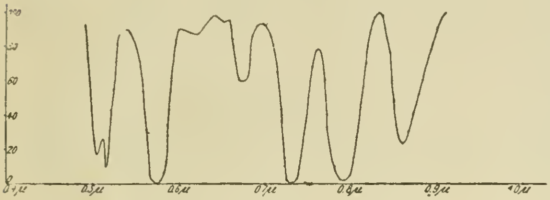


Fig. 8.

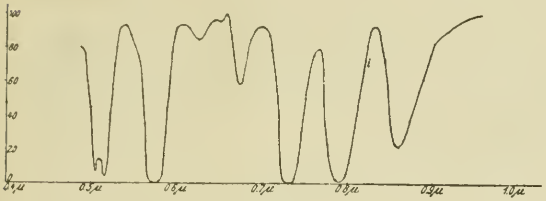


Fig. 9.

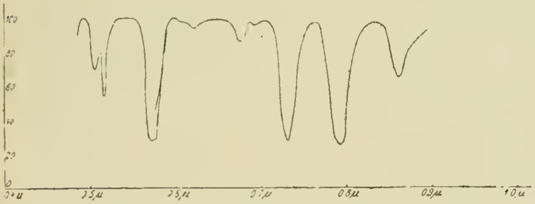


Fig. 10

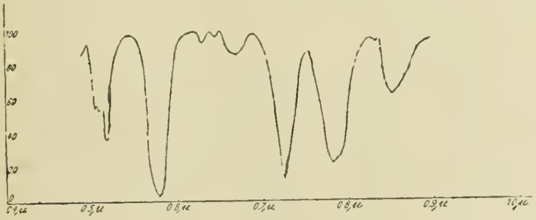


Fig. 11.

If we assume what is now generally accepted, that the absorption of light is a resonance phenomenon, it seems that analogous reasoning is justified here. In the most concentrated solutions, where the vibrators are close together, they so affect one another as to give imperfect resonance, and, consequently, the absorption bands are less intense.

In the dilute solutions where the vibrators are farther apart, and in most cases are protected by large amounts of water of hydration, the damping effect would not be so pronounced, and such a resonator would be freer to vibrate to its own wave-length and hence give a more intense resonance. The resonance being more nearly perfect would cause the absorption bands to be more intense.

This tentative suggestion to account for the above described fact is in agreement with the experimentally established facts.

Curves 10 and 11 show the transmission of neodymium sulphate and neodymium acetate; the concentrations being 0·118 normal and 8·84 normal respectively; corresponding depths of the solutions being 10 mm. and 2·5 mm.

It is seen that the absorption of the neodymium acetate solution for a given concentration is more intense than any other salt of neodymium thus far studied. This is in perfect accord with the results obtained for these various substances by the photographic method.

Beyond 1 μ the absorption of water is very great, and it is evident when working with very concentrated solutions we could not get comparable results by using the "water" cell and the "solution" cell of the same thickness. In the very concentrated solutions, such as the 3·43 normal solution of neodymium chloride, there is only about 50 per cent as much water as there is in the same depth of layer of pure water. In the region beyond 1 μ it was actually necessary to determine the water present and introduce a corresponding correction. This was not an important factor with the salts of neodymium, since no bands could be located in the region where water had a measurable absorption.

With praseodymium chloride and nitrate, however, bands were located down in the infra-red as far as 2 μ, and with these concentrated solutions the amount of water present had to be taken into account. This may be done in either of two ways. First, the specific gravity of the solution can be carefully determined, and knowing the concentration of the solution the percentage of water calculated. Knowing the actual amount of water present we can use a "water" cell of the proper thickness. If the very concentrated solution contains only 50 per cent of water, then to obtain comparable results we should use a cell 10 mm. thick for the solution and 5 mm. thick for the solvent. Under these conditions the amount of absorption due to water would be the same, since in the two cases there is the same depth of water in the path of the beam of light.

Another method is to keep the depth of the "water" and "solution" cells the same, and apply a correction to the final result. This has been done with the salts of praseodymium thus far studied; the results of which will be published at an early date.

Conclusions.

1. A very sensitive radiomicrometer has been devised and constructed.
2. The intensities of the known absorption bands of several salts of neodymium have been measured, and three new bands in the infra-red region have been detected and their wave-lengths determined. Their intensities have also been measured.
3. A suggestion based on the laws of resonance has been offered to explain the fact that when the conditions of Beer's Law were observed the transmission curves were not identical.

The work herein described in this preliminary communication is now being continued under grants from the Carnegie Institution of Washington, and is being extended to aqueous solutions of salts of cobalt, nickel, copper, iron, chromium, erbium, as well as to the aniline dyes and other organic coloured compounds.

As soon as the study of aqueous solutions is completed we shall extend this work to solutions in the various alcohols, acetone, glycerol, formamide, and other organic solvents; this being the quantitative counterpart of the qualitative work in locating the positions of the absorption bands in these solvents of these and other substances by means of the photographic method. We shall investigate also the aniline dyes in the various non-aqueous solvents.

In conclusion we wish to express our thanks to Dr. A. Springer, jun., who has assisted in making these measurements; to Dr. E. P. Wightman, who has kindly drawn the curves for us; to Dr. John Anderson, who was earlier engaged upon this work by the photographic method, for valuable suggestions during the progress of the work; and our thanks are especially due to Prof. A. H. Pfund, who first suggested the use of the radiomicrometer for studying infra-red absorption, who built for us the first radiomicrometer, and who has made a number of very valuable suggestions as the work progressed. The radiomicrometer used in making the measurements herein described was built by Dr. Guy.

It gives us especial pleasure to accept this opportunity to express our thanks to the Carnegie Institution of Washington for the financial aid so generously furnished, without which it would have been impossible to carry out this investigation.

THE QUANTITATIVE DETERMINATION OF PERCHLORATES.*

By ARTHUR B. LAMB and JOHN W. MARDEN.

In the course of a study of certain cobaltamines it became necessary to make accurate analyses of perchlorates. A study of the literature indicated that no really satisfactory method of analysis had been worked out, and a number of trials by several methods confirmed this conclusion. We finally located the disturbing factor in the simplest of these methods, and by a proper mode of procedure eliminated it altogether, so that now we can determine perchlorate with ease, speed, and accuracy.

A fusion method for the analysis of perchlorates, followed by the determination of the chloride formed, would seem to present no special difficulties. As a matter of fact, in spite of many attempts, it appears that no accurate results have heretofore been obtained in this way. Many different fusion mixtures and different methods of procedure have been suggested. The method of Bangley (Treadwell and Hall, "Analytical Chem.," vol. ii.), according to which the perchlorate is ignited with ammonium chloride, has been recommended, but it is admitted that an accuracy greater than 1 per cent cannot be expected. A method described by Carnot (*Comptes Rendus*, 1896, cxxii., 452) has also been recommended (Sutton, "Volumetric Analysis," 1904, p. 175). In this method the perchlorate is mixed with sand in a platinum crucible and this is heated to a dull red colour. Carnot claimed an accuracy of 0·1 per cent, but in spite of repeated trials we have been unable to approach this accuracy. The results of our last two trials, made with a pure sample of potassium perchlorate, were the best, and are given in Table I.

It will be seen that the errors are very considerable. It appeared in earlier trials as though these errors might be due to a loss by volatilisation, and the temperature was therefore kept as low as possible; but this could not be carried too far, as there was, on the other hand, the danger of incomplete decomposition due to too low a temperature. There is no sure way by this method of avoiding these alternative difficulties.

Dupré apparently appreciated these difficulties (*Journ. Soc. Chem. Ind.*, 1902, xxi., 825), for in determining the perchlorates in saltpetre by ignition, he used a platinum crucible surrounded by a specially constructed oven which maintained a constant temperature of 545°. His results appear to be somewhat better than those we have obtained by the Carnot method. The results of the only analyses he publishes, where adequate amounts of perchlorate were used, are given in Table II.

TABLE I.—*Analysis of Potassium Perchlorate by Carnot's Method.*

No. of expt.	Weight $KClO_4$ taken.	Weight AgCl calculated.	Blank.	Weight AgCl found.	Error (grm.).	Error (per cent).
1.	0·4562	0·4720	0·0000	0·4593	−0·0127	−2·69
2.	0·4677	0·4805	0·0000	0·4771	−0·0034	−0·70

TABLE II.—*Analyses of Potassium Perchlorate by Dupré's Method.*

No. of expt.	Weight $KClO_4$ taken.	Weight AgCl calculated.	Blank.	Weight AgCl found.	Error (grm.).	Error (per cent).
1.	0·0035	0·995	0·0000	0·986	−0·009	− 1·0
2.	0·0035	0·498	0·0000	0·492	−0·006	− 1·2
3.	0·0035	0·249	0·0000	0·250	+0·001	+ 0·4
4.	0·0035	0·099	0·0000	0·099	±0·000	0·0
5.	0·0035	0·050	0·0000	0·054	+0·004	+ 8·0
6.	0·0035	0·025	0·0000	0·028	+0·003	+12·0

These results are still very unsatisfactory.

TABLE III.—*Analyses of Potassium Perchlorate by Dietrich and Ballenbach.*

No. of expt.	Weight $KClO_4$ taken.	Weight AgCl calculated.	Blank.	Weight AgCl found.	Error (grm.).	Error (per cent).
1.	0·3924	0·4062	0·0000	0·4070	+0·0008	+0·19
2.	0·4436	0·4589	0·0000	0·4574	−0·0015	−0·32

Flux added: KNO_3 and KNO_2.

A method proposed by Dietrich and Ballenbach appears to be the most successful modification, so far, of the fusion method (*Ber.*, 1905, xxxviii., 751). These authors fused the perchlorate with a mixture of potassium nitrate and nitrite. The only results they have published are reproduced in Table III.

While better than any of the previously cited results their errors are still considerable.

Influenced by the ill success of these various modifications of the fusion method a number of investigators have worked out methods of reduction and analysis in solution (Rothmund, *Chem. Ztg.*, 1909, xxxiii., 1245; Sjollema, *Zeit. Anorg. Chem.*, 1904, xlii., 127; Kreiden, *Zeit. Anorg. Chem.*, 1895, x., 277). One by Rothmund (*loc. cit.*), using titanium sulphate, appears to be the most successful of them, but while apparently accurate enough, it is long and time consuming when compared with the direct fusion method. It seemed to us worth while, therefore, to locate the source of error in the fusion method and to remove it if possible.

The sign of the errors in all the modifications of this method so far tried has been almost always negative; that is, too little silver chloride has been obtained. Such a result would be caused by either of the two alternatives above mentioned, that is, either by incomplete reduction or by volatilisation.

To obtain evidence bearing upon these alternatives we fused samples of pure potassium perchlorate with many different fluxes; with potassium bisulphate and zinc, with sodium carbonate alone, and with sodium carbonate mixed with sodium sulphite or powdered charcoal, or with powdered charcoal and titanium sulphate. It is not necessary to give the results of these fusions in detail. Low results were again obtained in every case, but the error was fairly constant and never amounted to more than 1·0 per cent, even where no reducing agent was present. The fusions with the flux containing sodium carbonate, carbon, and titanium sulphate gave the best results, but even they were always from 0·2—0·4 per cent low. The use of a double crucible with a double cover seemed to be only a slight improvement. These experiments indicated that the reducing agent was of little importance, and that the small discrepancies were probably due not to incomplete reduction but to a slight loss by volatilisation.

To test this conclusion a number of fusions were carried on in a glass combustion tube through which a slow current of air was drawn. Plugs of asbestos wool were inserted near the outlet end of the tube, and to this two

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* Read before the Section of Inorganic and Physical Chemistry of the American Chemical Society at the Washington Meeting, December 28, 1911.—From the *Chemical Engineer*, xv., No. 6.

U-tubes containing beads wet with water were attached in series. The perchlorate with flux was placed in a platinum boat and heated for about twenty minutes. The plugs of asbestos and the moistened beads prevented the escape of any chloride vapour or fumes, for, although the water in the first U-tube usually gave a slight test for chlorides after a fusion, no chloride was ever detected in the second U-tube. After cooling, the contents of the combustion tube and the U-tube were washed upon a platinum Gooch filter with hot water, the chloride precipitated, and the silver chloride dried in an electric oven at 170—180°. Different fusion mixtures were employed; first, sodium carbonate mixed with powdered charcoal and titanium sulphate; later, the titanium sulphate and then the charcoal too were omitted. Since the charcoal, titanium sulphate, and asbestos were all found to contain traces of chlorides, blank determinations were made upon each of them and appropriate corrections, always very small, were applied. The use of warm water in washing resulted in a rapid removal of the silver and potassium nitrate from the precipitate, but according to the measurements of Böttger (*Zeit. Phys. Chem.*, 1903, xlvi., 603) and Kohlrausch (Kohlrausch and Holborn, "Leitvermogen," p. 216) must have entailed a slight loss of silver chloride. The temperature of the wash-water was about 60°, and its total volume, since it was applied in small quantities at a time, amounted only to between 50—75 cc. A saturated solution of silver chloride in pure water of this volume and temperature would have contained about 0·4 mgrm. of silver chloride, but since the washing was soon discontinued after the wash-waters showed no test for silver ions, the first two-thirds of the wash-water could have contained only a negligible quantity of silver chloride. The loss of silver chloride then must have been only about 0·1 mg. We have added this almost negligible correction to the observed weights of silver chloride. The results of these experiments are given in Table IV.

These results, with an average deviation from theory of only 0·2 mgrm. of silver chloride, or 0·1 per cent, demonstrate that accurate results can be obtained by the fusion method, that reducing agents are unnecessary, and that the low results of previous analyses by the fusion method must have been due to losses by volatilisation.

With these points established we resorted to a much simpler and yet equally efficient form of apparatus. It consisted merely of a thin glass (Jena) test-tube of 25—30 cc. capacity, fitted with two plugs of asbestos wool. The plugs were 15 mm. thick; the first was placed 50 mm., the second 95 mm. from the bottom of the test-tube. The perchlorate was weighed directly into the test-tube, the plugs inserted, the tube clamped in a nearly horizontal position, and the lower end gently heated. White fumes were formed as the oxygen was expelled, but these were completely retained by the first plug. When effervescence had ceased, a somewhat larger flame was applied until all the chloride was thoroughly fused. The time required for this heating varies between ten and fifteen minutes. It is a decided advantage to be able to watch the progress of the fusion. After cooling, the contents of the tube were washed upon a filter with warm water, the chloride was precipitated, and the silver chloride dried as before. The weights were carefully calibrated and vacuum corrections applied, taking 2·52 and 5·57 as the specific gravities of the potassium perchlorate and the silver chloride respectively. As before, a correction of 0·1 mgrm. was applied for the silver chloride dissolved by the warm wash-water.

The same sample of potassium perchlorate which was used in the combustion tube fusions was first analysed by this method. This sample had been found to be free from chlorides, chlorates, or sulphates, and from other metals than potassium. The results of these analyses are given in Table V.

The average deviation from the calculated value in the analyses is but 0·02 per cent.

Table IV.—*Fusion Analyses of Potassium Perchlorate in a Tube.*

No. of expt.	Weight $KClO_4$ taken.	Weight AgCl calc.	Blank.	Weight AgCl found.	Deviation.	
					Grm.	Per cent.
3.	0·2049	0·2119	0·0015	0·2134	0·0000	0·00*
4.	0·2005	0·2074	0·0015	0·2086	−0·0003	−0·15*
5.	0·2506	0·2592	0·0015	0·2603	−0·0004	−0·15*
6.	0·2605	0·2695	0·0010	0·2699	−0·0006	−0·22†
7.	0·2017	0·2086	0·0002	0·2085	−0·0003	−0·15‡

* Flux added: $Na_2CO_3Ti(SO_4)_2$ and C.
† Flux added: Na_2CO_3 and C.
‡ Flux added: Na_2CO_3.

Table V.—*Analysis of Sample No. 1 Potassium Perchlorate by Test-Tube Method.*

8.	0·2290	0·2369	+0·0002	0·2371	0·0000	0·00
9.	0·3455	0·3574	+0·0002	0·3577	+0·0001	+0·03
10.	0·3904	0·6107	+0·0002	0·6107	−0·0002	−0·03

Table VI.—*Analyses of Sample No. 2 Potassium Perchlorate by Test-tube Method.*

11.	0·4561	0·4718	+0·0002	0·4720	0·0000	0·00
12.	0·4437	0·4590	+0·0002	0·4590	−0·0002	−0·04
13.	0·4501	0·4656	+0·0002	0·4658	0·0000	0·00

Table VII.—*Analyses of Aquopentammine Cobalt Perchlorate by Test tube Method.*

14.	0·2900	0·2704	+0·0002	0·2706	0·0000	0·00
15.	0·3342	0·3121	+0·0002	0·3124	+0·0001	+0·03

A second sample of potassium perchlorate was prepared from the above sample by a double re-crystallisation from re distilled water in Jena glass flasks, using as low temperatures as possible. The resulting 50 grms. of salt was ground and then dried to constant weights at 130° in an electric oven. Analyses made upon it are given in Table VI.

These results are practically identical with those obtained with the previous sample and demonstrate the purity of both.

This method was now employed to analyse a newly prepared aquopentammine cobalt perchlorate. It was necessary to dilute the cobaltammine, else a rather explosive decomposition took place; pure sodium nitrate was used for this purpose. The results are given in Table VII.

They agree nearly as well with the requirements of theory as do the analyses of potassium perchlorate.

The above analyses demonstrate beyond question the accuracy of this method. The average duration from the calculated weight of silver chloride was less than 0·02 per cent, which is certainly equal to the attainable accuracy of the chloride determination itself under these conditions. Moreover, *every* analysis made by this new process has been here recorded. The apparatus is very simple; a hard glass test-tube is preferable to an ordinary soft one, but the treatment is not severe. We used the same thin glass test-tube for the first three analyses without any perceptible injury to it. The fusion can be easily controlled, and the whole analysis requires scarcely more than an ordinary chloride determination. If this latter determination is made volumetrically, the whole analysis becomes a very rapid one.

In conclusion, then, we can present the above as a very accurate, simple, and rapid method for the determination of perchlorates.

Physical Society's Annual Exhibition.—This Exhibition will be held on Tuesday, December 17th, 1912, and will be open both in the afternoon and evening.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY,

October 23, 1912.

The Medal of the Society was presented to Sir William Crookes, O.M., F.R.S., at a Dinner held at the Criterion Restaurant, London, on Wednesday, October 23rd, 1912, at which nearly 150 members and guests were present. The Chair was occupied by the retiring President, Dr. Rudolph Messel, F.R.S.

The toast of H.M. the King having been duly honoured,

The Chairman said their gathering that night might be looked upon as the final function of their Annual General Meeting, which had been held in New York, and at which the Medal had been unanimously awarded to Sir William Crookes. It had not been possible for Sir William personally to receive the Medal in New York; he had shrunk from the great fatigue which the voyage to and attendance in New York would entail. However, that had the advantage that they could that night celebrate the event and hand the medal to him in London. He was particularly delighted that they had such a representative gathering of the Society, and he felt greatly indebted to the Chairmen and the Secretaries of their Sections in England who had come to do honour to Sir William Crookes; and, likewise, that so many Scientific Societies were represented. He especially appreciated the honour that, for the first time, they had amongst them the President of the Royal Society. They all knew that was only reflected glory on them, and that it was all to the honour of Sir William Crookes: but all the same they most sincerely appreciated it. Sir William had excused himself for not going to New York on account of his advanced age; but he thought Sir William's 80 years sat very lightly on his shoulders. Looking back to the time when Sir William Crookes started working more than half a century ago—he founded the Chemical News in 1859 and discovered thallium in 1861—seeing him now daily at work—serious honest hard work, partly new and partly filling up gaps in work started more than half a century ago, they could only marvel and hope they might look forward to many years of active work by Sir William Crookes.

He had received many letters from Past Presidents and Presidents of kindred societies; the letters were invariably in the same laudatory strain, expressing admiration for this remarkable man, and regret for not being able to do honour to Sir William Crookes that night. Their new President, Professor Marston T. Bogert, wrote expressing sincere regret for not being able to be present, and offered his humble tribute to and his high appreciation of the long, distinguished, and fruitful career which had made Sir William Crookes's name a household word wherever chemistry was taught and a natural leader amongst his colleagues in all lands, which meant so much for the scientific progress of the world; the Society was adding one more famous name to the brilliant roll of its medallists, and was honouring itself in honouring Sir William Crookes; and he expressed the hope that Sir William would long be spared in health and happiness to continue his splendid work, and to enjoy the well-won fruits of his life; and that if, in the distant future, old age should descend upon Sir William it would be found that—

> " Age is opportunity no less
> Than youth itself, though in another dress;
> And as the twilight fades away,
> The sky is filled with stars invisible by day."

The sentiment expressed in this letter was that which really moved them all. In his (Dr. Messel's) Address at the presentation of the medal in New York (see *Journ. Soc. Chem. Ind.*, September 30, 1912, p. 857), he mentioned some of the work done by Sir William, but the world knew the work he had done, and it was not necessary to say anything further in that connection. Among the many acknowledgments which Sir William had received were the award of the Order of Merit and a Knighthood, as well as the Albert Medal, the Royal Society's Medals, and the Gold Medal of the French Academy, and many others—some thirty in all—and now, this Society offered its Medal to Sir William Crookes. To their Society it was a great honour to be allowed to enrol his illustrious name amongst their medallists, and they wished to show how sincerely they appreciated his services; but to him what can it mean? They hoped that he would look upon it as a proof not only that they so greatly appreciated his services, but also that they wished to hold him up as a model to future generations, that they valued pure science foremost, and that they would always regard it as the true foundation to progress and industry. As far as Sir William was concerned, he hoped he would look upon it as an appreciation of his services to science and as a mark of the high esteem in which he was held by 4000 or 5000 brother chemists—the members of our Society.

The Chairman then handed the Society's Medal to Sir William Crookes, with the remark that it was his proud privilege to present a Medal, which was the best the Society had to give.

Sir William Crookes, O.M., F.R.S., in acknowledging the receipt of the Medal, spoke as follows:—The first thing I must do is to crave your indulgence. Adequately to express my feelings on this occasion is beyond me. The kind things said about me, the cordial manner in which reference to works of mine has been received, and the flattering presence of this distinguished company of men eminent in the Society, give me vivid pleasure. I am no speech maker; all my life I have been grappling with mysteries only to be tracked by incessant work in the laboratory. But pray do not suppose I am indifferent to your friendliness. Sympathy is no less dear to workers in science than to those engaged in more popular pursuits. Indeed, it is more dear, since our work appeals to the few, not to the many.

To every student, to every investigator seeking to acquire deeper and clearer insight into the appalling wonders of what we call nature, recognition of success, especially from a distinguished scientific Society, naturally leads to further endeavour. That I should have been counted worthy to receive the Medal of the Society of Chemical Industry, a Society which numbers in its roll of former Medallists some of the brightest names in every department of applied chemistry, is an honour I keenly appreciate—an honour I shall never forget. If there be any element of truth in the old proverb, "*Nolo laudari nisi a laudato*," surely the highest aim of ambition must be to receive the praises of those who themselves are the most praised and the most praiseworthy.

Working as I have been for half-a-century with problems of radiant energy and radiant matter, there is a peculiar appropriateness in the design of my beautiful Medal. In the centre is Phœbus Apollo, the Divinity of radiance and light, associated by Euripides with the Sun god Helios, and the rays darting from him represent the atoms of helium, the discovery of which has aided the revival of the alchemists' dreams of the Middle Ages.

Chemical engineering and my own special lines of research lie at opposite ends of the science. You deal with enormous weights of raw material, with gigantic engine power, and with vast combinations of matter, labour, and machinery; I, on the contrary, have been absorbed in the mechanism of electrons, atoms, and molecules—millions of which unite to build up even one mote dancing in the sun-beam. You handle hundreds of tons of matter and thousands of horse-power; I deal with forces and dimensions compared with which the millionth of an atmosphere of pressure, the millionth of a grain of weight, and the millionth of a millimetre of length are large quantities. But here, as in other cases, extremes meet, and the infinitely great and the infinitely small are each governed by the same chemical and mechanical laws.

Industrial chemistry as we now know it is essentially a product of the Victorian age. What in my early days was a curiosity of the few, has now become the useful servant of the many. Supreme in the arts of peace as of war, industrial chemistry is indispensable in every department of life, and without it civilisation would soon come to an end and be non-existent.

In our overwhelming present we are apt to forget our past—to forget those who helped to make it for us. My first stock of thallium in quantities of over an ounce was extracted from flue-dust from Peter Spence's sulphuric acid works at Manchester, and quantities of crude thallium chloride were presented by him to me to be worked up in my private laboratory. Subsequently—nearly fifty years ago—I was under great obligations to Messrs. Hopkin and Williams for working up some flue-dust for thallium. Ten tons of dust, generously presented to me by Messrs. Allhusen, of Newcastle, yielded me more than a hundredweight of the pure metal. In more recent times I have been under great obligations to my good friend Mr. Tyrer, who worked up a considerable quantity of gadolinite for yttria and other rare earths, and later the same benefactor broke up half-a-ton of pitchblende and sent me all the different products for me to extract the radium from the most suitable specimen. My gratitude to this friend is not unmixed with a lively sense of favours to come, for in my laboratory I have a considerable quantity of crude scandium material which I hope to induce him to take in hand.

During my long life I have striven loyally with all my might for the truth. No one can be more fully conscious than I am how little I have won compared with what remains to be solved and achieved. Those of us who have attempted to penetrate from the known to the unknown, from the vague to the definite, are surprised not so much by the extent of our knowledge as by the depth of our ignorance. As I have proceeded in my investigations I have discerned new and unexplored regions opening out to the right and to the left. To some of these mysterious tracks I may return and endeavour to capture them and to bring them within the domain of science. Who shall dare to say what new treasures of truth and even of practical utility may there await the patient enquirer? I hope and believe I shall still be able to do good work in my research laboratory, and this notwithstanding the ominous assurances of friends that I grow younger every year!

It is a matter of great regret that I was unable to attend the meeting of the Society in New York. Our new President is a citizen of the United States, and I trust he will be able to come among us and preside at some of our meetings. I hope the most cordial relations and the most friendly rivalry may ever prevail between the men of science of that great Republic and the researchers of the little Mother Isle. May we labour harmoniously side by side in our great life-task—the interpretation of the chemical secrets of the universe!

In proposing the toast of "Kindred Societies," Mr. David Howard (Past-President) said that a great honour had been laid upon him and a very great responsibility, because how could he do justice to this toast, which meant so very much to the industrial chemist? "Kindred Societies" was a very generic term, but it was a special honour and pleasure to include, first of all, the parent society, the Royal Society, the oldest Society in England, and also the youngest, because Truth was ever young and there was no time in the Royal Society; it was as young as ever, and had all the common knowledge which was the foundation of all our applied knowledge. It was well to remember that science was not kept in water-tight compartments, for to think it was a fatal danger. No doubt it was one's duty to know, not science but the little tiny branches of science that one had to do with as well as one could; that meant knowing one's own ignorance. Applied Science was but a little corner of the great field of Science, which was the very foundation of them all. It had been the noble work of the Royal Society to link together all sciences, for they were all one, though so different; and to keep before their minds the great principle that they did not know everything. They welcomed most heartily the President of the Royal Society. There were other kindred societies represented there, including the Institute of Chemistry, the Society of Public Analysts, the Institute of Brewing, the Royal Photographic Society, and the Pharmaceutical Society; and they welcomed them all. Science was a tremendous subject, and, in order to achieve success in their own tiny compartments they should recognise the influence of others upon their own, and to appreciate the nobleness and magnificence of Truth for its own sake; and then they would realise what it meant to meet there, as they did, the representatives of pure Science and Applied Sciences, all working for one common object. All the progress of Science of which this twentieth century was so proud was but a tiny little bit of the great Truth; and if a little imperfect appreciation of Truth meant so much, what must be Truth itself? They were all applying to practical uses the central truths which it was the honour and glory of the Royal Society to teach. How much of their practical work was the result of the theoretical work of the pure scientist? Their success in Applied Science made them humble enough to appreciate the glories of Science for its own sake. He urged them not to think that useful knowledge was the only thing they had to study. They had to study Science for its own sake, and it might be that they might make it useful, but they should, first of all, remember that all Applied Science sprung from Science for its own sake; and, secondly, that all branches of Applied Science were akin to one another, linked to one another, one family who ought to love one another.

Sir Archibald Geikie, K.C.B., F.R.S. (President of the Royal Society) said it was an honour of which the President of the Royal Society was always very conscious when he was asked to respond for the "Kindred Societies." Two hundred years ago, there was only one Scientific Society, but the number had increased till every branch of Science had, not only its own society devoted to the cultivation of Pure Science, but had also its Society of Applied Science. The Chairman had said that he thought he had been mainly induced to come to the Dinner to do honour to Sir Wm. Crookes, and he admitted that was one object he had, and he was glad to add his humble word of praise of that great chemist and dear personal friend. It had been a great pleasure to him during the past four years to have served with Sir Wm. Crookes on the Council of the Royal Society; but Sir William's term of office was almost ended, and he looked forward with great regret to the termination of a long personal intimacy. But that was not his only object in wishing to be present at that Dinner; to a man who had devoted himself mostly to pure Science it was always a great pleasure to come into contact with those who had spent their lives in turning Science to practical use. He admired and wondered when he knew of the tons of material employed and of the intense heat in the electric furnace and the vast complications of processes they carried through. It was a great advantage and also a great pleasure to meet men engaged in a totally different sphere from one's own for in that way one obtained many new ideas. He thanked them for the pleasure that Dinner had given him; and he wished long success and happiness to the Society of Chemical Industry with its splendid *clientèle* of members. With such a brilliant past, they undoubtedly had a great future before them; and nobody would rejoice more in that than the Fellows of the Royal Society. He thanked them for the way this Toast had been proposed and received.

In proposing the toast of the "Society of Chemical Industry," Prof. Sir James Dewar, F.R.S. (Past President), said that it so happened that the toast which had been placed in his hands he had had the honour of proposing twenty-four years ago, when he presided over a meeting at Glasgow, at the time that he was the Society's seventh President. He was now about to propose their own healths and to congratulate themselves upon their thirtieth President. During that time the Society had increased with most extraordinary velocity from what was considered to be unexampled success, by the promoters of that great movement, in the year 1888, when the membership at the time of the meeting at Glasgow was a little over 2000, while now their numbers exceeded double that. That result had been achieved by a most judicious mode of advance in co-ordination and co-operation which would not have been possible but by the association of men of intellect in both abstract and Applied Science; it was the special design and object of the founders of the Society that it should be not only beneficial to industry but also to Science itself; because the co-operation of those two groups was essential for the future benefit of the human race. The men who carried this out in the early days were men not only of great originality but of unselfish power and devotion to their object. They laboured with joy at the foundation and at the success of the Society; and it was their initiative which had permeated and maintained the fruitful and spontaneous blood-stream of life which permeated it at this moment as vigorously as it did at the beginning. Such men, like Mond and many other Presidents and Secretaries, were those who had assisted in making this extraordinary success of the Society which was world-wide, with its 12 Sections extending not only throughout Great Britain but including one in Canada, two in the United States, and one in Australia. Verily they were now in contact with the whole of the intellectual and practical world. They had created in reality a great memorial body of Applied Chemical Science, an Imperial body in the highest and most important sense of the term. There was still so much to be done in other fields where what one might call Governmental forces were utilising, and necessarily utilising, Science more and more. They could only wish that the educational system of this country did something more to educate those who were responsible for the management of the great Departments of the State. If that were done, it would be not only a benefit to themselves but a great benefit to the nation and it would enable them to see, as sooner or later they must see, that a training in Science was absolutely essential to the management of such great undertakings. An individual mind responsible for great efforts ought to possess and could only possess the necessary power by early training and by the advice of other men. The Universities were moving rapidly, and he had seen at one of the oldest Universities what advances and enlightenment had taken place in the acknowledgment of Science and its claims. At the present time, in the Cambridge Laboratories extensions in every department would be found in physiology and geology; and large extensions on behalf of Agricultural Science, not to mention Botanical Science. They required to produce men who were really competent to aid in the practical application of Science. He did not doubt that this Society would be able to influence more and more even the older Universities, as well as the newer ones, in the extension of the great domain of Science. He then came to the acknowledgment of the services of their present President, Dr. Rudolf Messel, who was a worthy successor of any previous President. They were all proud when the Royal Society recognised the President's originality and merits as a great inventor and how his modest but determined, careful, and laborious life had accomplished great things which were now being imitated and applied in many ways; the catalytic process and its applications would always be associated with the name of Dr. Messel as one of the great applications of Science in our time; and he asked the Society to thank Dr. Messel for the admirable manner in which he had conducted the business of the Society. They wished him long life and good health and every possible success, and they congratulated him on his work and labour for the Society. Before asking the meeting to drink the health of the Society, he asked the Treasurer, Mr. Tyrer, to address the meeting.

Mr. Tyrer (Hon. Treasurer) said he had a very pleasing duty to perform, namely, to ask Dr. Messel to receive, on behalf of the Society, a token of their regard in the form of an album, containing photographs of the officers of the sections and of the Society, who had served under Dr. Messel during his presidency, together with portraits of Sir William Crookes and of the new President, Professor Bogert. Emblazoned on the cover of the album were the Arms of the British Empire, the United States, Canada, and Australia, together with the Stars of America and the Fleur de Lis, but no stripes—for brotherhood required none. In addition to being responsible for the design of the memento, he also had the honour to be the medium of handing to the Chairman this token of regard, and he hoped Dr. Messel's life would last as long as the Album was intended to do.

The Chairman said it was impossible to find words adequate to express to them his appreciation of their great kindness to him. How could he express it sufficiently? He knew that all they had said about him was prompted by their kind feelings and good fellowship; and he also knew how little worthy he was of much of what had been said. On one point, however, he would not give way, and that was that during the long time he had been in connection with the Society he had always tried to do his best and his level best in its interests. His year of office had nominally closed; but, because Professor Bogert would be unable to come to England for some time, he had been requested to undertake the duties of President during his year of office. The Council had by an unanimous vote begged him to accept, and therefore he should carry out the duties some little time longer. In Great Britain he had visited all the Sections; he had also visited New York, Boston, Toronto, and Montreal; in fact he had visited all their Sections, with the exception of New South Wales; and he was prevented from going there by the great distance. He had been most cordially received wherever he went, and he had found that the Society and its work were very greatly appreciated. There had been some fear that the membership of the Society might suffer owing to the activity in the Scientific Societies and in scientific literature in America; but, after making careful enquiries, he had come to the conclusion that they were not threatened in that way so long as they realised what was required of them and, above all, so long as they kept their Journal in a state of efficiency. It was of particular advantage to them to have Professor Bogert as his successor, because Professor Bogert, in addition to being a most accomplished scientist, was certainly a *personâ gratâ* in the United States, and he was a most active member of the American Chemical Society. There need be no antagonism between the Societies, and. so far as he knew, there was none. It gave him very great pleasure indeed to thank them for all the kindness they had shown him during his year of office; and he thanked them most sincerely for the way in which they had received him that night. He also most heartily thanked them for the delightful album, which he should treasure all his life as a memento of their kindness to him.

INSTITUTE OF CHEMISTRY.

Mr. Edmund White, B.Sc., F.I.C., delivered a lecture on "*Thorium and its Compounds*" before the members and students of the Institute of Chemistry, at Finsbury Technical College, on Friday, November 1st, Prof. Raphael Meldola, President, in the Chair.

The lecturer gave a short account of thorium since its supposed discovery by Berzelius in 1817 in the mineral gadolinite. Berzelius afterwards found that the substance he had christened thorium from the name of the Scandinavian god "Thor" was not an element, but he used the name in 1828 for an element which he discovered in the mineral called thorite. Thorium occurs in a large number of minerals in Norway which, are however, only found in small quantities; such as æschenite, euxenite, gadolinite, samarskite, xenotime, monazite, orangite, and thorite. The monazite sand deposits in Brazil form the chief commercial source of thorium at the present day. Monazite is found in many parts of Brazil, but the chief supplies have been drawn from sand found on the sea-shore. This sand was first shipped to Europe as ballast, but now that its value is known it is only allowed to be shipped after payment of royalties and other charges. Monazite sand also occurs in North America, India, Australia, Nigeria, Straits Settlements, and South Africa. The process of concentrating the crude sand deposits by means of running water, followed by magnetic treatment, was described and illustrated by lantern-slides, the problem being to remove the monazite in as pure a condition as possible from the complex mixture of minerals constituting the crude deposit. Purified monazite should contain not less than 5 per cent thorium oxide. The importance of thorium in the gas-lighting industry was referred to, and the world's requirements in gas-mantles was estimated at about 400 millions annually. The interesting mineral thorianite was referred to as an ideal mineral for the extraction of thorium, but not available in sufficient quantities to be of much commercial importance. The value of monazite depends upon the percentage of thorium oxide it contains. This proportion is determined by analysis, and the various processes of analysis were described. General methods employed in the extraction of thorium were also dealt with, attention being drawn to the difficulties which arise from the thorium being associated in monazite with ten to twelve times its weight of the cerite earths. The latter bodies so closely resemble thorium in their solubility and other properties of their salts, that a sharp separation in one or two operations is not possible. Hence, methods based upon fractional crystallisation and precipitation must be employed, thus rendering the extraction tedious and expensive. The finished product, thorium nitrate, is prepared in white crystalline masses or granules which are very soluble in water.

The commercial standards for purity of thorium nitrate were described and illustrated experimentally, the peculiar property of thorium nitrate in swelling up and yielding a voluminous ash forming a striking experiment. Delicate tests were given to detect the presence of possible impurities, such as cerium, lanthanum, didymium, phosphoric acid, iron, aluminium, calcium, magnesium, and sodium. The author exhibited an interesting collection of minerals and thorium compounds, and lantern-slides showing the composition of crude and purified monazite.

CORRESPONDENCE.

COPYRIGHT IN GOVERNMENT PUBLICATIONS.

To the Editor of the Chemical News.

Sir,—I am pleased to report that the President of the Board of Trade gave me an interview in which he said that his Department had no desire whatever to unduly restrict the right of Trade papers to extract from Government publications dealing with trade.

Mr. Buxton has since informed me that in future the *Board of Trade Journal* will contain the following notice:—

> *Crown Copyright Reserved.*—Extracts may be published if the source is duly acknowledged.

You are at liberty to announce the foregoing should you so desire.—I am, &c.,

S. J. Sewell,
Hon. Sec. London District.

Institute of Journalists,
October 29, 1912.

NOTICES OF BOOKS.

The Main Drainage of Towns. By F. Noel Taylor. London: Charles Griffin and Company, Ltd. 1912.

By the use of this book the engineer could get sufficient information to enable him to plan and carry out a complete sewage scheme of moderate size on the most modern and satisfactory lines. The principles of hydraulics and hydrostatics are thoroughly explained, and a very good chapter on practical calculations gives details of methods of working out problems connected with sewerage, special attention being paid to the case of sea-board towns. The author appears to underestimate the mathematical powers of the average engineer, but this is possibly a fault on the right side. Practical construction is well treated, and such questions as ventilation, storm overflows, &c., are thoroughly discussed. The arrangement and testing of house drains are concisely treated, and a short account is given of the theoretical side of sewage disposal as well as some account of works for the purpose. An appendix shortly describes the main drainage works of the City of Dublin and of Glasgow. There are plenty of sections and plans and diagrams to scale, but useless illustrations are altogether absent, and the book is of a thoroughly practical type in every respect.

Modern Copper Smelting. By Donald M. Levy, M.Sc., Assoc.R.S.M. London: Charles Griffin and Co., Ltd. 1912.

The lectures upon which this book is based were delivered before some of the senior students of the School of Metallurgy at the University of Birmingham. For the purpose of issuing them in book form they have been very considerably extended, and an introduction on the history, uses, and general metallurgy of copper has been added. The author has had a long and intimate experience in some of the largest copper works in America, where he had the advantage of being able to study the most advanced practice, and he puts his unique knowledge entirely at the disposal of his readers. The book gives the actual details of working, which are very often difficult to obtain, and contains excellent tabulations and summaries, as well as copious references to both English and foreign literature on the subject of copper smelting.

A New System for Preventing Collisions at Sea. By Sir Hiram S. Maxim. London, New York, Toronto, and Melbourne: Cassell and Co., Ltd. 1912.

This interesting pamphlet describes an ingenious piece of apparatus in terms which even the least scientific of readers can readily understand. The author first discusses the question of the supposed sixth sense of bats, the organ of which differs in form and size in different species, but is always situated somewhere on the head. By means of its wings the bat communicates to the air vibrations of too low frequency to be audible to the human ear; these are reflected by neighbouring objects, and the reflected and modified vibrations are perceived by the sixth-sense organ of the bat, which is thus made aware of the proximity of things which it cannot see. The author's device for warning ships of their approach towards objects which are invisible owing to fog is based upon the same principle. It consists essentially of a siren worked by the boiler steam and capable of producing similar inaudible vibrations, of, however, enormously greater energy. These vibrations, when reflected by such an object as an iceberg or another ship, are caught by a diaphragm, the vibration of which causes bells to ring. By an adaptation of the apparatus two ships both furnished with it could communicate with one another, using the Morse code.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 12, September 16, 1912.

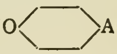
This number contains no chemical matter.

No. 13, September 23, 1912.

Conditions of Formation of Nitrous and Nitric Acids from Oxides of Nitrogen and Water.—E. Briner and E. L. Durand,—In presence of water the following reaction occurs :—$N_2O_3 + H_2O \rightleftharpoons 2HNO_2$. Thus in the aqueous phase colourless molecules of HNO_2 exist in solution and coloured molecules of N_2O_3. As the quantity of the latter is increased the limit of its solubility is reached, and then a liquid N_2O_3 phase is formed. Thus nitrous anhydride behaves like SO_3 and CO_2, except that in the gaseous state it dissociates into NO and $NO_2(N_2O_4)$. With NO_2 in presence of water the reaction is $2NO_2 + H_2O \rightleftharpoons NO_2H + HNO_3$.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlv., No. 11, 1912.

Preparation of Acroleïn.—A. Wohl and B. Mylo.—Any sulphate which gives free sulphuric acid at a comparatively low temperature can be used as a catalyser in the preparation of acroleïn from glycerin. Such sulphates are potassium bisulphate, aluminium, ferric, and copper sulphates. Sodium and potassium sulphates have no effect. For quantitative experiments magnesium sulphate is the best to use.

p-Nitroso-phenylarsinic Acid.— P. Karrer.— The oxidation of a neutral or faintly alkaline solution of atoxyl by means of neutral sulpho-monoper-acid solution gives *p*-nitroso-phenylarsenic acid, NO$AsO(OH)_2$. On acidifying the liquid the substance separates out in fine yellow needles, which are slightly soluble in cold water and dissolve easily on heating. The substance exhibits all the typical nitroso reactions. On being heated it does not melt, but turns brown or black at about 180°, and decomposes with an explosion at a higher temperature. It possesses no medicinal properties.

Derivatives of Anhydro-glucose.—Emil Fischer and Karl Zach.—Anhydro-glucose, recently prepared by the authors, shows great similarity to grape-sugar in its behaviour towards phenylhydrazine and alkalis, and in its relations to anhydromethyl glucoside. When it is treated with sodium amalgam it yields an alcohol, $C_6H_{12}O_5$, for which the authors suggest the name anhydrosorbite, and oxidation with bromine converts it into an acid, anhydro-gluconic acid.

o- and p-Mercapto-benzaldehydes.—P. Friedländer and Emil Lenk.—*o*- and *p*-Amido-benzaldehydes may be diazotised and their diazo-compounds give rhodan or xanthogen-benzaldehydes when treated with potassium rhodanate or xanthogenate. The action of alkalis or alkaline sulphides gives the mercaptan aldehydes in the form of their stable alkali salts. The free mercaptan aldehydes may be obtained from these salts, but they very readily undergo condensation. The disulphides of the two aldehydes are much more stable, and are crystalline substances which give the usual aldehydes reactions.

Action of Ozone on Alkali Hydroxides.—Wilhelm Traube.—When ozone acts on solid potassium hydroxide most of it is converted into ordinary oxygen, but a small portion is taken up by the alkali, giving a reddish yellow compound. The raw product is not a single substance, but contains, besides unchanged hydroxide, at least two higher oxides of potassium. One of these is characterised by the fact that in contact with water it gives up all the oxygen it contains in excess of that present in KOH, in the form of indifferent oxygen. Potassium tetroxide is also formed. At the ordinary temperature the "ozonised potash" gradually loses its colour, and is converted into a mixture of potassium hydroxide and tetroxide.

Atti della Reale Accademia dei Lincei. Vol. xxi. (ii.), No. 3, 1912.

Relation between Phototropism and Constitution.—M. Padva and L. Santi.—Apparently the rule established for the relation between constitution and phototropism in the case of the hydrazones cannot be applied to the osazones. With the fulgides phototropism is exhibited only when, of the four radicles, one or two are hydrogen atoms. With the osazones the derivatives corresponding tot1: diphenylfulgides are precisely those in which Biltz and the authors have observed phototropism. The substances corresponding to the completely substituted (tetraphenyl) fulgides are the osazones obtained from disubstituted hydrazines, like methylphenyl and diphenylhydrazine. The authors have prepared some of these derivatives, and have found that not one of the methylphenyl or diphenyl osazones is phototropic.

Bromo- and Chloro-guaiacols.—Temistocle Jona.—5-Bromoguaiacol can be prepared from the 5-nitro compound, by reducing it and then diazotising and brominating :— $C_6H_3(OH)(OCH_3)(NO)$ 1 : 2 : 5 → $C_6H_3(OH)(OCH_3)(NH_2)$ 1 : 2 : 5 → $C_6H_3(OH)(OCH_3)Br$ 1 : 2 : 5. The best way to prepare 3-chloro-guaicol is to start with 1 . 2 . 3 . 4 - *o* - nitro - vaniglinic acid, $C_6H_2(OH)(OCH_3)(NO_2)(COOH)$, reduce it by means of tin and hydrochloric acid, to give 3-amino-guaiacol, and then pass as before to the 3-chloro compound.

MISCELLANEOUS.

The Possibility of Silver in Manurials.—There is a possibility of silver being found in a mineral substance used commonly in this country as manure, possibly apatite or some calcium and phosphate combination. Solid lumps placed in a red-hot fire display an unusual property of being ejected with explosive violence, and the mineral closely resembles a class of mineral found in Canada and from which silver is extracted.—J. C. Thomlinson, B.Sc.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 4th inst. ; Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Dr. J. H. McBride and Miss Jane Worth were elected Members. The Honorary Secretary reported the decease of Prof. Henri Poincaré, an Honorary Member of the Institution, and a resolution of condolence with the family was passed.

Royal Institution.—The Eighty-seventh Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. Sir James Dewar, LL.D., D.Sc., Ph.D., F.R.S., Fullerian Professor of Chemistry, his title being "Christmae Lecture Epilogues." The Lectures will be experimentally illustrated, and the subjects are as follows : "Alchemy," Saturday, December 28, 1912; "Atoms." December 31 ; "Light," January 2, 1913; "Clouds," January 4 ; "Meteorites," January 7 ; "Frozen Worlds," January 9. The lecture hour is 3 o'clock.

MEETINGS FOR THE WEEK.

Friday, 8th.—Physical, 8. "Method of Measuring the Thomson Effect," by H. R. Nettleton. "An Improved Joule Radiometer and its Applications," by F. W. Jordan. "Attainment of a Steady State when Heat Diffuses along a Moving Cylinder," by Miss A. Somers. "Thermomagnetic Study of Steel," by S. W. J Smith.

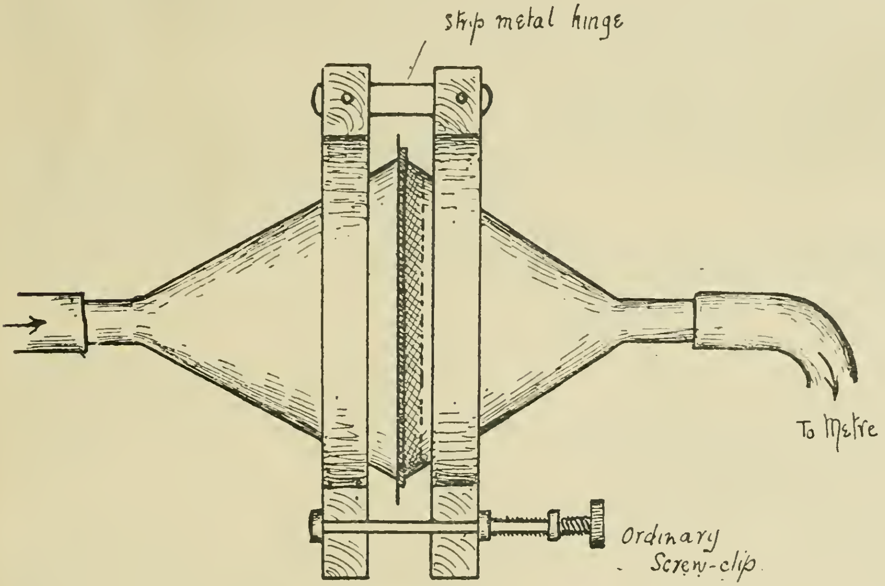
THE CHEMICAL NEWS.

Vol. CVI., No. 2764.

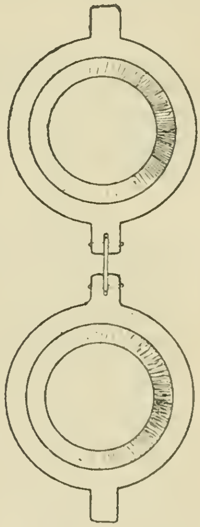
A SIMPLE APPARATUS FOR ESTIMATING DUST IN GAS.

By C. T. NESBITT, A.R.S.M.

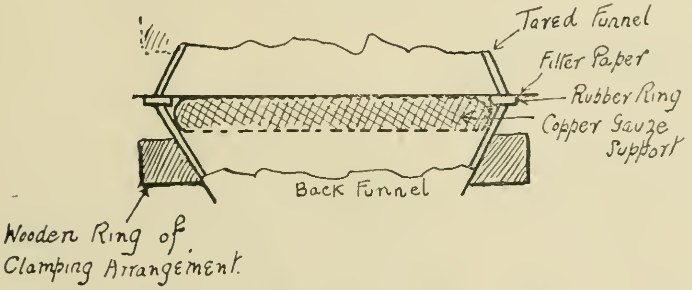
The accompanying diagrams represent a simple device for estimating dust in various gases. Many arrangements of U-tubes containing fibrous asbestos, wool, &c., were tried without satisfactory results. The funnel arrangement here described has been in use for some time, and yields excellent results.



APPARATUS IN USE.



Clamping Arrangement opened out. (One-fourth size).



Section showing Arrangement of Filter-paper, &c. (Half size).

Two smooth funnels (not ribbed) are chosen, the edges of which fit closely together, and two wooden rings (see Figs.) made and joined with a strip metal hinge. These two rings when in position on funnels are clamped by means of an ordinary gas screw-clip, and so grip the funnels closely together. Between the edges of funnels a circular ring of thin rubber (about $\frac{3}{16}$th inch wide) is placed, and ensures no leakage of gas. For convenience it is better to glue this ring to the edges of the back funnel. To support the filter-paper, which otherwise might break if the gas is very wet, a piece of copper-gauze is bent and placed in the back funnel so that its flat surface is flush with the edges of the funnel. A filter-paper is placed on the rubber ring and gauze, the other funnel placed on top, and the whole apparatus clamped firmly together.

The first funnel is tared before use, about 100 litres of gas run through the apparatus, and afterwards dried and weighed again. The filter-paper with dust on it is burnt off in a tared platinum crucible. The increase of weight of funnel added to dust so found gives the total dust in gas run through. Very good results are obtained with this simple apparatus. Tests with guard tubes show that absolutely no dust gets through the filter-paper when suitable paper is used. A very satisfactory paper is C. S. and S. No. 589 "Blue Band."

Brymbo Steel Works Laboratory,
October 12, 1912.

TRANSFORMATION OF CHLORO- AND NITRO-AMINOBENZENES INTO THE CORRESPONDING CHLOROANILIDES AND NITROANILINES.*

By Prof. K. J. P. ORTON.

In my attempt to contribute to the solution of the problem of substitution in derivatives of benzene, I have confined myself to a study of the chloro- and bromoamines, *i.e.*, the compounds of the form Ar.NClAc, and of the nitroamines, Ar.NH.NO_2.

Halogenation and nitration of anilines and anilides, forming *o*- and *p*-derivatives, and these only, is one of the most rapid and simplest of organic reactions. The halogenamines and the nitroamines respectively are converted so smoothly into the isomeric halogenated and nitrated compounds,—

$$C_6H_5.NCl.Ac \rightarrow o\text{- and } p\text{-}Cl.C_6H_4.NH.Ac,$$
$$C_6H_5.NH.NO_2 \rightarrow o\text{- and } p\text{-}NO_2.C_6H_4.NH_2,$$

that it has for long been thought, or perhaps I may say assumed, that they are necessary intermediaries in the process, and that their formation accounts for the readiness of these substitutions. as well as for the exclusiveness of the positions taken up by the substituents.

CHLOROAMINES.

Of the two classes of substances, the investigation of the halogenamines has been by far the simpler task, and has led to the most definite results. The part which they play, and the relation which they bear to the process of substitution in anilides, can now be stated with considerable certainty.

1. *Hydrogen Chloride the only Catalyst.*

The first important discovery was that of Armstrong in 1900 (*Trans. Chem. Soc.*, 1900, lxxvii., 1051), that the presence of hydrogen chloride was necessary to the convsrsion of chloroamines into the isomeric anilides.

This very singular circumstance, that *one* acid, and *one only is effective*, has been the subject of a careful search by myself and my collaborators.

It has been found (*Brit. Assoc. Reports*, 1910)—

(i.) That no other substance (or acids) will bring about the conversion; *e.g.*, chlorine and bromine have no action on chloroamines when free from the halogen acids.

(ii.) When conversion has occurred, apparently spontaneously, the presence of hydrogen chloride can always be demonstrated. It may be formed by impurity of the solvent or exposure to light.

A fact which has misled investigators is that the speed of the change may be affected by other substances when HCl is present; thus acids and chlorides both cause a slight increase of the rate of conversion.

2. *Presence of Chlorine during Conversion.*

In 1907 it was discovered (Orton and Jones, *Trans. Chem. Soc.*, 1909, xcv., 1456) that chloroamines and hydrogen chlorides interact, establishing the equilibrium:—

$$Ar.NCl.Ac + HCl \rightleftharpoons Ar.NHAc + Cl_2.$$

In a medium of 65 per cent acetic acid and below, the equilibrium is given by the equation:—

$$Ar.NCl.Ac + H^{\cdot} + Cl' \rightleftharpoons Ar.NHAc + Cl_2,$$

or—

$$K = [Ar.NCl.Ac] \times [HCl] \;/ [Ar.NHAc] + Cl_2,$$
$$K^1 = [Ar.NCl.Ac] \times [HCl]^2 / [Ar.NHAc] + Cl_2.$$

Composition of System made up from p-*Chloroacetanilide and Chlorine.*

Medium	50	65	75	90	100 p.c. $CH_3.CO_2H$
Per cent of Cl free	0·4	5·3	17	65	100

In all anhydrous media the system is composed of the right-hand side of the equation. In aqueous acetic acid below 50 per cent the system is composed almost completely of the left-hand side.

The proportion of free chlorine is determined by aspiration (*loc. cit.*, and Jones, *Trans. Chem. Soc.*, 1911, xcix., 392). These two facts suggest that the conversion of chloroamines into chloroanilides is nothing but a reaction of the chloroamine with hydrogen chloride followed by an interaction of the chlorine and the anilide, with the direct production of the C-chloro-derivative.

It follows that the chloroamines cannot be regarded as intermediaries in the chlorination of anilides.

To obtain confirmatory and conclusive evidence for this view a very large number of experiments and measurements have been made. A brief account of the results of some of the most decisive of these will be given.

(i.) *Interaction of an Anilide (which can be Chlorinated) with Chlorine in Various Media.*

(*a*) *Glacial Acetic Acid as Medium.*—In this and all other anhydrous media, C-chlorination follows an equation of the second order. The speed of the chlorination varies within very wide limits with the constitution of the anilide; *i.e.*, the position and nature of the substituents and the nature of the acyl group (Orton and King, *Trans. Chem. Soc.*, 1911, xcix., 1369).

TABLE I.

	$k_{II.}$=
Acetanilide	40
p-Chloroacetanilide	0·21
o-Chloroacetanilide	0·073
HCl + acetylchloroamino-*p*-chlorobenzene	0·21
Propionanilide	72
Formanilide	4·9
Oxanilide	2
Aceto-*p*-toluidide	77
Aceto-*o*-toluidide	9

It is very important that the acetic acid should be of great purity when the reaction is slow (Orton, Edwards, and King, *Trans. Chem. Soc.*, 1911, xcix., 1178). Highly confusing results are obtained if acetic acid contains reducing substances. This probably accounts for some of Acree's observations, which we have not been able to confirm.

(*b*) *In Aqueous Acetic Acid* two reactions take place side by side, reversible N-chlorination and irreversible C-chlorination.

$$Ar.NHAc + Cl_2 \begin{array}{l} \rightleftharpoons Ar.NCl.Ac + HCl \\ \rightarrow ClAr.NH.Ac + HCl \end{array}$$

Thus on adding a solution of chlorine to one of acetanilide or *p*-chloroacetanilide in 50 per cent acetic acid, one observes a sudden drop in the titer; in a given experiment from 25 cc. N/50 thio to 13·85 cc. within one minute. Since in this medium the left-hand side of the equilibrium is vanishingly small (only about 0·4 per cent of Cl_2 can be detected by aspiration immediately after the addition), the thio titer represents the chloroamine formed. The titer then slowly falls, as the chloroamine is converted in the C-chloro isomeride. (See Table II.).

(*c*) *Contrast with the Conversion of a Chloroamine into the C-Chloro Isomeride.*—In glacial acetic acid, the first very rapid effect is the attainment of equilibrium and the setting free of anilide and chlorine, which then react as just stated following a simple dimolecular reaction.

The effect of diluting the medium is shown by the curves in Diagram A.

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* A Paper read before the British Association (Section B), Dundee Meeting, 1912.

Table II.
Ratio : Chloroamine/Chloroanilide.

Medium. Per cent acetic acid.	Acetanilide.	*p*-Chloroacetanilide.
0	N.Cl/C.Cl = 0·07/1	N.Cl/C.Cl = —
30	„ 0·082/1	„ 0·93/1
50	„ 0·08/1	„ 1·25/1
65	„ 0·083/1	„ 1·55/1

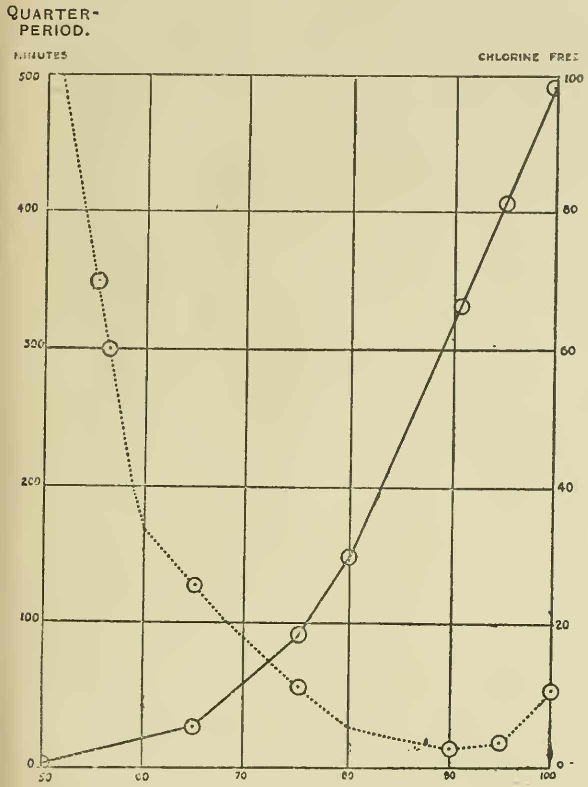

Diagram A.

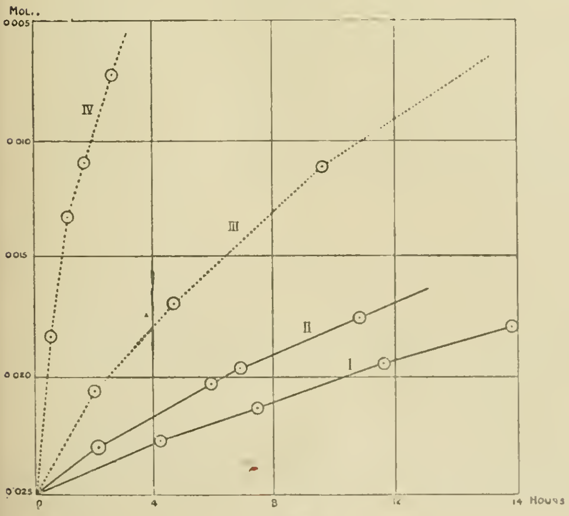

Diagram B.

The firm-line curve gives the percentage of chlorine originally as chloroamine, free in the system; the dotted line curve the quarter period in minutes of the formation of C-chloro-derivative. The speed at first increases, even though the concentration of free chlorine falls, but at 92 per cent acetic acid the dotted curve changes its direction, and the speed of formation of C-chloro-derivative becomes very slow at 50 per cent, where only a trace of free chlorine and anilide are present in the system. (N.B.—Addition of water to the medium favours the reaction in which C-chloro-derivative is produced—*cf.*, "Bromination").

In 50 per cent acetic acid the conversion of the N- to the C-chloro-compound is *apparently monomolecular*. The rate of conversion, quarter period = 500′, obviously shows a remarkable contrast to the instantaneous formation of the C-chloro-compound, which is observed when Cl reacts with the anilide.

(ii.) *The Reaction of a Chloroamine with an Anilide.*

Very remarkable evidence for the contention—(1) that chlorination of anilides does not proceed by way of chloroamines, and (2) that the conversion of chloroamines under the influence of HCl into the isomeride is preceded by the formation of chlorine and anilide, is found in the investigation of the reaction between chloroamines and anilides; *e.g.*, the system :—

$$\begin{matrix}\mathrm{ArCl_2.NCl.Ac} \\ +\mathrm{Ar.NH.Ac}\end{matrix} + \mathrm{HCl}.$$

Table III.—*Reacting System.*
(Medium : 50 per cent Acetic Acid).

		k_1.
I.	$C_6H_5.NClAc + HCl \rightarrow$ *o-* and *p*-$ClC_6H_4.NHAc$	0·00039
II.	*p*-$ClC_6H_4.NClAc + HCl \rightarrow$ 2 : 4-$Cl_2C_6H_3.NHAc$	0·00053
III.	*p*-$ClC_6H_4.NClAc + HCl + C_6H_5.NHAc \rightarrow$ *o-* and *p*-$ClC_6H_4.NHAc$	0·0016
IV.	2 : 4-$Cl_2C_6H_3.NClAc + HCl + C_6H_5.NHAc \rightarrow$ *o-* and *p*-$ClC_6H_4.NHAc$	0·01

The conversion of acetylchloroaminobenzene in the presence of a molecular proportion of HCl in 50 per cent, HA is a slow reaction apparently of the first order, k_1 (15°) = 0·00039 (Curve I. Diagram B). If, however, acetanilide is treated with molecular proportions of HCl and the N-chloro-2.4-dichloroacetanilide (an anilide which does not perceptibly chlorinate) the rate of formation of *o-* and *p*-chloro-derivatives is greatly increased, k_1 (15°) = 0·01 (Curve IV.). In the first system the amount of free chlorine is only just perceptible; in the latter it amounts to 1·5 per cent.

The results are still more striking in the case of interaction of acetanilide and the chloroamine of *p*-chloroacetanilide. The table (III.) and curves (Diagram B) show that the conversion of the latter into 2 : 4-dichloroacetanilide is more rapid than that of acetylchloroaminobenzene into *o-* and *p*-chloroacetanilides. When acetanilide is added to the chloroamine of *p* chloroacetanilide we get a very remarkable result. In the first place no detectable amount of 2 : 4-dichloroacetanilide is formed at all; the acetanilide is completely converted into the monochloroanilides; and secondly the speed of this change is considerably *greater* than the conversion of the chloroamine itself into chloroanilides (Curves II. and III.). It is difficult to account for this observation, except by a direct interaction between the chlorine and anilide. The reaction between chlorine and acetanilide is much faster than that between chlorine and *p*-chloroacetanilide (200 times in glacial acetic acid). The concentration of the acetanilide is relatively great in comparison with that of the *p*-chloroacetanilide. Under these favourable conditions of concentration, certainly less than 1/200 of the

2:4-dichloro compound would be produced from the *p*-chloroacetanilide.

These illustrations and measurements impress upon the mind the fact that the most rapid formation of C-chloro-compounds occurs *not* when the concentration of chloroamine is highest, but when that of the anilide and the chlorine are at a maximum.

It would appear, therefore, that chloroamines are rather by-products, and not intermediaries in the formation in the formation of chloroanilides.

Relation of Speed of Transformation to Concentration of HCl.

Much has been made of the fact that in dilute acetic acid solution the conversion of the chloroamine is a reaction of the first order, and that the speed is proportional to the second power of that concentration of the HCl catalyst. These relations can be deduced from the view here taken of the transformation.

$$d[\text{chloroanilide}]/dt = k_{\text{II}}[\text{anilide}][\text{Cl}_2].$$

But—

$$k[\text{chloroamine}][\text{HCl}]^2 = [\text{anilide}][\text{Cl}_2],$$

substituting—

$$d[\text{chloroanilide}]/dt = k_{\text{II}}(k.[\text{chloroamine}][\text{HCl}]^2).$$

But chloroamine is the only variable.

Therefore—

$$\begin{aligned} d[\text{chloroanilide}]/dt &= (k_{\text{II}}\,.\,k.[\text{HCl}]^2)\,[\text{chloroamine}). \\ &= (k_{\text{I}}\,.\,[\text{chloroamine}]. \end{aligned}$$

The concentration of the chloroamine is sensibly equal to the initial concentration in dilute acid, when, as stated, the amount of chlorine and anilide in the system is very small. Moreover, the speed is proportional to the $[\text{HCl}]^2$. We have shown, as would be expected, that these simple relations no longer hold for media containing more than 50 per cent acetic acid.

BROMINATION.

The bromoamines are less stable than the chloroamines, in that hydrolysis is always more extensive into hypobromous acid and anilide, in all media containing water, and hence owing to the instability of the former bromine appears. They react in an analogous way with hydrogen bromide, but if an equilibrium exists it is immensely in favour of the anilide or Br_2, The conversion of a bromoamine into a bromoanilide is therefore always identical with bromination with bromine.

Bromination is, however, complicated by the combination of Br' with Br_2, forming HBr_3, a combination which is the more marked in anhydrous solvents, *e.g.*, glacial acetic acid, the presence of 4HBr entirely inhibits the action of bromine on acetanilide. But in 75 per cent acetic acid bromination is still very rapid in the presence of 8HBr. Apart from the absence of HBr_3 in aqueous solution, water is the most favourable medium. The equilibria have been studied by the aspiration method (Jones, *loc. cit.*).

Transformation of Nitroaminobenzenes into Nitroanilines.

The transformation of nitroamines offers a very marked contrast to that of chloro- and bromo-amines (*Brit. Assoc. Reports*, 1906, p. 9).

1. No perceptible change takes place in the absence of an acid catalyst.

All acids and not one specific substance (as HCl in the case of chloroamines) bring about the transformation.

The relative effectiveness of different acids is generally proportional to their activities in other processes.

The reaction follows the equation of the first order.

When no side reactions occur the speed in anhydrous media is proportional to the first power, and in 50 per cent acetic acid and below to the second power of the concentration of the acid (when monobasic).

2. The best media for measurements are water or acetic acid, or mixtures of these. (Alcohol and acetone react with the nitroamines). Up to 50 per cent acetic acid there is little effect of the composition of the medium on the speed, but with higher proportion the speed rapidly rises, and in glacial acetic acid is several hunded times faster than in water.

3. Nitrous acid appears very generally during the transformation, and diazonium salts are produced in a side reaction. The presence of urea does not affect in any way the speed or the products of the change.

4. The nature of the nitroamine and of the catalyst has a very marked effect on the extent of the side reaction in which the diazonium salt is formed. The maximum amount of diazonium salt is found with 2:4-dichloronitroaminobenzene, much less with the corresponding bromo-compound, and none with 1-methyl-3-bromo-4-nitroaminobenzene.

The nature of the catalyst has a similar influence. When nitric acid is the catalyst no appreciable quantity of diazonium salt can be found. In the presence of perchloric acid the maximum amount of diazo-compound is produced; hydrogen chloride yields less, and sulphuric acid still less. The ratio of diazonium salt to nitroaniline for a given catalyst appears to be independent of the concentration of the catalyst and the composition of the medium. Thus in the case of hydrogen chloride and 2:4-dichloronitroaminobenzene in various mixtures of acetic acid and water, the ratio nitroaniline/diazonium salt = 3·7/1.

5. The solid crystalline nitroamine changes into the nitroaniline, the crystals of the latter apparently growing out of the former in a P_2O_5-dry atmosphere containing a certain proportion of hydrogen chloride.

6. (*a*) Although there is evidence, but of no certain kind, that the nitration of another substance by a nitroamine can occur (*e.g.*, of acetanilide, or 2:4-dichloroaniline by *s*-tribromonitroaminobenzene) under certain conditions, there is nothing corresponding to the remarkable chlorination of one anilide by the chloroamine of another. No radical (or ion) or substance which is a powerful nitrating agent appears to be free in the system.

(*b*) Under the conditions, *e.g.*, dilute aqueous solution, when smooth and nearly quantitative transformation of the nitroamine occurs, no way has yet been discovered of directly nitrating an aniline.

The experimental evidence just summarised permits of the provisional conclusion that the transformation of nitroaminobenzenes into nitroanilines differs from the conversion of chloroamines, and is probably "intramolecular."

That it is possible that under certain conditions cleavage into aniline and a nitrating substance occurs is indicated by the fact that the nitroamine from *s*-trichloroaniline yields *s*-trichloroaniline in an environment favourable to the isomeric transformation of nitroamines.

The question as to whether the nitroamines are intermediaries in the nitration of anilines depends on the relative velocities of the possible reactions under the given conditions.

$$\begin{tikzcd}
 & \text{Ar.NHNO}_2 \arrow[d] \\
\text{Ar.NH}_2+\text{HNO}_3(+\text{Ac}_2\text{O}) \arrow[ur] \arrow[r] & \text{Ar(NO}_2\text{).NH}_2
\end{tikzcd}$$

In the many experiments which have been made the intermediary formation of nitroamines has only been indicated when with a low concentration of nitric acid in the presence of acetic anhydride the speed of formation of the nitroamines is very great.

Prof. Holleman, who has made such a thorough study of nitration of aromatic substances ("Einführung von Substituenten in den Benzolkern," 1910), expresses the opinion that there is little, if any, evidence for the formation of intermediaries in nitration, or in fact in other substitution of anilines and anilides.

MODIFICATION OF THE ACID BATH IN ELECTRICAL ACCUMULATORS.

By A. DUFAY.

ADD to the solution of sulphuric acid in water used in electrical accumulators 10—15 per cent of a solution of potassium bichromate saturated in the cold.

Reactions.—In presence of a large excess of sulphuric acid the potassium bichromate dissociates into chromic acid and potassium bisulphate.

Action of the Charging Current.—Under the influence of the electric current the hydrogen peroxide formed reacts on the chromic acid to give perchromic acid, which combines with the hydrogen peroxide to give $Cr_2O_7.H_2O_2$, a compound of perchromic acid and hydrogen peroxide (M. Berthelot). But as this very unstable compound forms near the anode (positive pole) it dissociates immediately, giving up its oxygen to the lead, and returning to its primitive state, and then again forms the compound $Cr_2O_7.H_2O_2$. Thus there is no need to replenish the solution of potassium bichromate. Near the cathode (negative pole), the potassium set free being unable to exist in the metallic state, decomposes the water into its elements and sets hydrogen free. The sulphation of the negative bar cannot take place in these conditions. The charging and discharging of the accumulator occur very rapidly. The affinity of potassium for oxygen being greater than that of sodium, potassium bichromate is preferable to the sodium salt.

THE RELATIVE CORROSION OF IRON AND STEEL PIPE AS FOUND IN SERVICE.*

By WILLIAM H. WALKER.

THERE are few subjects relating to the corrosion of metals which have received so much attention, or around which there has centred so spirited a discussion, as the relative merits of iron (meaning thereby wrought iron) and steel. The fact that this matter is one still receiving attention, notwithstanding the great volume of accumulated and available literature, is due to a number of causes, among which may be mentioned:—First, that although the words "iron" and "steel" carry with them a definite idea as to general methods of manufacture and some of the more easily discernible properties, they convey no idea as to standards of value. It is possible to make very poor iron and very good steel, and it is just as possible to make the reverse. Hence when an investigator compared the corrosion of a poor iron with a good steel, he obtained results which favoured steel; when the material under study was the reverse, iron was shown to be the more resistant metal. Second, there is a woeful lack of uniformity of conditions obtaining in many, if not most, of the experiments which have been carried on for the purpose of comparing resistance to corrosion. Some specimens were large, some small; some cleaned of scale, others not; some immersed in deep water, others in shallow water, &c. The corrosion of iron is so sensitive to changing conditions of surface, oxygen concentration, salts in solution, and the like, that only when the most careful preparation is made to maintain all conditions constant, is a comparative test of value. We will not discuss these conditions here, but take pleasure in referring the reader to that most excellent book on "The Corrosion of Iron and Steel," by Dr. J. Newton Friend, where a complete treatment of the general subject will be found. Third, many times opinions are formed and expressed by the casual observer which fail to take into consideration not only the fundamental conditions necessary to accurate comparative work, but also less obvious conditions which make a comparison unreliable. For example, a person may notice the rapid rusting of a cheap grade of steel wire fencing which had originally but a wash of zinc as a substitute for galvanising, and thus become suspicious of the durability of all steel. Or he may notice holes in a metal roof put up in place of a material known to have lasted a much longer time than the new roof. He concludes that the latter is of less value without having any knowledge of the change of conditions in the locality, class of metal, and the thickness of the new roof, nature and thickness of the galvanising or other protective coating, and so forth.

Owing to the proverbial conservatism of New England the introduction of steel pipe has been slower in this territory than in other parts of the country. There is a tendency to pronounce any pipe which withstands corrosion as being wrought iron, while the fact that a pipe corrodes easily is considered by many proof in itself that it is steel.

To determine what the facts actually are in regard to the relative life of service pipes which have been in constant use for a number of years throughout New England, an investigation was undertaken in which it was proposed to seek out instances where steel and iron pipe had been used together in the same system; and further, where the two kinds of metal were separated in this system only by a coupling. Any influence which the coupling might have would be present equally with the iron and with the steel, while conditions of oxygen concentration, temperature, pressure, flow of water or steam, &c., would be as nearly identical for the two kinds of metal as it is possible to obtain. It was intended also to collect in this way material of known resistance or tendency to corrosion, in order to further test the applicability or truthfulness of the so-called "acid corrosion test." While the majority of the pipe so obtained was from hot and cold water feed systems, enough were selected from live and exhaust steam lines, hot water, and steam heating systems, &c., to make the conclusions drawn of general application. The investigation was necessarily tedious in that each pipe had to be examined to determine whether it was of iron or steel, and many instances were found that would have served our purpose well, but where it was impossible to remove the pipes from the system. The pipes were sent to the laboratory, where they were each split lengthwise into two halves and carefully cleaned from scale and rust by soaking in an ammonium citrate solution, with an occasional brushing. In this way the scale and rust were removed without dissolving any of the iron. An estimation of the extent of corrosion was made by measuring with a micrometer gauge the ten deepest pits per unit distance of length. I give the measurement of those samples of pipe which were rusted to practical destruction; that is, where either the iron or the steel showed pits over one-tenth of an inch in depth. (See next page).

The results are a splendid vindication, also, of the principle that if oxygen be excluded from water, no corrosion will take place. When the water in the lines examined was stagnant, as in the fire sprinkler system for buildings, or in lines where the water was circulated over and over again without exposure to the air, as in some hot water systems, no corrosion was to be observed. On the other hand, where fresh water was constantly added to the system, and heated within the system, corrosion was very rapid and in some cases excessive.

We were able to get sixty-four comparisons of iron and steel where the history of the installation was known. The results are as follows:—

Comparison where iron was found more corroded than steel	20
Comparison where steel was found more corroded than iron	18
Comparison where steel and iron were equally corroded	9
Comparison where corrosion was negligible..	17

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* Abstract of a Paper read before the New England Water Works Association, December 13, 1911. From the *Journal of Industrial and Engineering Chemistry*, iv., No. 7.

Sample number.	Depth of pitting.		
	Mean of ten deepest pits.	Deepest pit.	Least of ten deepest pits.
	Inches.	Inches.	Inches.
W 10. Iron	0·102	0·134	0·085
W 11. Steel	0·075	0·095	0·067
W 22. Iron	0·114	0·160	0·068
W 23. Steel	0·075	0·107	0·042
W 24. Iron	0·139	0·168	0·109
W 25. Steel	0·140	0·204	0·076
X 15. Iron	0·077	0·101	0·069
X 16. Steel	0·040	0·047	0·034
X 29. Iron	0·042	0·060	0·030
X 30. Steel	0·066	0·103	0·042
X 49. Iron	0·077	0·113	0·049
X 50. Steel	0·071	0·122	0·040
X 57. Iron	0·038	0·110	0·012
X 58. Steel	0·026	0·053	0·012
X 69. Iron	0·113	0·159	0·032
X 70. Steel	0·119	0·177	0·095
X 71. Iron	0·115	0·169	0·063
X 72. Steel	0·075	0·156	0·042

These results, again, demonstrate that taken *on the average* there is no difference in the corrosion of iron and steel pipe. Conversations held with the engineers in charge of plants during this investigation confirm the statement already made, that a pipe is frequently called steel when corrosion is found to be excessive, while it is set down as iron if it rusts but little.

In order to get some measurement of the influence of oxygen in the water of the modern hot water supply system a relatively large scale experiment was carried on at the plant of the Walworth Manufacturing Company in South Boston. Two coils made up from pieces taken from the same length of pipe were each fed with water from the same source at the same temperature. In one case the water was heated to 85° C. in an *open tank*, while in the other the water was heated to the same temperature in a *closed* tank. The feed water contained on the average 5·85 cc. of oxygen per litre, and passed through each coil at the rate of one-half gallon per minute. After running 1750 hours the coil fed with water heated in an open tank had lost 22 grms., while the coil fed with water heated in a closed tank had lost 155 grms. In neither case was the oxygen completely removed; if the water in the open tank had been gently *boiled*, corrosion in the coil fed with this water would have been entirely prevented.

In order to show what relation may exist between the so-called acid corrosion test and the real corrosion as found in service, eleven pairs of iron and steel were selected and subjected to 20 per cent sulphuric acid for four hours at room temperature. Four pairs were selected in which the steel was decidedly better than the iron in service, four in which the iron had shown decidedly better than the steel, and three in which there was no difference between the two metals.

In six instances the relative corrosion as shown by the sulphuric acid test corresponded with the corrosion as found in service. In five instances corrosion as shown by the acid test was exactly contrary to that found in service. Although the greatest care was taken to have the specimens of the same size, cleaned in the same way, and in the same physical condition, the results show that no reliance can be placed in this accelerated acid test, but that it may be entirely erroneous and very misleading. Not only did the acid test not agree with service test when steel was compared with iron, but the steels failed to agree among themselves, and the irons showed no agreement when considered by themselves.

I wish to express my appreciation of the work of Messrs. James J. Wilson and Francis Worcester, assistants in the Research Laboratory of Applied Chemistry, Mass. Institute of Technology, Boston, without whose aid this investigation could not have been made.

RECENT ADVANCES IN AGRICULTURAL SCIENCE.*

The Fertility of the Soil.

By A. D. HALL, M.A., F.R.S.

From an ordinary common-sense point of view the fertility of the soil is best defined as that property for which a man pays rent—the property which causes some land to let for £2 or £3 an acre, whereas the adjoining land may be dear enough at 10s. With the causes of this fertility I do not propose to deal at any great length this evening more than to indicate that it is the outcome of a very complex series of factors, among which we can enumerate the actual supply of plant food in the soil, its mechanical texture as conditioning the movements of water, and the particular micro-fauna and flora inhabiting the soil, for upon these lower organisms depend the facility with which the material contained in the soil will become available for the nutrition of the plant. For the purpose of the present argument it will be sufficient to fix our attention upon the amount of nitrogen in the soil as the main factor determining fertility, because, in the first place, nitrogen is one of the necessary and most expensive elements in the nutrition of the plant, and, secondly, because its amount in the soil is subject to both gains and losses from causes which are more or less under the control of the farmer. The other essential elements which the plant has to draw from the soil—for example, phosphoric acid and potash—are only subject to slight losses by solution in the drainage water, and cannot be added to except deliberately by the action of the farmer; but in the case of nitrogen we have in addition to the small stock of combined nitrogen in the soil the vast store of free gaseous nitrogen with which both soil and plant are in contact. We may take it as settled nowadays that the plant itself can make no use of nitrogen gas, but must draw combined nitrogen in one of its simpler forms, such as nitrates or ammonia from the soil. Among the bacteria of the soil, however, there are two great groups, one of which is capable of breaking up compounds of nitrogen and setting free the element as gas, whereas the other can take free gaseous nitrogen from the atmosphere and bring it into a combined form. Which of these two groups will be more active depends upon the conditions prevailing in the soil, and goes far to determine both its current fertility and the length of time during which it will be capable of bearing crops.

The question of the duration of the fertility of the land under continual cropping has excited much attention of late, chiefly because the United States has begun to take alarm about the reduced production of some of its most fertile lands, as, for instance, the old prairie lands of the middle West—a reduced production which, amongst other causes, has helped to set in motion a stream of migrants from the United States to the newer lands of the Canadian North-West. In the development of agriculture three distinct stages may be observed. In the first place, we may have a process of pure exploitation of the initial resources of the soil, when the farmer is to all intents and purposes mining in its fertility. This is the process which, in the main, has been going on in America, and, indeed, in all the newer countries which have been opened up to agriculture during the last two centuries. Not all virgin soils are rich, and the system of cropping alternately with wheat or maize which prevails over so much of North America has reduced great areas of the land in the eastern States to such a poverty-stricken condition that it has been allowed to go derelict. In the great plains, however, where the first settler found four or five feet of black soil, containing nearly half per cent of nitrogen, the land has kept up its productivity almost unimpaired for nearly a century. If we suppose the black soil only extended to a depth of three feet, and contained three-tenths per cent of

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* A Discourse delivered before the Royal Institution, May 24, 1912.

nitrogen, both limited estimates, there would still be 30,000 lbs. of nitrogen per acre—that is to say, nitrogen enough for five hundred crops larger than the American farmer has been accustomed to win from that land—and yet in less than a century such soils are beginning to show signs of exhaustion. The farming of the kind just described is destructive; but in the older lands of the west of Europe, which have been under cultivation for something like a century, a conservative system has been devised which is capable of keeping up the productive power of the soil, though not, perhaps, to a very high pitch. Perhaps the best example of this may be seen in the Norfolk four-course rotation prior to the introduction of artificial fertilisers. In this system a turnip crop, which was either consumed on the ground or converted into manure and so returned to the soil, was followed by barley in which clover was sown, and the clover, which also got back to the soil, was followed by wheat. The farming covenants prevented the sale of anything more than barley and wheat grain, and the meat that was produced by the consumption of the turnips and hay. Thus but a small proportion of the nitrogen taken out of the soil by the crop left the farm; the rest was returned and used over again, although considerable losses of gaseous nitrogen occurred during the making of the dung. Both losses, however, were more than replaced by the nitrogen which the clover crop gathered from the atmosphere during its growth. At any rate, we find that under such a conservative system of farming the productivity of the land remained pretty constant at about a level of twenty bushels to the acre from the time of Queen Elizabeth down to the beginning of the nineteenth century. This conservative farming about 1840 began to give place to the third stage in the development —intensive farming, rendered possible by the discovery of artificial fertilisers and the cheap freights which brought foreign fertility in the shape of cheap feeding stuffs to the soil of this country. By these means the average production of the land of the British Isles has been raised from the twenty-bushel level to something over thirty bushels, and the most intensive farmers reach an average level at least 25 per cent higher. In their case the soil has become practically a manufacturing medium transforming the nitrogen and other fertilising materials added to it into crops, giving nothing to those crops from its original stock, and, indeed, up to a certain point gaining rather than losing fertility with each year's cultivation. The inner history of these three stages in agriculture may be followed by a consideration of certain experimental plots at Rothamsted (Table I.). We may begin with the experimental wheatfield which is now carrying its sixty-ninth successive crop of wheat. One of the plots has been without manure throughout the whole of that period. The production, which fell steadily for the first ten years, has since that time remained so constant that the slow falling off which we still believe to be taking place is disguised by the fluctuations due to season. The average yield is about twelve bushels to the acre, almost exactly the average yield of the wheat lands of the whole world. Unfortunately, samples of soil were not taken at the very outset, but if we begin with the earliest analyses that were available in 1865 and draw up a balance-sheet for the nitrogen, we shall find that the removal in the crop is almost exactly balanced by the small amount that comes down in the rain and the decrease that has taken place in the amount of nitrogen in the soil. There are, however, other losses of nitrogen not brought into account; some is washed away by drainage water every year, and a further small unestimated amount gets removed as weeds. As these losses do not appear in the balance-sheet we must conclude that some recuperative action is at work keeping up the stock, though the process is not sufficient wholly to make up for the removals in the crop. The results of this plot show two principles at work—the tendency of the land under an unchanging system of farming to reach a position of equilibrium when the only variations in the crop are those brought about by seasons; and, secondly, that regeneration of the nitrogen stock in the soil is possible by natural causes alone.

TABLE I.—*Experiments on Wheat Broadbalk Field, Rothamsted.*

Average produce of Grain, first 8 years, (1844—51) and the successive 10-year periods 1852—1911.

	Plot 2. Farmyard manure. Bushels.	Plot 3. Unmanured. Bushels.
Averages over—		
8 years, 1844—1851.. ..	28·0	17·2
10 years, 1852—1861.. ..	34·2	15·9
10 years, 1862—1871.. ..	37·5	14·5
10 years, 1872—1881.. ..	28·7	10·4
10 years, 1882—1891.. ..	38·2	12·6
10 years, 1892—1901.. ..	39·2	12·3
10 years, 1902—1911.. ..	35·1	10·9
60 years, 1852—1911.. ..	35·5	12·8

We may now turn to one of the other plots which receives an excess of farmyard manure each year, the manure supplying about 200 lbs. of nitrogen per acre, whereas the crop only takes away about 50 lbs. (see Table II.). Naturally the land in this case increased in fertility, but after twenty or thirty years another position of equilibrium was attained at a level of about thirty-six bushels per acre, after which, despite the continued additions of manure, the crop again did not vary except as the result of exceptional favourable seasons. If we now consider a similar balance-sheet for this plot, we find that the additions of nitrogen are balanced neither by the removals in the crop nor by the accumulation of nitrogen in the soil; indeed, half of the nitrogen applied is unaccounted for. The soil has been getting no richer for the last twenty or thirty years, and the greater part of the nitrogen is wasted, doubtless because bacterial action sets the nitrogen free as gas. Here, then, we see another principle illustrated, that in very rich land the wasteful agencies are so speeded up as to prevent any continued accumulation of fertility out of the unused residues of the manures put on. Higher fertility means a higher level of waste, and this explains the rapidity with which the very rich virgin soils lose their fertility when they are put under arable cultivation. In this Rothamsted plot, the soil of which still contains less nitrogen than the less rich virgin soils of the prairies, three times as much nitrogen are wasted every year as is converted into crop, and the same or an even greater rate of wastage must attend the conversion of the rich virgin soils into land growing a succession of cereal crops.

TABLE II.—*Broadbalk Wheatfield.*

Nitrogen in Soil, lb. per acre.

In soil, 1865.	In soil, 1904.	Gain or loss in 39 years.	Added in manure.	Added in rain.	Removed in crop.	Unaccounted for.
Plot 3—Unmanured.						
2850	2290	−560	—	150	600	−110
Plot 2—Farmyard Manure.						
4470	4970	+500	7800	150	1990	−5460

(To be continued).

Aluminium Triphenyl.—Siegfried Hilfrey and Gerhard Grüttner.—By the action of aluminium on mercury diphenyl at 140° aluminium triphenyl can be obtained as a pale yellow viscous mass, which crystallises after some time. The preparation has to be performed in absence of air and moisture. Attempts to estimate the carbon and hydrogen in it ended in explosions, but it can be analysed by leading damp oxygen over it. With water it yields alumina, benzene, and diphenyl. It dissolves in alcohol, giving an infusible product which is not an alcoholate.—*Berichte*, xlv., No. 12.

SOAP LYE AND SAPONIFICATION CRUDE GLYCERINS.

British Standard Specifications.

The following Standard Specifications were drawn up by the British Executive Committee on Crude Glycerin Analysis, and approved at a General Meeting of Crude Glycerin Makers, Buyers, and Brokers, held in the Whitehall Rooms, London, on October 3rd, 1912. The following were the Members of the Committee:—W. W. Gossage (Chairman), Messrs. W. Gossage and Sons, Ltd., Widnes; Wm. Alexander, Messrs. Ogston and Tennant Ltd., Renfrew; J. Bruce, Messrs. Cape Explosives Co., Ltd., London, E.C.; D. T. Crighton, Messrs. Nobel's Explosives Co., Ltd., Glasgow; J. Griffiths, Messrs. Price's Candle Co., Ltd., London; C. Haslam, Messrs. J. Crosfield and Sons, Ltd., Warrington; F. E. Hyrons, Messrs. Henry Hill and Sons, London; J. Gray (Hon. Secretary), Messrs. Lever Brothers, Ltd., Port Sunlight.

Soap Lyes Crude Glycerin.

Analysis to be made in accordance with the International Standard Methods (I.S.M., 1911).

Glycerol.—The standard shall be 80 per cent glycerol. Any crude glycerin tendered which tests 81 per cent glycerol or over, shall be paid for at a *pro rata* increase, calculated as from the standard of 80 per cent. Any crude glycerin which tests under 80 per cent glycerol, but is 78 per cent or over, shall be subject to a reduction of one and a-half times the shortage, calculated at *pro rata* price as from 80 per cent. If the test falls below 78 per cent, the buyer shall have the right of rejection.

Ash.—The standard shall be 10 per cent. In the event of the percentage of ash exceeding 10 per cent, but not exceeding 10·5 per cent, a percentage deduction shall be made for the excess calculated as from 10 per cent at *pro rata* price, and if the percentage of ash exceeds 10·5 per cent, but does not exceed 11 per cent, an additional percentage deduction shall be made equal to double the amount in excess of 10·5 per cent. If the amount of ash exceeds 11 per cent, the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 3 per cent. A percentage deduction shall be made of three times the amount in excess of the standard of 3 per cent, calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3·75 per cent.

Saponification Crude Glycerin.

Analysis to be made in accordance with the International Standard Methods (I.S.M., 1911).

Glycerol.—The standard shall be 88 per cent. Any crude glycerine tendered which tests 89 per cent or over, shall be paid for at a *pro rata* increase, calculated as from the standard of 88 per cent. Any crude glycerin which tests under 88 per cent, but is 86 per cent or over, shall be subject to a reduction of one and a-half times the shortage, calculated at *pro rata* price as from 88 per cent. If the test falls below 86 per cent, the buyer shall have the right of rejection.

Ash.—The standard shall be 0·5 per cent. In the event of the percentage of ash exceeding 0·5 per cent, but not exceeding 2·0 per cent, a percentage deduction shall be made equal to double the amount in excess of 0·5 per cent. If the amount of ash exceeds 2 per cent, the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 1 per cent. A percentage deduction shall be made of twice the amount in excess of the standard of 1 per cent, calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 2 per cent.

October 7, 1912.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 25th, 1912.

Prof. C. H. Lees, F.R.S., Vice-President, in the Chair.

A paper on "*The Constitution of Mercury Lines Examined by an Echelon Grating and a Lummer-Gehrcke Plate*," by Prof. H. Nagaoka and Mr. T. Takamine, was read by the Chairman.

The authors have photographed the principal lines of mercury, using an echelon spectroscope crossed by a Lummer-Gehrcke plate. They find that the 5790 line consists of 8, the 5769 line of 4, the 5461 of 9, the 4359 of 11, the 4078 of 6, and the 4047 of 7 components, whose positions in general agree with those found by recent observers. They point out a simple relation between the distances of the components from the principal line in each case, and a further relation between the quotient of each of these distances by the wave-length of the principal line, which holds for all the lines. The relative intensities of the component lines were determined by interposing an echelon photograph between a constant source of light and a linear thermopile, and noting the changes in the deflection of a galvanometer in series with the pile as the plate was moved across the face of the pile. In every case there appears to be a simple relation between the position and intensity of each component line.

Prof. Stansfield was very much interested in the valuable work the authors had carried out, and objected only to their reflections on the character of the echelon spectroscope. He agreed with Prof. Lees that the ambiguity as to the order of spectrum lines at some distance from the principal line, mentioned by the authors, could in practice be readily avoided by employing a prism to increase or decrease slightly the echelon dispersion. The echelon he had employed showed some of its secondary diffraction maxima, as any diffraction grating approaching to perfection in its optical behaviour was bound to do. These secondary maxima were abnormally bright on one side of the principal maximum and very faint on the other. In the paper by Stansfield and Walmsley, referred to by the authors, this had been shown to be due to a cubic aberration produced by the one-sided clamping of the glass plates. In spite of this want of symmetry, however, he thought it was only fair to the instrument to call them secondary maxima, and he hoped that the authors of the paper would say whether the faint lines they referred to as ghosts were also secondary maxima. His own list of components for the green line only differed from that given by von Baeyer and the authors of the present paper in the omission of the faint line at $-54m$-A., and this did not represent any difference of opinion, as several of his photographs, including the one reproduced in his paper, gave some evidence of this line. A secondary diffraction maximum which happened to come in that position was so bright that the presence of a faint primary assisting it was strongly suspected. Fabry and Perot's early values for the green line, which differed considerably from the others quoted in the paper, were not regarded by their authors as accurate determinations. He was not aware that they had ever published them except in correspondence with Prof. Zeeman. He considered that the agreement between the results obtained by widely differing methods was fairly satisfactory.

Thanks were returned by the meeting to Prof. H. Nagaoka for having communicated his valuable paper to the Society.

A paper entitled "*Note on the Mutual Inductance of Two Coaxial Circular Currents*," by Prof. H. Nagaoka, was read by Dr. A. Russell.

Methods are given for the rapid calculation of the mutual inductance of two coaxial circular currents. Maxwell's first formula is converted into theta-functions, and then expanded in a Jacobian q series. The logarithmic values of this series for various values of q have been tabulated in a previous paper by the author. When the circles are near one another a series for M is given in terms of q_1, where q_1 is the complement of q. In this paper the author treats Maxwell's second formula in a similar way. A table of the values of these series found, computed to six decimal figures by T. Tishima, is given. The chief advantages of this table are that nearly all practical cases are included within a short range of the argument, and the calculation is simple, as the numbers in the difference columns are small. By the help of these tables and series the mutual inductance between two coaxial currents can be easily computed to a high degree of accuracy.

Mr. A. Campbell expressed great thanks for this communication. He had already used the tables given by Prof. Nagaoka in a former paper on the subject published in Japan very largely, and those given in the present paper covered still wider limits and enabled cases to be calculated which otherwise necessitated the use of Legrende's Tables of Elliptic Functions.

Dr. Russell expressed his interest in the paper. He pointed out that the value of the mutual inductance was given to seven figures. It was certainly a step in advance to be able to evaluate so easily and to such a high degree of accuracy the simple expression for the mutual inductance. But in practice the wires used had appreciable thickness, and it was highly desirable that a more accurate formula be obtained so as to take this thickness into account.

Mr. F. E. Smith said he would like to express personal thanks for the paper, and hoped that Prof. H. Nagaoka would also give tables for the mutual induction of a coil and a circle. The point raised by Dr. Russell of the thickness of the wires had been considered by Dr. G. F. C. Searle in a paper on the "Current Balance," who found that the effect was in general negligible. It was quite evident that the present paper was both labour and time saving.

A paper on "*The Absorption of Gases in Vacuum Tubes*," was read by Mr. S. E. Hill.

This paper is an account of experiments carried out to determine whether the absorption of gases caused by passing a discharge for some time through vacuum tubes is the result of a chemical action or is a mere physical absorption. In order to eliminate all electrode complications, the electrodeless discharge was used throughout. The bulbs examined were of soda, lead, Bohemia and Jena glass. The absorptions were noted at different pressures and curves plotted. Continued passage of a discharge causes a "saturation" effect in all the glasses. After two months none of the bulbs had recovered any of their absorptive power. If the action is chemical it is natural to expect various oxidation products to have been formed. Testing these bulbs with hydrogen we should expect a large initial absorption going to reduce these products. This was found to be the case for all the bulbs, the first reading for the soda glass giving 95 per cent absorption of hydrogen. Having now reduced the oxidation products we should expect a re-absorption of oxygen under the discharge. This was also found to be the case. The series of readings show great regularity, tbe order of absorption for oxygen holding also for hydrogen. That chemical actions are present is shown by peculiar deposits on the necks of the bulbs, these being unfortunately too small for analysis. The inert gases show correspondingly small absorption, as shown by Soddy and Mackenzie, and therefore the conclusion is that the disappearance is not due to physical absorption, but to definite chemical action.

Dr. R. S. Willows mentioned the fact that the inert gases, like argon and helium, also disappeared on running the discharge, but this might be due to their being carried down by the cathode deposit. He had known a case of a hydrogen vacuum tube made of lead glass and provided with outside electrodes that was used as a detector for high-frequency oscillations, which failed to work after long continuous running, owing to the disappearance of the hydrogen, but worked again if the tube was left on one side for a week.

Mr. C. E. S. Phillips thought the electrodes played an important part in the diminution of pressure on working. Mr. Hill's results seem to indicate that the glass may become aged. It might be possible to age the glass for X-ray bulbs artificially. The constant change in hardness of X-rays owing to the change of pressure was a most serious drawback especially in medical work, where it was holding back the progress of the applications of X-rays to medicine.

Dr. G. W. C. Kaye remarked that in X-ray bulbs the spluttering of the cathode absorbed the gas. Campbell Swinton found some years ago that by heating the walls of a vacuum tube small bubbles of gas were given off, which was mostly hydrogen, and found that they came from distances up to 0·15 mm. below the surface. Ramsay and Collie had recently found helium to be evolved in a similar case. It was difficult to explain these results on the penetration theory, as the charged atoms would not penetrate the thinnest aluminium foil. This theory also does not explain the differences in behaviour of different kinds of glass. The results may be due to chemical activity excited in the gas by the discharge, such as has recently been found by Prof. Strutt to be the case with nitrogen. The violet coloration often noted in the glass of vacuum tubes was due to a sub-oxide of sodium. He suggested Mr. Hill experimented with silica bulbs.

Mr. A. A. Campbell Swinton contributed the following remarks:—Mr. Hill alludes to my paper published in the *Proceedings of the Royal Society*, 1907, Series A, vol. lxxix., but does not seem to be aware of my further paper in the *Proceedings of the Royal Society*, 1908, Series A, vol. lxxxi., in which the criticisms of Soddy and Mackenzie and of others are dealt with. In Mr. Soddy's experiments, as also in those of Mr. Hill, forms of electric discharge were employed with which the amount of heat communicated to the glass would be very great as compared with the amount of cathode-ray bombardment; whereas, in the arrangements adopted in my experiments, the converse was the case. Consequently, I do not think that the cause of the absorption of gas is necessarily at all the same in the one case as in the other, particularly as in my crucial experiment I used helium, which does not combine chemically with anything at ordinary temperatures.

The Author remarked that he would be glad to carry out the experiments suggested.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, November 4th, 1912.

Mr. G. T. Holloway in the Chair.

The following papers were read and discussed:—

"*Nitrogenous Constituent of Para Rubber and its Bearing on the Nature of Synthetic Rubber.*" By Clayton Beadle and H. P. Stevens.

The raw material used in the experiments consisted of plantation sheet rubber, which was swollen in a large excess of benzene and allowed to stand. The insoluble nitrogenous matter separated out in the lower half, the upper half consisting of a clear orange-yellow fluid. The upper half was poured off and the nitrogen-free rubber obtained by spontaneous evaporation. The lower half, similarly treated, yielded rubber containing the whole of the insoluble nitrogenous matter. Each sample of rubber so obtained was vulcanised and tested alongside of the original rubber. A chemical analysis of the vulcanised rubber showed that the amount of sulphur entering into combination with the rubber was greatest in the case of the separated lower half containing the excess of insoluble nitrogenous matter, while the upper half free from nitrogenous matter showed a very small quantity of sulphur in combination with the rubber. The physical tests bore out the chemical analyses, the sample free from nitrogenous insoluble matter being very difficult to cure, and when cured inferior to the other samples.

Reference is made to other work of the authors dealing with rubber from which the resins had been separated, and showing that the removal of the resins also caused deterioration of the quality of the rubber. As synthetic rubber hydrocarbon would not naturally contain other insoluble nitrogenous matter or resin, it follows that it would not vulcanise satisfactorily. On the other hand, it is possible that by the artificial addition of these substances this defect might be overcome.

"*Corrosive Action of Dilute Solutions of Acids, Alkalis, and Salts upon certain Metals and Alloys.*" By A. J. Hale.

A brief review of the work already done is given, and references to papers dealing with this subject are given. The author then describes the manner in which the corrosion of eight metals and three alloys was studied, using sixteen different dilute solutions. The clean specimens of metal having an area of 2 sq. dcm. were completely immersed for fourteen days, and then, after cleaning, the loss in weight ascertained.

Comparable conditions were maintained throughout, and the results have been represented in a series of tables.

In the first table are shown the actual losses in weight observed as well as numbers representing the loss in weight of each metal and alloy per sq. dcm. per fourteen days, and attention is drawn to several important relations among the numbers.

The next two tables show the relative solvent power of the solutions used, and also the relative corrodibility of the metals and alloys, and here again observed relationships are discussed.

An attempt to find out how corrosion varies with the area exposed, and also with the time of immersion, is next described, and the results embodied in two tables and further represented by a series of graphs.

The impurities present in the metals and their amounts are stated, as well as the composition of the alloys used, and the influence of certain constituents on corrodibility is discussed.

"*Viscosity of Lubricating Oils.*" By A. E. Dunstan and F. L. Stevens.

This paper deals with the viscosity-temperature curve afforded by a variety of lubricating oils. The authors point out that such a curve would give reliable information about an oil at the working temperature to which it is subjected.

The apparatus used was modelled on that recommended by Ostwald, and consisted of a U-shaped viscometer, heated in an oil bath. Specific gravities were taken in a small 10 cc. pyknometer.

The apparatus was calibrated against pure phenol, the viscosity of which has been accurately determined at a variety of temperatures by Scarpa, Dunstan, and Thole.

The viscosities fall off very rapidly with rise of temperature and tend to become asymptotic to the axis of temperature. This will be seen from examples given in the paper.

"*Formylated Cellulose.*" By Edward C. Worden.

The author gives an historical summary, with bibliography, of the esters of cellulose. He points out that the high cost of acetic anhydride has militated against the commercial exploitation of cellulose acetates. In the search for other esters which, while at the same time uninflammable and non-explosive, could still be produced at a figure admitting of direct commercial competition with nitrocellulose, the industrial possibilities of formylated cellulose began to receive the serious attention of chemists. The fact that in the formylation of cellulose no counterpart of acetic anhydride—the most expensive constituent of the acetylating mixture—is required is, in the author's opinion, the principal factor for the great activity displayed in this field at present. It appears quite probable that in the near future the cellulose formates may be produced in unlimited amounts commercially at a cost at least not in advance of the present cost of nitrocellulose, starting with the same source of cellulose.

The author describes his own attempts, which so far have not been successful, at obtaining flexible coherent films of formylated cellulose.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, November 6th, 1912.

Mr. Leonard Archbutt, President, in the Chair.

Messrs. Stanley Winter Collins and Charles Blüthner Lessner were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Stanley Elliott, Penshurst, Windmill Hill, Enfield; Thomas Rigby Greenough, Beechwood, Leigh, Lancashire; Harold Lowe, 18, Hough Green, Chester; James P. Ogilvie, Homedale, Hendon Lane, London, N.; and John Algernon Lacy Sutcliffe, City Analyst's Laboratory, Broad Street, Birmingham.

The following papers were read and discussed:—

"*Detection and Estimation of Arachis Oil.*" By Norman Evers.

The author considers that the most satisfactory qualitative test for arachis oil in olive oil is that proposed by Adler, which is preferable to Bellier's test.

The sources of error in Bellier's quantitative method are pointed out, and a modification suggested which gives satisfactory results.

"*Examination of Chinese and Japanese Wood Oil.*" By A. Chaston Chapman.

The author deals with the chemical examination of Chinese and Japanese wood oils, and describes the methods which, in his opinion, are most suitable for the purpose, and which are most likely to lead to correct conclusions in regard to the purity or otherwise of the oil.

Analytical numbers are given for seventeen samples of genuine Chinese wood oils, and it is shown that these are subject to appreciable variations, dependent on geographical and botanical origin, on the conditions adopted in the manufacture of the oil, and on a number of other factors.

Analytical results are also given for the analysis of four samples of genuine Japanese wood oil, including one sample extracted by the author from the nuts of *Paulownia imperialis*, from which the oil is chiefly obtained.

"*Estimation of Manganese by the Bismuthate Method.*" By H. F. V. Little.

It is shown that, contrary to the opinion of Brinton, the bismuthate method gives accurate results in the determination of both high and low percentages of manganese, without the necessity of standardising the requisite solutions empirically. The manganese values of the permanganate and ferrous sulphate solutions may be readily and accurately calculated in the usual way from their relative values and the iron value of the permanganate.

The President exhibited an apparatus known as the Digby and Biggs "*Dionic Water Tester*" for testing water by measurement of its electrical conductivity.

A current at approximately constant voltage, generated by means of a small hand dynamo, is passed through the water between fixed platinum terminals and measured by means of a specially designed conductivity meter. The apparatus provides a rapid and delicate means of detecting leakage in surface condensers and also of controlling the concentration of boiler waters.

The results of tests were given showing the capabilities and limits of usefulness of the instrument.

NOTICES OF BOOKS.

Researches on Cellulose. III. (1905—1910). By Cross and Bevan. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

In describing the work that has been done on cellulose in the period 1905—1910, the authors have found themselves obliged somewhat to alter the plan adopted in the earlier parts of this book, and this third volume is to be regarded as a *résumé* and criticism of recent work on cellulose from the pens of the greatest authorities on the subject. The period has been one of great specialisation and important technical developments, and the authors' task has been far more difficult than when they were dealing with the preceding periods, which no doubt partly accounts for the fact that the book is written in a disjointed style, comparing unfavourably with that of the earlier volumes. All important articles and papers on cellulose published up to 1911 are abstracted, and the special cellulose industries are discussed, excellent samples of the new fabric cellophane, made by the Société Industrielle de Thaon, being given with the book. In the very interesting introduction brief allusion is made to the philosophical problems connected with the study of cellulose.

Notes on Foundry Practice. By J. J. Morgan, F.I.C. London: Charles Griffin and Co., Ltd. 1912.

The aim of this book is to give condensed and at the same time reliable information as to the materials and methods employed in iron-founding, and also to a certain extent in steel, brass, bronze, and phosphor bronze casting, and this aim it may be regarded as satisfactorily fulfilled. The author has restricted himself to giving the merest outline of his subject, but his information appears to be accurate as far as it goes, and the practical man as well as the student may well be glad to use the book as a summary of the essentials of the subject, in conjunction with a larger and more comprehensive work in which fuller details are to be found. It contains many useful tables, and a few explanations of typical methods of calculating results.

The Laboratory Book of Mineral Oil-testing. By Jas. A. Hicks. Second Edition. London: Charles Griffin and Co., Ltd. 1912.

The issue of a second edition of this very useful though unpretentious book, in answer to a general demand, has come so soon after the first that there was little time for revision. The author, whose death has recently occurred, had however gone over the text and made a few alterations, and an appendix has been added on the Redwood viscometer. This appendix gives a description and illustration of the latest form of the viscometer, which was designed by Sir Boverton Redwood for use in connection with the Admiralty specification for oil fuel, and also explains the method of using it.

First Year's Course of Chemistry. By James Sinclair, M.A., B.Sc., and George W. M'Allister, MA.. London: G. Bell and Sons, Ltd. 1912.

This is a good example of a useful type of school book suitable for putting into the hands of beginners. The experiments described in it are well selected and form an introductory course which is quite long enough for a full first year's work. The plan adopted of first describing a series of experiments to be performed on a single subject and then giving a discussion of the results appears thoroughly sound. The experimental directions are full and clear, and the explanations are usually well worded, though the authors are inclined to overload the book with matter and get into difficulties because some of the subjects they introduce are difficult to explain satisfactorily to beginners; for example, the short account of the Law of Mass Action is open to adverse criticism. Some additional experiments are introduced for the sake of the quicker workers, and there are plenty of questions which will test both the student's knowledge of the text and his ingenuity. It would be possible to alter the order of the chapters if considered desirable, and it is probable that many teachers would prefer to defer the quantitative study of water and take up carbon dioxide immediately after the atmosphere.

Matriculation Directory. No. 62, September, 1912. London: University Tutorial Press.

In this almost indispensable aid for the Matriculation candidate the usual features of previous issues appear. These include the full papers set in September, 1912, with solutions of many of them, and very outspoken but on the whole favourable criticisms. Sound advice on the choice of text-books finds a place in the book, as well as information relating to the classes and courses of the University Correspondence College.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlv., No. 12, 1912.

Action of Elements on Fused Caustic Potash.—M. Le Blanc and O. Weyl.—KOH can be obtained in an anhydrous state by heating to 400°; at 660° there is no dissociation, but evaporation occurs. Between 550° and 660° Au, Al, Mn, and K do not act on KOH in an atmosphere of nitrogen. Fe, CO, and Ni are attacked, but no H_2O, H, or K can be detected. With Cr, Mo, and W free K and H are formed, and the same reaction occurs with C and Mg. Si acts violently at 400°, hydrogen being evolved.

Constant Form of Combustion Cell.—Franz Fischer and Richard Lepsius.—Electrodes of ferroso-ferric oxide can be used in making a combustion cell. A nickel or iron crucible containing fused caustic soda is heated by means of a Bunsen burner, and the electrodes, a carbon and ferroso-ferric oxide rod respectively, are introduced into it. The latter is at first positive, but its polarity changes as the temperature rises, and at 550° the tension is 0·8 volt. When the circuit is closed with a resistance of 10 ohms the terminal voltage sinks to 0·6 volt, and the strength of the current remains constant at 60 milliamp. for hours.

Quantitative Determination of Active Hydrogen in Organic Compounds by means of Magnesium Methyl Iodide.—Th. Zerewitinoff.—The active hydrogen atoms in the lower fatty alcohols (methyl, ethyl, propyl) can be determined by means of methyl magnesium iodide, if pyridine is used as solvent. Compounds which contain two amido groups when treated with CH_3MgI at the ordinary temperature react with two hydrogen atoms, and, on warming, with three; the fourth active hydrogen will not react, even on heating. Hydrocarbons of the fluorene type react with CH_3MgI, but diphenyl, dinaphthyl, triphenyl, trinaphthyl, and trianisyl methane do not react either at the ordinary temperature or on warming.

Synthesis of Phenol-glucosides.—Emil Fischer and Hermann Strauss.—By shaking an alkaline solution of phloroglucine with an ethereal solution of acetobromglucose a product is obtained which after removal of the acetyl groups yields phloroglucin-*d*-glucoside. Resorcin-*d*-glucoside can be obtained in the same way. Both glucosides are split up by emulsin, and hence belong to the β-series. The authors have also prepared the glucoside of 2 . 4 . 6-tribromphenol, which differs from ordinary glucosides in its great instability towards alkalis, as might be expected from the strongly electronegative nature of tri bromphenol.

Behaviour of Phenols, Naphthols, and Phenol Carbonic Acids towards Tetravalent Titanium.—O.

Hauser and A. Lewite.—Titanic acid gives an intense red coloration with chromotropic acid (commercial 1.8-dioxynaphthaline-3.6-disulpho acid). The authors have now found that all phenols react similarly, and the coloration can be employed as a general method of detecting oxy-groups. A few drops of a concentrated solution of titanic acid in cold fuming HCl (or strong H_2SO_4) are added to some decigrms. of the phenol. On heating and adding some drops of alcohol or acetone as solvent a red or violet coloration is produced. In the case of salicylic acid salts of a di-titanic salicylic acid can be isolated.

Solubility of Argon and Helium in Solid and Liquid Metals.—A. Sieverts and E. Bergner.—The authors have investigated the solubility of argon and helium in solid and liquid copper, nickel, palladium, and iron; liquid silver, gold, aluminium, magnesium; solid tantalum and uranium. In all cases the results were negative. In the course of the experiments it was confirmed that the liberation of helium by cleveite depends on the temperature of heating. The simplest way to prepare helium is to heat the powdered mineral directly in a porcelain tube to 1000—1200°. Porcelain is much less permeable by helium than quartz glass at high temperatures. It was also found that metallic uranium probably absorbs hydrogen.

Ferric Benzoates.—R. F. Weinland and Alfred Herz.—By the addition of a solution of ferric chloride to a dilute solution of sodium benzoate a benzoate of formula $Fe_3(C_6H_5.COO)_7(OH)_2$ is precipitated. From this can be obtained derivatives of a hexabenzoato-triferric base, $[Fe_3(C_6H_5.COO)_6](OH)_3$, of a pentabenzoato base, $[Fe_3(C_6H_5.COO)_5](OH)_4$, and a tribenzoato base, $[Fe_3(C_6H_5.COO)_3](OH)_6$. The first of these readily gives well crystallised benzoates, as well as salts of inorganic acids. Crystallised benzoates can also be derived from the other two bases.

Atti della Reale Accademia dei Lincei.
Vol. xxi. (ii.), No. 6, 1912

Basicity of Acids containing Alcoholic Hydroxyl.—G. Calcagni.—In continuation of his work on the neutralisation of hydroxy acids by means of ammonia, the author has studied the neutralisation of the following acids by $Be(OH)_2$:—Glycolic, oxyisobutyric, malic, tartaric, and citric, and gives in this article the data obtained for the construction of the curve of conductivity of $Be(OH)_2$ neutralised by glycolic and oxyisobutyric acids. In the case of tartaric acid the author has obtained the potassium salt, $K_2O.2BeO.2C_4H_4O_5+2H_2O$, corresponding to the copper salt present in Fehling's solution, and the lead salt of tartaric acid, as well as the K, Na, and NH_4 salts of diberilliotartaric acid of formula $R_2O.4BeO.2C_4H_4O_5+x\text{Aq}$ and of the monoberilliotartaric acid of formula $R_2O.4BeO.2C_4H_4O_5+x\text{Aq}$, and of the monoberilliotartaric acid of formula $R_2O.2BeO.2C_4H_4O_5+x\text{Aq}$, and the similar malic acid salts.

Commercial Glycerophosphates of Sodium.—V. Pavlini.—The author has determined the water of crystallisation of various specimens of sodium glycerophosphate, and has found that they all correspond to the formula $Na_2(C_3H_7O_2)PO_4+5\frac{1}{2}H_2O$, and thus resemble the Poulenc salt. Commercial glycerophosphate consists chiefly of the symmetrical β-derivative.

MISCELLANEOUS.

Royal Society of Arts.—The 159th Session of the Royal Society of Arts will be opened on Wednesday evening, November 20th, by Lord Sanderson, G.C.B., K.C.M.G., Chairman of the Council, who will deliver an Address and distribute the Medals awarded last session. On November 27th, Mr. Harold Cox will read a paper on "The Interdependence of Morals and Economics"; Sir George Askwith, K.C.B., K.C., presiding. Mr. A. Zimmermann will describe "The Manufacture of Sugar from Wood, and its Economic Importance" on December 4th; Dr. F. Mollwo Perkin will read a paper on "Synthetic Rubber" on December 11th; and Mr. Joseph Pennell will deal with the "Pictorial Possibilities of Work" on December 18th, illustrating his paper with an exhibition of etchings, &c., which extend from the days of Rembrandt to the present time, and include some of the lithographs which he has lately made himself of the gigantic engineering works of the Panama Canal. In the Colonial Section, Prof. W. H. Warren will describe "The Hardwood Timbers of New South Wales," on November 26th, when Sir George Houston Reid will take the chair; and in the Indian Section, Mr. J. Forrest Brunton will read a paper on the rapidly-growing city of Karachi, on December 12th. A course of Cantor Lectures will also be delivered by Mr. C. R. Darling on "Methods of Economising Heat" on Mondays, December 2nd, 9th, and 16th.

City and Guilds of London Institute.—The Council of the City and Guilds of London Institute have conferred the Fellowship of the Institute upon Mr. Alfred Chatterton, C.I.E., B.Sc., and Mr. W. D. B. Duddell, F.R.S. This distinction is extended to those students who have obtained the Associateship of the Institute and spent at least five years in actual practice, and by original and valuable research work or otherwise have contributed to the advancement of the industry in which they are engaged. Mr. Chatterton was the first student on the City and Guilds Central Technical College Register. He entered at the beginning of 1885, and was awarded the Associateship in Civil and Mechanical Engineering in 1887. On leaving College he was appointed Professor of Engineering at the Government Engineering College and Inspector of Technical Schools in Madras. He is now Director of Industrial and Technical Inquiries, Madras Presidency, and has been awarded the Kaiser-i-Hind Medal. Mr. Duddell entered the Central Technical College in October, 1893, and obtained a Whitworth Exhibition in 1896; he continued at the College engaged in research work in the Electrical Department down to July, 1900, and has contributed many original and valuable papers on the results of his investigations to the Royal and other scientific societies. He is President of the Old Students Association of the College.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Microscopical, 8. "British Euchytraeids—IV., The Genus Henlea," by Rev. H. Friend. "Saccammina Psammasphoera (North Sea No. 2)," by E. Heron-Allen and A. Earland.

— Royal Society of Arts, 8. The Opening Address of the 159th Session of the Society will be delivered by Lord Sanderson, G.C.B., K.C.M.G., Vice-President and Chairman of the Council.

THURSDAY, 21st.—Royal Society. "Investigation of the Spectrum of Ionium," by A. S. Russell and R. Rossi. "The Absorption of β-Rays" and "The Similarity in Nature of X and Primary γ Rays," by J. A Gray. "Spectra of Fluorescent Röntgen Radiations," by J. C. Chapman. "Optical Investigation of Solidified Gases—II., The Crystallographic Properties of Hydrogen and Oxygen," by W. Wahl. "Electric Furnace for Experiments *in vacuo* at Temperatures up to 1500° C.," by R. E. Slade. "Investigation of the Dissociation Pressures and Melting-points of the System Copper—Cuprous Oxide," by R. E. Slade and F. D. Farrow. "The Capacity Coefficient of Spheres," by A. Russell.

— Chemical, 8.30. "The Change in the Boiling-points of the Trioxide and Tetroxide of Nitrogen on Drying," by H. B. and M. Baker. "Tendency of Atomic Weights to approximate to Integral and Semi-integral Values," by E. Feilmann. "Constituents of Taraxacum Root," by F. B. Power and H. Browning, jun. "Condensation of α-Keto-β-anilino-αβ-diphenylethane and its Homologues with Phenyl Carbimide and Phenyl Thiocarbimide," by S. A. Brazier and H. McCombie. "Neutral Salt Action—Part II., The Influence of Sodium Salts of Organic Acids on the Rate of Hydrolysis by Alkali," by G. Senter and F. Bulle. "Constitution of Aconitine," by O. L. Brady.

THE CHEMICAL NEWS.

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ANALYSIS OF RED EARTH FROM THE FLOOR OF AN ANCIENT HUT.

By J. O. HUGHES, B.Sc.

In various parts of England, especially along the western coasts of Wales and Cornwall, in Brittany, and in Ireland, traces have frequently been discovered of ancient habitations; to those found in Wales the term "Cyttiau'r Gwyddelod" (Irishmen's huts) has been applied. These ruins are generally in the form of a circular wall of stones, with an opening at one point, enclosing a space of a few yards' diameter; they are usually found in groups, thus forming a village, situated on high ground or in sheltered positions, and in many cases fortified by a rude outer wall. Excavations carried out at some of these villages have been attended with considerable success, implements, pottery, and coins being discovered, and in many cases the internal arrangement of the huts determined.

During an excavation, conducted by Mr. Harold Hughes, A.R.I.B.A., in the floor of some of the ancient huts forming the great stone fortress on the top of Penmaenmawr, Carnarvonshire, he found, amongst other things, a quantity of reddish brown earth containing bits of charcoal. Similar material has been observed before in some of the ancient huts, but so far as can be ascertained, has never been investigated; the result of a chemical examination of the substance may therefore be of some interest.

The material consisted of lumps of fine earth having a reddish brown colour. Two samples, collected from different positions in the floor of the ruined hut, were examined; analysis showed that their composition was practically identical, but that in one the percentage of gritty or sandy material was higher than in the other. Embedded in the material were two or three small bits of charcoal, about one-quarter inch long, the actual identity of this being proved by a chemical test.

The appearance of the substance, together with the presence of charcoal, suggested that it was simply baked soil or clay; but a preliminary analysis showed the presence of a considerable amount of phosphate and iron. A complete quantitative examination was therefore considered advisable, and the following results were obtained:—

	Per cent.
Residues insoluble in HCl, and soluble SiO_2	83·82
Al_2O_3	2·47
Fe_2O_3	4·71
MnO	trace
CaO	trace
MgO	1·45
$K_2O + Na_2O$	0·52
P_2O_5	1·22
SO_3	0·13
CO_2	trace
Cl	trace
H_2O (at 110° C.)	1·86
Loss on ignition	3·70
	99·88

It is seen that the analysis is not that of an ordinary soil or clay, the phosphate and the ratio of ferric oxide to alumina being higher than in a soil.

The high percentage of phosphate leads one to suggest that the material is of organic origin.

Taking into consideration the peculiar position where the material was obtained, the probable source is either (*a*) decomposition of animal remains or refuse, or (*b*) the ash of plants, or peat, or similar combustible material.

The following considerations enable us to arrive at a probable solution:—

Animal remains would contain their phosphate chiefly in the form of calcium salt, but analysis shows that calcium is present here only in minute quantity.

Peat ash usually consists of sand and clay, ferric oxide, phosphate, sulphate, and small quantities of lime, magnesia, and alkalis.

Some years ago I examined the peat ash from a peat-burning farm in Anglesey, and the composition and general appearance of the ash was very similar to that of this material; in that case the ash contained 1·75 per cent P_2O_5.

In view of these facts, viz., the locality where the earth was collected, the presence of pieces of charcoal, and the analysis of the substance, I am led to the conclusion that it is the ash of some combustible material, mixed with some of the surrounding soil. Whether the fuel was wood or peat is difficult to say; wood ashes contain a high percentage of alkalis, but this may have been washed out by rain water.

The investigation shows that those who inhabited these dwellings had their fires, at least in some cases, inside the huts, and this is confirmed by the discovery in some localities of fireplaces inside the walls of the huts (see Stanley's "Antiquities in Holyhead Island").

University College of N. Wales,
Bangor.

THE BACTERIOLOGY OF AËRATED WATER.

By G. D. ELSDON, B.Sc., A.I.C.

A short time ago the writer and another (Elsdon and Evers, *Analyst*, 1912, xxxvii.; see also Chemical News, vol. cvi., p. 223) described some experiments showing the action of carbon dioxide under pressure on the micro-organisms in water, and the number of organisms growing on jelly at 21° C. from many commercial samples of "soda water" were given. Some of these latter results are here tabulated, the figures being the number of organisms in 1 cc. of water growing on nutrient jelly in three days.

Nature of bottle.	Number of organisms.
Syphons	150, 3, 8, 20, 59, 45, 3, 5, 5, 21, 30, 4, 10, 10, 119, 2, 15
Codds..	70, 100, 87
Corked bottles	41, 3000, 1000, 2100
"Screw" bottles ..	540, 1100, 600

It will be seen from a perusal of these results that, in general, the number of organisms in water stored in syphons is low, whilst the number in waters stored in corked bottles is much higher; the number of organisms stored in "codds" (the automatically closing bottle with a globular glass stopper) is intermediate between these two.

Two factors may lead to these results. The first is that owing to their nature syphons cannot be used for miscellaneous household purposes, whilst bottles may be and often are. Besides this some bottles are not easily cleaned. The second, and more likely, reason is the difference in pressure which exists in the various vessels in which "soda waters" are sent out. Thus syphons are bottled at a higher pressure than any bottles, whilst codds are stoppered automatically with little escape of carbon dioxide. Other bottles (screw stoppers, corks, patent caps, &c.) have to be removed from the machine and bottled by hand, thus allowing a certain amount of carbon dioxide to escape and reducing the pressure.

From a consideration of the results given in the above mentioned paper it would seem very likely that the differences in the number of organisms are due to the differences of pressure. It is the intention of the author to investigate this question of the effect of the variation in pressure, and he hopes before long to publish some of the results.

City Analyst's Laboratory, Birmingham.

TWO NEW METHODS OF WEIGHING THE CORNETS IN THE ASSAY OF GOLD BULLION:

By which the Balance Readings give the Finenesses Directly, *i.e.*, the Weights of the Cornets Corrected for Surcharge; with Incidental Improvements in the Assay.*

By A. OCTAVIUS WATKINS, A.R.S.M., F.G.S.

General.

The term "surcharge," in the assay of gold bullion, is applied to the net correction to be made to the weight of a cornet, for the gains by retention of silver and occluded gases, and the losses of gold by volatilisation, absorption by cupel, and solution in the acid.

The method here set out, by which the balance readings give the finenesses directly, is suitable for assay offices where a large number of bullion assays of widely varying finenesses is made, and where it is desirable that all shall be treated alike from the time they are ready to be charged into the muffle till the cornets are annealed and ready for weighing. It is applicable to bullion containing more than about 1 per cent of gold provided that the base metals present are not of such a nature and quantity as to influence the surcharge.

Working from day to day under practically identical conditions, it is not necessary to pass, with each batch of assays or "fire," proofs or checks of approximately the same fineness as each sample of bullion, for although it is not possible to get the same surcharge for any given fineness, it is quite practicable to obtain the same difference in surcharge for equal differences in fineness. Usually the procedure has been to pass proofs for one fineness, and, after weighing the cornets, to compute, with the aid of a slide-rule, the surcharge for each cornet, allowing the same difference in surcharge from that of the proofs for equal differences in the weights of the cornets.

As there is the same difference in surcharge for equal differences in fineness, it follows that the surcharge of a cornet can be resolved into two parts—one (α) a correction proportional to the fineness of the bullion (or proof), but constant for all fires, and the other (β) a correction constant for all cornets in a fire, but varying in different fires (see Note).

Let e represent the α corection for a cornet weighing one assay pound to be deducted; and, in any given fire, let S represent the surcharge for pure or fine gold to be deducted; m the fineness of any given bullion (or proot) being assayed; and x the surcharge of its cornet to be deducted. Then will em represent the α correction to be deducted, and $S-e$ the β correction to be deducted, and therefore—

$$x = (em) + (S-e).$$

As these corrections have to be deducted when the value is negative, it has to be added.

The (em) corrections are made by adjustments applied to the weights and (ordinary) rider used, and the $(S-e)$ correction by placing an extra rider, called a surcharge rider, in the requisite position on the beam.

(Note.—From theoretical considerations, as the assays are all rolled to the same thickness, it can be concluded that the net correction (one part of α) for the gains by retention of silver and occluded gases, and the loss by solution in the acid, is proportional to the weight of the cornet, and since it is chiefly dependent upon quantity and strength of acid, time of boiling, and amount of washing, it is an easy matter to keep it practically constant for all fires. This is not the case, however, with the losses by volatilisation and absorption by the cupel, which largely depend upon the temperature and draught in the muffle, the control of which is not so complete, and therefore, since in practice the difference between a correction proportional to the weight of the cornet and one proportional to the fineness of the bullion (or proof) is negligible, it is surmised that the sum of these two losses can be resolved into a correction (the other part of α) proportional to the fineness, and a correction (β) constant for all cornets in a fire, the latter being dependent upon temperature and draught).

Particular.

The following are the details, except for a departure in a few minor points, of the methods as carried out at the Perth (Western Australia) Branch of the Royal Mint, where an assay pound of 10 grains is used:—

All the values below are given in assay pounds except where stated otherwise. For proofs the assay pound of proof gold is used, the fineness of which is never lower than 0·9998, that of pure gold being taken as unity. Silver is added to bring the ratio of silver to gold to 2½. If copper is not present 0·083 is added, this being the weight in an assay pound of standard gold (fineness, 0·916). The weight of lead used in every case is 84 grains.

Under the special conditions of working it is found tha the surcharge of the proofs varies from +0·0004 to +0·0008 in different fires, and that for finenesses between unity and 0·4 it diminishes by 0·00001 for each decrease of 0·01 in fineness; that is, $e = \dfrac{0{\cdot}00001}{0{\cdot}01} = 0{\cdot}001$. With finenesses below 0·4 the decrease is not quite regular, but proof gold is added to such bullion to bring the cornets obtained to 0·4 or more. The surcharge of the proofs is taken as that of pure or fine gold, but the maximum error so introduced is quite negligible, viz.,—

$$0{\cdot}001(1-0{\cdot}9998) = 0{\cdot}0000002 \quad . \quad . \quad . \quad (\mathbf{A}).$$

All the assays are made in duplicate, one by weighing the cornets with Foord's compensating weights with certain corrections explained below, against an assay pound, and the other sgainst ordinary direct weights with certain other corrections also explained below. (See "On a Proposed New Method of Weighing Applicable to the Gold Bullion Assay," by George Foord, *Trans. and Proc. Roy. Soc. of Victoria*, vol. xii.).

Each balance is fitted up for weighing cornets either by the compensating or the direct method, and for this purpose attached to each hanger is a small platform just above the removable pan, on which weights may be placed. There is also a short horizontal bar fixed to the centre of the rider-slide, and at right angles to it pointing away from the beam, at the end of which are two short bars running right and left parallel to the beam, and just within reach of the rider-carrier, so that two riders of different weights can be interchanged without having to use a pair of forceps.

Each arm of the beam of the balances is divided and notched into 50 parts, each fifth division being also marked with a dot below the division mark, thus dividing it into ten major divisions. No figures are marked on the arms, but under each even major division there is a vertical cross-piece. The position of a rider can thus be read as easily as if the major divisions were marked by figures underneath, and it can be read in either direction without any confusion which figures would cause. This permits of the balances being used without impediment for other work besides gold bullion assays, for in both the compensating and direct methods each arm is read from right to left; thus a right rider when on the extreme right, or a left rider when off the arm, reads nil.

The balances are so adjusted that a swing of one division from zero on the index scale represents 0·0001. The assay pieces and the cornets are always placed in the right-hand pan.

Before a cornet is weighed on the assay balance proper, the succeeding one is placed on the pan of a Law's auxiliary assay balance (*Journ. Chem. Soc.*, May, 1896, p. 526), sensitive to less than 0·01, and which comes to rest by the time the preceding cornet is weighed. By this means, as the weights differ by gradations of approx

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* Read at a Meeting of the Natural History and Science Society of Western Australia, October 8, 1912.

mately 0·01, the one required can generally at once be placed on the pan of the assay balance proper, thereby saving the time occupied in trying different weights.

The surcharge for fine gold is found by weighing the proof cornets against the assay pound, using the 0·001 rider on the left arm and the index scale. The fineness of the proof gold deducted from the mean weight of the proof cornets gives the surcharge for fine gold.

Compensating Weights Method.

To avoid having two riders on the same arm of the beam at a time, (*em* − *e*) is deducted instead of (*em*), by adjustments applied to the weights, and (ordinary) rider used; and (S) is deducted instead of (S − *e*) by placing an extra rider, called the surcharge rider, in the requisite position on the left-hand arm of the beam.

The actual weight of each compensating weight as devised by Foord was one assay pound less the sum of its nominal weight, and 0·01 (the weight of his rider).

To deduct (*em* − *e*), the compensating weights and (ordinary) rider are made 0·001 (that is, *e*) part heavier than his (Foord's). . . . . (B).

To deduct (S), a 0·001 rider, called the surcharge rider, is placed on the left-hand arm of the beam to give an effective weight of the surcharge for fine gold.

When the fineness of bullion being assayed is below 0·4, an addition of 0·5 of proof gold is made to the assay, and correction for this is made in weighing the cornet by deducting from the balance reading the weight of gold in the 0·5 of proof gold added.

The surcharge for fine gold having been placed on the left arm by means of the surcharge rider, to weigh a bullion cornet it is placed on the right-hand pan, and the weight (indicated by the Law's auxiliary balance) on the platform just above. The position of the right-hand rider is then adjusted to almost equipoise the left-hand system. The fineness of the bullion is then given by reading the weight, the right-hand rider (from right to left), and the index scale. . . . . (C).

Let S, as before, represent the surcharge for fine gold, W the nominal weight of the compensating weight used, R the nominal effective weight of the right-hand rider, N the weight the index scale shows the right is heavier than the left system, and x the fineness of the bullion. Then it must be shown that—

$$x = W + R + N.$$

From (A) the surcharge of the bullion cornet is—

$$S - 0{\cdot}001(1 - x),$$

i.e.,—

$$S - 0{\cdot}001 + 0{\cdot}001x.$$

From (B) the actual weight of the compensating weight is—

$$1 - (W + 0{\cdot}01) + 0{\cdot}001\,\{1 - (W + 0{\cdot}01)\},$$

i.e.,—

$$1 - W - 0{\cdot}01 + 0{\cdot}001 - 0{\cdot}001\,W - 0{\cdot}00001;$$

i.e.,—

$$0{\cdot}99099 - 1{\cdot}001\,W. \quad . \quad . \quad . \quad . \quad . \quad . \quad (D).$$

From (B) and (C) the actual effective weight of the right-hand rider is—

$$(0{\cdot}01 - R)\,\frac{0{\cdot}01001}{0{\cdot}01}$$

i.e.,—

$$0{\cdot}01001 - 1{\cdot}001\,R.$$

Now, the weight of the cornet represents the fineness of the bullion plus the surcharge of the cornet, and the load on the left arm plus the weight the index scale shows the right is heavier than the left system, is equal to the load on the right arm, *i.e.*,—

$$1 + S + N = \begin{cases} (x) + (S - 0{\cdot}001 + 0{\cdot}001x) + (0{\cdot}99099 \\ \quad - 1{\cdot}001\,W) + (0{\cdot}01001 - 1{\cdot}001\,R). \end{cases}$$

$$\therefore\ 1{\cdot}001x - 1{\cdot}001\,W - 1{\cdot}001\,R = N.$$

$$\therefore\ x = W + R + 0{\cdot}999\,N.$$

Then, as by adjusting the position of the right-hand rider N need never be allowed to exceed 0·0001, the value of one thousandth part of N need never exceed (0·0001 × 0·001 =)0·0000001, and therefore 0·999 N can be taken as N, especially as it is as often a plus as a minus quantity.

The equation then becomes—

$$x = W + R + N.$$

Calculated from the above formula, 0·99099 − 1·001 W, the compensating weights employed are given in Table I.

Table I.—*Compensating Weights.*

Assay Pounds.

Nominal and mark.	Actual.	Nominal and mark.	Actual.
0·98	0·01001	0·83	0·16016
0·97	0·02002	0·82	0·17017
0·96	0·03003	0·81	0·18018
0·95	0·04004	0·80	0·19019
0·94	0·05005	0·79	0·20020
0·93	0·06006	0·78	0·21021
0·92	0·07007	0·77	0·22022
0·91	0·08008	0·76	0·23023
0·90	0·09009	0·75	0·24024
0·89	0·10010	0·74	0·25025
0·88	0·11011	0·73	0·26026
0·87	0·12012	0·72	0·27027
0·86	0·13013	0·71	0·28028
0·85	0·14014	0·70	0·29029
0·84	0·15015	−0·3	0·30030

In addition the following two weights and two riders are required:—

Assay Pounds.

Nominal.	Actual.	
1	1·00000	Assay pound weight.
0·01	0·01001	Right-hand rider.
0·001	0·00100	Left-hand surcharge rider.
0·9167	0·0833833 (*a*) (theoretically)	

(*a*) Special compensating weight marked 0·9167 for weighing standard gold (0·916) cornets without a right-hand rider. The actual weight is calculated from the first statement of the formula (D) after striking out "0·01" (in two places) the nominal weight of the right-hand rider.

For cornets between 0·7 and 0·4 the −0·3 is used with another compensating weight, from which 0·3 is deducted in reading its nominal weight.

(To be continued).

THE PERMANENT FIREPROOFING OF COTTON GOODS.*

By WILLIAM HENRY PERKIN, Ph.D., LL.D., F.R.S.

When I had the honour of being asked to deliver one of the General Lectures, I had no choice but to accept, and yet it was at once evident to me that I should experience very great difficulty in finding a subject suitable to this occasion and interesting to the brilliant and distinguished audience which I see before me this afternoon.

This difficulty is due to the fact that, while I have always taken an interest in industrial questions and have repeatedly investigated industrial problems from the scientific point of view, my researches have, for the most part, lain in the path of pure Science, and any practical application of my researches to the Chemical and Allied Industries I have had to leave to others.

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* Lecture delivered at the Eighth International Congress of Applied Chemistry, September 10, 1912.

Among the problems of technical interest which I have worked at during many years are the manufacture of artificial camphor, of "synthetic" rubber, and more particularly the permanent fireproofing of cotton goods and other inflammable materials. In considering these subjects, I concluded that the problem of the manufacture of artificial camphor was too technical to be generally interesting, and my friend Prof. Duisberg wishes to introduce the subject of "synthetic" rubber into his General Lecture, so there remained the subject of permanent fireproofing, which in many respects is perhaps as interesting and important, and as difficult of accomplishment, as the other problems I have mentioned. The problem of the prevention of fire has always been one of the most pressing and at the same time one of the most difficult and perplexing with which mankind has had to deal. In very early times wooden houses caught fire and were burnt down, and it is said that the Romans attempted to render wood fireproof by dipping it in a bath made of vinegar and powdered clay.

This treatment, so strongly reminiscent of processes employed many years afterwards, would no doubt be effective in rendering the wood less liable to inflame, but it can hardly have had wide application, because vinegar, in those days, was not easily obtained in quantity and was consequently an expensive substance. I have made a search in a number of old books with the object of discovering some other of the actual methods used in early times in connection with fireproofing, and the first pamphlet on the subject which I have been able to find dates from 1638, when Nikolas Sabattini published a remarkable paper, in which he discussed the need of reform in the administration and construction of the theatres in Italy, and pointed out the danger, which is always present, of fire breaking out on the stage, not only owing to the inflammable nature of the wood employed in the construction of the theatre, and for the decorations and scenery, but also on account of the inflammability of the cotton material used in the scenery and for the dresses of the players.

He recommends, as a safeguard, that the colour used in painting the theatre and scenery should be mixed with clay and gypsum, but says nothing about the fireproofing of the dresses.

At a considerably later date—in 1735—Wild suggested a mixture of alum, borax, and sulphuric acid for the same purpose, and in 1740 Fagot, in a paper read before the Academy in Stockholm, recommended a mixture of alum and green vitriol, whereas, in the "Dictionnaire de l'Industrie," published in the year 1786, there is a paragraph in which it is stated that a mixture of alum, green vitriol, and salt is effective in making wood and other material fireproof.

After the disastrous fire in Munich on January 14th, 1823, which completely destroyed the Hof and National Theatre, a large number of experiments were made, with the result that the wood used in the construction of the roof and other parts of the new theatre was painted with several coats of sodium silicate and chalk.

A coating of this kind lasts for many years, and although it does not render the wood absolutely non-inflammable, it has at least this value, that the incipient fire, which as a rule begins in quite a small way, meets with resistance at the outset, progresses but slowly, and is easily extinguished.

At a somewhat later date, it was discovered that wood saturated with other salts, such as, for example, copper sulphate or ammonium phosphate, acquires the property of resisting flame, but of all the salts zinc chloride seems to be the most efficient for this purpose.

In the first place, zinc chloride has great affinity for, and therefore attaches itself readily to, woody fibre, and fibres of all kinds and material saturated with a solution of this salt and then dried are practically non-inflammable. This salt has also this valuable property, that it is a powerful antiseptic and therefore very suitable for fireproofing the wood used in the construction of hospitals and other public institutions of a similar nature.

But I do not propose to address you this afternoon at any length on the subject of the fireproofing of wood and other building materials, a subject on which I have made comparatively few experiments, and of which I, therefore, have little practical knowledge.

What I wish to discuss, and I hope that the subject will prove interesting to you all, is the problem of the permanent fireproofing of wearing materials, and especially of cotton and cotton goods, and by permanent fireproofing I mean protection which is not removed when the materials are subjected to the ordinary domestic wash.

Many disastrous accidents are on record which have been brought about by clothing catching fire; sometimes it is the case of a child whose garments have come in contact with a spark or lighted match, and sometimes disasters of much greater magnitude have resulted from the ignition of costumes made of tow or other inflammable material on the occasion of charity entertainments or fancy dress balls.

It has long been recognised that impregnation with certain salts very much reduces, and indeed may entirely destroy, the liability of cotton goods to inflame, and of these fireproofing agents I may perhaps be allowed to refer to a few only of the better known and more efficient. If a garment, after washing in the ordinary way, is rinsed in a solution containing alum, or is starched with a starch containing a proportion of alum, the material, after drying, shows a marked reluctance to ignite, but this treatment has many drawbacks. In the first place it makes the material very dusty; and secondly, the fireproofing is only of a temporary nature, since it is at once removed by contact with water, and the process must therefore be repeated every time the goods are washed. I can easily demonstrate this, and in these and all my other experiments I purposely take only very narrow strips in order that any smoke produced may not cause inconvenience in this Hall. Another solution which has been strongly recommended for the same purpose is made up with 3 parts of ammonium phosphate, 2 parts of ammonium chloride, and 1 part of ammonium sulphate in about 40 parts of water. If the material after washing is impregnated with this solution and dried, or if it is starched with starch made with the solution instead of with water, the dry material only ignites with difficulty, and, as it does not dust and is not prejudicially affected in any other way, this process has been used with advantage not only in connection with wearing material but also for the fireproofing of lace curtains and other inflammable decorations. But in this case also the fireproofing agents employed are all soluble in water, and one washing is sufficient to remove them entirely, leaving the goods at least as inflammable as before. The process must therefore be repeated every time the goods are washed, and this means expense which, in the long run, becomes considerable.

But a much more serious drawback to processes of this kind is the trouble they entail, since in order to fireproof the garment the washerwoman must have alongside the ordinary wash-tub a second tub containing the fireproofing solution, and this complication, added to the expense of the salts, has been shown to be so serious that processes of this kind are quite impracticable, especially in the homes of the poor. Again, unless the materials or garments after washing have been dried before immersion in the fireproofing solution, this solution cannot be kept uniform, since each garment being wet when put in leaves the solution weaker than before, and therefore of less protective value. To dry each garment between the washing and the fireproofing entails so much trouble and labour and expense that it would obviously prevent any general adoption of the practice. Although the substances I have mentioned, and the salts of ammonium in particular, possess in a high degree the property of rendering material fireproof, there is one substance which confers the property of resisting fire to cotton goods in such a remarkable degree that it has long attracted attention, and must be specially mentioned, and that is sodium tungstate.

A piece of muslin soaked in a weak solution of sodium tungstate and then dried is practically non-inflammable, but unfortunately this salt is again so excessively soluble in water that a mere rinsing in clean water is sufficient to remove it completely and the fireproofing is lost. And this applies not only to sodium tungstate but also to all the other salts which have from time to time been recommended for fireproofing purposes; the result is not permanent because the proofing is at once removed when the goods are washed in the ordinary way.

The problem on which I was engaged for several years, and which has now been successfully solved in a very simple manner, was that of attempting to discover some process which not only made the goods non-inflammable but also *permanently* non-inflammable, and the researches on this subject were originally started in connection with flannelette, a material very largely and widely used for clothing, especially by the poorer classes, and one of the most, if not the most, inflammable of all cotton goods.

Flannelette may be briefly described as a kind of calico, the surface of one or both sides of which has been "carded" or "raised" into a nap, the result being that the surface of the calico becomes covered with a fluff of minute fibres somewhat resembling a thin layer of cotton wool. This effect is produced by subjecting the surface of the calico to the action of a series of revolving rollers covered with a vast number of small pieces of sharp steel wire, which tear up the surface, and the material is passed over these rollers over and over again until the required amount of nap has been raised. The result of this superficial covering of nap is—as everybody who has handled flannelette will know—a warm, pleasant, and cosy feel, and this is no doubt due to a covering of air being imprisoned by the minute fibres, thus producing a layer which acts as a non-conductor much in the same way as in the case of flannel.

In the first two samples in the little book which you each received as you entered the Hall are calico and flannelette, and you will notice at once the great difference in the feel between the comparatively hard flat surface of the calico and the raised surface of the flannelette.

Flannelette is indeed little, if at all, inferior to flannel as a non-conducting material, and as it is very cheap and does not shrink in the wash, it has become very popular and is manufactured in enormous quantities, and almost universally used for the clothing of children, especially in the homes of the poorer classes.

But it was not long before its increasing use showed unmistakably that it has one terrible drawback—the nap, which is its peculiar feature, makes it highly inflammable and much more so than the calico from which it was manufactured.

Flannelette is, in fact, as I have already said, very much like calico, on the surface of which a thin layer of cotton wool has been spread, and this layer is, of course, highly inflammable.

I can easily demonstrate the difference in the inflammability of calico and flannelette by applying a light to strips of each, when it will be seen that while calico burns in the ordinary way, in the case of flannelette the flame flashes over the whole surface of the fluffy cotton layer and travels with extraordinary rapidity.

It is, of course, this property which makes flannelette one of the most dangerous of materials for clothing purposes. The alarming frequency of deaths by burning due to the wearing of flannelette became common knowledge; the coroners all over Great Britain repeatedly called attention to the matter, and by degrees the agitation against its use for clothing became so persistent that the Coroners' Committee of the Home Office was directed to enquire into the matter.

The Committee recognised that whilst, to quote the words of their Report, "We think the common opinion attributing to it (flannelette) a large share of the blame (of burning accidents) is not far wrong," that it was impossible to prohibit its use without causing great hardship; especially to the poor. Several years before this enquiry was held, one of the largest firms of flannelette manufacturers in Manchester, Messrs. Whipp Bros. and Tod, becoming alarmed at the frequent occurrence of fatal burning accidents, and fearing lest these might lead to the prohibition of the sale of the material, came to me and asked whether I would undertake a series of experiments with the object of endeavouring to find a remedy for this state of things, and, after looking carefully into the matter, I consented to do what I could. That the problem was a difficult one from many points of view will be readily understood if I briefly state the conditions which had to be kept constantly in mind while the experiments were being carried on. A process to be successful must in the first place not damage the feel or durability of the cloth, or cause it to go damp as so many chemicals do, and it must not make it dusty. It must not affect the colours or the design woven into the cloth or dyed or printed upon it; nothing (such as arsenic, antimony, or lead) of a poisonous nature, or in any way deleterious to the skin, may be used, and the fireproofing must be permanent, that is to say, it must not be removed even in the case of a garment which may possibly be washed fifty times or more. Furthermore, in order that it may have a wide application, the process must be cheap. What was really to be aimed at was to treat the flannelette in such a way that it acquired practically the properties of wool, which for all ordinary purposes may be taken as the standard of a safe material. Apart from the other conditions which I have laid down, when one considers the vigour with which the ordinary washerwoman scrubs garments with soap, not infrequently with the assistance of the scrubbing brush, and takes into account the wonderful mechanical appliances now so largely used for washing clothes with the least expenditure of time, it will not be thought surprising that the discovery of a process of fireproofing sufficiently permanent to resist all these conditions seemed to me at first to be almost an impossibility.

(To be continued)

RECENT ADVANCES IN AGRICULTURAL SCIENCE.*

The Fertility of the Soil.

By A. D. HALL, M.A., F.R.S.

(Concluded from p. 241).

We may now turn to another plot on the same field to illustrate the recuperative actions of which I have spoken (see Table III.). This is a part of the field that has been running wild since 1881, when the wheat it carried was not harvested but allowed to seed itself. A very few years sufficed to eliminate the wheat, which was unable to maintain itself against the competition of the weeds, and the land now carries a miscellaneous vegetation consisting mostly of grass. A soil sample was taken at starting, and when compared with another sample taken twenty-three years later showed that in the interval the land had gained nitrogen at the enormous rate of 92 lbs. per acre per annum. Making every allowance for possible errors in sampling and analysis, the accumulation of nitrogen is in marked contrast to its steady depletion in the equally unmanured arable land alongside. Now, the difference between the two plots lies in the fact that on the land running wild the vegetation is never removed, but allowed to die down naturally. Hence not only is the nitrogen taken out by the crop returned to the soil, but also a large stock of carbonaceous matter assimilated from the atmosphere, and this carbonaceous matter furnishes a bacterium

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* A Discourse delivered before the Royal Institution, May 24, 1912.

present in the soil, *Azotobacter chroococcum*, with the source of energy which will enable it to fix atmospheric nitrogen. *Azotobacter* is equally present in the soil of the unmanured wheat plot; but, as there the crop is removed, and only a little root and stubble left behind, there is but little carbonaceous matter for the *Azotobacter* to work upon, and a correspondingly small fixation of nitrogen, sufficient only, as we have seen, to repair the casual losses by drainage and weeding. This plot gives us a clue to the source of the vast accumulations of nitrogen in the old prairie soils. Vegetation alone, however long continued, cannot increase the stock of nitrogen in the soil; there is only a circulation of the initial stock removed by the plants, and then put back when the plant dies *in situ*. But if the conditions are also favourable to the development of *Azotobacter*, this organism derives from the carbonaceous part of the plant residues the energy it requires for the fixation of nitrogen, and a steady addition to the original stock goes on. We have found *Azotobacter* present in all these rich black soils, from both South and North America, the Russian Steppes, and similar virgin land in all parts of the world, and again we also find an abundance of lime, one of the other necessary factors for the growth of *Azotobacter*. Virgin soils are not necessarily rich; there are miserably poor ones, though they have equally carried some sort of vegetation for hundreds, indeed thousands, of years. They have remained poor because some of the other factors upon which depend the development of *Azotobacter* are lacking. With this far-reaching conclusion in sight, we have naturally tried at Rothamsted whether we could not bring about a similar heaping up of nitrogen in the soil by simply adding to it a carbohydrate containing no nitrogen, such as starch or sugar. In pots, the experiment is perfectly successful, and accordingly we selected one of the plots in the barley field which was in a very nitrogen-starved condition, because it had been manured for fifty years only with mineral fertilisers containing no nitrogen, and treated half the plot with sugar at the rate of a ton to the acre, the other treatment of the two halves of the plot being alike (see Table IV.). To our surprise, the half receiving sugar gave a miserable crop, much below the non-sugar half, for four years in succession, and a bacteriological examination of the soil showed that *Azotobacter* had not increased in response to the sugar, but that the number of merely putrefactive organisms had gone up greatly. These facts led Dr. Hutchinson to surmise that we had been putting on the sugar at the wrong time of year, in early spring or winter, some time before the barley was sown, when the soil is cold. Now *Azotobacter* is comparatively inactive at low temperatures, and the sugar was probably being wholly taken by the *Streptothrix*, &c., which are less affected by cold. As these organisms must also obtain nitrogen, they were robbing the barley of the small stock available in the soil, and so bringing about the observed reduction of crop. A change was accordingly made in the time of application of the sugar, which was put on as soon as the barley had been harvested when the soil still retained its summer heat, and the change was immediately followed by an increase in the succeeding barley crops, as compared with the non-sugar plots, that was as marked as the deficiency had been previously. This illustrates the many pitfalls which attend investigations in agricultural science. Under laboratory conditions one can define the issue sharply, but as soon as the experiments are extended to the open ground and living plant, so many extraneous and unsuspected factors come into play, that what is popularly called a conflict between theory and practice often becomes apparent.

TABLE III.—*Broadbalk Field, Rothamsted.*

Land allowed to run wild. Nitrogen in Soil, lb. per acre.

	In soil to 27 inches.		Added by rain.	Gain in soil per annum.
	1881.	1904.		
Broadbalk ..	5910	8110	90	92

TABLE IV.—*Hoosfield Barley.*

Effects of Sugar (or Starch) on the amount of Produce.
Plot 4 O. Complete Minerals.

Year.	Sugar (or starch) applied.	Total produce of barley (lbs.).	
		Without sugar.	With sugar.
1906	Spring	2485	(*a*)
1907 (*b*)	Spring	3578	3249
1908	Spring	1820	1404
1909	Spring	2563	2261
1910	Autumn	2082	2502
1911	Autumn	1244	1915

(*a*) Very small crop, not weighed.
(*b*) Starch applied instead of sugar in 1907.

We may now take a more complex example from the Rothamsted plots to illustrate what I have called the conservative systems of farming (see Table V.). One of the fields is farmed on a four-course rotation of turnips, barley, clover, wheat, but over half the field the clover is replaced by a year's bare fallow. Further, if we confine our attention to the one plot which never gets any nitrogen, but only mineral fertilisers, it is again divided at right angles into plots from which the turnip crop is wholly removed, and others on which it is returned, as so often occurs in practice when the turnips are eaten off *in situ* by sheep.

TABLE V.—*Nitrogen per cent in Soil of Agdell Field, Rothamsted.*

The plots receive Mineral Manures, but no Nitrogen.

	Fallow.		Clover.	
	Roots carted off, 13/14.	Roots returned, 9/10.	Roots carted off, 15/16.	Roots returned, 11/12.
1867 ..	0·1224	0·1240	0·1327	0·1380
1874 ..	0·1147	0·1238	0·1241	0·1321
1883 ..	0·1161	0·1228	0·1329	0·1383
1909 ..	0·1159	0·1195	0·1347	0·1498
Average, 1852—1903.				
Wheat .	31·2 bush.	32·2	32·2	35·1
Clover .	—	—	41·0 cwt.	47·7
Swedes	151·0 cwt.	268·0	160·0	187·0
Barley .	22·1 bush.	28·7	24·5	34·5

Table V. shows the average yield on these plots and also the changes in the nitrogen content of the soil at different dates. There are two possible recuperative actions to make up for the crops removed—the *Azotobacter* working upon the carbonaceous matter returned in the turnip crop, and the growth of the clover, for that crop as we know gathers nitrogen from the atmosphere by means of the organisms living in the nodules upon its roots. When neither clover is grown nor are the roots put back the soil is slowly losing nitrogen; when either occurs singly a fair production is maintained without loss of soil nitrogen; when both take place during the rotation the average removals from the soil become as high as thirty-five bushels per acre of wheat, thirty-four of barley, and more than two tons of clover-hay, yet the soil is if anything gaining rather than losing in fertility, though no extraneous nitrogen is being introduced.

Thus we see that we can maintain indefinitely a production of over four quarters per acre of wheat, and their equivalent in other crops, by natural agencies alone without recourse to external supplies of nitrogen, provided we repair the small annual losses of phosphoric acid and potash, which of course cannot be regenerated from the atmosphere. But such a level of production, though equal to the average of the British Isles, is below that which a modern intensive farmer must attain, and the lesson that we have to bear in mind is that at a higher level, say, that of five quarters of wheat, the wasteful actions of which we have spoken are increased out of all proportion. Hence we have to add as manurial nitrogen not merely the difference between that contained in the extra quarter of wheat, but four to five times that amount to repair the waste, and so on to an even greater extent if we still further raise the fertility and the production.

The essential wastefulness of highly intensive agriculture such as must be forced upon the race as the new countries fill up is a serious question, but the prospect of reducing the waste is not entirely hopeless. The losses, as we have seen, are due to bacteria, which attack the nitrogen compounds with liberation of nitrogen gas, the particular bacteria doing this being most active in soils rich in organic matter, until at Rothamsted we only recover in the wheat crop about one quarter of the nitrogen applied in the heavy dressing of farmyard manure. The problem before us is to bring the soil bacteria under control, and we already begin to see in various ways that such control is not impossible. For example, the researches of Drs. Russell and Hutchinson at Rothamsted have already proved that in one simple way we can so re-arrange the micro-fauna and flora of the soil as to obtain a much higher duty from the reserves of nitrogen therein contained.

It is too long a story to enter upon now. I can only briefly say that by putting the soil through various processes of partial sterilisation, such as heating or treatment with antiseptics, like chloroform or toluene, we can eliminate certain organisms which keep in check the useful bacteria in the soil—*i.e.*, the bacteria which break down the nitrogen compounds to the state of ammonia, a form assimilable by plants. Heating the soil to the temperature of boiling water for two hours will double its productivity, and such a process has been found to be commercially profitable in the case of greenhouse soils. The market growers of cucumbers and tomatoes make up an exceptionally rich soil of virgin loam and stable manure, but in a few years such soil, while still enormously rich on analysis, becomes incapable of growing a profitable crop. The partial sterilisation processes of which I have been speaking restore and even enhance its fertility by eliminating the injurious organisms, and we learn from the detailed results that after such treatment a much larger percentage of the soil-nitrogen is recoverable in the crop than normally prevails in untreated soil. At present the processes have not been extended to the open field, but progress is being made in that direction, and give some promise of a method by which ultimately the unseen fauna and flora of the soil will be domesticated, the useful races encouraged, and the noxious repressed, just as the larger flora and fauna have been reduced to our service since the days when primitive man first turned from hunting to agriculture.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 7th, 1912.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Scattering and Absorption of Light in Gaseous Media, with Applications to the Intensity of Sky Radiation.*" By Louis Vessot King, B.A.

The analysis of the present investigation seems to support the view that, at levels above Mount Wilson, molecular scattering is sufficient to account completely both for attenuation of solar radiation and for the intensity and quality of sky radiation. Even at sea-level the effect of "atmospheric dust" can be taken into account in a simple manner in the formulæ for absorption and scattering. Should future observations support the validity of the simple law expressed by equation (2) connecting the coefficient of attenuation with the wave-length, we may with considerable assurance make use of the law to obtain the coefficients for very short or very long wave-lengths when the direct method of calculation from high and low sun observations leaves room for considerable uncertainty owing to the small intensities in the solar spectrum at these wave-lengths, and owing to other experimental difficulties. Schuster (*loc. cit.*) points out in this connection the extreme importance of determining accurately the form of the solar intensity curve outside the earth's atmosphere for short wave-lengths, since the effect of a solar atmophere in absorbing and scattering radiation is to give rise to an intensity-curve which does not agree with that given by Planck's formula, especially for short wave-lengths.

Absorption and scattering of radiation by the sun's atmosphere, taken in conjunction with effects of self-illumination, constitutes a problem analogous to that just considered for the earth's atmosphere. By making a comparison between the calculated variation of intensity of radiation of different wave-lengths over the solar disc and the results of observation, it will be possible to determine from the intensity-curve of the normal solar spectrum outside the earth's atmosphere the intensity-curve at the radiating layer of the sun. This corrected curve may then be compared with that given by Planck's formula, and a closer approximation made to the temperature of the sun than the values now given. This investigation the writer hopes to be able to deal with in a future communication.

"*Standard Measuring Machine.*" By P. E. Shaw, D.Sc.

"*Spectro-photometric Comparison of the Emissivity of Solid and Liquid Gold at High Temperatures with that of a Full Radiator.*" By E. M. Stubbs and E. B. R. Prideaux, D.Sc.

1. The emissivity of solid and liquid gold at high temperatures, relative to the emissivity of a full radiator at the same temperatures, has been measured throughout the visible spectrum.

2. A sharp discontinuity in the emissivity takes place at the melting-point, the liquid gold emitting more strongly than the solid in the red and yellow, and less in the extreme blue. The shape of the "relative emissivity" curves is quite different in the two cases.

3. The curve of "relative emissivity" of solid gold at high temperatures is similar to that of absorptivity at low temperatures as determined from reflectivity measurements; whether it is identical, in which case the temperature coefficient of the absorptivity would be *nil*, could not be absolutely determined, owing to the change of structure which a polished surface undergoes on heating.

4. No temperature coefficient of "relative emissivity" could be detected for the liquid metal, through a range of over 100°.

5. "Black body" temperatures of solid and liquid gold at the melting-point have been calculated.

6. It has been shown that the general equation expressing the radiation of a selective radiator is of the form—

$$E_{\lambda}' = f(\lambda, T)c_1\lambda^{-5}e^{-c_2/\lambda T},$$

which in the case of gold and other metals cannot be reduced to the form of Wien's equation for a full radiator with changed values of the constants.

"*Optical Properties of Substances at the Critical Point.*" By C. Smith.

"*Absorption of Helium and other Gases under the Electric Discharge.*" By Hon. R. J. Strutt, M.A., F.R.S.

Attempts to repeat Berthelot's absorption of helium by carbon disulphide under the influence of the silent discharge have given absolutely negative results.

Helium is slightly absorbed by phosphorus under electric discharge, though in much less quantity than nitrogen or hydrogen. The absorption in the former case is regarded as mechanical, in the latter as chemical.

"*Discharge between Concentric Cylinders in Gases at Low Pressures.*" By F. W. Aston.

1. The relations beween pressure, voltage, and the

length of the Crookes dark space in the discharge between concentric cylinders take much the same form as those in the discharge between parallel planes.

2. Curvature of the surface of the cathode appears to have no influence upon the rate of alteration of the length of the dark space with change of current density, *so long as the latter is measured at the surface of the cathode.*

3. *Ceteris paribus*, the length of the dark space is greater for a convex cylindrical surface than a plane, and for a plane than a concave one.

"*Influence of the Nature of the Cathode on the Length of the Crookes Dark Space.*" By F. W. Aston.

1. The relations between the values of pressure, voltage, current, and the length of the dark space are determined for plane cathodes of many different materials, and found to satisfy the same form of equations as those previously given for aluminium, the constants varying considerably.

2. Roughness of the cathode surface does not appear to affect the discharge, if the dimensions of the irregularities are small compared with the length of the dark space.

3. The length of the dark space is shown, in the cases examined, to be greatest for silver and least for magnesium, the metals following the same order as in the case of the cathode fall.

4. The rate of change of length of the dark space with change of current density at the surface of the cathode seems much the same for all cathodes.

5. Difficulties in the way of arriving at a satisfactory explanation of these and other data connected with the dark space are indicated and shortly discussed.

Determination of the Absolute Unit of Resistance by Alternating Current Methods." By A. Campbell.

"*Some Unclassified Properties of Solids and Liquids.*" By A. Mallock, F.R.S.

This paper suggests that many qualities of solids and liquids, which, although well known and commonly recognised, are not classified (qualities, for instance, such as ductility and malleability), may be explained by reference to the relations of the limits of the principal elasticities of the substances.

A real homogeneous isotropic substance, whether solid or liquid, offers two distinct kinds of resistance to deformation, viz., resistance to alteration of volume and resistance to shear. There are also two distinct and different limits to each of these kinds of deformation—limits which cannot be exceeded without causing rupture or permanent alteration of the substance.

When a strain involves both shear and alteration of volume, the behaviour and properties of the strained material depend to a great extent on whether the limit of shear or the limit of volume alteration is the first to be overcome.

In the paper various examples of these effects are given.

"*Trichromatic Theory of Colour Vision. The Measurement of Fatigue of the Retina.*" By Sir W. de W. Abney, K.C.B., F.R.S.

CHEMICAL SOCIETY.

The Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:—

Whinfield, Salcombe, S. Devon,
Sept. 16th, 1912.

Gentlemen,—I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1913, together with a Table of Atomic Weights, which are submitted for publication in the Society's *Transactions* and *Proceedings*, as hitherto.

The Report draws attention to all the atomic weight determinations which have been published since the date of the preceding Report, but the only alteration suggested in the table which accompanied last year's Report is the inclusion of the element holmium, with Ho = 163·5, as the result of the work of Holmberg.—I am, Gentlemen, your obedient servant,

T. E. Thorpe.

The Hon. Secretaries, The Chemical Society,
Burlington House, London, W.

Annual Report of the International Committee on Atomic Weights, 1913.

Since the annual report for 1912 was prepared, a number of important memoirs on atomic weights have appeared. There are also one or two earlier researches which were received too late to be noticed at the proper time. These investigations may be summarised as follows:—

Nitrogen.—Wourtzel (*Comptes Rendus*, 1912, cliv., 115), by oxidising NO to N_2O_4, has re-determined the ratio between nitrogen and oxygen. Five concordant measurements give, in mean, N = 14·0068.

Potassium and Chlorine.—Staehler and Meyer (*Zeit. Anorg. Chem.*, 1911, lxxi., 368) have made careful analyses of potassium chlorate, with special precautions against contamination by the chloride. Their final series gives KCl = 74·5551, whence K = 39·097 and Cl = 35·458. For a discussion of their results, see also Guye (*Journ. Chim. Phys.*, 1912, x., 145), who concludes that the impurity above mentioned was, if not completely, at least sufficiently eliminated to be practically negligible.

Fluorine.—McAdam and Smith (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 592) have published two preliminary determinations of the atomic weight of fluorine. Sodium fluoride was converted into chloride by heating in dry gaseous hydrochloric acid, and from the ratio between the weights the atomic weight was calculated. The two values found are F = 19·0176 and 19·0133.

Phosphorus.—From analyses of phosphorus tribromide, Baxter, Moore, and Boylston (*Proc. Am. Acad.*, xlvii., 585; *Journ. Am. Chem. Soc.*, 1912, xxxiv., 259) find, in mean of three series, P = 31·027 when Ag = 107·88. This agrees fairly well with the former work of Baxter and Jones on silver phosphate. Further work on phosphorus trichloride is promised.

Mercury.—Easley and Brann (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 137), by analyses of mercuric bromide, find Hg = 200·64. This confirms the previous work of Easley on the chloride.

Selenium.—Kuzma and Krehlik (*Trans. Bohemian Acad. of Emperor Francis Joseph*, 19, No. 13, 1910; data furnished to the Committee by Prof. B. Brauner) have re-determined the atomic weight of selenium by reduction of SeO_2 with SO_2. The mean of ten determinations is Se = 79·26.

Tellurium.—Harcourt and Baker (*Trans.*, 1911, xcix., 1311) have thrown doubt upon the work of Flint, who claimed to have split up the supposed element into two fractions of different atomic weight. They repeated his method of fractionation, and from the fourth fraction, found Te = 127·54. This agrees with the figure found by Baker and Bennett in 1907. Similar fractionations have been carried out also by Pellini (*Atti. R. Accad. Lincei*, 1912, [v.], xxi., i., 218), who likewise failed to find any indication of a tellurium of low atomic weight.

Radium.—Hönigschmid (*Monatsh.*, 1912, xxxiii., 253), by careful analyses of relatively large quantities of radium chloride, finds Ra = 225·95. On the other hand, Whytlaw-Gray and Ramsay (*Proc. Roy. Soc.*, A, 1912, lxxxvi., 270), using very small quantities of material, and converting the bromide into the chloride, find Ra = 226·36, in agreement with previous work by Mdme. Curie and Thorpe. Until the discordance between Hönigschmid's low value and the higher is explained, it is undesirable to change the figure given in the table.

Tantalum.—The determinations of this atomic weight by Chapin and Smith (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 1497) were made by the hydrolysis of $TaBr_5$. The

International Atomic Weights. (1913).

		O = 16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

mean of eight determinations gave Ta = 181·80, a figure somewhat higher than that found by Balke from similar analyses of the pentachloride.

Iridium.—Hoyermann (*Sitzungsber. Phys. Med. Soz. Erlangen*, xlii., 278), by five reductions of $(NH_4)_2IrCl_6$ in hydrogen, finds Ir = 192·613.

Holmium.—Six determinations of the atomic weight of holmium by Holmberg (*Zeit. Anorg. Chem.*, 1911, lxxi., 226) gave Ho = 163·45. The well known sulphate method was employed.

There are also approximate determinations of the atomic weights of lead, zinc, and copper by Pecheux (*Comptes Rendus*, 1912, cliv., 1419), and of calcium by Œchsner de Coninck (*Comptes Rendus*, 1911, cliii., 1579). The figures obtained are not conclusive enough to justify their use in the table, for the methods employed were not of great accuracy.

Only one change is recommended in the table for 1913, namely, the insertion of holmium, for which hitherto, no good atomic weight determination has been available. Two or three other alterations of small importance might be made, but it seems undesirable to make changes too frequently.

(Signed) F. W. Clarke.
T. E. Thorpe.
W. Ostwald.
G. Urbain.

The following are abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions*.

189. "*The Essential Oil of the Leaves of* Atherosperma moschatum (‘*Australian sassafras*’)." By Margaret Emilie Scott. (*Trans.*, 1912, 1612).

The essential oil of *Atherosperma moschatum*, Labill., contains the following compounds in approximately the proportions indicated:—Eugenol methyl ether, 50 to 60 per cent; pinene, 15 to 20 per cent; camphor, 15 to 20 per cent; and safrole, 5 to 10 per cent.

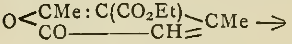
190. "*Harmine and Harmaline.* (Part I.). By William Henry Perkin, jun., and Robert Robinson. (*Trans.*, 1912, 1775).

A detailed description of work of which a preliminary account has already appeared (*Proc. Chem. Soc.*, xxviii., 153).

191. *The Chemistry of the Glutaconic Acids.* Part V. *The Preparation of Esters of the Labile Acids.*" By Norman Bland and Jocelyn Field Thorpe. (*Trans.*, 1912, 1557).

The esters of those labile acids of the series which, by reason of the presence of a methyl group on the central carbon atom of the three-carbon system, possess considerable stability, can be prepared by the dissociation of their sodium compounds, provided that such a compound contains a potentially mobile hydrogen atom within its molecule.

Thus the action of sodium ethoxide on ethyl *iso*dehydracetate (I.) yields the sodium compound (II.), and, by further action, ethyl acetate and the sodium compound (III.):—



$$\mathrm{O}<\begin{matrix}\mathrm{CMe:C(CO_2Et)}\\ \mathrm{CO}\text{————}\mathrm{CH}\end{matrix}\geqq\mathrm{CMe}\rightarrow$$

I.

$$\rightarrow \mathrm{NaO.CMe:C(CO_2Et)\cdot CME:CH\cdot CO_2Et}$$

II.

$$\rightarrow \mathrm{CH_3\cdot CO_2Et + NaO\cdot C(OEt):C\overset{*}{H}\cdot CMe:CH\cdot CO_2Et}$$

III.

This sodium compound contains a potentially mobile hydrogen atom (*); it therefore reacts with water, yielding the pure labile ester (IV.). The corresponding normal ester (V.) can be prepared by the esterification of the normal acid:—

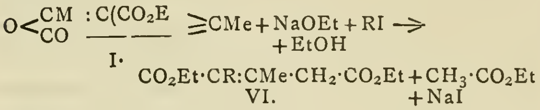
$$\mathrm{CO_2Et\cdot CH:CMe\cdot CH_2\cdot CO_2Et}$$

IV.

$$\mathrm{CO_2Et\cdot CH\cdot CHMe\cdot CH\cdot CO_2Et}$$

V.

The alkylation the sodium compound (II.) leads to the formation of the labile esters of the dialkylated acids (VI.):—



$$\mathrm{O}<\begin{matrix}\mathrm{CM\ :C(CO_2E}\\ \mathrm{CO}\text{———}\end{matrix}\geqq\mathrm{CMe+NaOEt+RI}\rightarrow$$

$$\mathrm{+EtOH}$$

I·

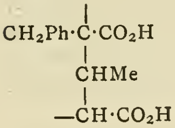
$$\mathrm{CO_2Et\cdot CR:CMe\cdot CH_2\cdot CO_2Et+CH_3\cdot CO_2Et}$$

VI. $\mathrm{+NaI}$

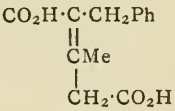
and by this means the labile forms of both αβ-dimethylglutaconic acid and of β-methyl-α-ethylglutaconic acid can be isolated.

192. "*The Chemistry of the Glutaconic Acids.* Part VI. *Conditions which Confer Stability on the* trans-*Forms of the Labile Acids*," By Norman Bland and Jocelyn Field Thorpe. (*Trans.*, 1912, 1739).

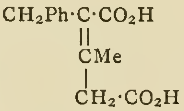
By increasing the weight of groups attached to the carbon atoms of the three-carbon system, sufficient stability is conferred on the labile state to render it capable of isolation in its *cis-* and *trans*-modifications; thus α-benzyl-β-methylglutaconic acid has been obtained as the normal form (I.) melting at 148°, the *trans*-modification of the labile form (II.) melting at 134°, and the unstable *cis*-modification of the labile form (III.) which passes into the hydroxy-anhydride (IV.) melting at 69°, when liberated from its salts:—



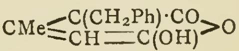
I.



II.



III.



$$\mathrm{CMe}\leqq\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH}=\!=\mathrm{C(OH)}\end{matrix}>\mathrm{O}$$

IV.

193. "4-*Alkyl*-1 : 4-*thiazans*." By Hans Thacher Clarke. (*Trans.*, 1912, 1583).

Alkyl derivatives of the cyclic compound thiazan, or thiomorpholine, $\mathrm{S}<\begin{smallmatrix}\mathrm{C_2H_4}\\ \mathrm{C_2H_4}\end{smallmatrix}>\mathrm{NH}$, in which the alkyl group is attached to the nitrogen atom, may be prepared by the interaction of ββ′-dichloroethyl sulphide and primary amines:—

$$\mathrm{S}<\begin{matrix}\mathrm{CH_2\cdot CH_2Cl}\\ \mathrm{CH_2\cdot CH_2Cl}\end{matrix}+\mathrm{R\cdot NH_2}\ =\ \mathrm{S}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{NR+2HCl}.$$

The *methyl-*, *ethyl-*, iso*amyl-*, and *benzyl-thiazans*, together with characteristic derivatives, are described.

194. "*The Triazo-group.* Part XXI. *Benzenoid Azoimides containing Multivalent Iodine.*" By Martin Onslow Forster and Johannes Heinrich Schaeppi. (*Trans.*, 1912, 1359).

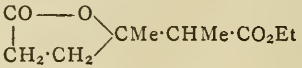
In order to ascertain whether any intramolecular action occurs between the azoimide nucleus and the iodoso- or iodoxy-group, the three iodophenylazoimides were prepared and converted into their respective triazophenyl iodochlorides, triazo-iodosobenzenes, triazoiodoxybenzenes and di-triazophenyliodinium iodides.

195. "*β-Hydroxy-αβ-dimethyladipic Acid and β-Hydroxy-ααβ-trimethyladipic Acid.*" By Victor John Harding. (*Trans.*, 1912, 1590).

When ethyl lævulate is condensed with ethyl α-bromopropionate by means of zinc in benzene solution, there is formed a mixture of diethyl β-hydroxy-αβ-dimethyladipate (I.) and the ethyl ester of the lactone of β-hydroxy-αβ-dimethyladipic acid (II.):—

$$\mathrm{CO_2Et\cdot CHMe\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CO_2Et}$$

I.

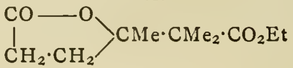


II.

A similar mixture of hydroxy-ester (III.) and lactone (IV.) is obtained by the condensation of ethyl lævulate and ethyl α-bromo*iso*butyrate:—

$$\mathrm{CO_2Et\cdot CMe_2\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CO_2Et}$$

III.

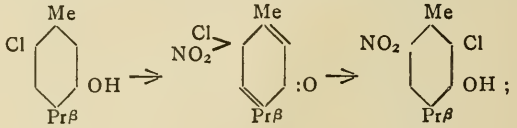


IV.

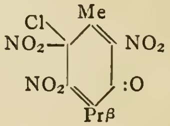
Acid hydrolysis results in the production of the lactonic acids. Attempts to prepare the unsaturated acids from the hydroxy-acids were without success.

196. "*The Migration of the Para halogen Atom in Phenols.*" By Philip Wilfred Robertson and Henry Vincent Aird Briscoe. (*Trans.*, 1912, 1964).

The observation that 6-bromothymol on nitration forms 2-bromo-6-nitrothymol (Robertson, *Trans.*, 1908, xciii., 793) has led the authors to investigate in more detail the cause of the migration of the halogen atom, and to extend the observations to other compounds. A similar migration takes place with 6-chlorothymol (I.) on nitration. It seemed probable that an intermediate hemiquinonoid compound (II.) is first formed, and actually the dinitro-derivative of this substance (IV.) has been isolated by the action of excess of nitrogen peroxide on 6-chlorothymol:—

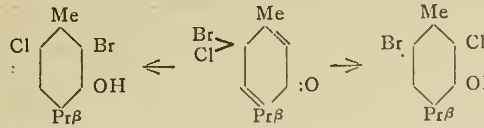


I. II. III



IV.

Not only is the nitro-group capable of causing a para-halogen atom to wander into the ortho-position, but also one halogen can cause another partly to migrate in the same manner, so that when 6-chlorothymol is brominated or 6-bromothymol is chlorinated a mixture of isomeric chlorobromothymols is obtained. These observations are easily explainable on the assumption of the intermediate formation of a hemiquinonoid compound, which yields two products, as indicated below:—



Similar changes have been observed in the case of certain derivatives of 2 : 2′-diphenol ; thus, 5 : 5′-dichloro-2 : 2′-diphenol and 5 : 5′-dibromo-2 : 2′-diphenol both yield on nitration compounds containing the halogen in the 3 : 3′-position.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, November 8th, 1912.

Prof. A. Schuster, F.R.S., President, in the Chair.

A paper "*On a Method of Measuring the Thomson Effect*" was read by Mr. H. R. Nettleton.

In this paper an investigation is made of the distribution of temperature down a conductor conveying an electric current and at the same time moving uniformly through two fixed temperature sources. The effect of the Thomson heat on the distribution is seen to be exactly similar to the effect of a small impressed velocity. This result is applied to mercury to measure the Thomson effect by comparing the alteration of temperature $\Delta\theta_1$ at a point near the middle of the gradient caused by reversing a current of C ampères with the alteration of temperature $\Delta\theta_2$ at the same point due to a flow of mercury of m grms. per second. It is shown that, without any approximation as to emissivity loss or magnitude of Joulian heat, $2C\sigma/ms = \Delta\theta_1/\Delta\theta_2$, where s is the specific heat of mercury and σ the specific heat of electricity. Working with currents of from 4 to 9 ampères and with flows of different magnitudes—but never exceeding 1 cm. per hour—consistent values of σ are obtained, the value at 61° C. being $-1{\cdot}52 \times 10^{-6}$ calories per degree Centigrade per coulomb. The thermo-junctions, which were of iron and constantan, were fused through the glass tubes with inappreciable distortion.

The President stated that the paper dealt with a difficult problem and gave an adequate and promising method of measuring the Thomson effect, but he queried whether it was justified to assume the velocity of flow was constant over the cross-section of the tube.

Dr. A. Griffiths stated that it was not assumed that the velocity over the cross-section was constant, but only that the temperature was constant, which on account of the extreme slowness of the flow would be justified. The author performed one experiment when the flow was stopped and obtained the same difference in temperature on reversing the current.

Dr. W. E. Sumpner pointed out that it was not realised how extremely slow the flow was—something of the order of 1 cm. per hour.

Prof. C. H. Lees was struck with the ingenuity of the method. There were, however, a number of small corrections to be considered, such as the heat transmitted through the glass. More accurate knowledge of the thermoelectric phenomena in liquids was urgently needed.

Mr. R. S. Whipple inquired how the iron and constantan wires were fused into the glass tube, to which the author replied.

A paper on "*An Improved Joule Radiometer and its Applications*" was read by F. W. Jordan.

The first part of the paper relates to improvements which have been made in order to convert the original Joule convection apparatus into an instrument for the exact measurement of small steady rates of evolution or absorption of heat. These improvements consisted in (1) replacing the badly conducting glass enclosure and cardboard partition by others made of brass and copper respectively ; (2) replacing the uncertain and variable magnetic control of the movement of the vane in Joule's apparatus by the elastic control of a quartz fibre ; (3) shaping the channels, in which the vanes moved, so that the angular deflection of the vanes was proportional to the rate of evolution of heat ; (4) reducing the size, so that a more uniform temperature of its various parts could be easily maintained by (5) placing the radiometer within a concentric brass tube to exclude all extraneous heat excepting that which might be directed through apertures in its side towards the radiometer.

The sensibility of the instrument was measured by passing a current through a resistance loop in one of the compartments of the partitioned tube, and found to be equal to 0·52 mm. per microwatt, as measured on a scale at a distance of 1 metre from the mirror. Thus the instrument may be used for the measurement of feeble oscillating currents, it being about as rapid as a Duddell milliammeter.

To convert the apparatus into an instrument for the measurement of radiant heat it is suggested that the radiant heat be directed through a small rock salt or fluorite window in the side of a compartment on to a thin blackened metal disc supported centrally by a badly conducting fibre within the compartment.

Its use for the quick measurement of the heat given out by radium is also suggested.

It is suggested that small steady rates of evolution or absorption of heat might be measured by the compensation methods of Callendar or Angström.

The second part of the paper relates to a suggested method of measuring the Thomson effect with this radiometer. The method hinges on an experiment described by the author in *Nature*, May 18, 1911, p. 380. In that apparatus the halves of a thin wire on either side of the partition are heated by the passage of an alternating current through thicker leads of the same metal. The Joule effects are compensated very nearly by an electro-deposit of the same metal, by scraping the thin wire, or by an auxiliary heating coil. The substitution of a direct current for the alternating current causes a slight heating in one and a cooling in the other half of the wire. The heating or cooling due to the Thomson effect in one half of the wire is compensated by passing a small measured current in the proper direction through the other half of the wire. This small current is passed through a thin lead of the same metal attached to the centre of the thin wire, and may be adjusted in four different ways. The temperature difference between the centre of the wire and the thick leads is measured with suitably attached thermojunctions.

The Thomson coefficient is expressible in terms of measurable quantities, and is equal to the product of the mean compensating current and the mean resistance of the halves of the wire divided by the temperature difference between the centre of the thin wire and its thick leads.

Dr. W. H. Eccles stated that he had worked a good deal with other forms of convection instruments. The better-known type consisted of a helix of wire which was caused to rotate by the draught up the tube. Forbes in 1890 patented a convection galvanometer with a screw propeller placed in the draught tube over the heater. He had developed this by using a fine paper screw propeller suspended by a quartz fibre, and used it for measuring small oscillatory currents, though his old instrument was fifty times less sensitive than Mr. Jordan's.

A "*Note on the Attainment of a Steady State when Heat Diffuses along a Moving Cylinder*" was read by Miss A. Somers.

The paper dealt with the case of a column of mercury moving with uniform speed between two fixed temperature sources. The differential equation for the temperature within the column was stated and its solution given, and it was shown how the time of attainment of a steady state could be obtained from the latter. The case of the diffusion of a salt in solution up a tube could be treated in the same manner.

Dr. A. **Griffiths** asked if some Fellow would solve the problem when the velocity, instead of being constant, was a periodic function of the time.

Mr. B. W. **Clack** stated that Miss Somers had referred to his work on diffusion, and in such a slow phenomenon it was important to save as much time as possible. The velocity of the liquid down the diffusion tube referred to was in his experiments natural and not artificial, depending on the change in volume of the solution as it became less concentrated by the diffusion. This velocity was very slow. In his apparatus it was of the order 1 cm. in four months, and he felt justified in assuming that this would not materially alter the time required to attain the steady state. Experiments showed that this assumption was legitimate.

Mr. R. **Appleyard** drew some analogies between the differential equation used and that for the flow of electricity along conductors.

A paper on the "*Thermomagnetic Study of Steel*" was read by Dr. S. W. J. **Smith**.

Thermomagnetic measurements make it increasingly evident that the magnetic properties of steels are frequently those of mixtures of magnetic substances, each possessing characteristic properties, which contribute in a comparatively definite way to the properties of the material as a whole.

In the case of a simple ferromagnetic substance, magnetising fields can generally be found in which the permeability variation with temperature is comparatively small except in the neighbourhood of the critical temperature. In such fields there is a very clearly marked peak in the permeability temperature curve for the substance. The explanation of this peak which the molecular theory affords is well known, and suggests that the phenomenon should be found common to all ferromagnetic substances. The immediate object of the present paper is to show that it is exhibited by the carbide of iron (cementite) which exists in annealed carbon steels. For this purpose it is not necessary to isolate the carbide, because, as shown in the paper, the phenomenon is quite clearly discernible in the permeability temperature curves for the steel. The particular steel examined contained 0·85 per cent of carbon. It was found that the fields necessary to evoke the comparatively sudden variations in the permeability of the carbide above described are small and such that the permeability variation of the iron present along with the carbide is slight in the neighbourhood of the critical temperature of the latter. The sudden gain and loss of permeability by the carbide as the temperature alters will be roughly equivalent to sudden removal and replacement of gaps in the magnetic circuit through the steel. They should therefore be attended by correspondingly sudden rise and fall of the apparent permeability of the material as a whole. This is found to be the case. There is a sharply marked peak near 210° C. upon the permeability temperature curve for the steel.

In the absence of measurements between 200° C. and 220° C. the peak would escape notice, and it is for this reason, probably, that it has not been recorded before. It could scarcely be found by accident. The search for it was prompted by the considerations outlined above in conjunction with results obtained in earlier work with Messrs. White and Barker.

The paper was discussed by the **President**, Prof. **Lees**, and Dr. **Russell**.

The **Author**'s replies to their remarks are incorporated in the abstract of the paper given above.

Anhydrous Sulphates.—V. de G. Calcagni and D. Marotta.—Lead sulphate forms no compound with lithium sulphate, and in this respect the latter resembles the sulphates of the alkaline earths. With sodium sulphate $PbSO_4$ gives a eutectic at 35 per cent Na_2SO_4 and 65 per cent $PbSO_4$.—*Atti della Reale Accademia dei Lincei*, xxi. [ii.], No. 4.

NOTICES OF BOOKS.

Chemical Theory and Calculations. By **Forsyth James Wilson**, D.Sc. (Edin.), Ph.D. (Leipzig), and **Isidor M. Heilbron**, Ph.D. (Leipzig), F.I.C., A.R.T.C. London: Constable and Co., Ltd. 1912.

This book is intended to provide an introduction to chemical theory, to accompany lectures on descriptive inorganic chemistry. It contains a great number of problems and calculations with explanations of the methods of working them, and in addition a very well arranged course of elementary theory, so that the student may advantageously work straight through the book, and will thus get a logically developed knowledge of the general principles of chemistry. For those who prefer to give their students a book devoted exclusively to theory rather than a general text-book on inorganic chemistry this may safely be recommended as likely to prove satisfactory for elementary work.

A Laboratory Manual of Inorganic Chemistry. By **John B. Ekeley**, Ph.D., Sc.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

This laboratory manual has been prepared to accompany Holleman's "Text-book of Inorganic Chemistry," which the author has found excellent for the use of his classes. The laboratory book could, however, be used independently; it gives directions for a great number of experiments in inorganic chemistry, both qualitative and quantitative, as well as some problems and a few theoretical questions. The chief unfavourable criticism to be directed against the book is the very great variation in the difficulty of the work put before the student, and, moreover, some of the experiments requiring the most skill in manipulation come at the beginning. In addition some of the experiments are more suitable for performance by the demonstrator, especially as the directions given are often very brief. For example, the beginner would hardly find it easy to manage the decomposition of water successfully without much more detailed instructions.

Photographic Copyright. By **George E. Brown**, F.I.C., and **Alexander Mackie**. London: Henry Greenwood and Co. 1912.

This book gives the full text of the Copyright Act of 1911, as far as it relates to copyright in photographs or reproductions of works of art by photography. The differences between the new law and the old are pointed out, and some sections are very fully discussed, with accounts of rulings bearing upon them, and full explanations and comments. Remedies for infringement are also discussed, and advice is given as to the course to be adopted when an infrigement has taken place. The question of international and foreign copyright and British copyright in America is shortly treated in one chapter, and the book contains much information of special interest to professional photographers.

MEETINGS FOR THE WEEK.

Tuesday, 26th.—Royal Society of Arts, 4.30. "The Hardwood Timbers of New South Wales," by Prof. W. H. Warren, LL.D., &c.

— Faraday Society, 8. "The Billiter Alkali-chlorine Cells," by A. J. Allmand. "Neutral Oil Emulsion as a Model of a Suspension Colloid," by R. Ellis. "Electrolysis of Nitric Acid Solutions of Copper," by J. H. Stansbie.

Wednesday, 27th.—Royal Society of Arts, 8. "Political Economy as a Code of Life," by Harold Cox.

THE CHEMICAL NEWS.

Vol. CVI., No. 2766.

TWO NEW METHODS OF WEIGHING THE CORNETS IN THE ASSAY OF GOLD BULLION:

By which the Balance Readings give the Finenesses Directly, *i.e.*, the Weights of the Cornets Corrected for Surcharge; with Incidental Improvements in the Assay.*

By A. OCTAVIUS WATKINS, A.R.S.M., F.G.S.

(Concluded from p. 249).

Direct Weights Method.

To deduct (*em*), the direct weights and the left-hand heavy rider are made 0·001 (that is, *e*) part heavier than their nominal weights. . . . . (E).

To deduct (S−*e*), or, in other words, to add (*e*−S), a 0·001 rider, called a surcharge rider, is placed on the right-hand arm of the beam to give an effective weight of (*e*) minus the surcharge for fine gold. As (*e*) happens, under the conditions of working being considered, to be of the same value as a surcharge rider, this is achieved by placing this surcharge rider in the requisite position to give a nominal effective weight of the surcharge for fine gold, reading from right to left. . . . . (F).

When the fineness of bullion being assayed is below 0·4, an addition of 0·4 of proof gold is made to the assay, and the correction for this is made in weighing the cornet by deducting from the balance reading the weight of gold in the 0·4 of proof gold added.

A surcharge rider having been placed in the requisite position on the right-hand arm of the beam to give a nominal effective weight, reading from right to left, of the surcharge for fine gold, to weigh a bullion cornet it is placed on the right and the weight on the left pan, and the position of the left-hand heavy rider is adjusted to almost equipoise the right-hand system. The fineness of the bullion is then given by reading the weight, the left-hand heavy rider, and the index scale.

Let S, as before, represent the surcharge for fine gold, W the nominal weight of the direct weight used, R the nominal effective weight of the left-hand heavy rider, N the weight the index scale shows the right is heavier than the left system, and *x* the fineness of the bullion. Then it must be shown that—

$$x = W + R + N.$$

From (A) the surcharge of the bullion cornet is—

$$S - 0{\cdot}001(1 - x),$$

i.e.,—

$$S - 0{\cdot}001 + 0{\cdot}001x.$$

From (E) the actual weight of the direct weight is—

$$W + 0{\cdot}001\,W,$$

i.e.,—

$$1{\cdot}001\,W. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (G).$$

From (E) the actual effective weight of the left-hand haavy rider is—

$$1{\cdot}001\,R.$$

From (F) the actual effective weight of the right-hand rider is—

$$0{\cdot}001 - S.$$

Now, the weight of the cornet represents the fineness of the bullion plus the surcharge of the cornet, and the load on the left arm plus the weight the index scale shows the right is heavier than the left system, is equal to the load on the right arm, *i.e.*,—

$$(1{\cdot}001\,W) + (1{\cdot}001\,R) + (N) =$$
$$= (x) + (S - 0{\cdot}001 + 0{\cdot}001x) + (0{\cdot}001 - S).$$
$$\therefore\ 1{\cdot}001x = 1{\cdot}001\,W + 1{\cdot}001\,R + N.$$
$$\therefore\ x = W + R + 0{\cdot}999\,N.$$

Then, as by adjusting the position of the left-hand heavy rider N need never be allowed to exceed 0·0001, the value of one-thousandth part of N need never exceed (0·0001 × 0·001 =) 0·0000001, and therefore 0·999 N can be taken as N, especially as it is as often a plus as a minus quantity.

The equation then becomes—

$$x = W + R + N.$$

Calculated from the above formula, 1·001 W, the direct weights employed are given in Table II.

Table II.—*Direct Weights.*

Assay Pounds.

Nominal and mark.	Actual.	Nominal and mark.	Actual.
0·99	0 99099	0·83	0·83083
0·98	0·98098	0·82	0·82082
0·97	0·97097	0·81	0·81081
0·96	0·96096	0·80	0·80080
0·95	0·95095	0·79	0·79079
0·94	0·94094	0·78	0·78078
0·93	0·93093	0·77	0·77077
0·92	0·92092	0·76	0·76076
0·91	0·91091	0·75	0·75075
0·90	0·90090	0·74	0·74074
0·89	0·89089	0·73	0·73073
0·88	0·88088	0·72	0 72072
0·87	0·87087	0·71	0 71071
0·86	0·86086	0·70	0·70070
0·85	0·85085	−0·2	0·20020
0·84	0·84084	−0·4	0·40040

In addition the following two weights and three riders are required:—

Assay Pounds.

Nominal.	Actual.	
1	1·00000	Assay pound weight.
0·01	0·01001	Left-hand heavy rider.
0·001	0·00100	Left-hand surcharge rider.
0·001	0·00100	Right-hand surcharge rider.
0·9167	0·9176167 (*a*) (theoretically)	

(*a*) Special direct weight marked 0·9167 for weighing standard gold (0·916) cornets without a left-hand heavy rider. The actual weight is calculated from the formula (G).

For cornets between 0·7 and 0·4 the −0·2 or −0·4 weight is placed on the platform just above the cornet, and 0·2 or 0·4, as the case may be, is deducted in reading the nominal weight on the left-hand pan.

Advantages Common to both Methods, or due to using both in Conjunction.

The surcharge corrections being accurately made by the weights and riders automatically:—

1. The work of computing and making the corrections is eliminated and the time taken saved.
2. Clerical errors in the procedure are obviated.
3. Standard gold (0·916) cornets are weighed especially accurately as the 0·01001 rider is not used, thereby avoiding the error due to any inaccuracy in its weight or position on the beam, and yet the index scale reading is only (0·9167 − 0·916 =) one-third of a division from zero when the exact assay pound has been taken for assay.
4. The weights and riders of neither method present any obstacles to their being used for bullion requiring specia

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* Read at a Meeting of the Natural History and Science Society of Western Australia, October 8, 1912.

synthetic proofs, on account of the nature and quantity of the base metals present, but, on the other hand, rather increase the accuracy where the exactly correct weight of gold has not been used for such proofs. The indicated fineness of the bullion has simply to be corrected by the difference between the indicated weight of the synthetic proofs and the gold they originally contained.

The addition of proof gold to finenesses below 0·4:—

5. Allows of a greater latitude in the estimation of the fineness for determining the weight of silver to be added for "inquartation"; and

6. Obviates, irrespective of the amount of silver contained in the bullion, the necessity for allowing any assay to break up in the acid; thus no assays have to be parted in flasks, but all are boiled in the platinum trays, thereby gaining the advantages due to their use, viz., accuracy and curtailment of work; and

7. Secures that more accurate surcharge corrections are made on account of the weights of the bullion cornets being nearer to that of the proofs.

Other advantages are:—

8. All the assays are treated exactly alike in every respect from the time they are ready to be charged into the muffle till the cornets are annealed and ready for weighing.

9. In weighing cornets for all finenesses over 0·7, it is necessary to place only one weight on the pan, and for lower finenesses never more than two.

10. Loss by wear of the compensating weights has an effect on the indicated fineness opposite to that produced by wear of the direct weights, and wear could therefore not be so easily overlooked.

11. With respect to bullion below 0·7 in fineness, if either the assayer using the compensating weights method or the assayer using the direct weights method, or both of them, omitted to deduct the nominal weight of the deduction weight from the nominal weight of the other weight used, or to deduct the gold in the weight, if any, of proof gold added, the possibility of the error not being discovered is precluded by the use of deduction weights of the different values, and by adding the different weights, if any, of proof gold.

Additional Advantages of Compensating Weights Method.

Those claimed by Foord, viz.:—

1. " . . . , Is in all respects equivalent to double weighing; it is independent of the relative lengths of the arms of the beam, whether arising from original imperfect workmanship, or from permanent molecular alteration, or from daily vicissitude"; and
2. "The weighments are all made with an uniform load, which satisfies another condition of accuracy more exactly than the common method, the sensitiveness of the beam varying with the load."

Another advantage, not mentioned by Foord, is:—

3. On account of the weights being lighter than ordinary direct weights, their loss by wear is less.

Against the advantages stated must set the complication resulting from using weights (an alloy of platinum and iridium) the correct values of which are different from their nominal values, but this disdvantage is of little moment where a high degree of accuracy is required, as it was found that the errors in the weights received from the makers were sometimes as great as 0·00005, and on this account, and also to guard against loss by wear, even when weights are used the correct values of which are their nominal weights, it is necessary to keep a register of the periodical determination of every weight and rider in use, to ensure that they are kept within the limit of error allowed.

I desire to acknowledge the assistance rendered by Mr. C. Burbury, A.B.S.M., and Mr. R. R. Kahan, B.Sc., in devising these methods of automatically making surcharge corrections.

THE PERMANENT FIREPROOFING OF COTTON GOODS.*

By WILLIAM HENRY PERKIN, Ph.D., LL.D., F.R.S.

(Concluded from p. 251).

In describing the course of the research, I may perhaps be allowed to give a brief sketch of the development of the subject and to outline the reasoning which led to the institution of the various experiments. Some idea of the difficulty of the subject will be gathered when I say that Mr. Samuel Bradbury, who so ably assisted me in the work, and has kept a record of each experiment, tells me that upwards of 10,000 separate burning tests were made before the solution of the problem was reached. Besides these, a great number of further experiments have since been made to see whether an even cheaper process than that which has now been in commercial use for nearly ten years could be discovered.

I suppose that everyone would agree that, at the outset of the experiments, the condition which seemed most difficult of realisation was that of finding a substance which not only fireproofs but which during the process becomes so permanently fixed that it will prove to be absolutely resistant to washing with soap and water or mechanical rubbing. Obviously the substance which is to fulfil these conditions must, in the first place, be insoluble in water; and, secondly, in order that it is not liable to be removed by mechanical rubbing and does not render the cloth dusty, it must be fixed in the fibre, and not be merely on the surface. I have already explained that when calico is dipped in a dilute solution of sodium tungstate, and then dried, the material possesses in a remarkable degree the property of resisting flame, and then, again, alum has often been recommended for the same purpose. Now when solutions of sodium tungstate and alum are mixed, an insoluble aluminium tungstate is produced, and it is clear that, if this insoluble salt could be fixed in the fibre, the material would certainly be fireproofed. It furthermore seemed reasonable to suppose that, as the salt is insoluble in water, it would remain in the fibre even after several washings, and therefore that permanent fireproofing might be achieved in this manner.

A piece of flannelette was therefore soaked in sodium tungstate, and, after passing through rollers to remove the excess of the solution, left for a considerable time in a solution of alum. It was then squeezed, dried, and was passed through the same process again, with the result that the material became almost as fire resistant as asbestos. When, however, the piece was thoroughly washed with soap and water, it was most disappointing to find that the greater part of the fireproofing was removed during the first washing, and after several washings the material was little better than the original flannelette.

While this unexpected result was being investigated, it was noticed that aluminium tungstate is soluble in acetic acid, and is re-precipitated when the acetic acid is removed by evaporation or by the action of steam, and as the precipitate formed seemed granular in appearance, it was thought that this process, if applied to the flannelette, might yield a better result than the process of double decomposition had done. Accordingly, a solution was made up of sodium tungstate, aluminium sulphate, and enough acetic acid to dissolve the precipitate; the flannelette was thoroughly soaked in this solution, dried, and then placed in an ordinary steamer and subjected to the action of steam until an odour of acetic acid could no longer be detected.

The material was, of course, non-inflammable, and when it was washed it was found that this property was distinctly more resistant to soap and water than was the case in the first experiment, but after several vigorous washings almost every trace of the fireproofing had disappeared.

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* Lecture delivered at the Eighth International Congress of Applied Chemistry, September 10, 1912.

These negative results seemed therefore to indicate that aluminium tungstate was not suitable for the purpose of permanent fireproofing. On the other hand, the failure of this salt was possibly due to some peculiarities in its specific properties, and was not considered valid evidence that other insoluble tungstates might not combine more completely with the fibre and thus resist removal by washing.

A careful examination of the tungstates was therefore made, and such insoluble salts only selected for experiment which, like aluminium tungstate, are colourless, since it is obvious that a fireproofing agent to be of any use must be capable of application to white cloth without staining it. Several hundred pieces of flannelette were treated under the most varied conditions with all sorts of combinations which it was known would precipitate insoluble tungstates in the fibre, but in no case was a satisfactory result achieved.

However, a fact was noticed which afterwards proved to be of value, and it was this, that of all the salts the tungstates of zinc and tin seemed to offer the most resistance to washing with soap and water. Thus, when the material had been thoroughly saturated with a solution made up of sodium tungstate, zinc sulphate, and enough acetic acid to prevent the precipitation of the zinc tungstate, and the goods after drying were thoroughly steamed, the fireproofing was certainly fixed to some extent, since it required several washings before the material burnt at all freely. But no amount of variation of the conditions produced a really good result, and this combination had therefore to be abandoned. Since the tungstate proved to be unsuitable to the exacting conditions of the problem, a general examination of almost every variety of salt, including ferrocyanides, aluminates, arseniates, antimoniates, zincates, and plumbates, was made. Many of these could not be employed in connection with wearing apparel in any case because of their poisonous nature, but it was thought that this general examination, which lasted several months, might yield some indication of the type of salt likely to prove resistant to soap and water, if, indeed, such type of salt existed at all. And, as a matter of fact, these experiments did prove to be most valuable, because when the results were all tabulated the generalisation gradually became apparent that certain soluble salts, such as aluminates, antimoniates, zincates, and plumbates, in which the oxide of the metal functions, as an acid, yielded precipitates, especially with zinc and tin salts, which exhibited much greater resistance to washing than the commoner insoluble salts such as barium sulphate or magnesium phosphate. This generalisation ultimately led to a very careful examination of the salts of tin, because, as is well known, the oxides of tin dissolve in alkalis to form stannites and stannates, and tin therefore belongs to the class of salts just mentioned, and it very soon became evident that these salts do actually possess the power of combining with the fibre to a greater extent than any of the salts which had previously been experimented with.

In one experiment it was noted that a piece of flannelette which had first been saturated with a solution of sodium stannate, and dried, and afterwards similarly treated with a solution of zinc chloride, was quite non-inflammable. After the sample had been subjected to a vigorous washing with soap and water a considerable amount of the fireproofing still remained, because when a light was applied to the cloth it only ignited with difficulty, burned very slowly, and either went out of itself or was easily extinguished on shaking the material.

This development was so promising that the experiment was repeated in a great variety of ways, but although several results were obtained which were much better than anything which had been seen before, it was disappointing to find that in all the cases the greater part of the fireproofing was lost after repeated washings.

In a later series of experiments the first solution was again sodium stannate, and the second consisted of sodium tungstate, zinc acetate, and sufficient acetic acid to prevent precipitation of the zinc tungstate formed. The result in this case was so good, the material being practically as safe as wool, even after repeated washings, that the first commercial permanently fireproofed flannelette which was placed on the market was made on these lines.

It was soon found, however, that the material thus treated had two serious drawbacks; it had a tendency to go damp, and an unpleasant smell of acetic acid remained even though the material had been steamed and washed, after the fireproofing process, before being sent out. And apart from these two faults, the fireproofing was still not sufficiently permanent, and the cost of the process was too great for it to be considered a satisfactory one.

A further series of careful comparative tests seemed to indicate that the undoubted advance which had been made was mainly due to the use of the stannate, and it was therefore decided to carry out a series of experiments, using salts of tin exclusively.

The fabric, after being treated with sodium stannate as before, was, in the earlier of these experiments, passed through a fixing bath containing stannous chloride. A very permanent fireproofing was again obtained, but the stannous chloride being a reducing agent tended to destroy or affect the colours of the material, and the process would, therefore, be generally applicable only to white cloth.

In order to get over this difficulty stannic chloride was employed, instead of the stannous salt, as the fixing agent, and to avoid any tendering of the material care was taken that the stannic chloride solution should be of such a strength that a little stannate was left unchanged in the material.

An excellent fireproofing was again obtained, for not only did the material show very little tendency to inflame after it had been washed several times with soap and water, but it had also in such other respects as appearance and feel almost ideal properties, the only objectionable feature being a slight tendency to dust on rubbing and shaking. Now in this particular experiment, in which sodium stannate and stannic chloride had been employed together, the substance which must have been produced in the fibre, and to which the fireproofing must therefore have been due, is stannic oxide, and it seemed clear that this oxide or its hydrate must have some remarkable power of combining with, or attaching itself to, the fibre which enables it to resist removal by washing and rubbing.

But this process still left something to be desired on the score of economy. A certain amount of the tin was undoubtedly wasted, for, in addition to that lost through a portion of the stannate being left unfixed, it was noticed that a considerable amount of the tin oxide which was formed by the action of the alkali of the stannate on the stannic chloride was not permanently fixed in the fibres of the material, and was therefore removed during the subsequent washing. Tin is so expensive that, in a process to be commercially successful, this loss must obviously be avoided.

There are many ways in which stannic oxide may be precipitated from sodium stannate, and one of these, commonly used in ordinary analytical chemistry, consists in adding certain soluble salts such as sodium sulphate or ammonium nitrate to the solution of the stannate, when the whole of the tin is precipitated as oxide or hydrate. In order to find out whether some process of this kind would precipitate this oxide in such a condition that it would remain permanently fixed in the fibre a number of pieces of flannelette were soaked in sodium stannate and, after thoroughly drying, separately passed through various solutions containing sodium or ammonium salts at the ordinary temperature and at temperatures up to the boiling-point. Although, as was to be expected, the results were not uniformly good, a certain degree of permanent fireproofing was always achieved, and consequently the matter was systematically followed up, with the result that a process was gradually evolved which yielded material possessing quite remarkable properties. The process is briefly this;—

The flannelette (or other material) is run through a solution of sodium stannate of approximately 45° Tw. in such a manner that it becomes thoroughly impregnated. It is then squeezed to remove the excess of the solution, passed over heated copper drums in order to thoroughly dry it, after which it is run through a solution of ammonium sulphate of about 15° Tw. and again squeezed and dried.

Apart from the precipitated stannic oxide, the material now contains sodium sulphate, and this is removed by passage through water; the material is then dried and subjected to the ordinary processes of finishing. A long series of trials, carried out under the most stringent conditions, have conclusively proved that material subjected to this process is permanently fireproofed. No amount of washing with hot soap and water will remove the fireproofing agent, or in other words, the property of resisting flame lasts so long as the material itself lasts. I will demonstrate this by exhibiting four different specimens:—(1) Material as it leaves the process and before washing; (2) material which has been washed ten times by hand; (3) material washed twenty times in a machine in a laundry; and (4) a portion of a garment which has been in actual use for two years, washed every week, and is, as you see, in rags. This extraordinary property of resisting soap and water seems to me to indicate that the oxide of tin is not present merely as an insoluble precipitate in the cloth, but must have entered into some actual combination with the fibre, yielding a compound which is not broken down by the action of the weak alkali of the soap. But a matter of hardly less importance from the practical point of view is that the material is not only permanently fireproofed by the process I have just described, it also retains and acquires properties which make it as perfect a material in all other respects as could be desired. In the first place, the treatment has no effect on the delicate colours which are now so generally employed in connection with the manufacture of flannelette and other cotton goods, and very careful experiments have demonstrated the fact that the insoluble tin compound in the fibre has not the slightest deleterious action on the most delicate skin. In addition, the presence of the tin compound in the pores gives the cloth a softer and fuller feel than that of the original flannelette, and what perhaps is the most unexpected result is the fact that the material is considerably strengthened by the process.

A series of tests made by the Manchester Chamber of Commerce proved that the tensile strength of flannelette is increased nearly 20 per cent as the result of the introduction of the tin compound into the fibre.

Further and very exhaustive tests made at the Municipal School of Technology, Manchester, on a machine specially designed for testing the wearing properties of fabrics, showed an even greater gain in durability in the case of the fireproofed flannelette. These separate and independent tests conclusively showed that the increase in strength and durability was approximately equal to the cost of the fireproofing treatment, so that garments made from the permanently fireproofed flannelette are, as a matter of fact, no dearer than those made from ordinary flannelette, and are at the same time as safe as if made from flannel. Some of these properties and statements may be easily tested by each of you independently with the samples in the little book which you received on entering the Hall.

This permanently fireproofed flannelette is now manufactured on the large scale by Messrs. Whipps and Todd in Manchester under the name of "Non-Flam," and, although its introduction has been slow, it is being increasingly used, and will in all probability ultimately entirely replace the ordinary inflammable variety. One of the difficulties experienced in connection with its general introduction is the fact, that owing to the high price of tin, which is now quoted at about £210 or 1050 dols. per ton, the cost of the process is not inconsiderable, but even with tin at this high price the extra cost is not more than 1d. (2 cents) per yard, or about 1½d. or 2d. (3—4 cents) for a child's garment. I have here on the table rolls of "Non-Flam" of different qualities, so that anyone who wishes for a larger sample than is contained in the little book can easily obtain it.

It is hardly necessary for me to say that this process can be applied to any cotton fabric, and is especially valuable in connection with muslin, because this material is so often used, especially on the stage, for dresses which, on account of their flimsy nature, are naturally highly inflammable. I have here two strips of the same muslin, one of which has been treated by the "Non-Flam" process without in any way affecting its ordinary properties, and was then washed ten times, and the difference in inflammability of the two samples is very striking. Whilst the first sample is highly dangerous, it is difficult to imagine that harm could come to anyone who happened to be dressed in the treated material, even if by accident a lighted match came in contact with the dress. Another direction in which the process may be used with great advantage is in connection with lace curtains. Many disastrous fires have occurred by reason of the ignition of lace curtains, and there can be no doubt that the greater majority of these would have been avoided if the curtains had been treated by the "Non-Flam" process. As an example of this, I have here a strip of lace curtain which has been subjected to the process and then washed a number of times, and it will be seen that if such material did accidentally come in contact with a lighted match, the danger of fire is reduced to a minimum, because even supposing the material did catch fire the flame is put out at once by the least shake.

It seems to me that it is obvious that if this process, or some other process capable of giving the same protection from fire, was adopted in the case of all inflammable cotton goods, and especially in the case of material used for garments, many disastrous fires and the appalling loss of life, especially among young children, might be avoided, and it is for this reason that I have ventured to bring the subject of the permanent fireproofing of cotton goods to your notice this afternoon.

VANADIUM AND CHROMIUM IN RUTILE AND THE POSSIBLE EFFECT OF VANADIUM ON COLOUR.

By THOMAS L. WATSON, University of Virginia.

VANADIUM and chromium are rather widely diffused in very small quantity in a variety of rocks and minerals, especially in igneous rocks.

(NOTE.—A good summary of the reported distribution of vanadium in rocks and minerals with references is given by F. W. Clarke, *Bull.* U.S. Geol. Survey, 1912, No. 491, 672. See also H. Moissan, "Traité de Chimie Mineralogie," 1905, ii., 100; and Thorpe's "Dictionary of Applied Chemistry," 1909; J. H. L. Vogt, *Zeit. Prakt. Geol.*, 1899, p. 274. For the distribution of chromium see *Bull.* U.S. Geol. Survey, 1912, No. 491, 664).

Clarke (*loc. cit.*) computes the average of 87 determinations of V_2O_3 in igneous rocks analysed in the laboratory of the U.S. Geological Survey to be 0·013 per cent, and for 256 igneous rocks 0·05 per cent of Cr_2O_3. In addition to its general presence in small amount in igneous rocks (shown by Hillebrand to be smallest in persilicic rocks and highest in subsilicic rocks, *Am. Journ. Sci.*, 1898, vi., 209; also see *Bull.* U.S. Geol. Survey, 1900, No. 167, 49), vanadium occurs in many sedimentary and metamorphic rocks, and in a variety of minerals (H. H. Hayes, *Proc. Am. Acad.*, 1875, x., 294). It occurs in some hydrocarbons, especially asphaltite from Peru and elsewhere (D. F. Hewitt, "Vanadium Deposits in Peru," *Trans. A.I.M.E.*, 1910, xl., 274), and in some coals (lignite and anthracite), and has been reported in some meteorites, in the ash of some plants, and in some natural waters. From available data it seems probable that chromium is more widely diffused than vanadium, Clarke's estimate in 1900 for the lithosphere being 0·01 per cent. It is common in some meteorites, but is most important in subsilicic rocks like peridotites and the serpentines derived from them, present in the form of the magmatic mineral chromite.

Both vanadium and chromium are not uncommon constituents in heavy ferric silicate minerals, such as some pyroxenes, amphiboles, and dark micas, biotite (Hillebrand, *loc. cit.*). They have long been known in titaniferous magnetites (Isidor Walz, *Amer. Chemist*, 1876, vi., 453; J. F. Kemp, Nineteenth Annual Report U.S. Geol. Survey, 1897-1898, Part III.).

Although vanadium was reported in rutile from St. Yrieux in 1859 (H. Ste.-Claire Deville, *Comptes Rendus*, 1859, xlix., 301), and chromium in a Swedish rutile from Käringbricka as early as 1803 (E. S. Dana, "A System of Mineralogy," 1900, p. 239), their presence in analyses of rutile and ilmenite are rarely indicated. Examination of the available analyses of rutile shows that with but few exceptions the oxides of titanium and iron, the latter usually reported as ferrous oxide, are the only constituents present. These, to be sure, are the chief constituents, but in light of recent investigations of rutile from various localities in the United States and Europe, vanadium is quite constantly present in variable small quantity, and in a majority of them chromium is also found.

By methods of spectrum analysis Hasselberg in 1897 reported the presence of vanadium in twelve rutiles from localities in the United States, Spain, Germany, France, Switzerland, Russia, Norway, and Sweden (*Astrophysical Journal*, 1897, vi., 22; Chemical News, 1897, lxxvi., 102; see also W. B. Giles, Chemical News, 1897, lxvii., 137). Vanadium was not detected in anatase from Switzerland. Hasselberg also reported the presence of chromium in ten of the twelve rutiles examined, it being absent in anatase from Switzerland and Magnet Cove, Arkansas. It is a noteworthy fact that of the twenty-two analyses of rutile quoted by Hintze ("Handbuch der Mineralogie," 1907, p. 1622) neither vanadium nor chromium is reported as being present in a single analysis. Of 100 analyses of ilmenites quoted by Hintze (*Ibid.*, 1908, pp. 1876—1881), Cr_2O_3, ranging from a trace to 0·56 per cent, is reported in eight, and vanadium is not listed in any.

In recent investigations of rutile by the Virginia Geological Survey accurate chemical analyses of several rutiles and ilmenite were made, and each analysis agreed in showing the presence of both vanadium and chromium in small and unequal but appreciable amounts. The results follow in the annexed tabular statement.

Partial Chemical Analyses of Rutile and Ilmenite.
(Wm. M. Thornton, jun., Analyst).

	I.	II.	III.	IV.
V_2O_3	0·15	0·20	0·55	0·24
Cr_2O_3	0·02	0·07	0·39	0·07
FeO	2·35	1·68	0·81	—

I. Red rutile from felspathic facies of syenite, Roseland, Nelson County, Virginia.
II. Very dark rutile from nelsonite on Warwick tract, 1½ miles north-west of Rose's Mill, Nelson County, Virginia.
III. Nearly black rutile from Krageroe, Norway.
IV. Black ilmenite from same locality as II.

Attention is directed in the analyses to the predominance of vanadium over chromium. Hesselberg (*op. cit.*) found for the rutiles he examined that when vanadium was present in very appreciable amount chromium was also present, but when vanadium was present in very small amount chromium was present either in trace or entirely absent. Although there are frequent exceptions vanadium is commonly though but slightly in excess of chromium in the known analyses of titaniferous magnetites. The exact form or combination in which these two constituents are present in rutile is entirely conjectural. As Washington remarks (*Trans. A.I.M.E.*, 1909, xxxix., 756) vanadium probably exists as V_2O_3, replacing Al_2O_3 and Fe_2O_3, in ferromagnesian silicate minerals, since it is essentially absent from such rocks as peridotites, of which olivine is the chief mineral, and the iron is ferrous oxide. It seems probable, as has been suggested by Kemp (*Trans. A.I.M.E.*, 1910, xl., 862), that V_2O_3 may be present in titaniferous magnetites replacing some of the ferric oxide, and he has remarked on the extremely sympathetic relations of Cr_2O_3 and V_2O_3 in the same ores (Kemp, Nineteenth Annual Report U.S. Geol. Survey, 1897-1898, Part III., p. 396).

A second fact, which at least is suggestive, is that the chemical analyses of rutiles that have been made under the direction of the writer indicate that difference in depth of colour is probably not to be attributed to iron oxide. On comparing the percentages of iron (FeO) with those of vanadium (V_2O_3) in the table above, it will be observed that vanadium increases with decrease of iron, and the colour increases in depth in the same direction. In other words, the rutile (I.) containing highest FeO and lowest V_2O_3 is red in colour, while the rutile (III.) showing lowest FeO and highest V_2O_3 is nearly black; II. is intermediate in colour, and shows less FeO and more V_2O_3 than I.

No conclusions, of course, can be drawn for rutiles in general, since complete analyses of the mineral are exceedingly few, but the above results are suggestive, and it will be of interest to ascertain whether the possible relation holds in future analyses of rutile. Sufficient work has been accomplished by recent students, however, to indicate that in future analyses of rutiles careful search should be made for both vanadium and chromium.—*Journal of the Washington Academy of Sciences*, ii., No. 18.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 14th, 1912.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Development of a Parasite of Earthworms.* By J. W. Cropper, M.B., M.Sc.

"*Study of the Inheritance of Hoariness in Stocks (Matthiola).*" By Edith R. Saunders.

"*Influence of Temperature on the Absorption of Water by Seeds of* Hordeum vulgare *in Relation to the Temperature Coefficient of Chemical Change.*" By Prof. A. J. Brown, F.R.S., and F. P. Worley.

"*Note on* Merlia normani *and the 'Monticuliporas.'*" By R. Kirkpatrick.

"*Chemical Action of* Bacillus cloacæ *(Jordan) on Citric and Malic Acids in the presence and Absence of Oxygen.*" By James Thompson.

(*a*) Malic acid is not fermented by *B. cloacæ* in the absence of oxygen.

(*b*) Malic acid is decomposed by *B. cloacæ* in the presence of oxygen into carbon dioxide, acetic acid, and succinic acid, with traces of alcohol. The decomposition probably goes on in two ways: oxidation by atmospheric oxygen to carbon dioxide and acetic acid, and oxidation at the expense of another portion of the malic acid, which is thereby reduced to succinic acid.

The respiratory coefficient CO_2/O_2 and the molecular ratio $CO_2/C_2H_4O_2$ found agree well with the values given by a reaction proceeding as follows:—

$$3C_4H_6O_5+5O_2=2C_2H_4O_2+8CO_2+5H_2O.$$

(*c*) In contradistinction to malic acid, citric acid is fermented by *B. cloacæ* in the absence of free oxygen. In addition to carbon dioxide, acetic acid, and succinic acids, the products resulting from aërobic fermentation, formic acid is produced, while there is an increased production of acetic acid.

The molecular ratio $CO_2/C_2H_4O_2$ found agrees with the value for the following equation:—

$$4C_6H_8O_7+4H_2O=9C_2H_4O_2+6CO_2.$$

(*d*) Citric acid is decomposed by *B. cloacæ* in the presence of oxygen into the same products as malic acid.

The values found for the respiratory coefficient and for the molecular ratio $CO_2/C_2H_4O_2$ are intermediate between those required for the following equations:—

1. $4C_6H_8O_7+4O_2=7C_2H_4O_2+10CO_2+2H_2O.$
2. $4C_6H_8O_7+2H_2O+2O_2=8C_2H_4O_2+8CO_2+2H_2O.$

This is probably due to the difficulty of maintaining complete aëration of the medium during the experiment, the decomposition being therefore partly anaërobic and partly aërobic in character.

(*e*) It is possible that the decomposition of citric acid by *B. cloacæ* takes place in the same way in the presence or absence of oxygen, according to the equation in (*c*), but that in the presence of oxygen a variable portion of the acetic acid is subsequently oxidised.

(*f*) Methylacetylcarbinol, which is produced by the action of *B. cloacæ* on mannitol and glucose, is not formed in the fermentation of malic acid or of citric acid by this organism.

"*Origin and Destiny of Cholesterol in the Animal Organism.* Part X. *On the Excretion of Cholesterol by Man, when fed on Various Diets.*" By G. W. Ellis and J. A. Gardner.

"*Comparative Anatomy and Affinities of the Araucarineæ.*" By Prof. R. Boyd Thomson.

"*Polymorphism of* Trypanosoma gambiense *in the Blood and its Relation to the Exogenous Cycle in* Glossina palpalis." By Muriel Robertson.

"*The Recovery of* Trypanosoma gambiense *from* Tragelaphus spekei *on the Islands of Lake Victoria Nyanza.*" By H. L. Duke.

"*Morphology of* Trypanosoma simiæ, *sp. nov.*" By Colonel Sir David Bruce, C.B., F.R.S., Majors Harvey and Hamerton, Dr. J. B. Davey, and Lady Bruce.

"*Some Observations on* T. pecorum (*Bruce*) *and* T. uniforme (*Bruce*)." By H. L. Duke.

"*Camel Trypanosome; with some Remarks on the Biometric Method of Diagnosing Trypanosomes.*" By H. L. Duke.

"*Cultivation of* Trypanosoma rhodesiense (*Stephens and Fantham*)." By H. Bayon, M.D.

"*Some Experiments with Arsenphenylglycin and* Trypanosoma gambiense *in* Glossina palpalis." By H. L. Duke.

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(Continued from p. 257).

197. "*The Resolution of* sec.-*Butylamine into Optically Active Components.*" By William Jackson Pope and Charles Stanley Gibson. (*Trans.*, 1912, 1702).

Externally compensated *sec.*-butylamine is readily resolved into its optically active components by crystallisation with *d*- and *l*-α-bromocamphor-π-sulphonic acids; a number of derivatives of the active bases have been prepared and characterised.

198. "*Relation between Residual Affinity and Chemical Constitution.* Part III. *Some Heterocyclic Compounds.*" By Hans Thacher Clarke. (*Trans.*, 1912, 1788).

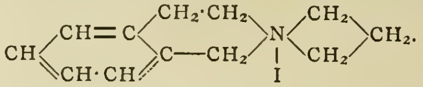
A series of compounds of the general formula $X<\begin{smallmatrix}CH_2.CH_2\\CH_2.CH_2\end{smallmatrix}>Y$, where X and Y are oxygen, nitrogen, or sulphur, has been examined. From a consideration of their chemical behaviour it is found that:—

1. The atoms X and Y exert a mutual influence which affects their reactive power;
2. When X and Y are atoms of the same element, the reactive power is abnormally great;
3. When X and Y are atoms of different elements, the reactivity is abnormally small.

The refractive and dispersive powers, and the molecular volumes, of these and other compounds are recorded, but no definite conclusions could be drawn therefrom.

199. "*The Configuration of Substituted Ammonium Compounds.*" By Humphrey Owen Jones and John Gunning Moore Dunlop. (*Trans.*, 1912, 1748).

The paper describes the preparation and attempted resolution of a dicyclic quaternary ammonium compound, namely, 2-*trimethylenetetrahydro*iso*quinolinium iodide*,—



On the "pyramid" configuration for quinquivalent nitrogen compounds this substance should exist in enantiomorphous forms, but no evidence that it can exhibit optical activity was obtained.

It is also to be expected that α- and β-substituted pyridinium compounds and also quinolinium compounds would exhibit optical activity. A number of compounds belonging to these classes has been examined previously (*Trans.*, 1893, lxxxiii., 1415; 1907, xci., 117), and more recently Miss M. B. Thomas has examined others, but no evidence of resolution has been obtained. It would therefore appear desirable to suggest some hypothesis to account for the apparent non-existence of enantiomorphous forms in these cases.

It is suggested tentatively that a quaternary ammonium compound may be regarded as having the four alkyl groups arranged around a central nitrogen atom forming a group (Na_4), which possesses enough residual valency to unite with an electronegative radicle, forming a salt, Na_4X.

200. "*Hydrolysis of Acetic Anhydride.*" By Kennedy Joseph Previté Orton and Marian Jones. (*Trans.*, 1912, 1708).

The hydrolysis of acetic anhydride in various media, acetic acids of various concentrations, and aqueous acetone, has been investigated by the aid of the method of determining acetic anhydride previously described (Edwards and Orton, *Proc.*, 1911, xxvii., 121). The results show that the hydrolysis of acetic anhydride is quite analogous to its reactions with hydroxy- and amino-compounds, and to the hydrolysis of esters, amides, &c.

In anhydrous media, acids are very powerful catalysts of the hydrolysis, but in water they have but a feeble influence. In aqueous solutions, alkalis and alkaline salts are most effective. Nitric acid behaves exceptionally; in a medium containing 50 per cent acetic acid or less, it has the normal catalytic effect. As the proportion of acetic acid is increased, its apparent activity decreases until in glacial acetic acid it is infinitesimal.

201. "*Acetic Anhydride. The Pure Material, its Physical Properties, and its Reaction with Bromine.*" By Kennedy Joseph Previté Orton and Marian Jones. (*Trans.*, 1912, 1720).

The complete separation of acetic anhydride from acetic acid can be effected by fractional distillation with a Young's "pear" still-head. The boiling-point of the pure anhydride is 139·55°/760 mm., the specific gravity 1·0876 at 15°/4°, and 1·0820 at 20°/4°, and the refractive index for the line Hc 1·39311 at 9·5° and 1·39069 at 15°.

Landolt (*Ann. Phys. Chem.*, 1864, [2], cxxii., 556) is the only observer whose values for these constants are in close agreement with the authors'; the most delicate analysis of acetic anhydride, containing acetic acid, is given by the method of Orton and Edwards (*Trans.*, 1911, xcix., 1181).

Pure acetic anhydride is stable to bromine and chlorine in the dark, but rapid action occurs in the presence of traces of strong acids, ferric chloride, or iodine ; aluminium chloride and other ferric salts are without effect. It is remarkable that the disappearance of the bromine is independent of the initial concentration, and directly proportional to the time and to the concentration of the catalyst. Addition of small quantities of water diminishes the activity of the catalyst except in the case of iodine.

202. "*The Action of Sulphur on Amines.* Part I. o-*Toluidine.*" By Herbert Henry Hodgson. *Trans.*, 1912, 1693).

When *o*-toluidine is treated with sulphur in the presence of *o*-toluidine hydrochloride or free hydrochloric acid, the product appears to be entirely *trithio*-o-*toluidine*, which may be readily isolated by means of its sparingly soluble *hydrochloride*. The *sulphate*, *oxalate*, *acetyl*, and *benzoyl* derivatives have been prepared, and also the m-*nitrobenzylidene* and *bisazo-β-naphthol* derivatives.

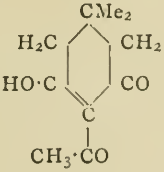
On reduction of the hydrochloride with zinc and hydrochloric acid, a mercaptan is produced which on oxidation furnishes *dithio*-o *toluidine*, of which the *hydrochloride*, *sulphate*, *oxalate*, *and acetyl* m-*nitrobenzylidene*, and *bisazo-β-naphthol* derivatives were prepared.

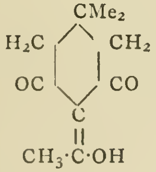
The bisazo-dyestuffs produced from trithio-*o*-toluidene are of remarkable fastness towards ordinary agents, particularly towards soap and alkalis.

203. "*Acyl Derivatives of the Dihydroresorcins.* Part I. *The Action of Hydroxylamine and of Phenylhydrazine on* C-*Acetyldimethyl- and* C-*Acetyltrimethyl-dihydroresorcins.*" By Arthur William Crossley and Nora Renouf. (*Trans.*, 1912, 1524).

The behaviour of C-acetyldimethyl- and C-acetyltrimethyl-dihydroresorcin towards hydroxylamine and phenylhydrazine has been investigated with the object of gaining more definite information as to the constitution of these substances.

C-Acetyldimethyldihydroresorcin behaves as a monobasic acid, and may be represented by one or other of the following formulæ, probably the latter :—

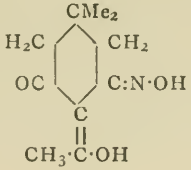




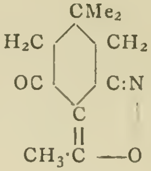
When acted on by hydroxylamine it gives an acid oxime (I), an *iso*oxazole (II.), and an oxime of the *iso*oxazole (III.), and with phenylhydrazine it behaves in a similar manner, giving an acid phenylhydrazone, a phenylpyrazole, and a phenylhydrazone of the phenylpyrazole.

C-Acetyltrimethyldihydroresorcin also gives an acid phenylhydrazone and a phenylpyrazole with phenylhydrazine, although all attempts to prepare a phenylhydrazone of the phenylpyrazole have so far failed.

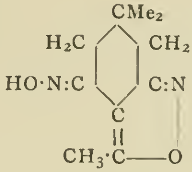
Reasons are given in the paper for assuming that these two C-acetyl derivatives are similarly constituted :—



I.



II.



III.

204. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part XVIII. *The Effect of Inorganic Salts on the Rotation of Ethyl Tartrate in Aqueous Solution and in the Homogeneous Condition.*" By Thomas Stewart Patterson and Duncan Geddes Anderson. (*Trans.*, 1912, 1833).

205. "*The Action of Aliphatic Amines on* s-*Dibromosuccinic Acid.* Part II. *Allylamine.*" By Edward Percy Frankland and Henry Edgar Smith. (*Trans.*, 1912, 1724).

The authors have prepared a *diallylaminosuccinic acid*—

$$C_3H_5\cdot NH\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot NH\cdot C_3H_5,$$

with properties similar to those of the dipropylamino- and dibutylamino-succinic acids previously obtained (*Trans.*, 1912, ci., 57), and have prepared from it a *monohydrochloride*, and *mononitroso* and *tetrabromo*-derivatives. The latter substance,—

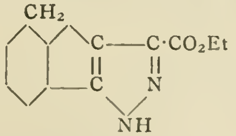
$$\begin{array}{l} CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CH\cdot CO_2H \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CH\cdot CO_2H \end{array},$$

undergoes decomposition when heated with acids, water, or alcohol, $\alpha\beta$-dibromopropylamine or its salts being liberated, and one molecule of carbon dioxide evolved.

The authors propose to apply this reaction to other brominated alkylamino-compounds.

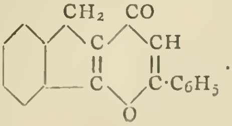
206. "*Studies on Cyclic Ketones.*" Part I. By Siegfried Ruhemann. (*Trans.*, 1912, 1729).

In connection with the work on triketohydrindene hydrate and its methylenedioxy-derivative, the cyclic ketones have been subjected to a closer study with the object of transforming them into polycyclic systems. The action of ethyl oxalate on a number of cyclic ketones was examined, and ethyl α-hydrindoneoxalate, $C_6H_4<{}^{CH_2}_{CO}>CH\cdot CO\cdot CO_2Et$, which is produced by this reaction, was condensed with hydrazine and phenylhydrazine to *ethyl* 4 : 5-*indenopyrazole*-3-*carboxylate*,—



and its 1-*phenyl* derivative.

It was further found that α-hydrindone reacts with ethyl phenylpropiolate in the presence of sodium ethoxide, like acetone or acetophenone, and yields 6-*phenyl*-2 : 3-*indeno*-4-*pyrone*,—



Attempts were also made to condense 1 : 3-dimethyl-Δ^5-*cyclo*hexen-5-one with *p*-nitrosodimethylaniline, with the result that an azomethine is not formed, but the nitroso-compound is reduced to tetramethyldiaminoazoxybenzene, whereas the ketone is probably oxidised to *m*-5-xylenol. This view is supported by the formation of ethyl Δ^1-*cyclo*hexene-3 : 6-dione-2 : 5-dicarboxylate on treatment of ethyl succinosuccinate with sodium carbonate and nitrosodimethylaniline.

207. "*Bromination of Phenol.* 2 : 4- *and* 2 : 6-*Dibromophenol.*" By Frank George Pope and Arthur Samuel Wood. (*Trans.*, 1912, 1823).

2 : 4-Dibromophenol is most rapidly prepared by the bromination of phenol in the presence of hydrobromic acid (D 1·49). The purified product melts at 40°, and has been characterised by conversion into its acetyl, benzoyl, and p-*nitrobenzoyl* derivatives and its methyl and *ethyl* ethers.

2 : 6-Dibromophenol can be obtained in good yields by the elimination of carbon dioxide from 3 : 5-dibromo-4-hydroxybenzoic acid. The acid may be obtained in about 90 per cent yield by bromination of *p*-hydroxybenzoic acid in presence of sulphuric acid, and the carbon dioxide eliminated from the carboxyl group by heating the acid under pressure with dilute sulphuric acid, water, or bases. The authors are of the opinion that the reaction is ionic, since the rate of elimination of carbon dioxide is slower the greater the concentration of the mineral acid, and more rapid in the presence of bases. The resulting phenol was characterised by conversion into its nitro-derivative and into its *methyl* and *ethyl* ethers.

208. "*The Action of Halogens on Silver Salts and on Potassium Cyanate in Presence of Water, with a Note on the Decomposition of Cyanic Acid in Aqueous Solution.*" By Charles William Blyth Normand and Alexander Charles Cumming. (*Trans.*, 1912, 1852).

The halogens react with silver salts to yield a silver halide, an acid, and one or more oxidation products of either the acid or the halide. The reactions, on account of secondary oxidations, are sometimes complex; for example, silver thiocyanate and iodine interact according to the equation :—

$$14AgCNS + 7I_2 + 10H_2O = 14AgI + 12HCNS + 2H_2SO_4 + HCN + NH_3 + CO_2.$$

The oxidation reactions are much more marked with chlorine and bromine than with iodine.

The main product obtained by treatment of silver cyanate with iodine is carbamide, formed probably by secondary decomposition of cyanic acid. Bromine and silver cyanate yield ammonium bromide, carbamide, cyanuric acid, and a little nitrogen.

For comparison, the action of bromine on potassium cyanate was studied, and found to be in accord with the equation :—

$$4KCNO + 4H_2O + 3Br_2 = 4KBr + 2NH_4Br + N_2 + 4CO_2.$$

It is suggested that the reactions are due to interactions between the silver salts and the products of the hydrolysis of the halogen by water; thus, a silver salt reacts with the chloridions formed by partial hydrolysis of chlorine: $Cl_2 + H_2O = H^{\cdot} + Cl' + HClO$.

Further interaction may occur between the hypochlorous acid and one of the reaction products. The experimental results are in accord with this hypothesis.

In connection with the formation of carbamide, some experiments on the decomposition of aqueous cyanic acid were tried, and these in conjunction with previous work led to the conclusion that cyanic acid decomposes in three different ways according to the conditions of experiment.

209. "*Refraction and Dispersion of Triazo-compounds.*" Part II. By James Charles Philip. (*Trans.*, 1912, 1866).

From the results of the earlier investigation (*Trans.*, 1908, xciii., 918) and the data recorded in the present paper, the figure 8·91 is deduced as the most probable refraction value (D-line) for the N_3-group in ordinary positions. The corresponding dispersion value $(H_\gamma - H_\alpha)$ is 0·348. In the case of *o*-triazoiodobenzene and $\alpha\gamma$-bistriazopropylene, two compounds in which the N_3-group is attached to a doubly-linked carbon atom, there is distinct enhancement of the optical values. This observation is in harmony with what was found in the earlier work.

An incidental refractometric investigation of the *o*-dihalogen derivatives of benzene shows the superiority of Eisenlohr's newer values for atomic refraction as compared with the older figures for these constants.

210. "*The Action of Acyl Chlorides on Primary Amides.*" By Arthur Walsh Titherley and Thomas Halstead Holden. (*Trans.*, 1912, 1871).

Whilst by long heating acetyl chloride acetylates benzamide, benzoyl chloride only gives very small yields of dibenzamide (decreasing with rising temperature) and large quantities of benzonitrile and benzoic acid at 140°. The action of benzoyl chloride on *p*-toluamide was studied in order to elucidate the mechanism of the reaction, which has been shown to follow two courses, involving the normal and pseudo-amide forms, namely :—

$$\text{(A)}\quad Ar{\cdot}CO{\cdot}NH_2 \xrightarrow{Ph{\cdot}COCl} Ar{\cdot}CO{\cdot}NH{\cdot}COPh$$

$$\text{(B)}\quad Ar{\cdot}C(OH){:}NH \xrightarrow{Ph{\cdot}COCl} Ar{\cdot}C(O{\cdot}COPh){:}NH \rightarrow Ar{\cdot}CN + Ph{\cdot}CO_2H.$$

In addition to the above products, benzonitrile is also formed in quantities which are relatively great when equimolecular proportions of *p*-toluamide and benzoyl chloride are taken, but small when an excess of amide is used. Its production has been traced to the decomposition of the secondary amide under the catalytic influence of hydrogen chloride, yielding a mixture of acids and a mixture of nitriles. This action is prevented by fixation of the hydrogen chloride when an excess of amide is used owing to the formation of amide hydrochloride. An important further secondary reaction is that between the amide hydrochloride and hydrogen chloride, yielding at 140° an acyl chloride and ammonium chloride, thus :—

$$Ar{\cdot}CO{\cdot}NH_2,HCl \xrightarrow{HCl} Ar{\cdot}COCl + NH_4Cl.$$

In the reaction between benzoyl chloride and *p*-toluamide, therefore, *p*-toluamide hydrochloride, ammonium chloride, *p*-toluoyl chloride, benzoic and *p*-toluic acids, benzonitrile, *p*-toluonitrile, and benzo-*p*-toluamide (and probably di-*p*-toluamide) are formed.

211. "*Action of Benzotrichloride on Primary Amides.*" By Arthur Walsh Titherley and Thomas Halstead Holden. (*Trans.*, 1912, 1881).

Salicylamide on heating with benzotrichloride readily condenses, yielding *o*-benzoyloxybenzonitrile (75 per cent of theory), together with small quantities of N-benzoylsalicylamide. The mechanism of this change has been elucidated by the study of the action of benzotrichloride on acetamide, benzamide, and *p*-toluamide. The first product of the change is the nitrile and benzoyl chloride, which in the latter cases enters into further action on the amide, yielding a secondary amide and benzoic acid, as shown by the authors (preceding abstract). Since with *p*-toluamide, benzotrichloride may under certain conditions yield benzonitrile along with *p*-toluonitrile (which is the main constituent when an excess of *p*-toluamide is used), as well as *p*-toluoyl chloride, two distinct condensation reactions appear to be involved when benzotrichloride acts on an aromatic amide, in which the normal and pseudo-forms participitate, probably thus :—

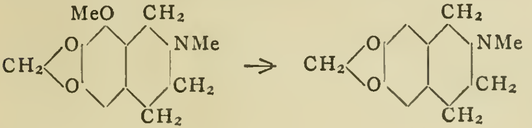
$$\text{(A)}\quad Ar{\cdot}CO{\cdot}NH_2 \xrightarrow{PhCCl_3} Ar{\cdot}CO{\cdot}NH{\cdot}CCl_2Ph \xrightarrow{-HCl} Ar{\cdot}CO{\cdot}N{:}CPhCl \xrightarrow{\text{split}} Ar{\cdot}COCl + Ph{\cdot}CN.$$

$$\text{(B)}\quad Ar{\cdot}C(OH){:}NH \xrightarrow{PhCCl_3} Ar{\cdot}C(O{\cdot}CCl_2Ph){:}NH \longrightarrow Ar{\cdot}CN + Ph{\cdot}COCl.$$

The first reaction is favoured by the presence of hydrogen chloride on account of the formation of the amide hydrochloride, $Ar{\cdot}CO{\cdot}NH_2,HCl$, which tends to react as in A, whilst the free amide tends to react as in B; and hence this reaction is favoured by an excess of *p*-toluamide. When three molecular proportions of the latter and one of benzotrichloride react at 140°, the chief products are *p*-toluamide hydrochloride, benzo-*p*-toluamide, *p*-toluonitrile, *p*-toluic acid, and benzoic acid. When equimolecular proportions are employed, the chief products are *p*-toluoyl chloride, benzoyl chloride, *p*-toluonitrile, and benzonitrile.

212. "Iso*Quinoline Derivatives.* Part VII. *The Preparation of Hydrastinine from Cotarnine.*" By Frank Lee Pyman and Frederic George Percy Remfry. (*Trans.*, 1912, 1595).

Hydrocotarnine (I.) is converted into hydrohydrastinine (II.) in a yield amounting to about 40 per cent of the theoretical by the action of sodium and alcohol:—



I. II.

Since hydrocotarnine is readily obtained by the reduction of cotarnine, and, on the other hand, hydrohydrastinine yields hydrastinine on oxidation, the latter alkaloid can now be prepared from cotarnine. Besides hydrohydrastinine, the following bases have been isolated from the products of the action of sodium and alcohol on hydrocotarnine:—6 *Hydroxy-2-methyltetrahydro*iso*quinoline*, 7-*hydroxy-2-methyltetrahydro*iso*quinoline*, 6-*hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline*, and 7-*hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline*.

213. "*The Rate of Reaction of Alkyl Haloids with certain Tertiary Bases.*" By Richard William Dades Preston and Humphrey Owen Jones. (*Trans.*, 1912, 1930).

The authors have studied the rate of combination of certain organic haloids (methyl-, ethyl, *n*-propyl, and allyl iodides, *o*-, *m*-, and *p*-xylyl bromides, and *p*-bromobenzyl bromide) with two tertiary amines (dimethylaniline and tri*iso*amylamine) in absolute alcohol solution at 40°, and in two cases at 25°.

The results show that the ratio of the velocity-constants for the haloids is (with one exception) practically independent of the nature of the tertiary amine, and that the relative reactivities of the xylyl bromides are in the order which would be expected from a consideration of the distribution of affinity in the molecule after the manner adopted by Flürcheim.

The rate of the reaction was measured by precipitating and weighing silver haloid. It has also been shown that change of conductivity of the solution can be used to measure the rate of the reaction.

214. "*Derivatives of* o-*Hydroxyazobenzene.*" By John Theodore Hewitt and William Henry Ratcliffe. (*Trans.*, 1912, 1765).

The authors have combined various substituted benzenediazonium salts with *p*-acetylaminophenol. During the progress of the work, Voroschtsoff (*Journ. Russ. Phys. Chem. Soc.*, 1911, xliii., 787) described *m*-acetylamino-*o*-hydroxyazobenzene (m. p. 226°), and its conversion into *o*-hydroxyazobenzene; his results are fully confirmed. In the following table the bases diazotised are given in the first column, the melting-points of the azo-compounds produced on combining with *p*-acetylaminophenol in the second:—

o-Chloroaniline	199—200°
m-Chloroaniline	206—207
p-Chloroaniline	217—218
o-Bromoaniline	206—208·5
m-Bromoaniline	217—218
p-Bromoaniline	222—223
o-Nitroaniline	216—217
m-Nitroaniline	231—233
p-Nitroaniline	235

p-Benzoylaminophenol was found to melt at 216—217°, benzoylaminophenyl benzoate at 235°, these figures substantially agreeing with those given by Reverdin. The former compound gives benzeneazo- and *p*-nitrobenzeneazo-compounds, which melt at 201° and 267—268° respectively.

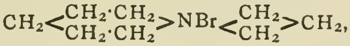
215. "*The Absorption Spectra of Nitro-compounds.*" By John Theodore Hewitt, Frank George Pope, and Winifred Isabel Willett. (*Trans.*, 1912, 1770).

The authors compare the absorption of benzoic acid and its *p*-bromo- and *p*-nitro-derivatives with their sodium salts. In each case salt-formation is accompanied by only slight diminution of the oscillation frequency, and the same holds good for phenylacetic acid and its nitrile. In all these cases the possibility of quinonoid change is precluded, but when alkali is added to *p*-nitrophenylacetonitrile a deep purple colour is produced, and a radical change in absorption spectrum occurs. Similar, although less marked, changes are observed in the case of ethyl *p*-nitrophenylacetate and *p*-nitrophenylacetic acid. Attention is drawn to the possibility of quinonoid re-arrangement taking place according to the scheme:—

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN \rightarrow NaNO_2{:}C_6H_4{:}CH{\cdot}CN.$$

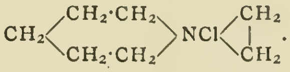
216. "*A Study of some Dicyclic Quaternary Ammonium Compounds.*" By John Gunning Moore Dunlop. (*Trans.*, 1912, 1998).

1 : 1-Trimethylenepiperidinium hydroxide, obtained by the action of silver oxide on 1 : 1-trimethylenepiperidinium bromide,—

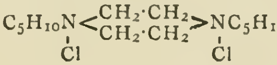

$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}NBr{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CH_2,$$

yields on distillation γ-hydroxypropylpiperidine, $C_5H_{10}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, together with traces of piperidine.

Marckwald and Frobenius (*Ber.*, 1902, xxxiv., 3557) stated that the product of the action of heat on β-chloroethylpiperidine, $C_5H_{10}N{\cdot}CH_2{\cdot}CH_2Cl$, is 1 : 1-ethylenepiperidinium chloride,—


$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}NCl{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}.$$

This is shown to be incorrect, the product being really diethylenedipiperidine dichlorine,—


$$\underset{\displaystyle Cl}{C_5H_{10}\overset{}{N}}{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}\underset{\displaystyle Cl}{N}C_5H_{10}.$$

(To be continued)

LONDON CHAMBER OF COMMERCE AND ASSOCIATION OF COAL-TAR DISTILLERS.

A joint meeting of members of the Chemical Trade Section of the London Chamber of Commerce and Association of Coal-tar Distillers took place at the offices of the Chamber on November 12th, when Mr. J. C. Umney, Chairman of the Chemical Trade Section, was voted to the Chair.

The object of the meeting was to consider what action should be taken, in the interest of the trades concerned, to represent their views before the Joint Committee of the Lords and Commons appointed under the following resolution passed on August 5th last;—

> "That it is expedient that a Joint Committee of Lords and Commons be appointed to consider and report whether any, and if any what, restrictions should be imposed on gas authorities with respect to the purchase and manufacture of the residual products resulting from the manufacture of gas by other authorities, or of other chemicals."

The Chairman referred to action taken earlier in the year relative to certain provisions in the Wandsworth, Wimbledon, and Epsom District Gas Bill and other Bills, which would have given unlimited powers to gas companies —possessing, as they do, what is in the nature of a statutory monopoly—to actively compete with manufacturers and traders by selling and dealing in residual products.

The Chamber has petitioned against this Bill, and the Association of Tar Distillers has also joined in the opposition thereto. As the result of protracted negotiations by the Chamber and other opponents when the Bill passed through Committee, the following new clause was inserted in lieu of that originally proposed :—

> "The Company shall be established for the purpose of manufacturing, storing, and supplying gas for lighting, heating, motive power, and other purposes within the limits of supply as defined by this Act, and may convert, manufacture, and sell all residual products resulting from the manufacture of gas by them, and generally may carry on any business usually carried on by gas companies, but the Company shall not purchase or use in any process of manufacture any materials other than those required for the making and supply of gas by them, or for the working up of their own residual products, or for the construction, maintenance, and repair of their gas-works, plant, and buildings, or for the maintenance and repair of gas-fittings."

After a brief discussion the following resolutions were unanimously adopted :—

> "That this joint meeting of the Chemical Trade Section of the London Chamber of Commerce (representing 373 members engaged in all branches of the Chemical Industry) and of the Association of Coal-tar Distillers of the United Kingdom (representing the leading firms in the Tar-distillers Industry) reaffirms previous resolutions passed by the said bodies objecting to the clause contained in certain Bills which have been before Parliament during the present Session of Parliament, which, until amended as the result of negotiations, would have given powers to certain Gas Companies to manufacture chemical products beyond those which they have hitherto possessed. That this meeting support by evidence the case to be presented by the Alkali Manufacturers' Association before the House of Lords and House of Commons to consider any, and if any what, restrictions should be imposed on Gas authorities with respect to the purchase and manufacture of the residual products resulting from the manufacture of gas by other gas authorities or of other chemicals."

A Special Committee was appointed (with power to act) to consider the resolution passed by the Joint Meeting, to decide as to the nature of the evidence to be given, and to select witnesses to appear before the Joint Parliamentary Committee.

Chloride of 1-4-Dichloroarsinobenzoic Acid. Ethers of Benzarsenious and Benzarsenic Acids.—MM. Fourneau and Ochslin.—The chloride of dichloroarsinobenzoic acid can be obtained by treating with phosphorus pentachloride either the benzarsenious dichloride, $AsCl_2.C_6H_4COOH$, or the non-chlorinated reduction products of benzarsenic acid—benzarsenious acid and oxide, $AsO.C_6H_4COOH$ and $As(OH)_2.C_6H_4COOH$. The authors have prepared and investigated the properties of various ethers of benzarsenious and benzarsenic acids.—*Bull. Soc. Chim.*, xi.—xii., Nos. 18—19.

NOTICES OF BOOKS.

Soil Conditions and Plant Growth. By Edward J. Russell, D.Sc.(Lond.). London, New York, Bombay, and Calcutta : Longmans, Green, and Co. 1912.

In this monograph an attempt is made to lay a foundation for the scientific study of the soil as an aim in itself and not mainly for economic purposes. A considerable amount of experimental work has been published, and our knowledge of the subject is by no means insignificant, but it certainly needs systematising and examining critically, as the author has done in this book. The first chapter, which is historical, shows the growth of our knowledge from its earliest beginnings, and gives a clear outline of its present state, and the author then passes to the consideration of the requirements of plants and the constituents of the soil. He necessarily includes a comparatively large amount of controversial matter, but he deals skilfully with rival hypotheses and makes the true situation always clear. In chapter VI. a very lucid summary is given of the soil in relation to plant growth, and excellent practical advice is offered to the agriculturist. A short appendix describes the analysis of the soil by the usual method adopted in England, together with references to literature for those who wish to use Continental or American processes.

Per-acids and their Salts, By T. Slater Price, D.Sc., Ph.D., F.I.C. London, New York, Bombay, and Calcutta : Longmans, Green, and Co. 1912.

For the Research or Honours student this monograph will be a valuable guide in his reading. It gives a complete account of the preparation of all the known inorganic per-acids and their salts, describes their properties in considerable detail, and enumerates their characteristic tests, also discussing their formulæ and composition, and making some allusion to any uses to which they may be put. Special attention is paid to modern research and recent theories, but the author is a little too diffident in giving the reader the benefit of his personal views, and is more inclined to refer him to the copious literature from which to form his own opinions in disputed matters.

Treatise on General and Industrial Inorganic Chemistry. By Dr. Ettore Molinari. Translated by Dr. Ernest Feilmann, B.Sc., Ph.D., F.I.C. London : J. and A. Churchill. 1912.

This is certainly a remarkable if not unique book, and the English translation should receive a cordial welcome. Prof. Molinari is a pioneer in the work of reforming the teaching of chemistry, so that the young chemist on the completion of his training may have a clear and definite knowledge of the practical and economic aspects of chemical industry, and not be at an entire loss when he is called upon to take some part in the management of chemical preparations on a large scale. The book opens with a short introduction which is historical and theoretical, and in the later descriptive parts lays special stress on industrial processes. Current prices of materials and products are frequently given for comparison, and patent literature, especially German, is freely quoted. The translation has been made as literally as possible, and the translator has contented himself with adding an occasional note, when some of the author's statements are open to criticism or when he shows himself to be unfamiliar with English practice or conditions.

Practical Chemistry. By P. A. Ellis Richards, F.I.C. Second Edition. London : Baillière, Tindall, and Cox. 1912.

This book is intended chiefly for the use of medical and dental students, for whom it gives a good introduction to elementary qualitative and quantitative analysis, such as is suitable for candidates for the practical examination of the Conjoint Board Preliminary Scientific. A chapter on very elementary toxicology is included; this gives no more than a short outline of methods of examining various substances for common poisons, but it contains some useful hints. In the second edition some alterations have been made in the detection tables, and additional reactions are given, as well as some extra volumetric work which is required for the First Examination for Medical Degrees of London University, but not in that of the Conjoint Board.

The Extra Pharmacopœia of Martindale and Westcott. Revised by W. HARRISON MARTINDALE, Ph.D., F.C.S., and W. WYNN WESTCOTT, M.B. (Lond.), D.P.H. Fifteenth Edition. Vol. I. and II. London: H. K. Lewis. 1912.

IN the fifteenth edition the Extra Pharmacopœia has been divided into two volumes, the first of which is slightly larger than the last edition, while the second runs into nearly 400 pages. The first volume contains all the information that the physician or pharmacist is likely to require for immediate reference. All out of date material has been cut out to make room for the addition of data concerning the newest drugs and chemicals used for pharmaceutical purposes, and many new formulæ are included. The chapter on tuberculosis has undergone extensive alteration, as well as that on vaccine; the question of sterilisation as applied to pharmacy is discussed, and in the case of radium some recent scientific developments are described, while important communications on its therapeutic uses are summarised. Volume II. of the Pharmacopœia deals with analytical and experimental work, and gives some of the results of the investigation of the causes of various diseases.

The Great Analysis. With an Introduction by GILBERT MURRAY. London: Methuen and Co., Ltd. 1912.

THIS book is one which will appeal to thoughtful people, who will probably find that it puts before them some new points of view. Briefly, the author propounds a scheme for the betterment of the condition of the world, a scheme which is based upon the establishment of equilibrium between Nature and Human Life. He believes that the time has come to take stock of the state of the world, and to begin to think on a larger planetary scale—to organise the quantitative study of social and economic problems. In his opinion it is high time that our leaders of thought should show that scientific prevision which Sir William Ramsay believes to be the true result of scientific progress, It is perhaps easy to criticise the details of the scheme as far as they are described, but the reader will find it more difficult to detect flaws in the author's reasoning, and even more so to suggest a better scheme.

Modern Research in Organic Chemistry. By F. G. POPE, B.Sc. (Lond.), F.C.S. London: Methuen and Co., Ltd. 1912.

THIS book is a valuable aid for lecturers on organic chemistry who wish to keep themselves abreast of the ever-increasing stream of research work and for advanced students. It opens with a short historical introduction by Dr. J. J. Hewitt, and contains a very clear summary of the advances which have been made in our knowledge of various groups of compounds; *e.g.*, the polymethylenes, the terpenes, and camphor, the purine group, alkaloids, &c. The bibliographies appended to each chapter are very complete, and all important work is carefully abstracted. A whole chapter is devoted to the mechanism of the Grignard reaction and its applications in synthesis, and another to the question of the relationship between colour and constitution. Certain groups of compounds, *e.g.*, the sugars, are not taken into consideration, but, on the whole, a very fair general view is given of recent research, and the references have been brought down to the latest possible date.

Bulletin of the Imperial Institute. Vol. X., No. 2, July, 1912. London: John Murray.

This volume of the bulletins of the Imperial Institute contains reports of the recent investigations undertaken at the Institute of silks and fibres from India, tobacco from Ceylon, oil-seeds from Hong Kong, and various products which appear to be capable of finding application as feeding substances, fertilisers, tanning materials, &c. Some general notices respecting economic products and their development are included, as, for example, cigar tobacco in Java, the cocoanut, shea-nuts, and shea-butter, and the Bulletin also contains a summary of the contents of the more important papers and reports published in the preceding quarter, in so far as they relate to tropical agriculture and the utilisation of the natural resources of the Colonies and India.

CORRESPONDENCE.

THE ALCHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—It will, I think, be admitted that the study of the origin and history of Science is one of considerable value and importance. So far as the majority of sciences are concerned, being of comparatively recent birth, what little history they have is well known. But the case is otherwise with ancient sciences like Chemistry, Mathematics, and Astronomy; to trace their origins we have to go back into the dim past, and these origins and the early history of such sciences are shrouded in considerable mystery. The societies which exist for the development of Science and the extension of its domains can hardly be expected to conduct historical researches into the origin and early history of the older sciences; and the field covered by the various societies devoted to general antiquarian research is far too vast for more than a very occasional investigation of these problems. There seems, therefore, to be a need for a Society specially devoted to these matters, or rather one for the historical investigation of each of the older sciences, since researches of this nature require very specialised knowledge. At least, I think this is certainly the case with regard to Chemistry, since so much diversity of opinion exists as to the origin and nature of its parent Alchemy, and so many interesting questions arise in connection therewith. The alchemists wrote in a language, so it seems, entirely their own. Surely it had a meaning for them. Yet what this meaning? Did their efforts to transmute base metals into gold arise from a belief that theological doctrines concerning the regeneration of the soul ought to be applicable to mineralogical problems? Or was it an outcome of the manufacture of artificial stones? Did the alchemists by their speculative methods grasp certain fundamental truths concerning the basic unity of matter, or were their theories utter folly unenlightened with any ray of truth? These are questions that need answering I think, and it is with great pleasure I announce the fact that I have been instrumental in organising a Society—to be known as *The Alchemical Society*—with the object of dealing with these obscure problems and allied questions. The Society proposes to hold about eight meetings in the year, and to publish a journal containing papers read at these meetings. The annual subscription has been fixed at half-a-guinea. Further particulars may be obtained from the Hon. Secretary, Mr. WALTER GORN OLD, 3, Taviton Street, Endsleigh Square, W.C. It is hoped that the Society will be warmly supported by the chemists of this country and America.—I am, &c.,

H. STANLEY REDGROVE, B.Sc.(Lond.), F.C.S.

The Polytechnic, Regent Street, W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 14, September 30, 1912.

New Form of Soluble Starch.—A. Fernbach.—If a 1 or 2 per cent suspension of starch is poured into a large excess of acetone a flocculent precipitate is obtained. If this precipitate is ground up with pure acetone and dried, a white mass is obtained which is soluble in both hot or cold water. This form of soluble starch has hardly any reducing power. It is readily saccharified by extract of malt, and its solution can be filtered through paper; it gives an intense blue coloration with iodine.

No. 15, October 7, 1912.

Volumetric Determination of Uranium.—V. Auger.—A solution containing iron and uranium can be analysed as follows:—The acid solution is reduced by means of amalgamated zinc, ammonium sulphocyanate is added, and the solution is oxidised with standard ferric solution till a persistent pink colouration, due to the formation of ferric sulphocyanate, is obtained. This method gives results which are correct to within 0·5 per cent with mixtures containing up to five parts of iron to one of uranium. Better results are obtained by effecting the reduction by means of a titanous solution in presence of a concentrated solution of sodium tartrate. The best indicator to use is azo-induline, the violet colour of which changes to yellow when there is an excess of titanous salt in the solution.

Bulletin de la Société Chimique de France. Vol. xi.—xii., Nos. 18—19, 1912.

Cryoscopy in Paraldehyde.—W. Louguinine and G. Dupont.—Paraldehyde is a very good cryoscopic solvent for substances of normal molecular weight. The rapidity with which it crystallises makes the determinations of fusing-points very exact, and the fact that its cryoscopic constant is high makes it possible to work with very small quantities of substance. After acetic acid and benzene it appears to be one of the most useful solvents. It must be pointed out the difference between the experimentally determined cryoscopic constant and that calculated by van 't Hoff's formula (70·5 and 65·5 respectively) is of about the usual order of magnitude found in attempts to verify the formula.

Character and Composition of Oil of Jatropha mahafalensis.—Henry Bimar.—The seed of *Jatropha mahafalensis* comes from the south of Madagascar. From its kernel about 60 per cent of oil can be extracted. It is an amber-coloured slightly fluorescent oil with the following physical and chemical constants.

Density at 15°	0·9213
Index of refraction at 20°	1·4648
Titer of fatty acids	21°
Index of saponification	194
Index of neutralisation of fatty acids ..	17·6
Iodine number	111·8
Iodine number of acid liquids	140
Acetyl number	17
Siccativity at 50°	26 hours

The oil is a semi-drying oil of the group of cotton-oils.

Analysis of Essence of Southernwood.—Victor Boulez.—The citronellal and geraniol in essence of southernwood can be determined as follows:—100 grms. of sodium bisulphite solution are added to 25 grms. of the essence, and well shaken. The bisulphite solution must be prepared by saturating a solution of commercial bisulphite with sodium sulphite. After allowing to stand for two or three hours 100 grms. of distilled water are added and the mixture is heated for some hours on the water-bath. The oily part is then separated in a separating funnel and the uncombined essence is received in a weighed flask, whence the quantity of citronellic aldehyde is determined by difference. The geraniol is determined in the uncombined essence by acetylation.

NOTES AND QUERIES.

Meteoric Diamond.—(J. McCann).—Diamonds were first discovered in the meteorite from the Canyon Diablo, in Arizona, by Dr. Foote, who found that his tools were injured when cutting sections of the meteorite. He examined the meteor chemically, and found in it black and transparent diamonds. This discovery was subsequently verified by Profs, Moissan and Friedel.

MEETINGS FOR THE WEEK.

Monday, Dec. 2nd.—Royal Society of Arts, 8. (Cantor Lecture). "Methods of Economising Heat," by C. R. Darling.

— Royal Institution, 5. General Meeting.

— Society of Chemical Industry, 8. "New Apparatus for the Examination of Mine Air," by L. A. Levy. "Slate Bed Treatment of Sewage," by W. J. Dibdin.

Wednesday, 4th.—Royal Society of Arts, 8. "The Manufacture of Sugar from Wood, and its Economic Importance," by A. Zimmermann.

— Society of Public Analysts, 8. "Value of the Guaiacum Test for Bloodstains," by H. S. Shrewsbury. "Detection of Adulteration in Linseed Oil," by G. D. Elsdon and H. Hawley. "Determination of Nitrates and Nitrites in Sewage Effluents," by A. Higginson. "Estimation of Citric Acid, and its Separation from Tartaric and Succinic Acids," by L. Gowing-Scopes.

Thursday, 5th.—Royal Society. "Physiological Observations made on Pike's Peak, Colorado, with special reference to Adaptation to Low Barometric Pressures," by C. G. Douglas, J. S. Haldane, Y. Henderson, and E. E. Schneider. "The Life-History of *Trypanosoma gambiense*, with a brief reference to the Cycles of *Trypanosoma nanum* and *Trypanosoma pecorum* in *Glossina palpalis*," by Muriel Robertson. "A Gregarine *Steinina rotundata*, nov sp., present in the Mid-gut of Bird Fleas of the Genus *Ceratophyllus*," by J H. Ashworth and T. Rettie. "The Size of the Aorta in Warm-blooded Animals and its Relationship to the Body Weight and to the Surface Area expressed in a Formula" and "The Size of the Trachea in Warm-blooded Animals and its Relationship to the Weight, the Surface Area, the Blood Volume, and the Size of the Aorta," by G. Dreyer, W. Ray, and E. W. A. Walker. "Studies of the Processes Operative in Solutions—XX., Conversion of Ammonic Cyanate into Urea, especially as influenced by Alcohols," by E. E. Walker; XXII., "Hydrolysis of Cane-sugar by Dilute Acids," XXIII., "Hydrolysis of Cane-sugar by Sulphuric Acid, with a Note on Improvements in Polarimetric Apparatus," and XXIV., "Hydrolysis of Methylic Acetate by Acids," by F. P. Worley; XXV., "The Nature of Hydrolytic Process," by H. E. Armstrong and F. P. Worley. "Direct Production of Characteristic Röntgen Radiations by Cathode Particles," by R. T. Beatty. "Penetrating Power of the γ-Rays from Radium C," by A. S. Russell. "The Photo-electric Behaviour of Iron in the Active and Passive State," by H. S. Allen. "Determination of the Radiation Constant," by H. B. Keene.

— Chemical, 8.30. "Study of Some Organic Derivatives of Tin as regards their Relation to the corresponding Silicon Compounds," by T. A. Smith and F. S. Kipping. "Contributions to the Chemistry of the Terpenes—Part XV., Synthesis of a Menthadiene from Carvacrol," by G. G. Henderson and S. P. Schotz. "Action of Halogens on Silver Salts," by H. S. Taylor. "The Formation of Tetrahydro-oxazoles from α-Hydroxy-β-anilino-$\alpha\beta$-diphenylethane and its Homologues," by H. L. Crowther and H. McCombie. "Precipitation of Lead Thiosulphate and its Behaviour on Boiling with Water," by W. H. Perkin and A. T. King. "Studies on Cyclic Ketones," by S. Rubemann and S. I. Levy.

THE CHEMICAL NEWS.

Vol. CVI., No. 2767.

EXTRACTION OF THORIA.*

By CHARLES BASKERVILLE, College of City of New York.

Thorium dioxide is obtained in the main from monazite sands, which, in round numbers, may be said to have this composition :—

	Per cent.
P_2O_5 (phosphates)	29
Ce_2O_3 (earths)	31
Di_2O_3 (earths)	31
SiO_2 (silicates)	1·50
ThO_2 (silicates and perhaps phosphates)	6·50

In the winning it is necessary to get rid of the phosphorus compounds as they materially interfere with the efficiency of the thoria when used for mantles. This is usually accomplished by converting the earths into insoluble oxalates after solution of the sand. Other methods have been proposed, and some are now used commercially for avoiding this by fusion with alkaline carbonates and leaching the phosphates out with water, dissolving the residue in suitable acids, and then making the separation of the earths.

Troost (*Comptes Rendus*, 1893, cxvi., 1227) prepared thorium carbide (ThC_2) by heating the oxide with carbon. Moissan and Etard (*Ann. Chim. Phys.*, 1896 [7], ix., 302; and 1897, [7], xii., 427; *Comptes Rendus*, 1896, cxxii., 573 and 1462) made elaborate studies on the formation and properties of thorium carbide. Muthmann, Hofer, and Weiss (*Ann.*, 1901, cccxx., 260; German Patent 129,416, Aug., 1901) fused monazite sand with carbon and dissolved the carbides and phosphides obtained in hydrochloric acid. Whereas the objectionable phosphoric compounds are removed in this manner, other practical difficulties arise, one being the hardness of the product which involves expense in grinding the fused product.

The work of Kress and Metzger (*Journ. Am. Chem. Soc.*, 1909, xxxi., 640) indicates that thorium does not occur as the silicate in monazite. It is a fact, however, that silica or silicate is a constant, but variable, constituent of the sand and must be taken care of, whatever means of extraction is applied. When the carbides are made by electric fusion of the sand with carbon some silicon carbide is produced which cuts the grinding machinery in the later process of pulverising. We have found that the addition of a small amount of fluorspar reduces this difficulty, yet the expense of some grinding remains.

In order to reduce this expense to a minimum, I decided to deliberately produce calcium carbide within the mass, which, when thrown into water, would disintegrate. (Application for letters patent on this method of disintegration of fused masses has been made). Although Moissan has shown that thorium and the rare earth (?) carbides are attacked by water, the speed of the reaction is very much less than with calcium carbide, and is also much dependent upon the fineness of the particles. Hence comparatively little of the thorium and rare earth (?) carbides would be decomposed by such treatment. Many experiments were carried out, with theoretical and practical mixtures, in various types of furnaces (Stokem, Moissan, Herault, and resistance) with direct and alternating currents. The numerous experimental details need not be recited. (The experimental work was done by Mr. S. G. Warner of my staff). Suffice it to say that a satisfactory charge may be had with a sand of the approximate composition given above as follows :—

	Pounds.
Monazite sand	1·0
Carbon (petroleum coke)	1·10
Lime	0·80
Fluorspar	0·15

The best results were obtained with such charges by using a current of 35 volts and 125 ampères for one and one-half hours.

The procedure is as follows :—

The mixture (unground sand being used) is made according to the principles outlined above, and then subjected to electric heat until phosphorus ceases to come off. (This phosphorus may be condensed). The mass is allowed to cool, and then to decompose slowly by exposure to the air or quickly by placing in water. In the latter case the acetylene may be utilised, the mass falling to a fine powder. The dissolved and suspended calcium hydroxide are removed by washing. The residue is treated with hydrochloric acid, and the thorium separated from the solution by sodium thiosulphate or other methods.

The process is controlled by the Welsbach Light Co., of Gloucester City, N.J., and is published with their consent and approval.

THE CONCENTRATION OF HYDROGEN ION IN SULPHURIC ACID.

By RICHARD C. TOLMAN and LUCIEN H. GREATHOUSE.

Sulphuric acid may dissociate according to either or both of the reactions :—

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$$

Since its method of dissociation is unknown, it is impossible to calculate, from conductivity measurements alone, either the degree of dissociation of the acid or the concentration of any of the ionic substances produced.

It occurred to the authors that the concentration of hydrogen ion in sulphuric acid could be most easily determined by the use of an indicator. The method consists in finding a solution of hydrochloric acid which imparts the same colour to a definite concentration of indicator as the sulphuric acid under consideration. (Indicators were first systematically used for determining hydrogen ion concentration by Friedenthal, *Zeit. Elektrochem.*, 1904, x., 119; see also Salm, *Zeit. Phys. Chem.*, 1907, lvii., 471).

We may consider an indicator as a weak acid which ionises according to the reaction $HI_n = H^+ + I_n^-$, the undissociated acid and its ion differing in colour.

The hydrogen ion concentration of the solution in which the indicator is present will determine the degree of ionisation of the indicator, and hence indirectly its colour. If we find a solution of hydrochloric acid which gives the same colour with the same amount of indicator as the solution of sulphuric acid under consideration, the two presumably have the same concentration of hydrogen ion which can be calculated for the hydrochloric acid from conductivity data.

Experimental.

Four dyes were finally chosen for use as indicators, and were made into stock solutions of the following suitable composition :—

1. 0·05 grm. malachite green, 5 cc. alcohol, 95 cc. water.
2. 0·0125 grm. methyl violet, 2½ cc. alcohol, 97½ cc. water.
3. 0·0166 grm. tropäolin 00 in 100 cc. 50 per cent alcohol.
4. 0·05 grm. methyl green, 100 cc. water.

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* Original communication from Eighth International Congress of Applied Chemistry.

TABLE I.—*Colour Comparison with that in* 0·2/N (× 1·0174) H_2SO_4.

Concentration of comparison acid.		Colour in comparison acid.			
		Malachite green.		Methyl violet.	
HCl.	HNO_3.	HCl.	HNO_3.	HCl.	HNO_3.
0·150 × (1·0033)	0·150 × (1·0121)	—	Greater	—	—
0·140 × (1·0033)	0·140 × (1·0121)	Greater	Greater	—	—
0·130 × (1·0033)	0·130 × (1·0121)	Slightly greater	Greater	Greater	Greater
0·120 × (1·0033)	0·120 × (1·0121)	Less	Slightly less	Less	Slightly less
0·110 × (1·0033)	0·110 × (1·0121)	Less	Less	Less	Less
Conc. HCl (1·0033) or HNO_3 (1·0121) equivalent to 0·2/N H_2SO_4 (1·0174) ..		0·1275	0·1225	0·1250	0·1225
Concentration HCl or HNO_3 equivalent to 0·2/N H_2SO_4		0·1257	0·1218	0·1233	0·1218
Concentration hydrogen ion		0·111	0·108	0·109	0·108

TABLE II.—*Colour Comparison with that in* 0·1/N (× 1·0174) H_2SO_4.

0·080 × (1·0033)	0·080 × (1·0121)	Greater	Greater	—	—
0·075 × (1·0033)	0·075 × (1·0121)	Greater	Greater	Greater	Greater
0·070 × (1·0033)	0·070 × (1·0121)	Same	Slightly greater	Same	Slightly greater
0·065 × (1·0033)	0·065 × (1·0121)	Less	Same	Less	Slightly less
0·060 × (1·0033)	0·060 × (1·0121)	—	Less	—	—
Conc. HCl (1·0033) or HNO_3 (1·0121) equivalent to 0·1/N H_2SO_4 (1·0174) ..		0·0700	0·0662	0·0700	0·0675
Concentration HCl or HNO_3 equivalent to 0·1/N H_2SO_4		0·0690	0·0659	0·0690	0·0672
Concentration hydrogen ion		0·0620	0·0597	0·0620	0·0609

TABLE III.—*Colour Comparison with that in* 0·05/N (1·0174) H_2SO_4.

Concentration of comparison acid.		Colour in comparison acid.			
		Tropäolin 00.		Methyl green.	
HCl.	HNO_3.	HCl.	HNO_3.	HCl.	HNO_3.
0·0425 × (1·0033)	0·0425 × (1·0121)	—	—	Greater	Greater
0·0400 × (1·0033)	0·0400 × (1·0121)	Greater	—	Same	Slightly greater
0·0375 × (1·0033)	0·0375 × (1·0121)	Greater	Greater	Slightly less	Same
0·0350 × (1·0035)	0·0350 × (1·0121)	Same	Same	Less	Less
0·0325 × (1·0033)	0·0325 × (1·0121)	Less	Less	Less	Less
Conc. HCl (1·0033) or HNO_3 (1·0121) equivalent to 0·05/N H_2SO_4 (1·0174) ..		0·0350	0·0350	0·0394	0·0381
Concentration HCl or HNO_3 equivalent to 0·05/N H_2SO_4		0·0345	0·0348	0·0389	0·0379
Concentration hydrogen ion		0·0315	0·0319	0·0356	0·0347

TABLE IV.

Colour shown by successive samples of comparison acid, contrasted with colour of H_2SO_4.	Equivalent concentration chosen as that which showed—
Greater—same—less.	Same colour.
Greater—less.	Less colour + ½ conc. interval.
Slightly greater—less.	Less colour + ¾ conc. interval.
Slightly greater—same—less.	Same colour + ¼ conc. interval.

TABLE V.—*Ratio of Hydrogen Ion Concentration to Normal Concentration* H_2SO_4.

Normal concentration.	Indicator method, approx. 24°.				Conductance and transference, 25°.	Picric acid expts., 25°.
0·100	1·11	1·08	1·09	1·08	1·05—1·16	1·04
0·050	1·24	1·19	1·24	1·22	1·13—1·24	1·10
0·025	1·26	1·28	1·42	1·39	1·23—1·35	1·20

Approximately 0·2/N solutions of sulphuric, hydrochloric, and nitric acids and of barium hydroxide were prepared and standardised. The acids were all titrated against barium hydroxide, and this in turn titrated against succinic acid. Furthermore, independent determinations of the strength of the sulphuric and hydrochloric acids were made by precipitation of barium sulphate and silver chloride. The various standardisations were in satisfactory agreement.

Indicator was added to solutions of 0·2/N, 0·1/N, and 0·05/N sulphuric acid, and the colour compared with that found in a series of differently concentrated solutions of hydrochloric and nitric acids, which were prepared by dilution from 0·2/N acid. The comparisons were made on a white background in Nessler tubes which had a depth of approximately 17 cm. to the 100 cc. mark. For the 0·2/N and 0·1/N acid, 50 cc. of the solutions were taken, and 0·1 cc. of the indicator solution added. For the 0·05/N acid 100 cc. of solutions were taken, and 0·2 cc. of indicator solution added. Malachite green and methyl violet were found to be sensitive indicators in 0·2/N and 0·1/N solution, methyl green and tropäolin 00 in 0·05/N solution. (For solutions as dilute as 0·005/N dimethylamidoazobenzene was the most suitable indicator tried, but even that lacked great sensitiveness). The indicator was added from a burette provided with an automatic stopcock which permitted the rapid delivery of 0·1 cc. portions. Since there is a tendency for the colour of the solutions to fade, the solutions to be compared were all placed in the Nessler tubes and the indicator added to them in quick succession. The comparisons were made at room temperature, approximately 24°.

Experimental Results.

The results of the experiments are given in Tables I. to III. The first column in the tables states the concentration of comparison acid whose colour was contrasted with that of the solution of sulphuric acid in question, and the other columns state whether the colour of the comparison acid corresponded to a greater or a less hydrogen ion concentration than that of the sulphuric acid.

The results of the experiments are summarised in the lower part of each table. The first line states the concentration of comparison acid decided on as having the same colour as the sulphuric acid used. The second line states the concentration of comparison acid having the same colour as sulphuric acid of exact normality, and the third line states the hydrogen ion concentration of this strength of comparison acid.

Table IV. indicates the conventions made in deciding what concentration of comparison acid would have the same colour as the sulphuric acid.

The concentration of comparison acid isohydric with sulphuric acid of exact normality was calculated by simple proportion from the normality factors of the two acids. The concentration of hydrogen ion in the comparison acid was calculated from the conductivity data of Kohlrausch at 18°, using the values for λ_0 determined by Noyes and Sammet (*Journ. Am. Chem. Soc.*, 1902-3, xxiv., 944; xxv., 165; *Zeit. Phys. Chem.*, 1903, xliii., 49—74) and Noyes and Kato (Carnegie Institution of Washington, Publication No. 63, *Journ. Am. Chem. Soc.*, 1908, xxx., 318), 396 for hydrochloric acid, 392 for nitric acid.

Conclusions.

From an examination of the last lines in Tables I. to III., it will be seen that the different acids and the different indicators lead to approximately the same values for hydrogen ion concentration in sulphuric acid. Small differences between the values obtained using different indicators and different comparison acids are to be expected from the probability of slight but unknown action between indicator and the acid radical. Nevertheless, assuming that conductivity measurements for uni-univalent acids give a true measure of degree of dissociation, we may conclude that the values we have presented for the hydrogen ion concentration in sulphuric acid are approximately correct. (For a consideration of the possibility that conductivity measurements do not give true values of the degree of dissociation, see an article by Tolman and Ferguson, *Journ. Am. Chem. Soc.*, 1912, xxxiv., 232).

A comparison of our values of hydrogen ion concentration with those recently presented in an article by Noyes and Stewart will be of interest (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1133). Their method consisted in determining the relative concentrations of hydrochloric acid and sulphuric acid which drive back the ionisation of picric acid to the same extent. Table V. gives values for the ratio of hydrogen ion concentration to the normal concentration of sulphuric acid, as obtained by the indicator method, and by the picric acid experiments of Noyes and Stewart. (The data of Noyes and Stewart presented in the table is that obtained using the values $\lambda_0 = 365$ for hydrogen ion). It has furthermore been shown by Noyes and Stewart by combining transference and conductivity data that certain limits can be calculated between which the hydrogen ion concentration must lie. These limits are also presented in the table. It will be noticed that none of the values for hydrogen ion concentration obtained by the picric acid method by Noyes and Stewart lie within the necessary limits which they have calculated. This probably means that the degree of dissociation of picric acid in the presence of the acids is not merely dependent on the concentration of hydrogen ion. Of the twelve different values obtained by the indicator method, using different indicators and different comparison acids, only two lie outside the limits, and these are the only ones in which methyl green was used as an indicator. The general conclusion may be drawn that a comparison of the results obtained with a number of different acids and different indicators will lead for simple solutions to values of the hydrogen ion concentration of reasonable reliability.

Using the same method, a determination of the hydroxide ion concentration in solutions of di-acid bases is now being carried out by one of the authors (L. H. G.).

The experimental work described in this article was done in the Chemical Laboratory of the University of Michigan. —*Journal of the American Chemical Society*, xxxiv., No. 4).

NOTE ON THE NEUTRAL PERMANGANATE METHOD FOR THE AVAILABILITY OF ORGANIC NITROGEN.

By JOHN PHILLIPS STREET.

When the neutral permanganate method was devised some years ago by the writer, a series of mixtures of known composition was prepared by which it was possible to determine the availability of the organic nitrogen, both in the raw material and when mixed with the usual phosphatic and potassic ingredients of commercial fertilisers. In these mixtures arbitrary amounts of acid phosphate and muriate of potash were used, the total weight of the mixtures always equalling 50 grms., the acid phosphate varying from 10 to 34·5 grms., and the muriate being constant at 10 grms. The mixtures, with one exception, each contained an equivalent of 1·50 per cent of organic nitrogen in varying forms. The agreement in availabilities of the organic form, when used alone and when mixed, was considered quite satisfactory; at any rate the figures obtained were sufficient, in the writer's estimation, to allow of a differentiation between the valuable and the relatively useless forms of organic ammoniates (*Journ. Industrial and Engineering Chemistry*, 1910, ii., 312).

A more extended series of tests, however, has shown that the method as originally published might give misleading results, which in certain cases would be most unfair to high-grade materials. In other words, under certain conditions, a high-grade material like dried blood, which showed a high permanganate availability unmixed, when mixed with acid phosphate and muriate of potash showed availabilities which would class it with garbage tankage and only a little above peat. Apparently the cause of this discrepancy in results lay either with the acid phosphate or the potash. Accordingly, another series of mixtures were made in which the quantity of these ingredients was varied, while the amount of organic nitrogen was kept constant at 0·0450 grm. These experiments showed at once that the muriate of potash had no effect on the results. A sample of dried blood which unmixed showed an availability of 97, when mixed with muriate showed 95 and 96. This same blood, however, when mixed with 2 grms. of acid phosphate, showed only 90, and with 4 grms. only 59. In three samples of blood the presence of 4 grms. of acid phosphate reduced the availabilities from 96, 94, and 96 to 53, 70, and 67 respectively. While this discrepancy was most marked in the case of dried blood, a decreased availability was also noted in tankage, fish, hide and skin meal, tartar pomace, solubilised organic nitrogen, and peat. With knuckle bone and cottonseed-meal the acid phosphate seemed to have less effect, and with garbage tankage the availability of the nitrogen in the mixture was, as has always been my experience, considerably higher than in the raw material.

	Nitrogenous material.	Acid phosphate.	KCl.	Na_2CO_3.	$KMnO_4$ solubility.	
					Raw material.	Mixture.
Blood, No. 22,160..	-0·34	2·00	0·50	—	96	83
	-0·34	3·00	0·75	—	96	70
	-0·34	4·00	1·00	—	96	53
	-0·34	2·00	—	1·00	96	96
	-0·34	4·00	—	1·00	96	90
Blood, No. 24,003..	-0·33	—	1·00	—	97	96
	-0·33	2·00	—	—	97	90
	-0·33	2·00	1·00	—	97	89
	-0·33	4·00	1·00	—	97	59
Blood, No. 22,406..	0·44	4·00	1·00	—	94	70
Blood, No. 22,965..	0·56	4·00	1·00	—	96	67
Tankage, No. 22,346	-0·96	2·00	0·50	—	91	80
	-0·96	3·00	0·75	—	91	82
	-0·96	4·00	1·00	—	91	78
	-0·96	2·00	—	1·00	91	94
	-0·96	4·00	—	1·00	91	85
Knuckle bone, No. 22,360	-1·17	2·00	0·50	—	97	88
	-1·17	3·00	0·75	—	97	84
	-1·17	4·00	1·00	—	97	90
	-1·17	4·00	—	1·00	97	93
Fish, No. 22,667	-0·70	2·00	0·50	—	93	89
	-0·70	3·00	0·75	—	93	88
	-0·70	4·00	1·00	—	93	85
	-0·70	2·00	—	1·00	93	92
Cotton-seed meal, No. 22,393	-0·75	1·95	0·67	—	92	90
	-0·75	2·00	—	1·00	92	95
Hide and skin meal, No. 24,009..	-0·58	2·00	1·00	—	75	60
	-0·58	4·00	1·00	—	75	45
Garbage tankage, No. 22,383	-2·25	0·75	0·75	—	47	70
	-2·42	4·00	1·00	—	47	55
	-2·42	2·00	—	1·00	47	68
Tartar pomace, No. 24,013..	-1·29	4·00	1·00	—	54	34
	-1·29	4·00	—	1·00	54	48
Solubilised organic nitrogen, No. 23,998 ..	-0·93	4·00	1·00	—	65	20
	-0·93	4·00	—	1·00	65	65
Peat, No. 23,392	-1·67	4·00	1·00	—	46	22
	-1·67	4·00	—	1·00	46	42
	-1·67	2·00	—	1·00	46	45

It was thought at first that the relatively large amount of acid phosphate (4 grms.), compared with the charge of dried blood (0·34 grm.), prevented complete action of the permanganate. Experiments carried on by Mr. J. E. Breckenridge, in which the permanganate mixture was agitated much more frequently than directed in the method, however, gave no better results. Thinking that the acidity of the acid phosphate might be the determining factor, another series of tests were carried out in which 1 grm. of sodium carbonate was added just prior to the introduction of the permanganate solution. The results obtained were most satisfactory, as the accompanying table shows. A 96 blood with 2 grms. of acid phosphate showed 96, with 4 grms. 90. A 91 tankage with the same amounts of acid phosphate showed 94 and 85. A 97 bone showed 93; a 93 fish, 92; a 92 cottonseed-meal, 95; a 54 tartar pomace, 48; a 65 solubilised organic nitrogen, 65; a 46 peat, 42. Garbage tankage again showed a high result, the availability increasing from 47 to 68, but even this high figure is too low to mislead any one as to its value.

The writer makes no attempt to explain just what causes these discrepancies. That they exist, however, is an undoubted fact, and the simple modification, at least in the materials tested, appears to give true and reasonable results.

In using the neutral permanganate method it must be remembered that it is not an absolute method, and that no pretence is made that by it the exact agricultural value of an organic nitrogenous material may be determined. A long series of tests, however, shows that it does differentiate between the good and the bad, materials of generally recognised value like blood, tankage, ground bone, dried fish, cottonseed-meal, and castor pomace rarely showing availabilites less than 90, while leather, mora meal, tobacco stems, peat, sheep manure, garbage tankage, tartar pomace, beet root manure, and fillerine show availabilities from 17 to 69. The method possesses the further advantages of simplicity of manipulation, of easy maintenance, of uniform conditions (a very important matter), and of measuring a definite chemical action, namely, the amount of organic nitrogen not decomposed by a definite quantity of permanganate of potash solution of fixed and uniform strength, acting for a definite time at a uniform temperature on a definite amount of organic nitrogen. Every condition can be definitely controlled, and the personal equation is almost negligible. The method as now used by the writer is as follows:—

Modified Neutral Permanganate Method.

Weigh a quantity of the fertiliser, equivalent to 45 mgrms. of water-insoluble organic nitrogen,* on a moistened 11 cm. filter-paper, and wash with successive portions of water at room temperature until the filtrates amount to

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* Determined by washing 1 grm. of the material on an 11 cm. filter with water at room temperature to a volume of about 250 cc. Dry and determine nitrogen in the residue, making a correction for the nitrogen in the filter-paper if necessary.

250 cc. Transfer insoluble residue with 25 cc. of tepid water to a 300 cc. low-form Griffin beaker, add 1 grm. sodium carbonate and 100 cc. of 2 per cent permanganate solution. Digest in a steam or hot-water bath for thirty minutes at the temperature of boiling-water, covering the beaker with a watch-glass and setting well down into the bath so that the level of the liquid in the beaker is below that of the bath. Stir twice at intervals of ten minutes. At the end of the digestion remove from the bath, add 100 cc. of cold water, and filter through a heavy 15 cm. folded filter. Wash with cold water, small quantities at a time, until total filtrate amounts to about 400 cc. Determine nitrogen in residue and filter, correcting for the nitrogen of the filter.—*Journal of Industrial and Engineering Chemistry*, iv., No. 6.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 21st, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Investigation of the Spectrum of Ionium.*" By A. S. RUSSELL and R. ROSSI.

The arc spectrum of an active preparation of ionium oxide mixed with thorium separated by Prof. B. B. Boltwood from the pitchblende residues loaned to Prof. Rutherford by the Royal Society, has been investigated with a large Rowland grating. The complete spectrum of thorium was obtained, but no new lines were observed that could be attributed to ionium. It was deduced that if ionium were half transformed in 100,000 years, the preparation should contain about 16 per cent of ionium oxide. By adding cerium and uranium to the preparation, it was found that 1 per cent of the former and 2 per cent of the latter could be easily detected spectroscopically. It was consequently concluded that the period of ionium cannot exceed 12,000 years.

This result, taken in conjunction with Soddy's results on the period of ionium, points to the existence of at least one new comparatively long-lived body between uranium and ionium in the disintegration series.

"*Absorption of β-Rays.*" By J. A. GRAY.

"*Similarity in Nature of X- and Primary γ-Rays.*" By J. A. GRAY.

The results of the experiments may be summarised as follows:—

1. Absorption experiments show that there is no fundamental difference in the absorption of X- and γ-rays.
2. The primary γ-rays of radium E excite the characteristic radiations (series K) of silver, tin, barium, cerium, praseodymium, and neodymium.
3. The scattering of the primary γ-rays of radium E is probably similar in character and magnitude to that of ordinary X-rays.

"*Spectra of Fluorescent Röntgen Radiations.*" By J. CROSBY CHAPMAN, B.Sc.

Radiations belonging to groups K L have been investigated as regards their X-ray properties. The absorption of the various radiations of both groups in copper, silver, and platinum has been found. In all cases it is shown that, if radiations from different groups suffer the same absorption in aluminium, then they are equally absorbed in any other element.

It happens that bromine and bismuth, though in different groups, emit radiations of equal penetrating power, so that as regards total energy absorption they are identical radiations. The intensity of the corpuscular radiation produced in tungsten and copper, and the ionisation resulting in ethyl bromide and nickel carbonyl, when equal amounts of energy of the two radiations were absorbed in the various substances, have been measured, and were found in each case to be independent of the radiator (bromine and bismuth).

The results prove that these two spectra of radiations of groups K L are identical in their nature, as is shown by measurements on radiations in both groups which test their (1) penetrating power in elements; (2) power of producing corpuscular radiation; (3) power of ionising. This suggests that the mechanism of production is the same though the elements emitting the radiation differ widely in atomic weight. The further light which this throws on the internal structure of the atom is discussed.

"*Optical Investigation of Solidified Gases. II. The Crystallographic Properties of Hydrogen and Oxygen.*" By WALTER WAHL, Ph.D.

"*Electric Furnace for Experiments* in vacuo *at Temperatures up to 1500° C.*" By R. E. SLADE.

This furnace was designed with a view to investigating, at temperatures up to 1500° C., certain cases of heterogeneous equilibrium in which the equilibrium is defined by the pressure of the system. Instances are the dissociation of oxides, nitrides, and carbonates, and the reduction of oxides by carbon.

The furnace consists of a platinum tube 17 cm. long and 2 cm. in diameter with walls 1 mm. thick. The ends of the tube fit into water cooled brass terminals. The tube is heated by a current of 200 to 500 ampères passing through it. One end of the tube is soldered to a silver capillary tube leading to the pump and pressure measuring apparatus; the other end is fitted with a ground silver stopper through which passes the thermo-couple. The furnace stands in an enclosure in which the pressure can be adjusted so as to be approximately the same inside and outside the tube. This is necessary as platinum becomes soft at high temperatures. The furnace works satisfactorily up to 1500° C., and holds a vacuum.

An investigation of the dissociation pressures of the system copper—cuprous oxide has been carried out in this furnace.

"*Investigation of the Dissociation Pressures and Melting points of the System Copper—Cnprous Oxide.*" By R. E. SLADE and F. D. FARROW.

The melting-point (temperature, composition) diagram of the system copper—cuprous oxide has been constructed. The following are the principal points:—

Melting-point of copper, 1083°.

Eutectic Cu_2O, 3·5 per cent; Cu, 96·5 per cent, 1065° (determined by Heyn).

Two liquid phases appear at 1195°; the denser one having the composition Cu_2O 20 per cent, Cu 80 per cent, and the lighter one Cu_2O 95 per cent, Cu 5 per cent.

Melting-point of cuprous oxide, 1210°.

The critical temperature at which the two liquid systems become identical is too high to be determined.

The dissociation pressures of the systems could not be determined below 1200°, because the pressures were so small and equilibrium was attained so slowly. No pressures were obtained of the system, solid Cu_2O, liquid gas, which cannot exist above 1210°. Values of the equilibrium pressure of the system liquid (1), liquid (2), gas were obtained at four temperatures.

We have not sufficient data of heats of reaction and specific heats to calculate these pressures thermodynamically, but it is shown that they are of the order which might be expected.

"*Electric Capacity Coefficients of Spheres.*" By ALEXANDER RUSSELL, M.A., D.Sc.

In connection with Mr. Jeffery's paper (*Proc. Roy. Soc.*, lxxxvii., 109), the author gives and refers to formulæ by means of which the values of the capacity coefficients of equal spheres can be easily found. He uses these formulæ to check the tables given in Mr. Jeffery's paper.

"*Motion of Viscous Liquid due to Uniform and Periodic Motion maintained over a Segment of an Infinite Plane Boundary.*" By W. J. HARRISON, M.A.

The first of the solutions obtained in this paper is that of the following problem:—Viscous liquid occupies the whole of space $y > 0$, being bounded by the plane $y = 0$. The infinite strip $-\xi < x < \xi$, $y = 0$, of the boundary is cut away, and underneath, in contact with it, is placed a second plane, which is made to move with uniform velocity in the direction of the axis of x. The result is that a uniform tangential velocity ω of the boundary is maintained over the strip. The remaining problems are similar; the sliding piece is given a periodic velocity $\omega \cos pt$, and both cases are also solved when the liquid is further limited by a second plane boundary parallel to the first.

The stream lines are exhibited for four particular cases of steady motion. When the liquid is bounded by a single plane, the total traction on the sliding strip per unit of its length is found to be $\omega d(\rho\mu p)^{\frac{1}{2}}$, where $\omega \cos pt$ is the velocity of the boundary, d the breadth of the strip, μ the coefficient of viscosity of the liquid, ρ its density. When the liquid is bounded by two planes a small distance b apart, the traction in the steady motion is $4\mu\omega d/b$; and in the periodic motion its maximum value is $4\mu\omega d/b$, when the period is greater than a certain limit, and increases up up to $\omega d(\rho\mu p)^{\frac{1}{2}}$ for motion of very small period.

"*Elastic Hysteresis of Steel.*" By Prof. B. HOPKINSON, F.R.S., and G. TREVOR-WILLIAMS.

A bar of steel, the reduced portion of which is 4 inches long by ¼ inch diameter, is subjected to alternating stress in the high-speed fatigue-testing machine described in a previous communication. This machine gives direct axial stress up to range of 30 tons per square inch or more, between equal limits of tension and compression, at a rate of about 120 cycles per second. The elastic hysteresis is measured by determining, with the aid of thermo-couples, the fall of temperature between the centre of the piece and each end when it is undergoing alternating stress within the elastic range. The dissipation of energy corresponding to a given fall of temperature is determined by heating the pecimen with an electric current, and measuring the watts dissipated by resistance.

In the mild steel used in the experiments the energy dissipated per cycle when the limits of stress are ± 12½ tons per square inch (giving a range of 25 tons, which is within the limiting elastic range as determined by ordinary fatigue experiments) is about 25,000 ergs per cc., and gives a fall of temperature of about 5°. This is of the same order of magnitude as that due to the magnetic hysteresis in similar material under strong magnetic forces. The elastic hysteresis varies approximately as the fourth power of the stress range.

The elastic hysteresis of the same sample was observed statically by means of a specially designed extensometer, the cycles of stress being performed slowly in a testing machine. It is probable that the area of the hysteresis loop so obtained does not differ by more than 30 per cent from the corresponding quantity at 120 cycles per second, and that if there is any difference, the high-speed cycle involves the less dissipation of energy. Under a range of stress of 20 tons per square inch the width of the hysteresis loop on the stress axis is about 0·08 tons per square inch, a result which agrees as regards order of magnitude with that obtained by Ewing with long wires, and a similar range of stress. With a range of 10 tons per square inch the width only amounts to about 30 pounds per square inch, a quantity which would hardly be detected by static measurements. The resulting dissipation is, however, measurable with fair accuracy in the high-speed machine.

"*Ionic Size in Relation to Molecular Physics, together with a New Law relating to the Heats of Formation of Solid, Liquid, and Ionic Molecules.*" By W. R. BOUSFIELD, M.A., K.C.

In a former paper it was shown that ionic volumes (derived from mobilities) and solution volumes were connected by an empirical linear relation—

$$EV_s = a - bI_v.$$

In the present paper a new empirical relation is established of the form—

$$D^{-1} = p - qN(I_v - K)$$

where D is the effective molecular freezing-point depreston, *i.e.*, $\Delta/N(1 + a)$.

In the former paper the experimental data were given for KCl and NaCl, and in the present paper for LiCl, which data determine the constants a, b, p, q for each salt.

It is now shown that we can express in terms of these constants:—

(1) The factor required to reduce arbitrary ionic volume units to absolute units; (2) the volume of the ionic nuclei; (3) the volume and mean density of the "watery atmospheres" associated with the ions.

Hence we arrive at the following figures for the three salts at "infinite" dilution:—

	KCl.	NaCl.	LiCl.
Associated molecules of water—n =	9	13	21
δV =	47·0	29·9	18·7

δV is the difference in cc. between the atomic volumes of the elements which compose each salt and the molecular volume in the ionic state.

It is also shown for a group of 14 solid and liquid salts and acids that their heats of formation are given by the expression—

$$7/8\,\delta V + H_1 + H_2,$$

where δV is the reduction of volume (or contraction) which takes place on combination, and H_1 and H_2 are constants for the elements of which they are composed.

It is found that the heats of ionisation of the three salts may also be expressed under the same law as—

$$\Sigma\, 7/8\,\delta V + H_1 + H_2 + 1{\cdot}3n - 29,$$

where δV includes volume change of combined water as well as of ionic nuclei, n is number of molecules of combined water, and -29 is a constant which represents endothermic changes involved in ionisation.

The theory of the compressibility of the atom accords with these results, and interprets the heat component $7/8\,\delta V$ as the change of internal energy of the atom owing to atomic contraction which takes place on combination.

The fact that there is a considerably greater reduction of volume of salt in the state of ionic combination than in the solid state is in accord with the view that combination of water with ionic nuclei is the chief factor in aqueous ionisation, and furnishes the large amount of energy required for dissociation of the solid salt into its elements.

"*Synthesis of a Silicalcyanide and of a Felspar.*" By Dr. J. EMERSON REYNOLDS, M.D., Sc.D., F.R.S.

During recent years the writer has obtained many compounds of silicon in which that element is directly united with the nitrogen of various organic groups, and amongst these silico-cyanogen, SiN, in combination. The proof so obtained that silicon has a strong attraction for trivalent nitrogen in organic substances, suggested that a similar capacity is operative in the mineral kingdom, but in respect of trivalent aluminium acting in the nitrogen *rôle* towards silicon. It seemed probable that some at least of the more important rock-forming minerals may be regarded as fully oxidised products of alumino-*silicides* somewhat analogous to SiN.

The experimental work recorded in the paper supports this view, and has resulted in the formation of a remarkably stable substance termed *calcium silicalcyanide*, $Ca(SiAl)_2$ analogous to ordinary calcium cyanide, $Ca(CN)_2$. From this silicalcyanide a furthur synthesis of the felspar *anorthite*, $CaSi_2Al_2O_8$, has been effected. In the course of this work some clues have also been obtained which tend to make clearer the chemical relations of anorthite and albite—the two chief members of the great group of plagioclasic felspars.

"*Method of finding the Conductivity for Heat.*" By Prof. C. Niven, F.R.S., and A. E. M. Geddes, B.Sc.

Aniversary Meeting, November 30th, 1912.

At this meeting the following Fellows were elected as Council and Officers for the ensuing year :—

President—Sir Archibald Geikie.

Treasurer—Sir Alfred Bray Kempe.

Secretaries—Sir John Rose Bradford, Prof. Arthur Schuster.

Foreign Secretary—Dr. Dukinfield Henry Scott.

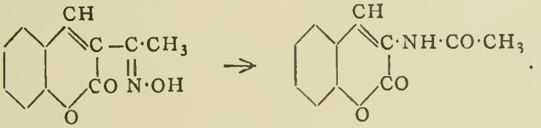
Other Members of Council—Lieut.-Col. Alfred William Alcock, The Right Hon. Arthur James Balfour, Sir William Crookes, Dr. Frank Watson Dyson, Prof. William Gowland, Mr. William Bate Hardy, Prof. Micaiah J. M. Hill, Sir Joseph Larmor, Prof. Ernest William MacBride, Sir Ronald Ross, Prof. Grafton Elliott Smith, Prof. Arthur Smithells, Dr. J. J. Harris Teall, Prof. Silvanus Phillips Thompson, Sir Joseph John Thomson, Sir Philip Watts.

CHEMICAL SOCIETY.

(Continued from p. 267).

217. "*3-Aminocoumarin.*" By Frank William Linch. (*Trans.*, 1912, 1578).

3-*Acetylaminocoumarin* was prepared by the condensation of salicylaldehyde with glycine, or more advantageously from the oxime of 3-acetylcoumarin by means of the Beckmann transformation :—



It crystallises in white silky needles, melting at 201°, and on hydrolysis gives 3-*aminocoumarin*, which forms cream coloured needles melting at 130°. This compound behaves as if it possessed the imino-structure ; for example, nitrous acid gives an iso*nitroso*-compound, and on hydrolysis 3-ketocoumarin is produced, with the liberation of ammonia.

7-*Bromo*-3-*acetylcoumarin*, prepared by the condensation of 5-bromosalicylaldehyde with ethyl acetoacetate, forms pale yellow needles melting at 217° ; the *oxime* decomposes at 220°.

7-*Bromo*-3-*acetylaminocoumarin*, prepared from the above oxime by means of the Beckmann reaction, crystallises from most organic solvents in needles melting at 266°. On acid hydrolysis it gives 7-*bromo*-3-*aminocoumarin*, which forms pale cream coloured needles melting at 205°.

218. "*Studies in the Azine Series.*" (Part II.). By Kathleen Balls, John Theodore Hewitt, and Sidney Herbert Newman. (*Trans.*, 1912, 1840).

The question of the ortho- or para-quinonoid nature of the safranines has been examined, and several reactions lead to the detection of only one amino-group at a time in the phenosafranine molecule (monacid salts) ; thus not only can one amino-group alone be diazotised in solutions of medium acid concentration, but phenosafranine condenses with one molecule of benzaldehyde ; whilst tetramethylsafranine unites with one molecule of methyl iodide.

The absorption spectra of several derivatives of phenylphenazonium have been measured.

219. "*Properties af Mixtures of Allyl Alcohol, Water, and Benzene.*" (Part II.). By Thomas Arthur Wallace and William Ringrose Gelston Atkins. (*Trans.*, 1912, 1958).

Pure allyl alcohol has D^{0}_{0} 0·86911 and boils at 97·06°. It forms the following mixtures of constant boiling-point :—

Alcohol, per cent.	Benzene, per cent.	Water, per cent.	Boiling-point.
72·00	—	28·00	88·00°
17·36	82·64	—	76·75
9·16	82·26	8·58	68·21

The alcohol when mixed with water shows a large, and with *n*-propyl alcohol a slight, contraction in volume ; with benzene, however, there is a small expansion.

The above data show that by distillation of the aqueous alcohol, and subsequent addition of benzene to the alcohol-water binary mixture, a pure anhydrous allyl alcohol may be obtained in quantity.

220. "*Some New Diazoamino- and* o-*Aminoazo-compounds.*" By George Marshall Norman. (*Trans.*, 1912, 1913).

Aminoazo-compounds have been obtained from 4 : 4′-dibromo- and 4 : 4′-dichloro-diazoaminobenzene by heating these compounds at 65° with excess of the corresponding amine and one molecule of its hydrochloride.

4 : 4′-*Dibromo-2-aminoazobenzene*,—

$$C_6H_4Br{\cdot}N_2{\cdot}C_6H_3Br{\cdot}NH_2,$$

forms red needles, m. p. 146—147°.

4 : 4′-*Dichloro-2-aminoazobenzene* forms bright red plates with a green reflex, m. p. 140°.

3 : 3′-*Dibromodiazoamino*-p-*toluene*,—

$$CH_3{\cdot}C_6H_3Br{\cdot}N_3H{\cdot}C_6H_3Br{\cdot}CH_3,$$

crystallising in yellow needles, m. p. 111°, could not be transformed into an azo-compound by heating with 3-bromo-*p*-toluidine and its hydrochloride.

β-Naphthalenediazoamino-p-*chlorobenzene*,—

$$C_6H_4Cl{\cdot}N_3H{\cdot}C_{10}H_7,$$

crystallises in dark yellow needles, m. p. 156°.

β-Naphthalenediazoamino-*p*-toluene, when heated with *p*-toluidine and its hydrochloride, gave a good yield of *p*-tolueneazo-β-naphthylamine.

o-*Tolueneazo-β-naphthylamine*,—

$$CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2,$$

forms long dark red needles, m. p. 122°. It is produced either by the action of *o*-toluenediazonium chloride on β-naphthylamine, or by the action of β-naphthalenediazonium chloride on *o*-toluidine.

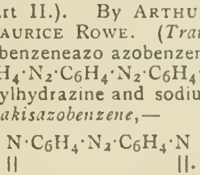
m-*Tolueneazo-β-naphthylamine* is produced by the action of *m*-toluenediazonium chloride on β-naphthylamine. It crystallises in small orange-red needles, m. p. 102°.

By the action of β-naphthalenediazonium chloride on *m*-toluidine there is produced in small quantity *β-naphthalenediazoamino*-m-*toluene*, $CH_3{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_{10}H_7$, which crystallises in thin yellow plates, m. p. 183°.

The action of nitrous acid on the azo-compounds, and of β-naphthol on some of the diazoamino-compounds mentioned, has also been studied.

221. "*The Alkaline Condensations of Nitrohydrazo-compounds.*" (Part II.). By Arthur George Green and Frederick Maurice Rowe. (*Trans.*, 1912, 2003).

When bisnitrobenzeneazo azobenzene (dinitrotrisazobenzene, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$, is reduced with phenylhydrazine and sodium hydroxide, it is converted into *tetrakisazobenzene*,—



$$\begin{array}{l} N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N \\ \| \qquad\qquad\qquad\quad \| . \\ N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N \end{array}$$

This is a red granular substance of high melting-point, which is the nitrogen analogue of Mikado-orange, and like this dye stuff it dissolves in concentrated sulphuric acid with a pure blue colour. The analogy between the condensations which give rise to bisnitrobenzeneazo-azobenzene and those by which the stilbene dye stuffs are formed, is thus confirmed.

As a by-product in the reduction there is also produced the bisaminobenzeneazo-azobenzene,—

$$NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2,$$

recently described by Witt and Kopetschni (*Ber.*, 1912, xlv., 1147). This crystallises from xylene in garnet-red crystals, which melt at 294°.

222. "*The Absorption Spectra of Simple Aliphatic Substances in Solutions, Vapours, and Thin Films.* Part I. *Saturated Aldehydes and Ketones.*" By JOHN EDWARD PURVIS and NIAL PATRICK MCCLELAND. (*Trans.*, 1912, 1810).

A comparative study of the absorption spectra of various simple aliphatic aldehydes and ketones has been made in order to determine in what direction, and how far, the absorption of light is affected when they are in different physical conditions. The phenomena are discussed from a consideration of the vibrations having their primary oscillations originating in definite oscillation centres.

223. "*The Influence of certain Salts on the Dynamic Isomerism of Ammonium Thiocyanate and Thiocarbamide.*" By WILLIAM RINGROSE GELSTON ATKINS and EMIL ALPHONSE WERNER. (*Trans.*, 1912, 1982).

In continuation of the work already published (*Trans.*, 1912, ci., 1167), experiments have been made in the hope of obtaining evidence likely to throw further light on the reversible isomerism of the above two compounds, The action of heat on the compounds $(CsN_2H_4)_4$,KI, m. p. 189°, $(CsN_2H_4)_4$,CsI, m. p. 191°, and $(CsN_2H_4)_4$RbI, m. p. 202°, has been studied; in each case the equilibrium percentage of thiocarbamide was lowered, as compared with the normal 25 per cent. It was found to be about 14 per cent in the case of the potassium iodide compound, and about 16 per cent with the other two.

The influence of the chlorides, bromides, and iodides of potassium, sodium, and ammonium on the reversion of thiocarbamide and ammonium thiocyanate at 170° has been studied; sodium iodide differs from the other salts by effecting an almost complete reversion of thiocarbamide.

The action of heat on the compound $(CsN_2H_4)_3$,KSCN has also been examined; in this case the normal equilibrium was not disturbed.

Several new additive compounds of thiocarbamide with saline iodides have been prepared for comparative study. Whilst tetramethylammonium iodide does not form a compound with thiocarbamide, the additive compound $(CsN_2H_4)_2$,NMe_3EtI, m. p. 141°, was readily obtained.

224. "*The Molecular Condition of some Organic Ammonium Salts in Bromoform.*" By WILLIAM ERNEST STEPHEN TURNER. (*Trans.*, 1912, 1923).

In continuation of the author's investigation (*Trans.*, 1911, xcix., 880), the molecular complexities of twelve salts of organic ammonium bases have been determined in bromoform. The results confirm the author's previous conclusions based on the use of chloroform as a solvent, and indicate that these salts are strongly associated, the extent depending on the character of the salt, on the concentration of the solution, and on the solvent employed.

Association in bromoform is even more pronounced than in chloroform, and the conclusion is drawn that the probable cause is to be traced to the lower dielectric constant of bromoform. The effect of the solvent on the molecular weight differs, however, from salt to salt.

225. "*The Action of Sodium Methoxide on* 2 : 3 : 4 : 5-*Tetrachloropyridine.*" (Part II.). By WILLIAM JAMES SELL. (*Trans.*, 1912, 1945).

The action of sodium methoxide on 2 : 3 : 4 : 5-tetrachloropyridine has been studied on a fairly large scale at the ordinary pressure in a flask heated by immersion in a water-bath, the experiments being conducted in two series, namely, (1) in which the sodium methoxide solution was of moderate strength, the main product being 3 : 5-dichloro-2 : 4-dimethoxypyridine; no methyl ether was produced. (2) In which the sodium methoxide was of such strength as to solidify on cooling, and the only products were 3 : 5-dichloro-4-hydroxy-2-methoxypyridine and methyl ether. The methyl ether is believed to be the product of the further action of sodium methoxide on the pyridine methoxide first produced, thus:—

$$(a)\quad RCl+CH_3{\cdot}ONa = NaCl+RO{\cdot}CH_3.$$
$$(b)\quad RO{\cdot}CH_3+CH_3{\cdot}ONa = RONa+(CH_3)_2O.$$

Some evidence is adduced as to the constitution of the chief products of this reaction, and it is indicated that at a temperature below the boiling-point of water the 4-methoxy-group in the 3 : 5-dichloro-2 : 4-dimethoxy-compound is converted into the hydroxy-group, but that it requires a considerably higher temperature to effect the conversion of the methoxy-group in the 2-position.

226. "*Preparation of Glycogen and Yeast-Gum from Yeast.*" By ARTHUR HARDEN and WILLIAM JOHN YOUNG. (*Trans.*, 1912, 1928).

The method previously described for the preparation of pure glycogen from yeast (*Trans.*, 1892, lxxxi., 1224) has been simplified by adopting the procedure of Pflüger for the preliminary extraction and purification. By the process described, glycogen is obtained which contains no nitrogen and only 0·02 per cent of ash. From the filtrate, after removal of the glycogen, yeast-gum is obtained as a white powder dissolving in water to a clear solution, which gives no red colour with iodine, produces a bulky flocculent precipitate when warmed with Fehling's solution, and yields mannose when hydrolysed by boiling with acid.

227. "*Studies of Chinese Wood Oil. β-Elæostearic Acid.*" By ROBERT SELBY MORRELL. *Trans.*, 1912, 2082).

Further investigation of the glyceride produced when Chinese wood oil is exposed to light seemed advisable in view of the diversity of opinion as to the structure of elæostearic acid. The results obtained confirm many of the statements of previous investigators. β-Elæostearic acid (m. p. 72°) and its glyceride (m. p. 61—62°) are stereoisomerides of α-elæostearic acid (m. p. 48°) and its liquid glyceride. With the exception of the potassium salt, the derivatives of the acid absorb oxygen with great rapidity, and in several cases it was impossible to prevent oxidation before analysis. Oxidation of the potassium salt by alkaline permanganate gave *n*-valeric and azelaic acids, together with substances showing the pyrrole reaction. Tartaric and succinic acids could not be detected among the oxidation products. Ethyl β-elæostearate (b. p. 232°/14 mm.) undoubtedly contains only two doubly linked carbon atoms. The reactions of elæostearic acid are best expressed by the constitutional formula proposed by Majima (*Ber.*, 1909, xlii., 674), namely,—

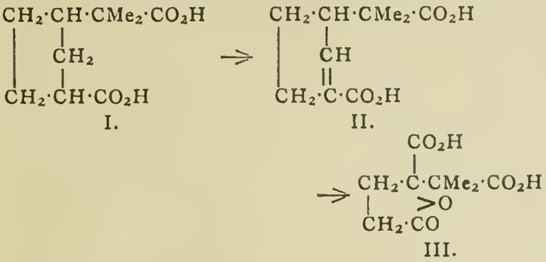
$$CH_3{\cdot}[CH_2]_3{\cdot}CH{:}CH{\cdot}[CH_2]_2{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CO_2H,$$

Preliminary investigations of the action of oxygen and air on the salts of β-elæostearic acid have shown that the gain in weight depends on the nature of the salt. During the oxidation of the glyceride a change from crystalline to spongy character occurs without alteration in colour. If the temperature is raised to 100° there is a sudden change in colour and oxidation products (aldehydes and acids) are expelled.

228. "*Constitution of Camphene.* Part I. *The Structure of Camphenic Acid.*" By WALTER NORMAN HAWORTH and ALBERT THEODORE KING. (*Trans.*, 1912, 1975).

Aschan (*Annalen*, 1910, ccclxxv., 336) ascribes to camphenic acid the constitution (I.); to dehydrocamphenic acid (II.); and to the product of the oxidation of this with nitric acid, the lactonic acid formula (III.).

By the aid of a Reformatsky condensation between ethyl α-ketoglutarate and ethyl α-bromo*iso*butyrate, the authors have synthesised a lactonic acid having the constitution represented by (III.), which, however, is not identical with the lactonic acid obtained by Aschan by the oxidation of dehydrocamphenic acid. Consequently, some modification of the above accepted structure (I.) for camphenic acid must be adopted.



I. II. III.

229. "*Studies in Phototropy and Thermotropy.* Part III. *Arylideneamines.*" By Alfred Senier, Frederick George Shepheard, and Rosalind Clarke. (*Trans.*, 1912, 1950).

The effect of light on the Schiff's bases, which are phototropic at the ordinary temperature, has been studied at temperatures up to their melting-points, and some bases which are not phototropic at the ordinary temperature have been submitted to the action of light at lower temperatures in order to find out if they might not exhibit phototropy under such conditions. In the first case it has been found that whilst some Schiff's bases are phototropic at temperatures up to their melting-points, others have a limiting temperature, above which they are not phototropic; secondly, of the compounds examined at lower temperatures, two, namely, salicylidene-*p*-anisidine and 2-*hydroxy*-3-*methoxybenzylidene*-p-*xylidene*, were found to be phototropic.

The colour changes which take place in salicylidene-β-naphthylamine (Senier and Shepheard, *Trans.*, 1909, xcv., 1950) have been further investigated, and it has been found that this compound is phototropic at the ordinary temperature, but that the darker phototrope only changes very slowly into the lighter one. Salicylidene-β-naphthylamine, similar to some other anils of this series, can be obtained tn two forms, yellow and red, by varying the method of preparation, and it is now shown that these modifications are identical with the light and dark phototropes.

To the list of phototropic Schiff's bases already known, the following compounds have been added:—*Salicylidene*-o-*anisidine*, *disalicylidene*-m-*phenylenediamine*, and 2-*hydroxy*-3-*methoxybenzylidene*-p-*xylidene*, which have not hitherto been described, and salicylideneaniline, salicylidene-*o*-bromoaniline, salicylidene-*p*-bromoaniline, and salicylidene-*p*-anisidine, already described, but with no mention hitherto of their phototropic properties.

230. "*Studies of the Constitution of Soap in Solution: Sodium Myristate and Sodium Laurate.*" By James William McBain, Elfreida Constance Victoria Cornish, and Richard Charles Bowden. (*Trans.*, 1912, 2042).

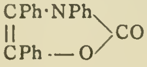
The anomalous conductivity curve for sodium palmitate at 90° is closely paralleled by that of the very much more mobile sodium myristate solutions. The curve for sodium laurate is much less anomalous in that the maximum and minimum are obliterated. Only the degree, and not the position, of the abnormality in the curves is altered in passing down the homologous series from stearate to laurate. The conductivity curves of sodium myristate at a number of temperatures between 90° and 40° reveal a very high temperature-coefficient, which, however, is nearly uniform for all concentrations, so that the position and degree of development of maximum and minimum is largely unaffected. Finally, a number of qualitative observations closely bearing on the colloid theory of soap solutions and "supersaturation" of gelatinisation are discussed. The coagulation of a suspensoid or gelatinisation of an emulsoid does not appear to be connected with change in the degree of dispersion of the colloid in certain cases.

231. "*Condensation of α-Keto-β-anilino-αβ-diphenylethane and its Homologues with Ethyl Chlorocarbonate and Thionyl Chloride.*" By Hamilton McCombie and John Wilfred Parkes. (*Trans.*, 1912, 1991).

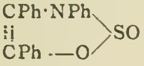
Some of the acyl derivatives of α-keto-β-anilino-αβ-diphenylethane were found by Everest aud McCombie (*Trans.*, 1911, xcix., 1746) to undergo condensation with ammonia to yield glyoxalines. In continuation of this work, the authors have prepared the carbethoxy-derivatives of α-keto-β-anilino-αβ-diphenylethane (I.) and its homologues. The carbethoxy-compound (I.), when heated with ammonia in a sealed tube, was found to yield 2-keto-3:4:5-triphenyl-2:3-dihydro-oxazole (II.), the ammonia merely acting as a hydrolysing agent. It was found that this oxazole could be prepared more conveniently from the carbethoxy-compound by the action of alcoholic potassium hydroxide, or directly from α-keto-β-anilino-αβ-diphenylethane by the action of carbonyl chloride in presence of pyridine:—

$$COPh\cdot COPh\cdot NPh\cdot CO_2Et$$

I.



II.



III.

The dihydro-oxazoles, which have been prepared, are found to be very stable towards acids and alkalis, they resist the action of reducing agents, and are not sufficiently basic to form salts.

The reaction between thionyl chloride and α-keto-β-anilino-αβ-diphenyl ethane and its homologues was also investigated. In this case, the compounds obtained (III.) were analogous to the oxazoles described above, having the CO-group replaced by the SO-group. The authors suggest the name oxasulphinazole for this new heterocyclic ring, so that compound (III.) would be 3:4:5-triphenyloxasulphinazole.

Like the oxazoles, the oxasulphinazoles were found to be extremely unreactive.

Attempts were also made to substitute sulphuryl chloride for thionyl chloride in this reaction, but no ring compounds were obtained, only chloro-derivatives of the original α-keto-β-anilino-αβ-diphenylethane being produced.

232. "*Carbon Disulphide as Solvent for the Determination of the 'Refraction Constant.*" By Frédéric Schwers. (*Trans.*, 1912, 1889).

Some new experiments have been made on the density and refractive index of binary mixtures, and the results calculated according to the formula which was theoretically explained in previous papers.

Measurements were made with mixtures of carbon disulphide with aliphatic salts (acetic, *iso*butyric, *iso*valeric) and alcohols (ethyl and *iso*butyl), and the refraction constant "A" was calculated and compared with the value for the corresponding solutions in water. Some differences are to be noted between the two kinds of solutions, namely, (1) there occurs a dilatation of both density and refractive index in the case of carbon disulphide mixtures, and not a contraction as in the case of aqueous solutions; (2) the absolute values of "A" are much smaller than for the corresponding solutions in water; moreover, there does not exist an absolute proportionality between these A-values in carbon disulphide and aqueous solutions. On the other hand, solutions in carbon disulphide have important points in common with those in water, namely, (1) by comparing solutions of carbon disulphide with the different terms of a series, it appears that "A" diminishes with the increase of the molecular weight; (2) increase of temperature produces increase of "A"; (3) the refraction constant diminishes from the red to the violet end of the spectrum.

232. "*Electrochemistry of Solutions in Acetone.* Part II. *The Silver Nitrate Concentration Cell.*" By Alexander Roshdestwensky and William Cudmore McCullagh Lewis.

Employing a more sensitive form of capillary electrometer, further measurements have been carried out on the E.M.F. of concentration cells containing silver nitrate in acetone. The E.M.F. values were found not to be affected by the interposition of a silver nitrate solution of arbitrary concentration; and taking this into account along with results previously obtained, the conclusion is drawn that the Nernst formulæ are applicable. On this basis the transport numbers of the ions of silver nitrate in acetone have been calculated.

Measurements have also been carried out with saturated ammonium acetate as the middle liquid.

234. "*Influence of Neutral Solvents on Velocity of Reaction.* Part II. *Transformation of Anissynaldoxime in Various Solvents.*" By Thomas Stewart Patterson and Harvey Hugh Montgomerie.

The influence of neutral solvents on the velocity of transformation of anis*syn*aldoxime into anis*anti*aldoxime has been studied, the transformation being rendered apparent by a corresponding alteration in the rotation of ethyl tartrate used as an indicator.

235. "*Condensation of Pentaerythritol with Aldehydes.*" By John Read. (*Trans.*, 1912, 2090).

The condensation products of pentaerythritol with a number of aldehydes have been made and investigated with a view to their resolution into enantiomorphously related isomerides.

236. "*Interaction of Iodine and Thiocarbamide. The Properties of Formamidine Disulphide and its Salts.*" By Emil Alphonse Werner.

Iodine and thiocarbamide interact in presence of an ionising solvent in accordance with the equation:—

$$2CSN_2H_4 + I_2 \rightleftharpoons \underset{\text{Formamidine disulphide hydriodide.}}{NH_2{\cdot}C(:NH){\cdot}S_2{\cdot}C(:NH){\cdot}NH_2,2HI}$$

The amount of the hydriodide of the base produced is inversely proportional to the concentration of the products when equilibrium is established, and directly proportional to the ionising power of the solvent. In presence of nitric acid a quantitative yield of the dinitrate, $C_2S_2N_4H_6,2HNO_3$, is obtained. Three final results can be realised under different conditions, namely, (1) quantitative formation of formamidine disulphide, (*a*) with concentrated solutions of the components, (*b*) in a high degree of dilution, and (2) a condition of equilibrium in which the base and thiocarbamide are present in equivalent proportions, $C_2S_2N_4H_6 : 2CsN_2H_4$. An additive compound, $(CsN_2H_4)_2I_2$, is formed only when iodine and thiocarbamide are allowed to interact in presence of benzene or chloroform. It melts at 87°, and when brought in contact with water, or other ionising solvent, is converted into formamidine disulphide hydriodide (m. p. 81°).

Claus's compound, $(CSN_2H_4)_2Cl_2$ (*Annalen*, 1875, clxxix., 139), is the hydrochloride of the base.

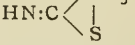
The *picrate* (m. p. 154°), *platinichloride*, and the *compound* $C_2S_2N_4H_6,2HI,I_2$ are described.

The action of potassium iodide in increasing the dissociation of the hydriodide, with generation of thiocarbamide and iodine has been examined, and its influence on the estimation of thiocarbamide by N/10 iodine solution is pointed out. The production of formamidine disulphide by oxidising agents, such as potassium permanganate, nitrous acid, and hydrogen peroxide, on thiocarbamide, only takes place in presence of strong acids, whilst with iodine the base is produced just as readily in neutral solution. An explanation of the probable mechanism of the interaction is given, which accounts for the formation of the base by the action of iodine under conditions different from those necessary with the oxidising agents mentioned.

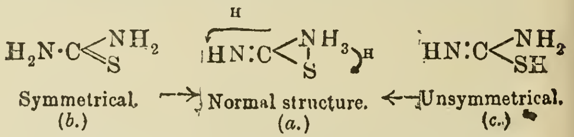
237. "*Action of Nitrous Acid on Thiocarbamide and on Formamidine Disulphide. A New Structural Formula of Thiocarbamide.*" By Emil Alphonse Werner.

When nitrous acid and thiocarbamide interact, the change proceeds in two different directions according as a weak or a strong acid is present.

In the presence of a weak acid the interaction is expressed by the equation $CSN_2H_4 + HONO = HSCN + N_2 + 2H_2O$, as proposed by A. E. Dixon (*Trans.*, 1892, lxi., 526), with a strong acid present, formamidine disulphide, $C_2S_2N_4H_6$ (Storch, *Monatsh*, 1890, xi., 452), is first produced thus: $2CSN_2H_4 + 2HONO = C_2S_2N_4H_6 + 2NO + 2H_2O$, and this is decomposed by further action of nitrous acid with production of thiocyanic acid and evolution of nitrogen. The changes have been studied quantitatively, and the secondary reactions, which takes place to a small extent in both cases, have been explained.

Thiocarbamide can be used for the rapid and accurate assay of nitrites. To account for the different phenomena described, neither the symmetrical nor the unsymmetrical formula of thiocarbamide is sufficient, but a new formula,  $HN{:}C\left\langle\begin{matrix}NH_3\\ |\\ S\end{matrix}\right.$, is proposed, as probably representing the true structure of thiocarbamide in a neutral solution, or in presence of a weak acid.

This formula shows a much closer connection between thiocarbamide and ammonium thiocyanate than the other two, and readily explains how the compound may give rise to derivatives of the symmetrical or unsymmetrical structure, under different conditions, by the migration of an atom of hydrogen in either of the directions shown below.



The change from (*a*) to (*c*) is determined by the presence of a strong acid or other strong negative reagent.

(To be continued).

Royal Institution.—The following are the lecture arrangements at the Royal Institution before Easter:—Prof. Sir James Dewar, Fullerian Professor of Chemistry, a course of six experimentally illustrated lectures, adapted to a juvenile auditory, on Christmas Lecture Epilogues: "Alchemy," Dec. 28; "Atoms," Dec. 31; "Light," Jan. 2; "Clouds," Jan. 4; "Meteorites," Jan. 7; "Frozen Worlds," Jan 9. Prof. W. Bateson, Fullerian Professor of Physiology, six lectures on "The Heredity of Sex and some Cognate Problems." Prof. H. H. Turner, three lectures on the "Movements of the Stars—The Nebular Hypothesis; The Stars and their Movements; Our Greater System." Mr. Seton Gordon, two lectures on "Birds of the Hill country." Prof. B. Hopkinson, two lectures on "Recent Research on the Gas Engine." Sir Sidney Lee, three lectures on "The Dawn of Empire in Shakespeare's Era." Mr. W. B. Hardy, two lectures on "Surface Energy." Dr. H. Walford Davies, three lectures on "Aspects of Harmony—Chord Progression (illustrated from Handel, Beethoven, and Brahms); Added Dissonance (illustrated from Schumann and Wagner); the New Whole Tone Chord and its Predecessors (illustrated from Bach and Debussy)." Prof. Sir J. J. Thomson, Professor of Natural Philosophy, six lectures on "The Properties and Constitution of the Atom." The Friday Evening Meetings will commence on January 17, when Prof. Sir J. J. Thomson will deliver a Discourse on "Further Applications of the Method of Positive Rays." Succeeding Discourses will probably be given by Prof. J. O. Arnold, Mr. G. M. Trevelyan, Sir John Murray, Prof. A. Gray, Mr. S. U. Pickering, Mr. C. T. R. Wilson, Prof. the Hon. R. J. Strutt, Dr. A. E. H. Tutton, and other gentlemen.

NOTICES OF BOOKS.

A Scheme for the Detection of the more Common Classes of Carbon Compounds. By Frank E. Weston, B.Sc. (Lond.), F.C.S. Third Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

The scheme described in this book by which a student is enabled to assign a given organic substance to a class, or actually to identify it completely, remains in essentials the same as that put forward in earlier editions, but some alterations have been made in matters of detail, and there are some important additions. These include the identification of aldehydes and ketones by the formation of their semi-carbazone derivatives, and the identification of sugars by the microscopic investigation of their osazones, photomicrographs of which are given. A quick method of determining the density of a small quantity of liquid is also described. The book will be found a useful practical guide to accompany lectures on organic chemistry, either for beginners, who might perform selected typical experiments only, or for more advanced students.

Modern Road Construction. By Francis Wood, M.Inst.C.E., F.G.S. London: Charles Griffin and Co., Ltd. 1912.

Engineers, surveyors, and members of local authorities will find in this book much useful information concerning the materials used in road construction, the wearing of different kinds of roads, methods of repairing, and cost of maintenance. Data concerning tractive effort on various surfaces are also included, as well as typical road board specifications relating to the construction of new roads and surface tarring. The author warns his readers that his opinions are sometimes not to be regarded as orthodox, but in such cases he always gives very fully his reasons for his departure from the usual opinion, and his statements will undoubtedly carry weight as representing the views of a practical expert.

The Materials Used in Sizing. By W. F. A. Ermen, M.A. London: Constable and Co., Ltd. 1912.

In the introduction of this book the author explains the necessity for sizing cloth and the results to be aimed at, and he then considers all the ingredients of a sizing mixture in turn, describing their physical and chemical properties and giving details of methods of analysis. The works' chemist should have no difficulty in pronouncing on the nature and purity of a given mixture if he makes intelligent use of the book, and he should also be able to compound by its help a suitable sizing mixture for any purpose. Weighting and softening materials and antiseptics are all discussed, and the uses of different ingredients are fully explained, as well as the complete analysis of a sample of warp or cloth.

Enzymes. By Otto Cohnheim. New York: John Wiley and Sons. London: Chapman and Half, Ltd. 1912.

This book contains six lectures which were delivered under the Herter Lectureship Fund at the University and Bellevue Hospital Medical College in New York in 1910, before an audience of medical students and physicians. From the nature of his audience the lecturer was not obliged to explain the elements of the subject, but could plunge straight into the discussion of the most modern theories. He first describes methods of obtaining and purifying enzymes, passing thence to the consideration of their general properties, and finally reviewing in detail the individual enzymes. He always states very explicitly and fully his own opinions, as, for example, on the theory of enzymes as catalysers propounded by Ostwald and Bredig. It is perhaps unavoidable that his criticism should be rather tantalisingly destructive, but no worker in the regions of biochemistry can afford to be ignorant of his opinions.

Brewing. By A. Chaston Chapman. Cambridge: At the University Press. 1912.

The general principles underlying the process of brewing are discussed in this little manual in such a way as to render them easily intelligible to the average well-informed reader who already knows a certain amount of elementary chemistry. The book, which is one of the Cambridge Manuals of Science and Literature, is in no way intended for the technical man, nor to be used as a practical guide, but it presents the subject in its most interesting aspect, and explains the results which have been attained by the chemical and biological investigation of the brewing process. The process is followed from beginning to end, and the chemical reactions and the practical considerations underlying each step are fully and thoroughly explained, from the materials used to the distribution of the product. The author has made a judicious selection of material for fuller discussion, and the general reader who is interested in applied science, and specially in the brewing industry, will appreciate the good literary style of the manual.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 16, October 14, 1912.

New Sensitive and Characteristic Reaction of Free Bromine.—Georges Denigès.—When an aqueous solution of bromine is poured into a solution of bisulphite of rosaniline in water, a purple or violet colouration is formed at first, and finally a violet precipitate is deposited. Upon this fact a very sensitive test for free bromine can be based. Two cc. of bisulphite of rosaniline and 2 cc. of hydrogen peroxide are shaken together in a test-tube, 1 cc, of chloroform is added, and then the solution to be tested. If the chloroform becomes coloured the liquid to be tested contains bromine. 0·01 mgrm. of bromine can be detected thus by its amethyst colouration, or by the characteristic absorption spectrum. A paper which can be used to test for bromine can very readily be prepared by dipping filter-paper in the bisulphite solution, and drying. The paper has to be moistened with water containing 1 or 2 per cent HCl before use.

Synthesis of Galactosides of Alcohols by Emulsine. β-Ethylgalactoside.—Em. Bourquelot and H. Hérissey.—The emulsine of almonds is really a mixture of several ferments, and it possesses a hydrolysing action on lactose. This property is due to the presence of lactase by means of which β-ethylgalactoside can be synthesised from galactose and ethyl alcohol.

Atti della Reale Accademia dei Lincei. Vol. xxi. (ii.), No. 7, 1912.

Boric Acid in Minetal Waters of Salsomaggiore.—R. Nasini and C. Porlezza.—In the mineral waters of the Salsomaggiore springs about 2·5 grms. of boric acid are present per litre. This large amount of boric acid would give a pronounced antiseptic action to the waters, and its presence is a fresh confirmation of its harmlessness.

Solid Solutions of Haloid Salts of a given Element.—G. B. Bernardis.—Antimony bromide forms mixed crystals in all proportions with the iodide and chloride, both the solidification curves belonging to Roozeboom's Type III. Antimony chloride forms mixed crystals with the iodide in limited proportions only, ending at a concentration of about 45 per cent of $SbCl_3$. Thus with antimony as with silver, thallium, and copper, an increase in the difference between the atomic weights of the halogens diminishes the affinity between the derivatives. Silver bromide, for example, forms mixed crystals in all proportions with both the chloride and iodide, but the two latter give solid solutions with one another to a limited degree only.

Basicity of Acids containing Alcoholic Hydroxyl.—G. Calcagni.—From the study of the specific conductivity of solutions of acids containing varying proportions of $Be(OH)_2$ it is found that glycolic, lactic, and oxybutyric acids form two series of salts in which the ratios between the acid and base are respectively 1 : ½ and 1 : 1. Thus they behave like dibasic acids; malic acid appears to be tribasic, forming three series of salts:—1 : ½, 1 : 1, 1 : 1½. Tartaric acid forms three series of salts:—1 : ½, 1 : 1, and 1 : 2, and citric acid four:—1 : ½, 1 : 1, 1 : 1½, and 1 : 2. These results may be generalised as follows:—The alcoholic hydroxyls contained in organic acids of the fatty series behave like carboxylic hydroxyls, and they confer on the acid a basicity which is numerically equal to the sum of the carboxylic and alcoholic groups.

Action of Sodium Alcoholates on Carbopyrrolic Ethers.—A. Calacicchi and C. Bertoni.—It is possible to introduce alkyl groups into the pyrrol nucleus by a much less prolonged heating and at a much lower temperature than were employed in the previous research. When dimethylacetyl carbopyrrolic ether is heated to 220° with sodium ethylate for sixteen hours, contrary to expection a large amount of the tetra-substituted product is formed, together with a small quantity of the trialkyl pyrrol.

Compounds of Uranium with Hydrazine.—Roberto Salvadori.—When hydrazine hydrate is precipitated with uranyl nitrate in the cold, a yellow compound of constant composition, represented by the formula $(N_2H_5)_2O.5UO_3.8H_2O$ is obtained. This compound is stable up to 100°, at which temperature it decomposes completely, losing its nitrogen. The precipitate obtained by heating uranium nitrate and hydrazine hydrate together has not a constant composition. The reduction of uranate by hydrazine seems to tend towards a limit which can be expressed by the formula $(N_2H_5)_2O5UO_3.6H_2O.UO_2$. When sulphuretted hydrogen is passed into an excess of nitrate or sulphate of uranyl, a yellow precipitate is obtained; if the excess of H_2S is removed by a current of oxygen, and hydrazine hydrate is added till the liquid is alkaline, hydrazine uranium-red is obtained in the form of a vermilion-red precipitate. Its composition corresponds to the formula $5UO_3.2(N_2H_5)_2O.N_2H_5.H_2S.4H_2O$. It slowly loses the unstable molecule of hydrazine, absorbing a molecule of water, and is thus transformed into the fundamental compound of uranic-red $5UO_3.(2N_2H_5)O.H_2S_2.6H_2O$.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xlv., No. 13, 1912.

Iron Salts which Combine with Carbon Monoxide.—Wilhelm Manchot.—When ammonia acts on sodium nitroprusside a trisodium-ferropentacyanamin of formula $Na_3FeCy_5NH_3 + 6H_2O$ is obtained. This substance possesses the power of absorbing carbon monoxide, nitric oxide, and oxygen. Ethylene and acetylene are not absorbed.

Asymmetric Phosphorus.—E. Wedekind.—The perfectly asymmetric phosphonium salts, $PR_1R_2R_3R_4X$, where X is a halogen, must exist in optically active forms, but the experimental difficulties of splitting them up into their isomers are very great. The author has obtained indications of such a decomposition in a few cases only. The two salts with which he has worked are *p*-tolyl-phenyl-ethyl-methyl phosphonium iodide, and *p*-tolyl-ethyl-phenyl-benzyl phosphonium iodide.

Colour Reactions of Unsaturated Ketones.—G. Reddelien.—α-β-Unsaturated ketones give, with concentrated sulphuric acid, coloured solutions which undergo a characteristic change of colour when a little nitric acid is added to the diluted solutions. The following are some of the changes observed:—

Benzal-acetone	Reddish yellow to bright yellow.
Anisal-acetone	Reddish yellow to bright yellow.
Benzal-acetophenone ..	Orange to yellow.
Anisal-acetophenone ..	Orange-red to yellow.
Dibenzal-acetone . ..	Red to yellow.
Dicinnamenyl acetone .	Violet to orange.
Mesityloxide..	Yellow to bright yellow.
Phorone	Orange to yellow.
Fluorenone	Purplish red to reddish yellow.

Some Peculiarities of Metal Wools.—O. Ohmann.—Steel wool will remove the exothermic heat of an explosive gas mixture even if it is already kindled, and will thus stop the spreading of the explosion. The burning of zinc wool is an effective lecture experiment. When lead wool is heated in the blowpipe flame it melts, forming tiny oxidised drops, and volumes of smoke are formed. Magnesium wool is explosive.

MISCELLANEOUS.

Sir John Cass Technical Institute.—The Prizes and Certificates gained by Students during the past Session will be distributed by Prof. Selwyn Image, M.A., on Tuesday, December 10, 1912, at 8 p.m.

Industry and Chemistry of Sugar.—By an oversight we omitted to state that the abstracts of the papers read before Section V.*a* at the Eighth International Congress of Applied Chemistry (Chemical News, cvi., 218, Nov. 1, 1912) were prepared and forwarded to us by Prof. W. D. Horne, President of the Section.

Royal Institution.—A General Meeting of the members of the Royal Institution was held on the 4th inst.; the Duke of Northumberland, President, in the Chair. Mr. P. B. Brown, Mr. H. B. Grylls, Mr. G. Kennett-Barrington, Mr. W. H. Player, Dr. S. W. Richardson, Major G. O. Squier, Mr. H. H. Turner, and Mr. F. W. Willcox were elected Members.

Institute of Chemistry.—At the Final Examination for the Associateship in the Branch of Biological Chemistry (October 14th to 18th, 1912), the following candidates passed:—Robert Philip Keith, Royal Technical College, Glasgow; Eric Richards, B.Sc. (Lond.), under Dr. George McGowan, F.I.C. (for Fellowship); Frederic Robinson, M.Sc.Tech. (Manc.), Municipal School of Technology, Manchester.

Physical Society's Annual Exhibition.—This Exhibition, which is to be held on Tuesday, December 17, at the Imperial College of Science, South Kensington, will be open in both the afternoon (from 3 to 6 p.m.) and in the evening (from 7 to 10 p.m.). Mr. S. G. Brown will give a Discourse at 4.30 p.m., and again at 8 p.m., on "Some Methods of Magnifying Feeble Signalling Currents." Some thirty firms will be exhibiting. We understand that invitations have been given to the Institution of Electrical Engineers, the Institution of Mechanical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission in all cases will be by ticket only, and therefore members of the Societies just mentioned (including also the Physical Society) desiring to attend the Exhibition should apply to the Secretary of the Society to which they belong.

MEETINGS FOR THE WEEK.

Monday, 9th.—Royal Society of Arts, 8. (Cantor Lecture). "Methods of Economising Heat," by C. R. Darling.

Tuesday, 10th.—Faraday Society, 8. "The Electromotive Forces of Concentration Cells," by A. P. Laurie.

Wednesday, 11th.—Royal Society of Arts, 8. "Natural and Synthetic Rubber," by Dr. F. Mollwo Perkin.

Thursday, 12th.—Royal Society of Arts, 4.30. "Delhi, the Metropolis of India," by Sir Bradford Leslie, K.C.I.E.

THE CHEMICAL NEWS.

Vol. CVI., No. 2768.

NOTE ON THE ELECTROLYSIS OF NITRIC ACID SOLUTIONS OF COPPER.*

By J. H. STANSBIE, B.Sc., F.I.C.

In the electrolytic deposition of copper from nitric acid solutions it is practically impossible to deposit the whole of the metal upon either a rotating or stationary cathode under ordinary conditions, and in considering the results of experiments in which a copper coated cathode was caused to rotate in a nitric acid solution with no current passing, the probable cause of the failure of the current to deposit the last traces of copper from a nitric acid solution suggested itself.

The object of the preliminary experiments was to determine the difference in the rate of reaction of dilute nitric acid with copper at rest and in motion. For this purpose a platinum cathode was thickly coated with copper by electrolytic deposition. After drying and weighing it was rotated in 50 cc. of nitric acid (sp. gr. 1·108) containing about 10 grms. of HNO_3 and less than 0·1 mgrm. of HNO_2. When the rotation was stopped the cathode was at once removed, washed, dried, and re-weighed. It was then immersed in a similar solution, but was allowed to remain at rest for the same length of time. The beaker was immersed in a vessel containing water at room temperature. All the conditions were kept as constant as possible, except that the metal was rotating in the one case and at rest in the other. The following remarkable results were obtained:—

Mgrms.

i. Rotated for one hour, weight of copper dissolved .. .. = 6·5

Rest for one hour, weight of copper dissolved .. .. = 780·6

ii. Rotated for two hours, weight of copper dissolved .. .. = 15·4

Rest for two hours, weight of copper dissolved .. .. = 3486·3

It is well known, but often overlooked, that nitrous acid plays a very important part in the dissolution of copper in nitric acid, and that the lower acid, or nitrite, accumulates in the solution. In solutions containing only traces of nitrous acid, the action is very slow at first, but gradually increases as more nitrite is formed. It this is allowed to remain on the surface of the metal the general reaction is rapidly accelerated, but if it is hurried away into the mass of the solution the reaction is retarded. This is the most obvious explanation of the results given above.

Now in the ordinary electrolysis of nitric acid solutions of copper the solution is boiled, in the first instance, to decompose nitrous acid and nitrite, and to expel the products of their decomposition; but nitric acid is again reduced to nitrous acid by the current during electrolysis, and all the conditions for the dissolution of copper from the cathode are present. At first the current deposits the metal very much faster than it is re-dissolved, but finally, when only traces of metal are present in the solution, dynamic equilibrium is reached, and no further permanent deposition of the metal can take place. This furnishes another argument in favour of the rotating cathode over the stationary one when purely nitric acid solutions are used.

The following experiments were then made as a further test:—Five grms. of electrolytic copper were dissolved in 50 cc. of 1·2 nitric acid, and the solution evaporated to one fifth its bulk to decompose nitrous compounds. It was then made up to 500 cc., and the free nitric acid in 50 cc. determined. This was found to be 236 mgrms. The remaining solution was electrolysed with a rotating cathode in 50 cc. lots. Additions of free acid were made as shown in the table, and the other conditions were kept as constant as possible. The measured volume with additions was made up to 100 cc. in each case.

The potential difference between the terminal of the rotor carrying the cathode and the anode = 3·2 volts. Current = 1·5 ampères. Duration of experiment = 40 minutes.

Table of Results.

Experiment.	1. Weight of copper deposited. Mgrms.	2. Free nitric acid present.	5. Nitrous acid found.	4. Free sulphuric acid present.
1.	474·3	236	33·0	—
2.	497·4	236	28·8	—
3.	497·3	236	16·3	4500
4.	455·0	1236	33·5	—
5.	495·5	2236	30·9	—
6.	495·7	3236	31·3	—
7.	424·8	4586	38·1	—
8.	314·7	6326	60·3	—
9.	494·0	6326	14·2	4500

It will be seen from the table that the more or less perfect deposition of the copper depends upon the concentration of nitric acid and of nitrous acid in the solution, the smaller deposit corresponding to the greater concentration of the higher acid, while for the same concentration of the "ic" acid the smaller deposit corresponds to the greater concentration of the "ous" acid. From Experiments 5 and 6 it would appear that up to 3 grms. of HNO_3 per 100 cc. of solution the deposits are good, providing the nitrite keeps low; but beyond that the deposit is poor.

Before the introduction of the rotating cathode the method adopted by the author was to evaporate the nitric acid solution with sulphuric acid before electrolysis, as it was found impossible to deposit the whole of the metal without getting rid of the nitric acid, on account of the low current density used. But with the rotating cathode it is sufficient to keep the nitric acid low, and add from 2 to 3 cc. of strong sulphuric acid. The usual plan is to dissolve about 0·5 grm. of the metal in 10 cc. of 1·2 nitric acid, boil down to decompose nitrites, and make up to 100 cc. with addition of 2 cc. of concentrated sulphuric acid. After forty minutes' electrolysis the exhausted solution will very rarely give any coloration with sulphuretted hydrogen. To prevent any resolution of the metal when the circuit is broken the following simple plan has been found very effective:—A wash-bottle with a long rubber tube attached to the mouthpiece is arranged so that when the rotation is stopped a jet of water can be directed upon the cathode, while the current is gradually broken by lowering the beaker. The fixed wash-bottle with the flexible tube allows the operator to use both hands in manipulating the apparatus.

The action of the sulphuric acid is probably twofold:—(*a*) Its ions help to carry the current and thereby to check the formation of nitrous acid; (*b*) it unites with nitrous acid to form a nitro-compound which is much less effective in bringing about resolution of the metal. Comparison of the results of Experiments 2, 3, and 8, 9 makes the first part of this explanation clear. The second part was suggested by the late Dr. Edward Divers in discussing the results of some experiments on the reactions of metals and alloys with nitric acid, which the author had carried out.

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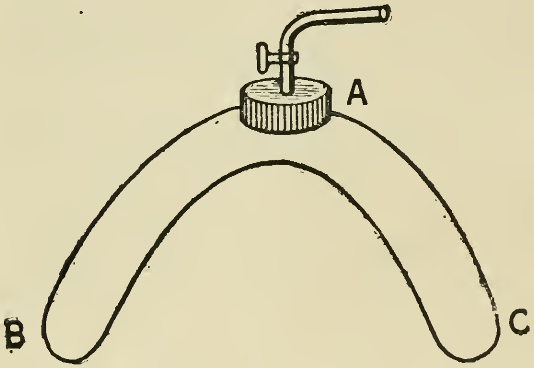
* A Paper read before the Faraday Society, November 26, 1912.

A SIMPLE APPARATUS FOR THE ESTIMATION OF CARBON DIOXIDE.

By W. R. FORBES, B.Sc.

A glass tube of suitable bore is bent into the shape shown. It is provided at A with a ground stopper carrying a delivery tube and tap. In use the acid is placed in limb C and the carbonate in limb B, the action being commenced by tilting the apparatus.



The apparatus is simple in construction and easy to keep clean.

THE ATOMIC WEIGHT OF BROMINE.

By H. C. P. WEBER, U.S Bureau of Standards.

A considerable amount of work has been done in order to determine the atomic weight of bromine, and the oft-repeated comparison of the atomic weights of silver and bromine makes it seem that this ratio is known with considerable accuracy. The value accepted for bromine, however, rests almost entirely upon that of silver, and it is of interest and importance to obtain a ratio between it and some other element. For chlorine a number of determinations of the ratio of hydrogen to chlorine in hydrochloric acid have been made, both by purely physical and by chemical methods. For bromine similar comparisons have not been made. Since the determination of the ratio chlorine : hydrogen was carried out with reasonable ease, it seemed probable that the method might be advantageously applied for the purpose of determining the ratio between hydrogen and bromine.

The method which was employed by Noyes and Weber (U.S. Bureau of Standards, 1908, *Bull.* 4, 345) was found to give good results in this case. The initial difficulties to be overcome were somewhat greater, which was rather unexpected. They were largely due to the physical properties of hydrobromic acid gas, and were eliminated after the method had been studied for some time and slight alterations in the method of manipulation had been introduced.

The results obtained are given in the accompanying table. The column headed "discrepancy" gives the differences between H + Br and HBr. The remainder of the table is self-explanatory.

In the ten experiments 9·00369 grms. of hydrogen were combined with 714·05722 grms. of bromine, and yielded 723·05828 grms. of hydrobromic acid. The value obtained from these two sums is respectively 79·307 (1) and 80·306 (9).

The final ratio obtained from these figures for H : Br is 79·306 (7), with a probable error of 0·0022. The ratio found from H : HBr is 80·306 (4), with a probable error of 0·0018. Combining the two the value is 79·306 (6) ± 0·0014. The numerical value of the probable error is somewhat larger than that of the chlorine ratio obtained in a similar manner. Relatively it is approximately the same or even somewhat smaller.

Expt.	H. Grms.	Br. Grms.	HBr. Grms.	Discrepancy. Mgrms.	H : Br.	H : HBr.
1.	0·77300	61·28837	62·06052	−0·85	79·2863	80·2853
2.	0·86060	68·25033	69·11144	+0·54	79·3055	80·3061
3.	0·77607	61·54733	62·32198	−1·42	79·3064	80·3046
4.	0·96927	76 88221	77·85135	−0·15	79·3197	80·3195
5.	1·07545	85·29562	86·37092	−0·15	79·3114	80·3114
6.	0·99689	79·06834	80·06424	−0·99	79 3150	80·3140
7.	0·74966	59·45275	60·20500	+2·59	79·3063	80·3097
8.	0·98161	77·85554	78·83758	+0·43	79·3141	80·3145
9.	1·00131	79·39533	80·39658	−0·06	79·2915	80·2914
10.	0·81983	65·02140	65·83867	−2·56	79·3108	80·3077
	9·00369	714·05722	723·05828	−2·63	79·3067	80·3064
					± 0·0022	± 0·0018
			Combined		79·3066	± 0·0014

Taking the atomic weight of hydrogen as 1·00779 (Clarke, "Re-calculation of Atomic Weights," 1910, p. 41), the value for bromine on the oxygen basis becomes 79·924, as against the value 79·920 given by the International Commission for 1912.—*Journal of the Washington Academy of Sciences*, ii., No. 19.

THE ESTIMATION OF LEAD, NICKEL, AND ZINC BY PRECIPITATION AS OXALATES AND TITRATION WITH POTASSIUM PERMANGANATE.

By H. L. WARD.

Determination of Lead.

Reis (*Ber.*, xiii., 502) in some investigations on the use of oxalates in analysis precipitated lead as the oxalate by adding ammonium oxalate to a neutral solution of a lead salt and breaking up the resulting soluble double oxalate with a large excess of acetic acid. The insoluble lead oxalate was filtered off and ignited, and the lead was weighed as the oxide. It was thought that lead oxalate precipitated under these conditions might be of such composition that titration with permanganate would give a true estimate of the amount of lead present.

In the experiments of Table I. the oxalate was precipitated by the addition of solid ammonium oxalate to the boiling solution of lead nitrate, containing the amount of acetic acid specified. The precipitate was collected on asbestos in a perforated crucible, and washed with small amounts of water. The oxalic acid was then set free by treatment with warm dilute sulphuric acid and titrated with potassium permanganate.

It will be noticed in the first part of Table I., where the amount of acetic acid does not exceed one-fourth of the solution, that precipitation is incomplete. If, however, glacial acetic acid makes up one-half the volume of the solution the results are accurate.

Oxalic acid has been used as a precipitant for lead by a number of investigators (Böttiger and Pollatz, *Chemical Abstracts*, ii., 645; Mohr - Classen, "Lehrbuch der Chemische Analytische Titermethode," 228; Low, *Journ. Am. Chem. Soc.*, xxx., 587). The determinations of Table II. were made by adding crystallised oxalic acid to a boiling solution of lead nitrate, filtering, washing, and titrating the oxalate with permanganate as before. When no acetic acid is present, precipitation is not quite complete, but the errors are much less than when ammonium oxalate is used as a precipitant, as may be seen from a comparison with Table I. Acetic acid added in equal volume to the solution secures complete precipitation even in the presence of considerable amounts of ammonium or potassium salts, provided the amount of lead salt present is not too small.

Determination of Nickel.

Classen (*Zeit. Anal. Chem.*, xvi., 470) has shown that nickel may be completely precipitated by treating the soluble nickel potassium oxalate with a large amount of acetic acid. The oxalate formed under these circumstances may be ignited to the oxide and weighed as such. It seemed desirable to determine whether this oxalate is of such composition as to allow the estimation of nickel by titrating the oxalate radical with potassium permanganate. The procedure first tried was that recommended by Classen. To a solution of a known amount of nickel sulphate was added a considerable excess of potassium oxalate and the liquid heated to boiling, when the oxalate first formed went into solution as nickel potassium oxalate. Two volumes of acetic acid were then added to precipitate the nickel oxalate. It was found necessary, in order to secure a product which could be filtered, to heat the acetic acid and to run slowly, with constant stirring, into the boiling solution of the double salt. Upon this treatment a flocky precipitate formed, which on standing for some time at 60—70° went over to a fine powder. By filtration and titration with permanganate it was discovered that the oxalate obtained under these conditions had a tendency to include some of the precipitant, causing high results on titration. On ignition also large positive errors were obtained, but if the oxide was washed to remove the potassium carbonate formed, a very good estimation of the amount of nickel present was secured.

It seemed possible that the use of oxalic acid as a precipitant might eliminate the errors due to inclusion, but it was found that if oxalic acid was added to the boiling solution of a nickel salt containing an equal volume of acetic acid, the oxalate formed came down quickly and in an extremely finely divided condition. The first experiment of Table III. was made in this manner, but in the majority of instances filtration proved to be impossible. If, however, precipitation was made in water solution and acetic acid added later to throw out the last traces of nickel, the oxalate came out more slowly and in a form suitable for filtration.

The nickel sulphate taken for analysis was dissolved in water, and the solution standardised both by precipitation as nickelic hydroxide and ignition to the oxide and by throwing out as metallic nickel on the rotating cathode. To a definite amount of this solution, diluted to the required volume and heated to boiling, was added an excess of crystallised oxalic acid. Upon cooling, acetic acid was run in and the precipitate allowed to settle over night. The smaller amounts of nickel did not come out from the water solution, and even after adding acetic acid it was necessary to heat it to start precipitation. The nickel oxalate was filtered off on asbestos in a perforated crucible and washed with small amounts of water. The crucible was placed in a beaker containing about 25 cc. of dilute (1 : 4) sulphuric acid, and heat applied to effect the solution of the oxalate. The volume of the solution was then made up to about 200 cc. and cobalt sulphate added until a slight pinkish tinge appeared. This procedure, recommended by Gibbs, was necessary to secure a definite end-point, as the green colour of the nickel masked the complementary pink of the permanganate. The contents of the beaker were then heated to boiling, and titration made in the usual manner. The results appear in Table III. The positive errors may be assigned to two causes, inclusion of the precipitant and uncertainty of end-point when titrating in coloured solutions.

Determination of Zinc as the Oxalate.

It was found to be possible to estimate zinc volumetrically as the oxalate by the process already outlined for nickel. In this case, no coloured salts being present in the solution on titration, a more definite end-point was secured, and the results obtained are much more accurate, as appears in Table IV.

Table I.—*The Determination of Lead by Precipitation with Ammonium Oxalate in the presence of Strong Acetic Acid.*

Lead present as the nitrate.	Volume at precipitation.	Acetic acid present.	Ammonium oxalate.	Lead found.	Error.
Grm.	Cc.	Cc.	Grms.	Grm.	Grm.
0·0050	100	25	3	0·0016	−0·0036
0·0250	100	25	3	0·0246	−0·0004
0·0500	100	5	3	0·0454	−0·0046
0·0500	100	10	3	0·0480	−0·0020
0·0500	100	25	3	0·0496	−0·0004
0·0500	200	50	7	0·0477	−0·0023
0·0050	100	50	4	0·0048	−0·0002
0·0050	100	50	4	0·0045	−0·0005
0·0250	100	50	4	0·0256	+0·0006
0·0250	100	50	4	0·0250	—
0·0500	100	50	4	0·0505	+0·0005
0·1000	200	100	8	0·1002	+0·0002

Table II.—*The Determination of Lead as Oxalate by Precipitation with Oxalic Acid in the presence of Strong Acetic Acid.*

Lead present as nitrate.	Volume at precipitation.	Acetic acid.	Oxalic acid.	Salts present.	Lead found.	Error.
Grm.	Cc.	Cc.	Grms.	Grms.	Grm.	Grm.
0·0500	50	—	2	—	0·0491	−0·0009
0·0500	100	—	4	—	0·0488	−0·0012
0·1000	50	—	2	—	0·0994	−0·0006
0·1000	100	—	4	—	0·0990	−0·0010
0·0050	50	25	1	—	0·0050	—
0·0250	50	25	1	—	0·0256	+0·0006
0·1000	100	50	2	—	0·1002	+0·0002
			Potassium Acetate present.			
0·1000	50	—	2	0·2	0·0962	−0·0038
0·1000	100	—	4	0·2	0·0988	−0·0012
0·1000	100	50	2	0·2	0·0997	−0·0003
0·1000	100	50	2	0·2	0·0100	—
			Ammonium Acetate present.			
0·0050	50	25	1	3	0·0040	−0·0010
0·0250	100	50	2	5	0·0227	−0·0023
0·1000	100	50	2	2	0·1000	—

Table III.—*The Determination of Nickel by Precipitation with Oxalic Acid and Treatment with Acetic Acid.*

Nickel as sulphate.	Volume of water solution at precipitation.	Oxalic acid.	Acetic acid added.	Nickel found.	Error.
Grm.	Cc.	Grms.	Cc.	Grm.	Grm.
0·0503	100	2	50	0·0502	−0·0001
0·0050	100	2	100	0·0054	+0·0004
0·0251	100	2	100	0·0258	+0·0007
0·0503	50	2	100	0·0514	+0·0011
0·0503	100	2	100	0·0502	−0·0001
0·1257	100	2	100	0·1271	+0·0014

Table IV.—*The Determination of Zinc by Precipitation with Oxalic Acid and Treatment with Acetic Acid.*

Zinc as acetate.	Volume at precipitation.	Oxalic acid.	Acetic acid.	Zinc found.	Error.
Grm.	Cc.	Grms.	Cc.	Grm.	Grm.
0·0055	100	2	100	0·0056	+0·0001
0·0274	100	2	100	0·0276	+0·0002
0·0548	50	2	50	0·0553	+0·0005
0·0548	100	2	100	0·0550	+0·0002
0·1370	100	2	100	0·1372	+0·0002

The oxalate of zinc obtained by the method of Classen (*Zeit. Anal. Chem.*, xvi., 470) was contaminated with potassium oxalate, and therefore could not be used to determine the amount of zinc present. On ignition and washing of the oxide obtained, it was shown that all the zinc was recovered.

Summary.

Experiments have been given to show that lead may be determined by precipitation, either with ammonium oxalate or oxalic acid, in the presence of large volumes of acetic acid and titration of the oxalate formed with permanganate.

Nickel has been estimated by precipitation by oxalic acid in water solution, the addition of acetic acid to separate the metal remaining in solution, and titration with permanganate. Errors may occur in this method from inclusion of the precipitant or indefiniteness of the end-point.

Zinc may be estimated very accurately by the method used for nickel.—*American Journal of Science*, xxxiii., 334.

THE DETECTION OF FORMIC ACID IN FRUIT PRODUCTS.

By F. L. SHANNON.

In *Bull.* 195 of the Dairy and Food Department of the State of Michigan, the author called attention to the fact that formic acid was being used in this country as a preservative of food products.

It has been the general belief among chemists, for some time, that some preservatives other than the ones ordinarily found were being used in the preservation of fruit products, and investigations have been made in various laboratories throughout the country for the purpose of determining the identity of the substance used. Owing to its use in Germany, a number have suspected formic acid, and have built up their investigations with that substance in mind, but because of the unsatisfactory and indirect methods of identification it has been difficult to reach a positive conclusion.

A search of the literature on the subject revealed the fact that the detection of formic acid did not depend upon its isolation and subsequent identification, but mainly upon the indirect method of its reducing power, principally upon silver nitrate and mercuric chloride solution. For example, the older literature states that formic acid is a constant constituent of many plant and animal products, a statement based on the fact that when they are subjected to steam distillation some substance is obtained in the distillate which reduces silver nitrate and mercuric chloride solution. However, in view of recent investigations along this line, it seems that this whole subject of the natural occurrence of formic acid needs further study, as it has been found possible to subject a host of substances which were known to contain no formic acid, to steam distillation, and obtain a distillate which gave a pronounced reduction with both silver nitrate and mercuric chloride solution. From none of these substances, however, has it been possible to isolate and identify formic acid as such. Therefore it is evident that we are not justified in designating as formic acid every substance obtained by steam distillation which reduces silver nitrate and mercuric chloride solution. It was found, for example, that when phosphoric acid was subjected to distillation, the distillate possessed the reducing properties generally ascribed to formic acid. Furthermore, in a number of methods in which the formic acid recovered by steam distillation is neutralised using phenolphthalein as indicator, the indicator itself was found to have a reducing action on mercuric chloride.

One of the most satisfactory indirect methods for the detection of formic acid is based on its reduction to formaldehyde by means of magnesium and dilute sulphuric acid. Fenton (*Journ. Chem. Soc.*, 1907, xci., 687) has shown that carbonic acid may be reduced in the same way, but Bacon (*Circ.* 74, U.S. Dept. Agric. Bur. of Chem.) has called attention to the fact that this is of theoretical importance only, there being no danger of confusing the two in practice. However, every step in this method must be carried out with absolute precision, or erroneous conclusions may be drawn.

The qualitative method as applied to the products used in this investigation is as follows:—To about 200 to 500 cc. of the syrup or crushed fruit in a 2 litre long necked round bottom flask provided with a Reitmeier bulb, add about 50 to 100 cc. of water. Subject to steam distillation, collecting the distillate (usually about 2500 cc.) until it ceases to give an acid reaction with litmus). Exactly neutralise the distillate with $N/1NaOH$, using litmus as an indicator. Evaporate on a steam- or water-bath to about 50 cc., transferring from the large evaporating dish to smaller ones as the volume decreases. Transfer to an Erlenmeyer flask, provided with a glass tube about 3 feet long as an air condenser, add a few pieces of pure magnesium ribbon or wire, and a slight excess of dilute sulphuric acid, and set in a cool place for one hour, adding dilute sulphuric acid through the tube from time to time as the reaction ceases. Transfer the liquid to a suitable distilling flask, and collect the first 10 cc. of the distillate, which will contain most of the formaldehyde, if the original syrup contained formic acid.

There are a number of methods published for the detection of formaldehyde, and nearly every analyst has his favourite test. However, the methods which proved the most satisfactory in this work were Leach's method (*Bull.* 107, p. 185, U.S. Dept. Agric. Bur. Chem.), phloroglucinol method (*Ibid.*), Rimini's method (*Ibid.*), and the resorcin method of the United States Pharmacopœia. A positive reaction with *these four tests* was considered conclusive evidence of the presence of formaldehyde.

Crystallographic Identification.

Inasmuch as practically all methods for the detection of formic acid previously reported are indirect methods depending upon the decomposition of the formic acid or upon its reducing powers, it seemed desirable to attempt the isolation of formic acid in the form of an insoluble salt.

The usual procedure in determining the identity of an organic acid in plants is to prepare some readily crystallisable salt, sparingly soluble in water. Of the various formates the lead salt crystallises readily without water of crystallisation, is very stable, and requires 63 parts of water for solution. The formation and identification of lead formate would therefore constitute a direct and positive proof of the presence of formic acid. After numerous attempts the following procedure was adopted:—

Steam distil about 1000 to 1200 cc. of the syrup as in the first operation, collecting the distillate (2500 to 3000 cc.) in a receiving flask to which about 5 cc. of lead cream has been added. (This is made as follows:—Precipitate a solution of lead nitrate with potassium or sodium hydrate in the presence of phenolphthalein until a faint pink colour appears. Wash by decantation eight to ten times). Shake the flask occasionally, and as the lead hydrate is dissolved add a few cc. more, until all the formic acid is combined. Concentrate the liquid in a large dish on a steam- or water-bath to about 50 cc. Filter, and transfer to a suitable crystallising dish and set aside in a desiccator. If formic acid was present in the original material, needle-like crystals of lead formate will form. Wash the crystals with absolute alcohol, to remove any lead acetate which may be present, spread on filter-paper, and dry. To the dry crystals apply the following tests:—

(*a*) Aqueous solution will reduce $AgNO_3$ upon warming.

(*b*) Aqueous solution will reduce mercuric chloride solution upon warming.

(*c*) Aqueous solution will reduce platinum chloride upon warming.

(*d*) To a portion of the crystals in a dry test-tube add sulphuric acid, and warm. Carbon monoxide is generated which will burn in the tube with a blue flame when ignited. Further note that the lead formate is not discoloured.

(*e*) Transfer some of the crystals to a small distilling flask, treat with concentrated phosphoric acid, and distil. The distillate, which is formic acid, will react as follows:—

1. Acid to litmus and acid taste.
2. Reduces silver nitrate on warming.
3. Reduces mercuric chloride on warming.
4. Reduces platinum chloride on warming.
5. Is reduced to formaldehyde by magnesium and dilute sulphuric acid.

As previously mentioned it was found that when phosphoric acid and water alone were distilled, the distillate would reduce silver nitrate and mercuric chloride solution. Therefore, before test (*e*) was carried out the phosphoric acid was subjected to distillation until it no longer gave a distillate that would reduce silver nitrate or mercuric chloride. The crystals of the lead compound were then added, and the distillation continued.

Although the chemical evidence that the volatile acid obtained from the fruit products used in this investigation is conclusive, it was thought desirable to submit the crystals to Dr. Edward H. Kraus, Professor of Geology and Mineralogy, University of Michigan, and he reports as follows:—

"The crystals, which were examined crystallographically, were obtained by slow crystallisation from an aqueous solution of the material furnished by Fern L. Shannon, State Analyst, Lansing, Michigan. They are prismatic in habit, and about 2 to 3 mm. in length, and of slightly yellowish colour. All crystals were clear and transparent. Although the crystals were, in general, doubly terminated, readings were made only upon the faces of the prism zone, the end faces being extremely small and, hence, difficult of adjustment. The images obtained were very good, considering the size of the crystals.

"The measured angles, compared with the values given by Plathan (Groth, *Chemische Krystallographic*, 1910, iii., 16), for lead formate are as follows:—

	Kraus.	Plathan.
m : *m* (110) : (110).. ..	73° 26′	73° 28′
m : *m* (110) : (110).. ..	53° 17½′	53° 16′

"This comparison shows that the agreement in the values for this material and those given by Plathan for lead formate are exceedingly close.

"Parallel extinction was observed upon all the faces examined. The indices of refraction are higher than that of methylene iodide, as determined by the Becke and the Schroeder van der Kolk methods.

"The above crystallographic-optical properties, together with the fact that a distinct reaction for lead is easily obtained upon the plaster tablet with the blowpipe, indicates conclusively that the substance examined is lead formate."

To further substantiate the proof, a number of fruit syrups that were known to contain no added formic acid were subjected to steam distillation and an attempt made to separate a lead compound. In some instances a few crystals were obtained, but at no time would the crystals give the characteristic tests for lead formate.

It would seem then that the formation of formaldehyde coupled with the formation of lead formate and their subsequent identification would furnish a conclusive and positive proof of the presence of formic acid.

The author desires to take this opportunity to thank Dr. Edward H. Kraus for his co-operation in this work.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

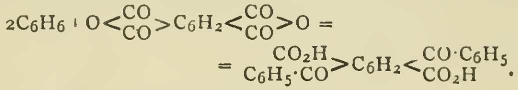
(Concluded from p. 280).

238. "*The Oxidation of some Benzyl Compounds of Sulphur.*" (Part I.) By JOHN ARMSTRONG SMYTHE. (*Trans.*, 1912, 2076).

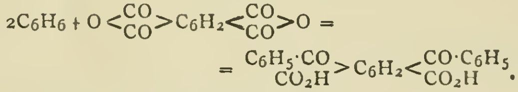
The comparative study of a number of benzyl compounds of sulphur has been undertaken. Oxidation is carried out with hydrogen peroxide in solution of glacial acetic acid. The simple monosulphidic compounds are converted quantitatively into higher oxy-derivatives, but the polysulphidic compounds suffer rupture. Benzyl disulphide yields benzyl disulphoxide, benzylsulphonic acid, benzaldehyde, and sulphuric acid, and the last three are among the products of reaction of benzyl disulphoxide, benzyl mercaptan, and benzoyl benzyl sulphide. An explanation of this peculiarity is sought in the hydrolysis of the disulphoxide, and subsequent reaction of the hydrolytic products.

239. "*The Synthetical Production of Derivatives of Dinaphthanthracene.*" By WILLIAM HOBSON MILLS and MILDRED MILLS.

Under the influence of aluminium chloride, pyromellitic anhydride condenses with benzene, forming a mixture of 2:5-*dibenzoylterephthalic acid* and 4:6-*dibenzoylisophthalic acid*, as shown by the following equations:—

1. 

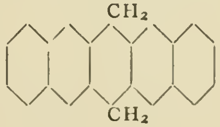
$$2C_6H_6 + O<^{CO}_{CO}>C_6H_2<^{CO}_{CO}>O = \; = {}^{CO_2H}_{C_6H_5\cdot CO}>C_6H_2<^{CO\cdot C_6H_5}_{CO_2H}.$$

2. 

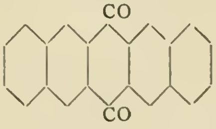
$$2C_6H_6 + O<^{CO}_{CO}>C_6H_2<^{CO}_{CO}>O = \; = {}^{C_6H_5\cdot CO}_{CO_2H}>C_6H_2<^{CO\cdot C_6H_5}_{CO_2H}.$$

The constitution of these acids has been established by fusion with potassium hydroxide, which decomposes them into benzoic acid, on the one hand, and terephthalic and *iso*phthalic acids respectively on the other. When warmed with concentrated sulphuric acid, both of these acids lose two molecules of water, and give rise to *dinaphthanthradiquinone*, $C_6H_4<^{CO}_{CO}>C_6H_2<^{CO}_{CO}>C_6H_4$.

This diquinone when reduced with zinc dust and alkali is converted into *dihydrodinaphthanthracene* (I.); when heated with hydriodic acid and phosphorus it gives rise to two isomeric *α*- and *β*-*tetrahydrodinaphthanthracenes*.



I.



II.

α-Tetrahydrodinaphthanthracene on oxidation is converted successively into dihydrodinaphthanthracene (I.) *dinaphthanthrone*, $C_{10}H_6<^{CO}_{CH_2}>C_{10}H_6$, and *dinaphthanthraquinone* (II.). The constitution of dinaphthanthraquinone is established by the fact that it is decomposed by sodium hydroxide into a mixture of benzoic and *β*-naphthoic acids.

240. "*The Preparation of Durylic and Pyromellitic Acids.*" By WILLIAM HOBSON MILLS.

The conditions are specified under acetyl-*ψ*-cumene, which can readily be obtained in any quantity from *ψ*-cumene by the Friedel-Crafts reaction, can be converted easily and with a satisfactory yield into pyromellitic acid. The process consists in the transformation of the ketone by sodium hypobromite into durylic acid, and the subsequent oxidation of the latter with potassium permanganate.

241. "*Organic Derivatives of Silicon.* Part XV. *The Nomenclature of Organic Silicon Compounds.*" By Frederic Stanley Kipping.

Some suggestions are made for systematising the nomenclature of different types of silicon compounds, more especially those described in the following papers.

242. "*Organic Derivatives of Silicon.* Part XVI. *The Preparation and Properties of Diphenylsilicanediol.*" By Frederic Stanley Kipping.

The hydrolysis of pure dichlorodiphenylsilicane under various conditions has been studied, and it has been found that the isolation of diphenylsilicanediol, $SiPh_2(OH)_2$, from the product is an exceptionally difficult task, partly owing to the readiness with which the diol undergoes condensation, giving compounds which it adsorbs from solutions.

Pure diphenylsilicanediol usually decomposes with effervescence at about 128—132°, but it is dimorphous, and in the neighbourhood of its decomposition point it may pass into a more stable crystalline modification, which does not decompose and effervesce until about 150—160°; this change seems to occur always when the crystals of the diol contain relatively small quantities of some of its condensation products, but seldom takes place when the compound is pure, so that impure specimens appear to have a much higher decomposition point than the pure substance.

The isomeric "diphenylsilicols" described by Martin (*Ber.*, 1912, xlv., 403) as melting at about 140° and 160° respectively were probably impure specimens of diphenylsilicanediol, and the methods which he gave for the conversion of these supposed isomerides into one another do not bring about any isomeric change.

243. "*Organic Derivatives of Silicon.* Part XVII. *Some Condensation Products of Diphenylsilicanediol.*" By Frederic Stanley Kipping,

Diphenylsilicanediol very readily undergoes condensation in presence of acids or alkalis, and in the preparation of the diol from dichlorodiphenylsilicane by different methods, various oily or glue-like products are obtained in considerable quantities. These products are usually mixtures of three or more compounds, which are formed from the diol by a process of condensation, and of which the following four have so far been isolated:—

$HO \cdot SiPh_2 \cdot O \cdot SiPh_2 \cdot OH$

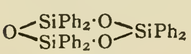
I.

Anhydrobisdiphenylsilicanediol.

$HO \cdot SiPh_2 \cdot O \cdot SiPh_2 \cdot O \cdot SiPh_2 \cdot OH$

II.

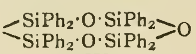
Dianhydrotrisdiphenylsilicanediol.



$$O<\begin{matrix}SiPh_2 \cdot O\\SiPh_2 \cdot O\end{matrix}>SiPh_2$$

III.

Trianhydrotrisdiphenylsilicanediol.



$$O<\begin{matrix}SiPh_2 \cdot O \cdot SiPh_2\\SiPh_2 \cdot O \cdot SiPh_2\end{matrix}>O$$

IV.

Tetra-anhydrotetrakisdiphenylsilicanediol.

The conditions under which these four condensation products are obtained from the diol have been studied, and also methods for the conversion of the two hydroxy-compounds (I. and II.) into their respective anhydro-derivatives (IV. and III.). The results of these and of further experiments which are in progress may throw some light on the constitutions of the complex mineral silicates.

244. "*Organic Derivatives of Silicon.* Part XVIII. *Dibenzylsilicanediol and its Anhydro-derivative.*" By Robert Robison and Frederic Stanley Kipping.

The further study of the compounds described as α-dibenzylsilicol and β-dibenzylsilicol (*Trans.*, 1908, xciii., 441) has shown that the former is a dibenzysilicanediol of the constitution $Si(CH_2 \cdot C_6H_5)_2(OH)_2$, whereas the latter is an *anhydrobisdibenzylsilicanediol* of the constitution $HO \cdot Si(CH_2 \cdot C_6H_5)_2 \cdot O \cdot Si(CH_2 \cdot C_6H_5)_2 \cdot OH$, crystallised with one molecule of water; although, therefore, the two compounds have the same composition they are not isomeric.

Dibenzylsilicanediol is the primary product of the hydrolysis of dichlorodibenzylsilicane, and methods for the preparation of the pure diol are described. When heated, or when treated with various reagents, dibenzylsilicanediol undergoes condensation, yielding products from which anhydrobisdibenzylsilicanediol and trianhydrotrisdibenzylsilicanediol may be isolated, the former in hydrated crystals. These hydrated crystals lose their water at 100°, and give anhydrobisdibenzylsilicanediol as a viscid oil, which is so very hygroscopic that it passes into the hydrated crystals on exposure to moist air.

245. "*Organic Derivatives of Silicon.* Part XIX. *The Preparation and Properties of some Silicanediols of the Type* $SiR_2(OH)_2$." By Robert Robison and Frederic Stanley Kipping.

Phenylethylsilicanediol, $SiPhEt(OH)_2$, *benzylethylsilicanediol*, $SiEt(CH_2 \cdot C_6H_5)(OH)_2$, and *phenylbenzylsilicanediol*, $SiPh(CH_2 \cdot C_6H_5)(OH)_2$, may be obtained by carefully hydrolysing the corresponding disubstituted dichlorosilicanes with an aqueous solution of ammonium hydroxide. These three crystalline compounds, like diphenylsilicanediol and dibenzylsilicanediol, give soluble derivatives with solutions of the alkali hydroxides; they are all very easily changed by heat, and also by various reagents, giving oils which are doubtless mixtures of their condensation products.

Anhydrobisphenylethylsilicanediol,—

$$HO \cdot SiPhEt \cdot O \cdot SiPhEt \cdot OH,$$

is formed when purified phenylethylsilicanediol is kept at the ordinary temperature, and also when an aqueous solution of the last named compound is treated with a very little dilute hydrochloric acid.

246. "*The Purification, Density, and Expansion of Ethyl Acetate.*" By John Wade and Richard William Merriman.

Defects in the methods of preparing dry esters, used by previous workers, are pointed out and overcome. The density at 0° compared with water at 4° was found to be 0·92454, which is higher than the values obtained by Perkin (*Trans.*, 1884, xlv., 492), and by Young and Thomas (*Trans.*, 1893, lxiii., 1216). Reasons for this difference are given.

Taking the specific volume at 0° to be unity, the specific volumes at 10°, 20°, and 30° were found to be 1·01301, 1·02663, and 1·04080 respectively. A method of using a Dewar vacuum vessel as a constant temperature bath is described.

247. "*The Vapour Pressure of Ethyl Acetate from 0° to 100°.*" By John Wade and Richard William Merriman.

For temperatures above 15° the boiling-point of ethyl acetate was determined at constant pressure in the manner previously described by the authors (*Trans.*, 1911, xcix., 989). At each pressure a complete fractionation of 100 grms. of pure ester was made, the temperature recorded being that at which Δ per cent was a maximum (Wade, *Trans.*, 1905, lxxxvii., 1656). At 100° the pressure found was 1536 mm., as compared with 1515 mm. obtained by Young and Thomas (*Trans.*, 1893, lxiii., 1216). Reasons are advanced for regarding the new value as correct.

Below a pressure of 900 mm. the agreement with Young and Thomas is almost perfect. A new method was used for finding the vapour pressures below 150°.

248. "*Halogen Derivatives and 'Refraction Constant.'*" By Frédéric Schwers.

The anomalies with regard to the "refraction constant" shown by mixtures containing a halogen derivative have been submitted to a closer investigation. It appears that the irregular behaviour (as compared with other mixtures) of the C_v and C_n curves is related to the number of halogen atoms, and affects the density much more than the refractive index, which shows more regularity. Particularly curious are the mixtures alcohol-chloroform and acetone-chloroform; their density variations are positive for certain concentrations and negative for others, whereas the refraction changes in quite a different manner and in the most regular way. Interesting is the fact that mixtures of halogen derivatives with fatty acids do not show the same phenomena. For the explanation of the observed phenomena, the hypothesis of an atom nucleus with variable volume (Richards) seems more necessary than ever.

The following communication has been received during the vacation:—

249. "*Bimolecular Glycollaldehyde.*" (A Correction). By NIAL PATRICK MCCLELAND.

The author regrets that a mistake was allowed to pass unnoticed in the above paper (*Trans.*, 1911, xcix., 1827):—

On p. 1829, line 17, for $C = \frac{M - 60}{60}$ should be read $C = \frac{M - 60}{M/2}$.

With this alteration the values of k become:—

i. 0·00140 not 0·00210.
ii. 0·00196 not 0·00303.
iii. 0·00381 not 0·00561.

The variation from the mean value is only one instance exceeding 4 per cent.

This alteration in no way affects the conclusions arrived at in the paper.

At an Extra Meeting of the Chemical Society, held in the Large Theatre of Burlington House (by the kind permission of his Majesty's Office of Works) on Thursday, October 17th, 1912, at 8.30 p.m., Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair, Sir Oliver Lodge, D.Sc., F.R.S., delivered the Becquerel Memorial Lecture.

A vote of thanks to Sir Oliver Lodge, proposed by Sir WILLIAM CROOKES, O.M., F.R.S., and seconded by Prof. H. E. ARMSTRONG, F.R.S., was supported by the PRESIDENT and carried with acclamation.

PHYSICAL SOCIETY.

Ordinary Meeting, November 22nd, 1912.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

A PAPER on "*A Column Testing Machine*" was read by Prof. E. G. COKER.

The conditions of fixture of the ends of columns, and the large influence this has upon their strength, generally make it necessary to use special testing machines for these members, in which the end plates applying the load are accurately parallel, and remain so during a test.

If only rough measurements of the load are required this offers no serious difficulty, but accurate measurement involves elaborate mechanical devices, some of which are briefly referred to in the paper.

This difficulty is overcome in a simple manner by supporting one pressure plate by two or more annular diaphragms spaced at considerable intervals, and clamped at their outer edges to a fixed casing in such a manner that only one degree of freedom is possible. This construction is carried out in the machine described in the paper. The total load on the pressure plate supported in this way can be measured by a loaded lever system or other suitable means. The other pressure plate may be carried on guides, and the load applied by screws, hydraulic pressure, or other suitable means.

Rectangular plates or wires may also be used in place of annular diaphragms, and a model showing an application to a compression machine is described.

Photographs of celluloid columns are shown under stress, and the colours produced by temporary double refraction indicate that the loads are satisfactorily applied in a machine of this type.

Sir R. HADFIELD thought this paper opened out an important field of research.

Mr. C. E. LARARD asked if the machine was meant for testing metals or only xylonite, as in the former case the conical pivot at the top would be a source of weakness.

The AUTHOR replied that for heavier machines the conical pivot could be replaced by a narrow strip of thin steel plate which was preferable to a knife edge.

A paper on "*The Law of Plastic Flow of a Ductile Material and the Phenomena of Elastic and Plastic Strains*" was read by Mr. C. E. LARARD.

The author gave an account of the twisting to destruction at a uniform angular velocity of a cylindrical steel specimen 3 in. diameter, and of his deductions from the experimental data. The following deductions were made:—

1. The rate of increase of the torque with the time varies inversely as the time.

2. The acceleration of the torque velocity which is negative or, as it may be called, the de-celeration, varies therefore inversely as the square of the time.

3. The variables, time t, and torque T, are connected by the compound interest law.

More exactly $t + t_0 \quad a\epsilon^{b\mathrm{T}}$, where t_0 is a time constant. Corresponding results in terms of the angle of torsion θ and T obviously followed, since $\theta \quad \omega t$, where ω is the angular rate of straining.

The author next proceeded to summarise certain other conclusions he has formed as a result of many experiments extending over five years, illustrating his arguments by means of original diagrams, but reserving the full account for later publication.

1. *The Elastic Period.*

(*a*) Plastic strain is always produced by applied stress, and when its amount becomes large enough to be detected by the strain instrument the actual linearity between stress and strain is no longer directly obvious.

(*b*) The *recorded* limit of elasticity depends on the degree of accuracy to which the strain instrument is capable of indicating the strain—*i.e.*, there is no definite limit of elasticity, the recorded limit being merely an instrument limit.

(*c*) In the case of a tension test where the increase of strain is measured in the direction of the applied stress linearity between stress and strain is apparently very pronounced, but in the case of a torsion test very small increases in the elongation of helically twisted generating lines of the specimen are accompanied by the relatively large angles of torsion measured by the twist-strain instrument, with the result that plastic strain is observed very early in the test, giving low instrument limits of elasticity.

(*d*) There is elastic strain, whether it is obscured by plastic flow or not, which is closely proportional to the torque (or load) for all values of the torque (or load) up to the maximum, and it is given by $\theta_e/\mathrm{T} = \theta_1/\mathrm{T}_1$, where T is any torque not exceeding the maximum load, and T_1 and θ_1 are any observations of torque and twist respectively during the elastic period of instrumental linearity between stress and strain. Consequently the usual formula may be used for calculating elastic strains, provided the torque is not greater than the maximum.

(*e*) The total strains produced under applied stress even before the yield period is reached depend on the time as well as on the torque (or load).

(*f*) The linearity between strain and applied stress may be rendered obvious up to a high value of the load by suppressing the plastic flow.

2. *The Yield Period.*

(*a*) The plastic strain phenomena under constant load during this period depend on the time. If the load is imposed on a specimen either *very* slowly or *very* quickly there is no yield period; the former case corresponding very closely to isothermal straining and the latter to adiabatic.

(*b*) *Most General Case.*—When the yield torque (or load) is reached, and where equilibrium is maintained between the load and the resistance, the velocity of the plastic strain is rapidly and increasingly accelerated for a short period of time due to some rapidly and increasingly softening process going on in the material, the acceleration θ rapidly reaching a maximum value followed for a short period by a rapidly decreasing acceleration, the velocity θ still increasing until the acceleration reaches zero value with momentary uniform velocity. From this point, and for by far the greater part of the yield, the velocity θ undergoes constantly decreasing retardation (due to some gradual and increasingly hardening process going on in the material) until the curve in θ and t becomes, or tends to become asymptotic to the axis of time with a uniform value of θ.

(*c*) From what has been stated above it follows that the yield period is produced when from the conditions of loading acceleration of plastic flow is produced, and further, that where the torque-time and torque-twist ratios are kept below certain critical values, and, therefore, where there is no acceleration but only a retardation, no yield period is produced and the elastic-torque-twist line and the plastic-torque-twist curves are compounded into a smooth and continuous resultant torque-twist diagram.

(*d*) The yield period may be due to the production of a fluid state (liquefaction) in parts of the material under the acceleration, with subsequent relegation and hardening producing de-celeration after the parts have adjusted themselves to their new positions. The torque-twist curve which is continuous denotes a condition of semiplastic flow.

(*e*) the yield period which takes place under the circumstances indicated can be raised by strain to almost any position with respect to a torque-twist curve.

3. *Total Strain.*

If the above results are accepted the total strain is the sum of the elastic and plastic strains, where the elastic strain is a linear function of the load for all ordinary speeds of loading and where the plastic strain is function of both load and time.

Sir ROBERT HADFIELD said he thought the results presented marked an epoch, and he gave some additional information on some experiments of his own on straining and toughening material, which tended to confirm some of the author's conclusions.

Dr. CHREE thought the results would have been clearer from a physical standpoint if the author had employed t (time) throughout as the independent variable in his mathematical expressions. If he had taken dT/dt as ordinate and t as abscissa in Fig. 4 his theoretical curve would have been a rectangular hyperbola, which would have served satisfactorily to show the agreement between the observations and the theory. The real physical significance of the experiments seemed to be that under the conditions of test $\theta dT/dt$ was a constant. Had the author tried whether this relation held when θ did not increase uniformly with the time? The formula required some restriction as it made dT/dt initially infinite.

Mr. APPLEYARD suggested that the constant b in the author's equations could be given a better numerical value, and suggested 25·8, which would render t_0 zero.

Mr. F. L. HOPWOOD remarked that Andrade in 1910 had shown that for tension tests on lead and copper the elastic yield persists during the plastic yield.

Prof. MARGETSON suggested that if the results had been stated in terms of θ and T, instead of between t and T, the results would have been more in accordance with the author's previous statement of the compound interest law in the form $\theta = a_t{}^{bT}$.

Replying to the discussion, the AUTHOR thanked Sir Robert Hadfield for his remarks. With respect to Dr. Chree's suggestion, the reason the author had presented the diagrams and results in the form given was so as to make them readily intelligible to the engineer, to whom they might prove useful. Further, the torque-twist diagrams were given as they would be taken in practice. Mr. Appleyard was quite in error; the value of the constant given in the paper agreed very closely with the experimental result. Replying to Mr. Hoowood, the Author called attention to papers of his published in 1907 and 1909, in which he had established the same result.

Some "*Kinematograph Illustrations of the Twisting and Breaking of Large Wrought-iron and Steel Specimens*" were exhibited by Mr. C. E. LARARD.

The tests illustrated the Northampton Institute testing machine in operation, showing torsion tests on the following:—

1. A piece of mild steel, $2\frac{1}{2}$ in. diameter.
2. A piece of wrought-iron of the same dimensions.
3. A wrought-iron shaft, $2\frac{1}{2}$ in. square.
4. A rectangular bar of steel, $3\frac{1}{2}$ in. by $1\frac{1}{2}$ in.
5. A steel tube, $3\frac{1}{2}$ in. diameter, with the wall $\frac{3}{8}$ in. thick.
6. A tension test showing the development of the Lüder lines.

SOCIETY OF CHEMICAL INDTSTRY.
(LONDON SECTION).

Ordinary Meeting, December 2nd, 1912.

Mr. G. T. HOLLOWAY in the Chair.

THE following papers were read and discussed:—

"*New Apparatus for the Examination of Mine Air.*" By Dr. L. A. LEVY.

A new type of oxidation tube for effecting the rapid estimation of combustible gases is described. This consists of a capillary tube of silica through which a platinum wire is stretched axially. This wire is heated to incipient whiteness by a current supplied through molybdenum terminals fused into the silica. The expansion of the wire on heating is taken up by means of a molybdenum spring. The tube is incorporated into two new types of apparatus designed for the routine examination of mine air according to the provisions of the Coal Mines Act, 1911.

One of these is intended for the estimation of fire-damp only, and an accurate analysis can be completed in about five minutes. The other provides means for the estimation of carbon dioxide and oxygen as well as of fire-damp. Both instruments are absolutely safe, and can be taken into the most fiery mine without any danger of causing an explosion. Both are very simple to manipulate, and are capable of great exactitude.

"*Slate-bed Treatment of Sewage.*" By W. J. DIBDIN.

In the present paper an account of the success of the slate-bed process was given in continuation of previous papers in 1904-6.

The introduction of this process marks the utilisation of one waste product, slate *débris*, to effect the conversion of offensive organic waste into an inoffensive earthy form which has some manurial value.

The action of the slate-beds may be summarised as follows:—The solid matters in the sewage are allowed to settle on shelves of slate supported by slate blocks at a distance of about two inches, these being superposed to a depth of one to five or six feet, as required. In consequence of the alternate filling and emptying and resting empty, the deposit becomes the home of many types of organisms that digest the matters and render them inoffensive in like manner to the action by which earth-worms produce a humus from organic *débris*, and throw it to the surface in the form of worm-casts. In the slate-bed the deposit of earthy matter thus formed on the surface of the layer of mud on the slates is washed off by the receding effluent when the bed is emptied, and forms a black slurry, consisting of mineral and indigestible matter with numerous organisms from the bed. This slurry is then placed on a suitable drainage bed for the water to drain off, and to allow time for the full digestion of any crude material that may have come from the bed, and, finally, to allow the host of infusoria gradually to extinguish themselves by the natural process of the "survival of the fittest."

As a result of experiments during a period of eighteen months at High Wycombe, it was found that the quantity of residual matter was equal to only 3·4 tons of 90 per cent moisture per million gallons of normal sewage.

On the assumption that farmers will remove the air-dried humus at their own cost, the capitalised annual economy will repay the cost of the slate-beds. There is the further advantage that the whole of the nuisance of sludge disposal is abolished.

How far the assumption that farmers will remove the humus free of cost is warranted may be judged from the fact that Messrs. Barr and Sons, of Taplow, report that it is evident that while it possesses undoubted manurial properties it has a very beneficial mechanical advantage in lightening heavy soils. It would be an excellent medium for mixing with potting soils for general purposes, in addition to being a good manurial agent to dig into the soil.

Taken in conjunction with the fact that the Corporation of Manchester is making and selling at 25s. per ton a good manure made from the washings of the clinker contact beds, which are of the same character as that from the slate-beds, this evidence of the utility of the only residue from sewage treated by the aerobic method in slate-beds more than fully justifies the belief that, when once farmers realise the difference between this residue and ordinary "sewage sludge," they will readily remove it free of cost.

It was shown by the Royal Commission that:—"Provided that the sewage is not allowed to remain too long in the slate-beds, the slate-bed sludge differs from ordinary sewage or septic tank sludge in that it possesses only a slight odour, resembling that of sea-weed, is full of minute forms of animal life, and is in an active process of inoffensive decomposition as it lies on the slates.

"Compared with other preliminary processes of sewage purification slate-beds will probably be found to be expensive as regards capital outlay, but on account of the sludge being comparatively odourless we think that the claims of the process deserve consideration in cases where the reduction of smell at a sewage installation is of primary importance.

"On two occasions when a slate-bed was opened no offensive odour could be detected in the bed, even when standing at the bottom of it on a hot day. In fact, it smelt no worse than an ordinary damp cellar."

These results were confirmed by the Bureau of Survey upon the purification of the sewage of Philadelphia, 1910, and by various Russian as well as many English works.

In connection with the Exhibition of the Royal Sanitary Institute at Belfast in 1911, the Council of the Institute awarded the highest possible award, the Silver Medal.

The permanence of the slate has a distinct bearing on the question of the period for which loans could be granted. For land treatment sixty years are allowed for repayment. For artificial systems thirty years only are allowed. The indestructibility and permanent character of the slate justify the consideration whether the rate might be lessened, and a period of sixty years allowed for repayment in order that part of the cost might be laid on the next generation who will profit by the installation as in the case of land.

The evidence now available clearly demonstrates that by means of the slate-bed treatment the foul matters in sewage are resolved into an inoffensive residue which has a distinctly manurial value. Our ideas respecting sewage works and nuisance must be modified in view of the benefits secured by the conversion of the solid matters into a valuable aid to agriculture. The long expressed wish for the economical utilisation of the chief waste products of the community is satisfied by the healthy functions of aerobic organisms.

FARADAY SOCIETY.

Ordinary Meeting, November 26th, 1912.

Dr. H. Borns in the Chair.

Dr. A. J. Allmand read a paper on "*The Billiter Alkali-Chlorine Cells.*"

Dr. J. Billiter, of the University of Vienna, has, in recent years, designed two successful types of non-mercury alkali-chlorine cells. The Billiter-Siemens cell has already been described in several places. It has diaphragms, these being placed horizontally instead of vertically, as is usually the case. The floor space needed is greater, but the diaphragms are stabler chemically and the current efficiencies are high. Several installations of this cell are working on the Continent and in America. The Billiter-Leykam cell is a modified bell-jar cell. The cathodes are, however, arranged *underneath* the bell-jar, being contained in porous asbestos hoods to catch the hydrogen. The brine leaving the bell-jar does not therefore change the direction of its motion before reaching the cathodes. A far more uniform flow is thus obtained, and the current efficiency is consequently high. The porous asbestos hoods offer very little resistance to the passage of the current. The cell being furthermore heated by means of hot liquids flowing through earthenware pipes, the voltage is low. At 85°, 12—13 per cent $NaOH$ can be made at 92 per cent current efficiency, using 3·1 volts. The first installation in Gratwein, Austria, works very satisfactorily. Attendance charges are low, and unpurified brine is used.

"*Electrolysis of Nitric Acid Solutions of Copper.*" By J. H. Stansbie, B.Sc., F.I.C. (See p. 283).

Mr. Ridsdale Ellis, B.Sc., read a paper entitled "*A Neutral Oil Emulsion as a Model of a Suspension Colloid.*"

The interface potential at the surface of the oil globules of an emulsion was measured by means of a microscope slide apparatus. The interface potential was found to be little affected by organic impurities in the oil, but to be altered enormously by acids, and to a lesser degree by alkalies. The maximum interface potential was found to correspond to a concentration of about 0·001/N alkali, and this was found to be the point of maximum stability of the emulsion. Surface tension measurements showed that the stability did not depend on the surface tension, but on the interface potential.

Determinations were made of the concentrations of salts with mono-, di-, and tri-valent cations required to just neutralise the charge on the oil globules. The ratio of these concentrations was found to form a geometrical series agreeing with that obtained by coagulation experiments. The coagulation of oil emulsions by colloidal ferric hydroxide was next tried, and it was found that the oil was completely precipitated within two well-defined limits on either side of the iso-electric point of the oil emulsion.

The coagulation appears to be due to surface precipitation effects taking place between the oil globules somewhat analogous to the condensation of water-vapour on surfaces of various curvatures.

Mr. E. Hatschek said it might be of interest to state that the size of the oil globules in Mr. Ellis's experiments was about 2 μ, which was of course very much larger than anything in suspension colloids. He found it very difficult to realise how the electrical "double-layer" would prevent collision between the globules; the theory was useful mathematically but very obscure physically. Whetham's theory with regard to the ratio of concentrations of salts with mono-, di-, and tri-valent cations required to neutralise the charge on the oil globules was, in his opinion, untenable, as, for one thing, it was based on the assumption that the particles were stationary. After some criticism of the author's ferric hydrate theory, Mr. Hatschek concluded by expressing the hope that the work would be continued in emulsions free altogether from electrolytes—from ions—if that were possible.

Prof. Alfred W. Porter, F.R.S., controverted some of the remarks of the previous speaker. Whetham's theory merely depended on relative motion taking place. The coming together of two globules with "double-layers" would have the effect of mutually disturbing the perfect uniformity of their electric charges, and then the particles would repel one another.

Prof. F. G. Donnan, F.R.S., in a written communication which was read to the meeting, pointed out that no distinction could be made between "suspensions" and "emulsions" if based merely on the liquid or solid state of the disperse medium. The author's oil emulsions behaved as typical suspensions, forming a very striking model of a suspension colloid. Bredig's "Lippmann Effect" theory of the stability of suspensions was not borne out by Mr. Ellis's results. Further work on emulsions is being carried out in the Muspratt Laboratory.

Mr. H. M. Ridge remarked on the great interest of the subject in connection with the theory of oil flotation processes now largely in use for ore separation.

Dr. G. Senter referred to some recent work of Freundlich in which geometrical ratios in the coagulating effects of mono, di-, and tri-valent cations were not observed. He agreed that the author's work did away with any real distinction between suspension and emulsion colloids.

Dr. E. Feilmann said it had long been known that slightly alkaline media favoured the formation of stable suspensions, but he gave instances where slightly acid media had the same effect. He criticised the author's suggestion that dyeing might be due to capillary coagulation of the colloidal dye.

NOTICES OF BOOKS.

Practical Measurements in Radio-activity. By W. Makower, M.A., D.Sc., and H. Geiger, Ph.D. London, New York, Bombay, and Calcutta: Longmans, Green, and Co.

Coming directly from the Physics Laboratory of the University of Manchester the above book will be welcomed by all workers in the rapidly increasing field of radio-activity. Although primarily intended as a laboratory course the scope has been enlarged to meet the requirements of those engaged in original investigation. It is assumed that the reader has an elementary knowledge of the subject, so no historical introduction is given, and chapter I. opens directly with illustrations and descriptions of the measuring instruments used in the research. Special reference is made to the Dolezalek electrometer, its construction, and the method of using it for the measurement of ionisation currents. Chapter II. deals with the various forms of electroscopes now in common use, and gives practical hints for the construction of these instruments. The Wilson tilted electroscope is described, and also the less well-known quartz fibre electroscope devised by Wulf, which can be used for very refined measurements. Chapters IV. and V. are devoted to the discussion of α-, β-, and γ-radiations, and the value of the scintillations produced on a blende screen, first observed by Sir William Crookes, for indicating the "range" of the α-particle. A chapter is devoted to the subject of radio-active transformations, followed by one on standard measurements. This latter contains a fund of valuable information, and directions are given for making measurements by all the best known methods, including that recently described by Messrs. Rutherford and Chadwick by balancing the γ-radiations from a radium product against those from uranium; the method of measurement by counting the scintillations produced upon a blende screen *in vacuo* is also fully described, but the excessive refinement of manipulation needed is likely to prevent its coming into general use. The final chapter deals with the separation of radio-active substances, many chemical and physical processes being described in a practical manner. An appendix at the end of the book is devoted to radio-active constants, decay tables, and measuring instruments generally. The authors are to be congratulated upon having produced a practical and useful book that will be appreciated by all workers in the intensely interesting field of radio-activity. The illustrations are good, and there is a full index.

A Text book of Rand Metallurgical Practice. Volume II. By C. O. Schmitt, M.Inst.M.M. London: Charles Griffin and Co., Ltd. 1912.

The second volume of this treatise is the work of one author only, and is devoted to the Designing and Construction of Reducing Plants and the Transport of Materials. It deals very fully with the designing and building of sorting, breaking, crushing, amalgamating, &c., plant, and the difficult question of estimating cost is discussed in a very practical spirit. The general transport of ore, sand, slime, as well as of stores and sundry materials is treated in the second part, and the book will certainly be of value to others besides Rand metallurgists, by whom it will undoubtedly come to be regarded as indispensable.

A Second Year Course of Organic Chemistry for Technical Institutes. The Carbocyclic Compounds. By F. B. Thole, B.Sc. (Lond.). London: Methuen and Co., Ltd. 1912.

This is a book which will be a useful addition to the library of almost any student who is attending a course of lectures on organic chemistry, whatever other books he may possess and use. It can be thoroughly recommended as giving a summary of the preparation and properties of the carbocyclic compounds, which though brief is systematic and well arranged. Some account is given of the industrial and other uses of the substances described, but this more technical part is not emphasised at the expense of more purely scientific and theoretical aspects, and questions relating to constitution, &c., are fully discussed. A short chapter on Steric Hindrance gives a very clear outline of the subject, and the chapter on some important synthetical reactions generally associated with the names of their discoverers will be found useful for revising for examination purposes and for reference. A certain amount of practical work is described, including the identification of a few common organic substances.

Forty-eighth Annual Report on Alkali, &c., Works. By the Chief Inspector. London: His Majesty's Stationery Office. 1912.

This Report contains an account of an investigation of the chromate method of determining lead in chimney gases, which has been found to give very accurate results if certain precautions are adopted. A measured excess of standard chromate solution must be added to the lead solution, and the titration completed with standard lead nitrate, using silver nitrate as an indicator. The behaviour of oxide of iron in purifiers in gas works has also been the subject of a careful research, which has not yet been brought to a conclusion. In one respect the result is negative, for no clue has been found to the cause of the "souring" of the oxide, but, on the other hand, the report contains a detailed discussion of the conditions which make for the maximum efficiency of the substance.

The Scientist's Reference Book and Diary, 1913. Manchester: Jas. Woolley, Sons, and Co., Ltd.

This is a very handy little diary and reference book, and contains a large amount of information, both of general and scientific interest, which is well selected and well arranged. Besides the calendar and diary for 1913 and plenty of space for manuscript notes and memoranda, tables of weights and measures, conversion tables, and chemical factors for analysis will be found in it. Astronomical, meteorological, and physiological notes are also included, as well as an index of scientific definitions and the most important chemical laws. The miscellaneous data include many world statistics and hints for first aid in cases of accident and poisoning.

Ebonite Tubing, Pumps, Taps, and other Articles. London: The Indiarubber, Gutta Percha, and Telegraph Works Co., Ltd. 1912.

This price list contains full details as to price, size, &c., of all the ebonite tubing, taps, elbows, gauge cocks, pumps, &c., manufactured by the Indiarubber, Gutta Percha, and Telegraph Works Co., Ltd., of Silvertown, London. The articles are intended chiefly for use in chemical and vinegar works, for hydrochloric and acetic acids, in which ebonite is employed for storing and pumping apparatus, &c. Although the prices quoted are necessarily much higher than they were a few years ago, the great advantages of the material will probably soon compensate for its initial cost.

Methods for Sugar Analysis and Allied Determinations. By Arthur Given, B.S. Philadelphia: P. Blakiston's Son and Co. 1912.

In this handbook the author describes the methods of sugar analysis which he has found most satisfactory and the best adapted for their special purposes. Usually he describes but one method, believing that the novice, for whom the book is intended, is only confused if given a choice of processes, and is very likely to attain to proficiency and accuracy in none of them. Each process is described fully, but the student is supposed to have a knowledge of the ordinary operations of analytical chemistry and to have done some work with the polariscope. Some useful methods for determining sugars in cattle foods and similar substances are described, and the analysis of honey, condensed milk, &c., is included. All necessary tables and one or two alternative methods are given in the appendices.

Lectures Delivered at the Centenary Celebration of the First Commercial Gas Company to Sell Gas as an Illuminant. New York City: American Gas Institute. 1912.

This volume contains a short account of the Celebration of the Centenary of the Introduction of Gas as an Illuminant held in the early part of the year in Philadelphia under the auspices of the American Philosophical Society, the Franklin Institute, the American Chemical Society, and the American Gas Institute. In it are reproduced the catalogue of the Loan Exhibition, and an interesting chronological table of the development of gas lighting, which dates back to 1450 B.C., when artificial light was first employed. The full text of the five lectures delivered on the occasion is also included. These lectures were given by men who are eminent in the chemical or engineering worlds, and dealt with the By-products of the Industry, its Commercial and Financial Aspects, the Technique of Gas Manufacture, the Use of Gas as an Illuminant, and Methods of Testing Gas. Many of them were of considerable interest to the consumer as well as to the manufacturer, and the Gas Institute was well advised to publish them in book form.

Die Analyse der seltenen Erden und der Erdsäuren. ("The Analysis of the Rare Earths and the Acid Earths"). By Prof. Dr. R. J. Meyer and Dr. O. Hauser. Stuttgart: Ferdinand Enke. 1912.

In this volume of Margosches's "Chemische Analyse" the qualitative and quantitative analysis of the rare earths is very fully discussed. The actual separation and preparation of the individual earths is not included, but no well-established and thoroughly tested method of estimating or detecting any of them is passed over. On the other hand, very little attention is paid to processes which have been superseded or are of historical interest only. Many new and as yet unpublished observations are included, especially in the chapters on Qualitative Analysis; spectroscopic work is fully described, analysis by the aid of the absorption spectra being treated in detail, as being of the greatest practical assistance to the chemist.

Magnetische Analyse flüssiger Kristalle. ("Magnetic Analysis of Liquid Crystals"). By O. Lehmann. Leipzig: S. Hirzel. 1912.

This paper is reprinted from the 13th volume of the *Physikalische Zeitschrift*, and contains a highly interesting account of the influence of transverse and longitudinal magnetic fields on the molecular structure of para-azoxy-anisol, para-azoxyphenetol, and anisaldazin. The illustrations, which are beautifully clear, are very striking, and the article throws new light upon the author's work on the formation and structure of liquid crystals.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clv., No. 17, October 21, 1912.

Preparation of Mineral Oxides.—Maurice Billy.—To prepare Ti_2O_3 an intimate mixture of dry titanic anhydride and an excess of titanium is heated to 700° in absence of air. The substance obtained after purification is a crystalline homogeneous dark blue powder. To obtain TiO the same mixture as before must be heated to 1500°, when a brown crystalline powder is obtained. To dissolve out the excess of metal the finely divided substance can be left in contact with tetrachloride of titanium in hydrochloric acid at 60°, when the metal dissolves, giving the violet trichloride. A more rapid method of purification consists in attacking the finely divided substance with concentrated caustic potash solution (20 grms. KOH, 10 grms. H_2O) at about 130° for four or five hours. To dissolve the titanate thus formed hydrochloric acid diluted with its own volume of water is used, the temperature not being allowed to exceed 60°. The oxide is not attacked. Similar reductions can be carried out with tungstic anhydride, molybdic anhydride, &c., with very satisfactory results.

No. 18, October 28, 1912.

Racemic Dilactic Acid and Inactive Dilactic Acid.—E. Jungfleisch.—Raw dilactic acid is dissolved in water and neutralised with magnesium hydroxide or carbonate, and the liquid is evaporated. The inactive dilactylate, being much less soluble than the racemic salt, is deposited first in small crystals, which may be separated off by decantation from time to time. When a certain concentration is reached the liquid is allowed to cool, and large crystals of racemic salt are obtained mixed with a few crystals of the inactive salt. The racemic acid is separated from the salt by dissolving in sulphuric acid and heating the solution *in vacuo*, when it finally separates into two layers, the less dense of which is a syrupy solution of racemic dilactic acid, which may be extracted with ether. The inactive acid is separated by a similar method from the inactive salt.

Photochemical Hydrolysis of Solutions of Chloroplatinic Acids.—Paul Job and Marcel Boll.—From measurements of conductivity it is found that the ions of the chloroplatinic series are hydrolysed in two stages. In very dilute solution (dimilli-normal) they first undergo a photo-chemical reaction, which always gives the same monochlorodiplatinic compound, with formation of the corresponding number of chlorine ions. Secondly, they undergo a purely chemical reaction by which the platinum is precipitated in the form of platinic hydrate.

Decomposition of Glucose and Galactose by different Radiations.—Daniel Berthelot and Henry Gaudechon.—In decompositions by means of light the vibratory frequence of the radiations plays the same part as temperature in decompositions by heat. Thus with glucose and sugars of aldehydic function wave-lengths between 0·30 and 0·25 μ gasify the aldehyde function COH and photolysis gives exactly two volumes of CO to one of H. More rapid vibrations attack the alcoholic functions, and the proportion of hydrogen increases until it is the predominant constituent of the mixture; at the same time the liquids become acid, and exert a reducing action in the cold, increasing quantities of CO_2 and methane being evolved.

Double Sulphites of Alkalis and Mercury.—H. Baubigny.—A double sulphite of sodium and mercury can be prepared by pouring a solution of sublimate into an excess of sodium sulphite. When the crystals thus obtained are heated to 100° they are not completely decomposed after two hours, and no trace of dithionic acid is obtained. The decomposition of the double salt in the cold also gives no trace of dithionic acid.

Action of Hydrogen Peroxide on Trithienyl.—Maurice Lanfry.—When H_2O_2 acts on trithienyl, $C_4H_3S—C_4H_2S—C_4H_3S$, one of the thiophenic radicles loses its atom of sulphur, and then two or four atoms of oxygen are fixed, according to intensity and duration of the oxidation. The dioxygenated compound has the formula $C_{12}H_8S_2O_2$. The tetroxygenated compound, $C_{12}H_8S_2O_4$, has already been isolated by Renard, by the oxidation of trithienyl by means of fuming HNO_3 at 150° or chromic acid in acetic solution.

Action of Formic Acid on Triaryl Carbinols.—A. Guyot and A. Kovache.—Experimenting with very different types of aryl carbinols the authors have found that they all liberate CO_2 when heated with formic acid, but in a great majority of cases the reaction is not quantitative. If, however, some anhydrous sodium formate is previously added to the formic acid the transformation into methane derivative is integral, and the weight of the CO_2 disengaged agrees exactly with that deduced from the reduction equation. The alkaline formate seems to oppose the dehydrating action of the formic acid by diluting it.

Derivatives of Phenylisoxazolone.—André Meyer.—Phenylisoxazolone condenses with cyclic aldehydes to give a new series of colouring substances, the chromogen of which is benzoyl phenylisoxazolone. The author has prepared various substances of this type, and has found that the dyes with a free phenol function are of a darker shade than their ethers. Acylation alters the shade more than methylation. The position of the auxochromes, OH, has an influence on the shade. The ortho-compound is generally less intensely coloured than the para derivative; but in sulphuric and alkaline solutions the reverse holds good.

Annales des Falsifications. No. 45, 1912.

Determination of Rice in Adulterated Flour.—P. Andouard.—The percentage of rice present in adulterated flour may be determined by the following gravimetric method:—The gluten is extracted from a known weight of the flour, the residue is freed from any granules of wheat or tares, washed, dried, and weighed. A second equal quantity of the flour is treated similarly, but the residue is saccharified before weighing. If 33·33 grms. of the flour are taken, and r is the difference between the weights of the residues, the percentage of rice is given by $x = \frac{r \times 100}{42} \times 3$.

Preservation of Samples of Milk intended for Analysis.—X. Rocques.—Potassium bichromate is an excellent preservative for samples of milk, but if any alteration in the composition of the milk has begun to take place it is no longer effectual. Apparently any lactic acid present acts as a reducing agent and converts the bichromate into salts of chromium. Lactose favours this reducing action of lactic acid, but lactose is not altered by bichromate when the latter is present only in the proportions used for preserving purposes. It is important to proceed with the analysis as quickly as possible, before the bichromate is reduced, if any alteration in the samples has begun.

Coffee Essence.—L. Farcy.—The sample examined, which was of Swiss origin, consisted of a brown powder, composed of shining and dull granules and smelling of coffee. From the results of the chemical and microscopical examinations it was concluded that it contained about 50 per cent of caramel, 25 per cent of chicory, 10 to 12 per cent of roasted barley, and about the same proportion of coffee.

MISCELLANEOUS.

New Works and New Editions.—Messrs. J. and A. Churchill have pleasure in announcing the following:—

"A History of Chamistry." From the Earliest Times till the Present Day. By the late James Campbell Brown, D.Sc. (Lond.), LL.D. (Abdn.), Professor of Chemistry at Liverpool University. With a Frontispiece Portrait of the Author, and 106 Illustrations.

"Notes on Chemical Research." An Account of Certain Conditions which apply to Original Investigation. By W. P. Dreaper, F.I.C., F.C.S. With a Frontispiece Portrait of Michael Faraday. (This is the first of a series of text-books of Chemical Research and Engineering, just about to be published).

"A Text-book of Anatomy for Nurses." By Elizabeth R. Bundy, M.D., Member of the Medical Staff of the Women's Hospital, Philadelphia. Second Edition, with much additional matter and new illustrations.

"Who's Who in Science (International), 1913." Edited by H. H. Stephenson. Containing biographies of the leading followers of the following sciences:—Agriculture, anatomy, anthropology, astronomy, bacteriology, botany, chemistry, engineering, forestry, geography, geology, mathematics, medicine, meteorology, mineralogy, pathology, pharmacology, physics, physiology, psychology, surgery, zoology. Including also a Comprehensive list of the World's Universities, a Classified Index, and a List of the Scientific Societies throughout the World. 500 Pages. Much enlarged.

MEETINGS FOR THE WEEK.

Monday, 16th.—Royal Society of Arts, 8. (Cantor Lecture). "Methods of Economising Heat," by C. R. Darling.

Wednesday, 18th.—Royal Society of Arts, 8. "The Pictorial Possibilities of Work," by Joseph Pennell.

—— Microscopical, 8. Lantern Demonstration on Insect Intelligence, by F. Enock.

Thursday, 19th.—Chemical, 8.30. "Dibenzyl and Diphenyl Silicols and Silicones," by G Martin. "An Attempt to Harmonise the Relation between Temperature and Rotation for Light of all Refrangibilities of certain Active Substances, both in the Homogeneous State and in Solution," by T. S. Patterson. "Photography of Absorption Spectra," by T. R. Merton. "Constitution of Ortho.diazoimines—Part II., The p-Tolylnaphthatriazoles," by G. T. Morgan and F. M. G. Micklethwait. "Co-ordination Compounds of Vanadium—Part I., The Acylacetonates," by G. T. Morgan and H. W. Moss. "Optically Active Glycols derived from the Phenyl-lactic Acids," by A. McKenzie and G. Martin "Diphenylene," by J. J. Dobbie, J. J. Fox, and A. J. H. Gauge. "New Method for the Estimation of Hypochlorites," by H. G. Williams.

THE CHEMICAL NEWS.

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THE DIFFUSE REFLECTING POWER OF VARIOUS SUBSTANCES.

By W. W. COBLENTZ, Bureau of Standards.

This paper gives an account of an investigation of the reflecting power of matte surfaces of various substances for the spectral regions of 0·54, 0·60, 0·95, 4·4, 8·8, and 24 μ. The diffusely reflected radiations were collected by means of a hemispherical mirror, and projected upon a surface thermopile of bismuth and silver, which was used to measure the intensity of the incident and reflected radiations.

The substances examined include lampblack, platinum black, pigments, white paints, green leaves, dyed cloth, and building material. The object of the investigation was to find the blackest and the whitest substances; the former to be used as absorbing surfaces of radiometers, the latter to be used as a covering for buildings exposed to intense sunlight.

Methods are given for preparing standard black surfaces; and quantitative data are given for the loss by reflection of the same. The blackest deposits of soot are obtained from an acetylene flame, the reflecting power being only about 0·6 per cent. Lampblack paint made by mixing the dry material with turpentine reflects about 3 per cent in the visible spectrum to 3·5 per cent in the extreme infra-red. Thick deposits of platinum black reflect about 1 per cent in the visible spectrum, and 2 to 3 per cent in the extreme infra-red.

Bricks, granolith, dusty asphaltum pavements, and green leaves fall in the same group with a reflecting power about 25 per cent for green leaves. But there is a vast difference in their effect upon the surrounding atmosphere and consequently upon the comfort of the community. The building material continues to re-radiate energy long after the sun has set, while in the growing leaf the absorbed energy is at once used in photo-chemical processes, with practically no rise in its temperature. It is evident that, until traffic demands the full width of it, a great portion of a street should be covered with grass and trees instead of granolith and asphalt, thus adding to the comfort of the community as well as decreasing the cost of maintenance. Observatories should be surrounded with grass and evergreen shrubbery, which will absorb the solar rays without warming the atmosphere by re-radiation.

As a covering for an observatory dome the problem is to find a white paint that reflects a maximum amount of visible rays and a minimum amount of infra-red rays of wave-lengths between 6 and 10 μ. In this manner a large portion of the solar rays will be reflected into space; and the rise in temperature resulting from the solar rays that are absorbed will be prevented by re-radiation, which is facilitated by a high emissivity (low reflectivity) at 6 to 10 μ. Unfortunately the paint (zinc oxide) that fulfils the latter condition cannot be used for exterior work. The next best primary paint for exterior work is white lead. Radiometrically it would therefore be better to use a mixture composed of white lead and as high a proportion of zinc oxide as is permissible to form a good paint.

The carbonates, sulphates, and silicates have bands of strong metallic reflection in the region of 7 to 9 μ, which suppresses re-radiation of the absorbed solar rays. In binary mixtures, sulphates and silicates are less desirable than carbonates; for their infra-red reflecting power is higher and the bands do not lie close to those of lead carbonate. This suppresses the emissivity over a wider range of the infra-red spectrum. Of course a few (5 to 8) per cent of silica or china clay which is said to improve white lead mechanically, cannot seriously affect the radiating properties of the primary, viz., white lead. The combinations of calcium sulphate and of barytes with white lead appeared much darker than a similar combination with calcium carbonate.

The white paints examined quantitatively for reflection were samples which had been ground in linseed oil, under standard conditions (*Proc. Am. Soc. for Testing Materials*, 1911, xi., 226). There was no marked difference in the reflecting power of white lead made by different processes (American, Dutch, and French), the reflecting power of various samples varying from 74·3 to 76·0 per cent. Similarly the samples of zinc oxide paints reflected from 68 to 69 per cent. This agrees with previous observations on the dry pigments which show that lead carbonate has a higher reflecting power than zinc oxide. A mixture of equal parts of white lead and of zinc oxide reflected 71 per cent.

In view of the fact that the reflecting power of aluminium is high (69 per cent) in the visible and in the ultra-violet, it was of interest to determine whether sheet aluminium would be more satisfactofy than white paint for protecting a building against warming by solar rays. The difference in reflecting power of aluminium and white paint is not so marked in the visible spectrum as in the infra-red. Both materials absorb considerable sunlight; but aluminium has the lower emissivity for radiations at 6 to 12 μ. Hence it cannot radiate the absorbed energy as rapidly as the white paint, and its temperature rises above that of white paint.

This conclusion is borne out by the following experiments in which the temperature of two similar plates of aluminium was observed before and after one plate was painted with white lead ground in pure linseed oil. Two sizes of sheet aluminium were tested; A = 46 by 48 by 0·718 mm., B = 68 by 69 by 0·245 mm. Thermocouples of copper and constantan wires were inserted and riveted in holes drilled through the aluminium plates, and as a further attempt to obtain good contact the junctions were tightened with Wood's alloy. The constantan wire was 0·31 mm., and the copper wire was 0·40 mm. in diameter. The cold junctions were kept in ice. The aluminium sheets were mounted side by side upon a board of yellow poplar, 20 by 19 by 0·18 cm., and exposed to direct sunlight. The temperature of the pairs of sheets, A and B, and the difference in temperature was measured by means of a potentiometer.

Sheets No. II. of both A and B were given two coats of pure white lead paint, and when dry they were exposed to sunlight. The sky was perfectly clear (10-7-1912) with only a slight breeze blowing. Without glass coverings, which is the test of most interest, the bare aluminium plate was the hotter. For A—I, the temperature of the unpainted aluminium sheet was 3·0° to 3·1° higher than the exactly similar sheet having two coats of white lead paint. The actual temperature of A—I was about 44·7°. Similarly, for B—I the temperature excess of the unpainted aluminium sheet was 2·3° to 2·4°, the actual temperature being about 43·7°. The intensity of the solar radiation, Q, was about 1·16 grm. cal. cm^2. min.

These tests were repeated, using three coats of paint. The weather was perfectly clear (10-10-1912) and no breeze blowing. The intensity of the solar radiation was 1·157 grm. cal. cm^2. min. The plates were exposed directly to the sun, *i.e.*, no glass intervening. For A—I the temperature excess was 4·1° to 4·3°, the actual temperature being about 45° C. Similarly, for B—I (unpainted aluminium) the temperature excess was 3·0° to 3·2°, the actual temperature being about 42·7°.

From these tests it is evident that a metal roof painted with several coats of white paint is far superior to one of bright metal. As already mentioned this is owing to the fact that white paint has a higher emissivity than metals in the infra-red.

The unpainted sheets of aluminium (A—I, B—I) were then given three coats of zinc oxide paint. When thoroughly dry, the sheets containing the zinc oxide paint appeared to be at about the same (+0·1°) temperature as obtained in the white lead. Another coat of paint was then applied (making four coats in all) to each sheet. When exposed directly to solar radiation, the temperature excess of the zinc oxide paint for the thin sheets, B, was ± 0·1°, and for the thick sheets it was about +0·5°. From this appears that, in comparison with white lead, what is gained in higher emissivity in the infra-red in the zinc oxide paint is lost by its higher absorption (lower reflecting power) in the visible spectrum, so that radiometrically it is no more efficient than white lead.

The white lead paint was removed from the sheets, A—II and B—II, which were then painted with a matte layer of the lampblack used in the experiments already described. When exposed directly to the sun the temperature of the lampblack sheet A—II was about 16° higher than the zinc oxide paint A—I; the actual temperature of the lampblack being about 52·2° for solar radiation of intensity, Q = 1·16. Similarly the temperature of the lampblack sheet B—II was 17·5° higher than the zinc oxide plate B—I, the actual temperature of the aluminium sheet covered with lampblack paint being about 53·3° C. and the room temperature being about 23·1° C. The infra-red reflecting at 8·8 μ differs but little for these two substances, hence there is no great difference in their emissivities for low temperatures. In the visible spectrum the absorptivity of the zinc oxide is only about 30 per cent, and for lampblack it is 97 per cent. Hence the lampblack must become the hotter; for it absorbs energy at three times the rate, and it emits energy (low temperature radiation) at practically the same rate, as does the zinc oxide paint.—*Journal of the Washington Academy of Sciences*, ii., No. 19.

HE OXALATE-PERMANGANATE PROCESS FOR THE DETERMINATION OF COPPER ASSOCIATED WITH CADMIUM, ARSENIC, IRON, OR LEAD.*

By H. L. WARD.

It has been shown by Peters in a paper from the Kent Chemical Laboratory of Yale University (*Am. Journ. Sci.*, [4], x., 359) that copper oxalate may be precipitated by oxalic acid with practical completeness from solutions of a copper salt, provided the volume of the liquid is not too great and that the amount of copper present exceeds a minimum value, somewhat dependent on conditions. Still more recently (Gooch and Ward, *Am. Journ. Sci.*, [4], xxvii., 448), it has been shown that the condition of supersaturation which is responsible for failure in the precipitation of minimum amounts of copper oxalate may be easily overcome by freezing the solution, by addition of alcohol to the amount of 50 per cent of the solution, and, in a higher degree, by evaporation to dryness or by the addition of large amounts of acetic acid. The best and most convenient procedure for the precipitation of large as well as small amounts of copper oxalate ideal in composition, consists in adding 2 grms. of oxalic acid to 50 cc. or 4 grms. to 100 cc. of the 50 per cent acetic acid solution of the copper salt containing 5 to 10 per cent of nitric acid. The permanganate titration of the washed oxalate, in the presence of sulphuric acid, gives a very accurate determination of the copper.

The present paper is an account of attempts to apply the latter two processes in separations of copper from cadmium, arsenic, and iron, and in the determination of copper after separating the lead as sulphate.

In the experiments of the first part of Table I. a standard solution of copper sulphate was treated with 1 grm. of oxalic acid, added in the solid form to the boiling solution of about 50 cc. volume, and the liquid was then evaporated on the steam-bath. Extraction was made with the amounts of nitric acid indicated and water to make up a volume of 50 cc. The liquid was then boiled for ten minutes in contact with the precipitate and allowed to cool. The oxalate was collected upon asbestos in a perforated crucible and washed carefully with small amounts of water. The crucible with its contents was placed in a beaker and covered with about 200 cc. of hot water, containing 25 cc. of dilute sulphuric acid (1 : 4), and approximately N/10 potassium permanganate of known standard added to coloration.

The experiments of the second part of the table were performed similarly, except that the active mass of the oxalic acid was increased by the addition of more of the crystals before extraction. It will be noticed that when the concentration of the oxalic acid is slight, even the smaller amounts of nitric acid cause considerable errors, and that these errors increase with the percentage of nitric acid present. When, however, oxalic acid is added nearly to the saturation point of the liquid, the losses are not large and do not increase materially even when very large quantities of nitric acid are used in the extraction. It is evident, also, that about 1 mgrm. of copper goes into solution and the process is only accurate up to this amount.

The Separation of Copper from Cadmium as Oxalate.

It was found that the procedure outlined above does not secure a complete separation of copper from cadmium, as some of the latter element is included with the copper and cannot be dissolved even on treatment with concentrated solutions of hot nitric acid. If, however, nitric acid is added before precipitation, the oxalate of cadmium separates out only on evaporation, when it readily dissolves on treatment with more acid.

The first process used for the separation of copper and cadmium is as follows:—To the boiling concentrated solution of the nitrates or sulphates of copper and cadmium, containing 5 cc. of strong nitric acid, is added 4 grms. of crystallised oxalic acid. The solution is evaporated to dryness on the steam-bath and the residue is taken up with cold water containing nitric acid, it being unnecessary to heat the acid to bring about the solution of the cadmium. The precipitate is transferred to the perforated crucible by means of the filtrate, and washing is done with small amounts of water. The crucible is then placed in a beaker containing about 25 cc. of dilute (1 : 4) sulphuric acid and 200 cc. of water heated to boiling, and the dissolved oxalate is titrated with permanganate. It is necessary to use a large excess of oxalic acid in the precipitation, for some of it is destroyed by the nitric acid on evaporation to dryness. It will be seen from Table II. that when 10 per cent nitric acid is used in extraction, the errors, while all negative, are within permissible limits. On using 20 per cent acid, however, a considerably greater amount of oxalate goes into solution. This process, at best, is not extremely accurate.

It has been shown in the previous paper (*Am. Journ. Sci.*, 1909, [4], xxvii., 448) that copper may be precipitated very completely from solutions of its salts by oxalic acid, provided one-half the volume of the solution consists of glacial acetic acid, and that considerable amounts of nitric acid may be present without causing appreciable error. In separating copper from cadmium by this second process, precipitation is brought about by oxalic acid in a solution one-half of whose volume is glacial acetic acid containing free nitric acid. The oxalic acid is added in the solid form to the boiling solution and the resulting oxalate allowed to stand over night. Filtration, washing, and titration are made in the same manner as in the former method.

It will be noticed that in the first part of Table III., where small amounts of oxalic acid have been used in the precipitation, the results have a tendency to come low, especially when the larger amounts of nitric acid are present. At least 3·5 grms. to 4 grms. of oxalic acid

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* From the *American Journal of Science*, xxxiii., p. 423.

Table I.—*The Effect of Desiccation and Extraction with Nitric Acid.*

Copper taken. Grm.	Volume at precipitation. Cc.	Volume of liquid used in extraction. Cc.	Nitric acid. Cc.	Oxalic acid. Grms.	Copper found. Grm.	Error. Grm.
			A.—Small Amounts of Oxalic Acid.			
0·0504	50	50	1	1	0·0497	−0·0007
0·0504	50	50	2	1	0·0492	−0·0012
0·0504	50	50	3	1	0·0487	−0·0017
0·0504	50	50	4	1	0·0479	−0·0025
0·0504	50	50	5	1	0·0469	−0·0035
			B.—Large Amounts of Oxalic Acid.			
0·0504	50	50	3	6	0·0495	−0·0009
0·0504	50	50	4	6	0·0495	−0·0009
0·0504	50	50	5	6	0·0491	−0·0013
0·0504	50	50	5	6	0·0495	−0·0009
0·0504	50	50	10	6	0·0486	−0·0018
0·0504	50	50	15	6	0·0486	−0·0018
0·0504	50	50	20	6	0·0487	−0·0017
0·0504	50	50	25	5	0·0491	−0·0013
0·0504	50	50	25	5	0·0491	−0·0013
0·0504	50	50	40	5	0·0494	−0·0010

Table II.—*Separation of Copper from Cadmium by Desiccation and Extraction.*

Copper present. Grm.	Cadmium present. Grm.	Nitric acid on precipitation. Cc.	Volume at precipitation. Cc.	Oxalic acid. Grms.	Liquid used in extraction. Cc.	Nitric acid used in extraction. Cc.	Copper found. Grm.	Error. Grm.
0·0514	0·01	5	50	4	50	5	0·0507	−0·0007
0·0514	0·06	5	50	4	50	5	0·0506	−0·0008
0·0051	0·10	5	50	4	50	5	0·0048	−0·0003
0·0504	0·10	5	50	4	50	5	0·0502	−0·0002
0·0514	0·10	5	50	4	50	5	0·0508	−0·0006
0·0514	0·20	5	50	4	50	5	0·0508	−0·0006
0·1542	0·20	5	50	4	50	5	0·1537	−0·0005
0·0516	0·30	5	50	4	50	5	0·0507	−0·0009
0·0504	0·10	5	50	2	50	10	0·0488	−0·0016
0·0504	0·10	5	50	4	50	10	0·0494	−0·0010
0·0514	0·20	5	50	4	50	10	0·0500	−0·0014

Table III.—*Separation of Copper from Cadmium by Precipitation from a Solution containing a large amount of Acetic Acid.*

Copper present. Grm.	Cadmium present. Grm.	Volume at precipitation. Cc.	Oxalic acid. Grms.	Acetic acid. Cc.	Nitric acid. Cc.	Copper found. Grm.	Error. Grm.
0·0051	0·10	50	1	25	5	0·0052	+0·0001
0·0051	0·10	100	2	50	5	0·0045	−0·0006
0·0051	0·10	100	2	50	5	0·0043	−0·0008
0·0253	0·20	100	2	50	10	0·0251	−0·0002
0·0511	0·20	100	2	50	5	0·0512	+0·0001
0·1533	0·20	100	2	50	5	0·1545	+0·0012
0·1533	0·20	100	2	50	10	0·1525	−0·0008
0·0051	0·20	100	4	50	5	0·0049	−0·0002
0·0255	0·20	100	4	50	10	0·0257	+0·0002
0·0510	0·20	100	4	50	10	0·0512	+0·0002
0·1530	0·20	120	3·5	50	10	0·1533	+0·0003
0·0051	0·30	100	4	50	5	0·0053	+0·0002
0·0511	0·30	100	4	50	10	0·0520	+0·0009
0·0511	0·30	200	8	100	10	0·0510	−0·0001
0·1533	0·30	100	4	50	10	0·1556	+0·0023
0·1533	0·30	100	4	50	20	0·1556	+0·0023
0·1629	0·30	200	8	100	10	0·1643	+0·0014
0·1629	0·30	100	4	50	10	0·1636	+0·0007

Table IV.—*Separation of Copper from Arsenic by Desiccation and Extraction.*

Copper present. Grm.	Arsenic present as arsenate. Grm.	Volume at precipitation. Cc.	Oxalic acid. Grm.	Solution used in extraction. Cc.	Nitric acid used in extraction. Cc.	Copper found. Grm.	Error. Grm.
0·0051	0·10	50	1	50	2	0·0047	−0·0004
0·0504	0·05	50	1	50	2	0·0499	−0·0005
0·0504	0·05	50	1	50	2	0·0501	−0·0003
0·0504	0·10	50	1	50	2	0·0503	−0·0001
0·0504	0·10	50	1	50	2	0·0497	−0·0007
0·0504	0·20	50	1	50	2	0·0498	−0·0006
0·1533	0·20	50	1	50	2	0·1528	−0·0005

Table V.—*Separation of Copper from Arsenic by Precipitation in a Solution containing a large amount of Acetic Acid.*

Copper present.	Arsenic present as arsenate.	Volume at precipitation.	Oxalic acid.	Acetic acid present.	Nitric acid.	Copper found.	Error.
Grm.	Grm.	Cc.	Grms.	Cc.	Cc.	Grm.	Grm.
0·0051	0·20	100	2	50	0·2	0·0052	+0·0001
0·0051	0·30	100	4	50	0·4	0·0054	+0·0003
0·0511	0·30	100	4	50	0·4	0·0505	−0·0006
0·1530	0·20	100	4	50	10·0	0·1530	—
0·1533	0·30	100	5	50	10·0	0·1530	−0·0003

should be used for every 100 cc. of solution, but more causes trouble by crystallising out. It is then necessary to dissolve the crystals in water, which may cause a slight error due to solubility, or to use the mixture of equal parts water, acetic acid, and alcohol recommended by Classen (*Zeit. Anal. Chem.*, xviii., 175). When very little copper is present not more than 5 cc. of nitric acid should be added before precipitation. With amounts exceeding 50 mgrms. 10 cc. should be used to 100 cc. of liquid. A separation may be thus secured from 0·20 grm. of cadmium. With 0·3 grm. of cadmium and 50 mgrms. of copper it is possible to obtain satisfactory results when the volume on precipitation is increased to 200 cc. If 0·15 grm. of copper is present, even under these conditions, some of the cadmium comes down with the copper. Increasing the volume of nitric acid present to 20 cc. does not entirely eliminate the error when the volume is kept at 100 cc. Another method, used in the last experiment of the table, is to precipitate in water solution and add the acetic acid afterward to throw out the last traces of copper. This secures a somewhat sharper separation in the case of the larger amounts of the metals.

The Separation of Copper from Arsenic as Oxalate.

In the first attempt to separate copper from arsenic the evaporation process used for cadmium was tried. No nitric acid was added on precipitation, as the arsenic comes down only on evaporation and may be dissolved again. Less nitric acid was also used in the extraction. In the experiments of Table IV. the arsenic was present in the form of potassium arsenate, as it was found much easier to make a sharp separation when the arsenic was in the higher condition of oxidation. Even then it was difficult with the larger amounts to bring the arsenic entirely into solution.

On precipitation from a solution containing a large amount of acetic acid according to the procedure before described for cadmium, a very sharp and satisfactory separation was secured. The results of some experiments appear in Table V. In the case of the larger amounts of copper it was found necessary to add nitric acid before precipitation to render the precipitate crystalline and suitable for filtration.

(To be continued).

BLOOD CORPUSCLES AND LEATHER.

By J. C. THOMLINSON, B.Sc.

The quality of leather may to some slight extent be judged by examining it for blood corpuscles.

Osmosis may be useful in the process of preparing; as a safe guide of the processes which furnish the best finished leather all blood corpuscles would be removed or ruptured.

They rarely occur microscopically discernible in good leather, and all processes in preparing it should be regulated to just rupture the blood corpuscles osmotically and render other cells efficient as making the tissue as plastic as would be rendered by turgid protoplasm. In curing, the osmotic pressure of solutions would be so rendered that it is always below that of the corpuscles and tissue cells, thus producing rupture of blood discs and the above turgid condition of living protoplasm containing cells.

THE DETERMINATION OF TOTAL MANGANESE IN SOILS.

By ROSS A. GORTNER and CLAYTON O. ROST.

Introduction.

It is a well-known fact that the gravimetric estimation of small quantities of manganese, such as occur in rocks or soils, is highly inaccurate even when great care is used. The inaccuracy may be caused by a number of factors, including incomplete separation from the iron and aluminium, incomplete precipitation, and contamination of the precipitate by other substances. These errors, because of the small amounts of manganese present, can not be depended on to balance each other (see Hillebrand, *Bull.* 422, 116, U.S. Geological Survey). The usual method which is now employed is to determine the manganese colorimetrically after oxidation to permanganic acid. Various means of effecting this oxidation have been employed. The oldest method is the oxidation of the manganese in nitric acid solution by the addition of lead peroxide (Pichard, *Comptes Rendus*, Dec. 30, 1872). This material proved unsatisfactory owing to the necessity for the removal of the excess of the lead peroxide, which settled very slowly.

Acting on the suggestion of Marshall (Chem. News, 1901, lxxxiii. 76), Walters (*Ibid.*, 1901, lxxxiv., 239) substituted ammonium persulphate for the lead peroxide. All of Walters' determinations were made either on steel, pig irons, or blast furnace cinders. This method was later adopted by Hillebrand (*loc. cit.*) and Washington ("The Chemical Analysis of Rocks," 1910) for the determination of total maganese in rocks.

Essentially the method consists in decomposing the rock powder in a platinum basin by means of hydrofluoric and sulphuric acids, expelling the excess of hydrofluoric acid by repeated evaporation with small amounts of sulphuric acid, evaporating almost to dryness, diluting with 1 : 1 nitric acid, filtering, and oxidising the manganese to permanganic acid by the addition of ammonium persulphate. The permanganic acid solution is then diluted to a known volume and the colour read against a solution of known strength in a colorimeter.

In applying this method to Nebraska soils, following the detailed directions of Washington (*loc. cit.*) we have found that in many cases we could not obtain concordant results on duplicate determinations, the variation between duplicates being sometimes as much as 200 per cent. Brinton (*Journal of Industrial and Engineering Chemistry*, 1911, iii., 237) has already noted that in some iron ores the treatment with sulphuric and hydrofluoric acids does not give complete extraction of the maganese, and we have found that this is the case with all of the soils which we have investigated. In most of these soils, three, and in some cases four, extractions with hydrofluoric and sulphuric acids were necessary before all of the manganese was obtained in solution. Inasmuch as each extraction requires nearly three hours, it will be seen that to accurately determine manganese in soils by this method is a very tedious operation. We have, therefore, endeavoured to devise a method which is much more rapid, more accurate, requires less attention, and eliminates all fumes of hydrofluoric acid or sulphur trioxide. The smaller amount of platinum required in the process is also a decided advantage.

As an oxodiser we have used sodium bismuthate instead of ammonium persulphate, inasmuch as it gives a better oxidation, always giving the true permanganate colour, while the persulphate oxidation often produces a reddish tint that is difficult to read accurately. Blair (*Journ. Am. Chem. Soc.*, xxvi., 793; also "Chem. Anal. of Iron," 7th ed., p. 121) and Brinton (*loc. cit.*) seem to recognise the superiority of the "bismuthate" oxidation by stating that "for samples containing not over 2 per cent. of manganese the bismuthate is the most accurate method known." Walters (*loc. cit.*) states that the persulphate oxidation does not always progress smoothly, for when the salt is dry "the reaction is very incomplete and irregular and not to be depended on," a fact that is not mentioned in the description of the method by Hillebrand or Washington. By moistening the persulphate much more concordant results are obtained, but we have found that the bismuthate is much more reliable than than the persulphate. In some instances we were unable to oxidise all of the manganese by means of ammonium persulphate, but when these same solutions were reduced with sulphurous acid and reoxidised with bismuthate the correct percentage of manganese was obtained. The bismuthate method has the added advantage over the persulphate in that it is not necessary to add silver nitrate to catalyse the reaction.

Experimental.

The Estimation of Manganese in Soils by Walters' Method.—The soil, which had been ground to pass through bolting cloth of 0·1 mm. mesh, was treated with hydrofluoric and sulphuric acids as described by Washington (*loc, cit.*) and the manganese determined in the extract. The first part of table 1 shows the results which were obtained on eight different soils. Soil No. 3490 was selected to determine whether or not all of the manganese was rendered soluble with one extraction, and it was found that in some instances four extractions were necessary to completely remove all traces of manganese. In those samples where several extractions were made, the total amount of manganese obtained was nearly a constant, but even in these there is too great an error for exact work, for, although the maximum difference between duplicates is only 0·10 per cent, this error represents almost 10 per cent of the total manganese present.

The Estimation of Manganese in Soils by our Method.—One grm. of soil is intimately mixed with 4 grms. of manganese-free, dry, sodium carbonate and fused in a 20 cc. platinum crucible over a blast lamp until the melt is quiet, usually after about ten minutes' fusion. The liquid mass is then poured into a platinum basin and the basin rotated in order to obtain the melt in a thin film, thus providing for more rapid solution. The melt and the crucible are then treated with about 100 cc. of distilled water and heated on a water-bath in either a platinum or a porcelain dish until the fused product is completely integrated. (Glass should not be used inasmuch as the alkali might attack the glass and dissolve out some of the manganese which is present in most laboratory glass, including Jena apparatus. See Gortner, *Am. Chem. Journ.*, 1908, xxxix., 157.) The crucible is then removed from the dish, any adhering solution washed off, and the mixture acidified with 130 cc. of 35 per cent (by weight) sulphuric acid, and diluted to 250 cc.

(This exces of sulphuric acid is employed inasmuch as the oxidation progresses more rapidly and basic bismuth salts do not prceipitate. The same results may be obtained when half of this quantity of acid is used, but the oxidation requires several minutes' boiling and the permanganic acid solution must be filtered through asbestos in order tofree the solution from precipitated bismuth salts).

Should there be a heavy precipitate of silica at this point it is advisable to filter, using a Buchner funnel and filtering by suction. This is seldom necessary, however, for in most cases the silica does not precipitate to any extent, but merely produces a slight opalescence which does not interfere with the premanganate readings. 100 cc. of this solution are then placed in a beaker and from 0·25 grm. to 1 grm. of sodium bismuthate added, depending on the quantity of manganese present. We have found that 0·25 grm. is sufficient where the manganese content does not exceed 0·20 per cent. The oxidation mixture is then heated to boiling and the boiling continued until the liquid has the true permanganate tint. If there is any red coloration the boiling has not been continued long enough. The solution is then cooled and read in a colorimeter or Nessler's glasses against a standard solution of permanganic acid which has been prepared by reducing a solution of potassium permanganate in 20 per cent sulphuric acid by the cautious addition of sulphurous acid, and re-oxidising with bismuthate. This standard solution should contain about 0·2 mg. of MnO per 10 cc. From the ratios thus obtained the quantity of manganese in the original sample is calculated. After a little practice, the complete operation can be carried out in an hour and a half, so that in this respect alone the method is greatly to be preferred.

When duplicate determinations are desired only one fusion is necessary, for two separate oxidations may be taken from the total 250 cc. In the data which are given in the last column of table 1 each figure represents a separate fusion and oxidation, and in the sixteen determinations, representing duplicate fusions on eight different soils, the maximum difference between duplicates amount to only 0·002 per cent. No determinations were discarded in compiling this table.

Table I.—*Percentage of MnO Found by Walters' Method as Described by Washington, and by our New Method.*

Expt. No.	Soil No.	Walters' method. MnO in extractions I. to IV.					Authors' method.
		I.	II.	III.	IV.	Total.	
1.	3490	0·082	0·020	0·004	Trace	0·106	0·109
2.	3490	0·080	0·027	0·005	?	0·112	0·111
3.	3490	0·060	0·042	Trace	?	0·102	
4.	3490	0·095	0·013	Trace	?	0·108	
5.	3490	0·095	0·013	Trace	?	0·108	
6.	3490	0·064	0·016	(*a*)			
7.	3490	0·046	0·029	(*a*)			
8.	3486	0·045		(*a*)			0·107
9.	3486	0·052					0·105
10.	3487	0·018					0·111
11.	3487	0·028					0·110
12.	3488	0·020					0·111
13.	3488						0·112
14.	3489	0·025					0·120
15.	3489	0·031					0·119
16.	3491	0·044					0·123
17.	3491	0·044					0·125
18.	3483	0·060					0·096
19.	3483	0·060					0·098
20.	3459	0·033					0·067
21.	3459						0·067

(*a*) Not determined.

Summary.

1. We have found that Walters' method for the determination of small quantities of managanese, as described by Washington and Hillebrand, is not applicable to Nebrasks soils, but that in some instances four extractions on a 1-grm. sample with hydrofluoric and sulphuric acids were necessary before all of the manganese was obtained in solution.

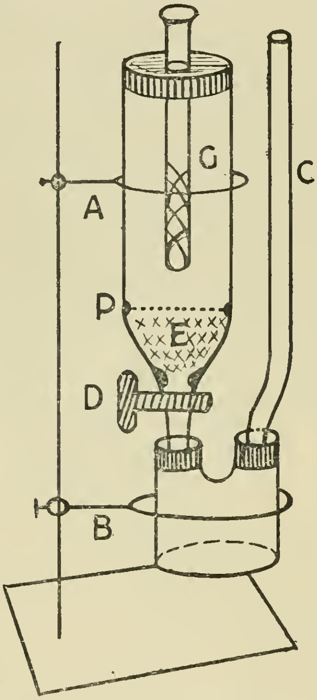
2. We have found that when such soils are fused with sodium carbonate and the solution of this melt is acidified with sulphuric acid and oxidised by means of sodium bismuthate, that all of the manganese is oxidised to permanganic acid, and may easily be estimated colorimetrically.

3. We claim for this method greater rapidity, absence from irritating fumes, less danger of loss by spattering, more ease of operation in unexperienced hands, duplicate determinations on one sample of soil, and much greater accuracy.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

THE DETERMINATION OF SOLUBILITY.

By W. R. FORBES, B.Sc.

The apparatus described below is modified from that of Goldschmidt (*Zeit. Phys. Chem.*, 1895) as figured by Findlay ("Phase Rule," 1906). The stirrer has been simplified, the filter area widened, and the use of rubber eliminated, thus increasing the range of the apparatus. It has also been rendered more compact. Water and the salt are placed in A, and the tap D closed. When the solution is saturated D is opened and the solution is sucked into the weighing bottle B by exhausting through C. B is then taken from its ground unions with A and C, dried, and weighed. G is the stirrer.



While in use the apparatus is fitted in the stand as shown, and placed in a water-bath.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1912.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society through death:—On August 7th, 1912, of Mr. Robert Holford MacDowall Bosanquet, F.R.S (who was elected a Fellow on February 2nd, 1865); on August 15th, 1912, of Dr. H. O. Jones, F.R.S., and of Dr. John Wade.

The President read the following Address, which had been presented to the Royal Society on the celebration of the 250th Anniversary of its Foundation in July, 1912:—

The Chemical Society to the President, Council, and Fellows of the Royal Society.

Greeting,—Amongst the many Learned Bodies represented here to-day there is certainly none which can wish to offer you more sincere and heartfelt congratulations than the Chemical Society.

The Officers, Council, and Fellows of our Society desire to associate themselves with you in celebrating the Two-hundred-and-fiftieth Anniversary of the birth of a scientific corporation which in the distinction of its history is assuredly second to no similar body in the World. The great army of diligent and determined workers who are united by the solemn covenant to extend Man's knowledge of Nature look with reverence and gratitude on the Society which, during two and a-half centuries, has kept alive in these Islands the sacred fire of Research, and has included within its Fellowship men whose names and achievements are amongst the most imperishable glories of the human race.

We desire to take this opportunity of expressing, however imperfectly, our indebtedness to the Society of *Boyle*, of *Cavendish*, of *Priestley*, of *Dalton*, and of *Davy*, and we are proud to remember that these early masters of our Science, by the stimulus which their investigations gave to the growth of Chemical Knowledge, led to the origin of our Society by a natural process of gemmation from your body. It is, therefore, in the capacity of children, and as an act of filial piety, that we desire to offer to you, our parents, dutiful felicitations to-day.

We would take this opportunity again of gladly and freely acknowledging before all men that whatever success our own Society may have achieved, whatever may be the dignity to which we have attained, and whatever service to Science and to Mankind we may have been privileged to perform, we largely owe to the inspiration which our founders drew from the magnificent traditions of the Royal Society. This quickening influence has been, and, we we trust, may long be, maintained by a close association with you, by the community of Fellowship which exists between your Society and ours, and by the kindred ideals and aspirations which animate us both.

Signed on behalf of the Chemical Society,

Percy F. Frankland, President.
Alexander Scott, Treasurer.
Arthur W. Crossley } Secretaries.
Samuel Smiles }
Horace T. Brown, Foreign Secretary.

Sealed in Council this Twentieth Day of June, One Thousand Nine Hundred and Twelve.

It was announced that, during the vacation, the rooms of the Society had been redecorated throughout, and that a fan had been installed with the object of securing more efficient ventilation in the Meeting Room.

Messrs. T. V. Barker and W. E. Hawkins were formally admitted Fellows of the Society.

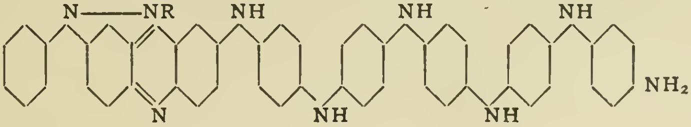
Certificates were read for the first time in favour of Messrs. James Henry Young Baker, 86, Chestnut Avenue, Hamilton, Ontario; Douglas Anderson Bowack, 15, Belsize Square, Hampstead, N.W.; Richard Westmann Challinor, Quidington, Emmerick Street, Leichardt, Sydney, N.S.W.; Frank Andrew Coombs, Sydney Technical College, Sydney, N.S.W.; Walter Henry Dixon, 51, High Street, East Grinstead; H. H. Dodds, M.Sc., Explosives Works, Umbogintwini, Natal; George Davidson Elsdon, B.Sc., City Analysts' Laboratory, Birmingham; Harold Heath Gray, B.Sc., University Hall, More's Gardens, Cheyne Walk, Chelsea, S.W.; Ardesir Naserwanji Peston Jamas, M.A., B.Sc., Karrim Building, Grant Road, Bombay; Edgar Jobling, B.Sc., H.M. Patent Office, Southampton Buildings, W.C.; Frederick Russell Lankshear, B.A., M.Sc., Dalton Hall, Victoria Park, Manchester; Stanley Isaac Levy, B.A., B.Sc., St. John's College, Cambridge; Ernest Lawson Lomax, M.Sc., Mowbreck, Farington, Preston; George Francis Morrell, Ph.D., B.Sc., 7, Claylands Road, Kennington Gate, S.W.; Ernest Moore Mumford, B.Sc., 75, High Street, Chorlton-on-Medlock, Manchester; Leslie Frank Newman, B.A., Downing

College, Cambridge; William Moore Nicholls, 17, Ferrybridge Road, Castleford; Maximilian Nierenstein, Ph.D., 30, Cavendish Road, Henleaze, Bristol; Lionel Orange, B.Sc., 148, Barkworth Road, N. Camberwell, S.E.; John William Patterson, 88, Park Road, West Dulwich, S.E.; Charles Etty Potter, B.Sc., 9, Church View, Church Lane, Heckmondwike; Jitendra Nath Rakshit, 11/1, Bahar Urijapur Road, Calcutta; Martin Remers, L.R.C.P., L.R.C.S., 24, Chorley Old Road, Bolton; Albert Sasson, Department of Agriculture, Alexandria, Egypt; Harold Archibald Scarborough, B.Sc., 60, Highbury Terrace, Hill Street, Coventry; Walter Scott, 2, Wordsworth Avenue, Cardiff; Kunjo Behary Seal, 5, Nilmony Dutt Lane, Calcutta; Cyril Edgar Sladden, B.A., 12, Charleville Circus, Sydenham, S.E.; Thomas Alfred Smith, B.Sc., 3, Colgrave Street, Lincoln; William Charles Smith, Church Lane, Lowton, Newton-le-Willows; Victor Steele, 438, New Cross Road, New Cross, S.E.; Alfred Ernest Stephen, Bank of New South Wales, Sydney, N.S.W.; William Compton Till, M.Sc., Barnacle House, Coventry; Paul Jenner Ure, c/o Dr. Ure, George Street, Brisbane, Queensland.

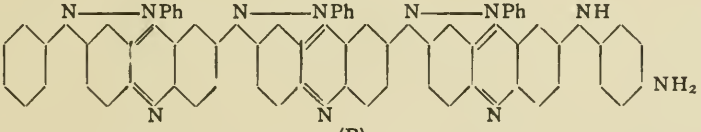
Of the following papers those marked * were read:—

*250. "*Aniline-black and Allied Compounds.*" Part III. By Arthur George Green and Salomon Wolf.

The authors have studied the action of various primary amines on nigraniline. They find that this base, when in a finely divided state, reacts readily in the cold with neutral or weakly acid solutions of amine salts, giving compounds in which 1 molecule of amine has entered into combination with 1 molecule of nigraniline. The products obtained are represented as monoarylazonium compounds of the constitution (A).



(A).



(B).

In their formation a portion of the quinonoid groups has undergone reduction, and the product resembles protoemeraldine in character, although considerably blacker in colour. By treatment with hydrogen peroxide or chromic acid, by which the compound is reoxidised to a higher (probably tri-) quinonoid stage, it is enabled to react again with a further quantity of a primary amine; and on several repetitions of these alternate treatments 3 molecules of amine can eventually be introduced. At this stage the product (when aniline is the amine employed) has all the properties characteristic of "ungreenable aniline-black" produced on the fibre in the usual way. The analyses and properties agree with the constitution (B).

By employing *p*-bromoaniline in place of aniline, the corresponding tribrominated aniline-black, of very similar properties to the above, was obtained, the analyses of which substantiated the above formula.

Monoarylazonium compounds were also prepared and analysed, in which the reacting amines were *o*-toluidine, *p*-toluidine, *m*-bromoaniline, β-naphthylamine, tolidine, and diaminodiphenylmethane. All these products are very similar to the aniline condensation product.

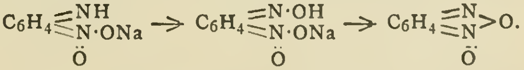
*251. "*Alkaline Condensation of Nitrohydrazo-compounds. Part III. Influence of Ortho-groups on their Formation and Condensation.*" By Arthur George Green and Frederick Morris Rowe.

The presence of sulpho- or nitro-groups in the ortho-position with respect to basic nitrogen prevents or impedes the normal reactions; thus 2 : 4-dinitroaniline and *p*-nitroanilinesulphonic acid cannot under ordinary conditions be oxidised to the azo-compounds, nor can their corresponding hydrazines be condensed with chloronitro-compounds to give hydrazo-compounds, except with the extremely reactive picryl chloride. A search for the cause of this impeding action, which is the exact reverse of that observed in the derivatives of *p*-nitrotoluene, pointed to its being due to the occurrence of condensation between the basic nitrogen group and the *o*-nitro- or *o*-sulphonic group. This was confirmed by the observation that when *o*-nitroaniline is oxidised with hypochlorites in alkaline solution it is converted entirely into benz*iso*oxadiazole (benzfurazan) oxide ("dinitrosobenzene") (see following abstract), whilst the normal oxidation to 2 : 2′-dinitroazobenzene only occurs when strictly neutral conditions are maintained, that is, when isomerisation of the nitroamine into the quinonoid form is prevented.

A similar condensation appears to occur when the hydrazo-compounds containing *o*-nitro-groups are treated with alkalis, and consequently the blue quinonoid salts of these compounds are very unstable. The conditions of formation and reaction were studied for the following azo- and hydrazo-compounds:—The 2 : 2′-dinitro, 2 : 4 : 2′ : 4′-tetranitro-, and 2 : 2′-dichloro-4 : 4′-dinitro-azobenzenes; the 2 : 2′-dinitro-, 2 : 4 : 4′-trinitro, 2 : 4 : 2′ : 4′-tetranitro-, 2 : 4 : 6 : 4′-tetranitro-, 2 : 4 : 6 : 2′ : 4′-pentanitro-, 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitro-, and 2 : 2′-dichloro-4 : 4′-dinitro-hydrazobenzenes.

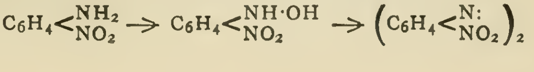
*252. "*Existence of Quinonoid Salts of* o-*Nitroamines and their Conversion into Oxadiazole Oxides.*" By Arthur George Green and Frederick Morris Rowe.

In the course of the previous investigation it was observed that when *o*-nitroaniline is oxidised with hypochlorites in strongly alkaline solution it is quantitatively converted into the compound hitherto known as "dinitrosobenzene" or "*o*-benzoquinonedioxime peroxide." This reaction, together with several other considerations, has led the authors to believe that the compound and its analogues are more correctly represented as benz*iso*oxadiazole (benzfurazan) oxides, and that the change takes place thus:—



$$\mathrm{C_6H_4}\begin{array}{l}\mathrm{=NH}\\ \mathrm{=N\cdot ONa}\\ \quad\ddot{\mathrm{O}}\end{array} \rightarrow \mathrm{C_6H_4}\begin{array}{l}\mathrm{=N\cdot OH}\\ \mathrm{=N\cdot ONa}\\ \quad\ddot{\mathrm{O}}\end{array} \rightarrow \mathrm{C_6H_4}\begin{array}{l}\mathrm{=N}\\ \mathrm{=N}\\ \quad\ddot{\mathrm{O}}\end{array}\!>\mathrm{O}.$$

This formula for the product involves no migration of an oxygen atom, either here or in Zincke and Schwartz's method of formation from *o*-nitrotrisazobenzene. If its correctness is admitted, the reaction affords strong support for the existence of *aci*-quinonoid salts of *o*-nitroamines, and this conclusion is still further strengthened by the observation that *o*-nitroaniline dissolves in alcoholic potassium hydroxide with an orange-red colour, and that the oxidation in neutral solution takes an entirely different and more normal course, giving 2 : 2′-dinitroazobenzene:—



$$\mathrm{C_6H_4}<^{\mathrm{NH_2}}_{\mathrm{NO_2}} \rightarrow \mathrm{C_6H_4}<^{\mathrm{NH\cdot OH}}_{\mathrm{NO_2}} \rightarrow \left(\mathrm{C_6H_4}<^{\mathrm{N:}}_{\mathrm{NO_2}}\right)_2$$

The formation of benz*iso*oxadiazole (benzfurazan) oxides by alkaline oxidation of *o*-nitroamines appears to be a general one, and affords a convenient method of preparing these compounds.

*253. "*The Essential Oil of Cocoa.*" By James Scott Bainbridge and Samuel Henry Davies.

The authors find that the aromatic principle of the cocoa bean is an essential oil.

Two thousand kilos. of cocoa nibs were subjected to distillation with steam. From the distillate 24 cc. of a purified oil were isolated, which proved to be a mixture of esters formed during the fermentation of the cocoa bean with the true essential oil. The latter consists chiefly of a *d*-linalool. Octoic acid and other fatty acids probably derived from cocoa-butter were present, and a small proportion of a stable nitrogenous compound, which was not identified.

*254. "*Studies in Chemical Crystallography. Part I. Co-ordination, Isomorphism, and Valency.*" By Thomas Vipond Barker.

Some new cases of isomorphism of unusual types were described, the bearing of which on chemical and crystallographic theory was discussed. The conclusion was drawn that the ordinarily accepted theory of valency structure is incapable of offering any useful information concerning the structure of the compounds in question. Co-ordination structures, on the other hand, bring out pronounced chemical analogies, from which it is inferred that such structures are not only supported by the crystallographic evidence, but also are more general in inorganic compounds than was formerly suspected. The theories of Sollas and of Barlow and Pope were criticised from the point of view of isomorphism, and the conclusion was drawn that Barlow and Pope's theory in its present form is certainly incapable of general application to inorganic compounds. The view is entertained that the true volume unit in crystalline structures is the atomic rather than the valency volume.

*255. "*The Oxidation of Aconitine.*" By Francis Howard Carr.

It was shown that a neutral substance, *oxonitin*, $C_{22}H_{29}O_9N$, together with acetaldehyde, results from the oxidation of aconitine with potassium permanganate in acid solution. Oxonitin crystallises in white prismatic crystals, m. p. 276—277°; it is sparingly soluble in all solvents, neutral in reaction, and does not combine with acids or alkalis, nor does it give a precipitate with the common alkaloidal reagents. Methyl iodide, hydroxylamine, and acetic anhydride fail to act upon it. It contains three methoxyl groups, and since it gives, like aconitine, acetic and benzoic acids on hydrolysis, it contains also an acetyl and benzoyl group. It may be presumed that the $N{\cdot}CH_3$-group contained in aconitine is unchanged; its constitution may therefore be represented thus:— $C_{10}H_9O_2NMe(OBz)(OAc)(OMe)_3$.

Oxonitin yields different products according as the hydrolysis is brought about by alkali or by hydrochloric acid; in the former case a neutral substance, and in the latter an alkaloid, is produced; in both instances acetic and benzoic acids are formed. The investigation is being continued with a view to the elucidation of the constitution of the hydrolytic substances and of the hypothetical base, $C_{10}H_{15}O_2N$.

Discussion.

Mr. Brady said that he had been working on the compound described for some time, but had not been able to establish the presence of the acetyl group, and inquired how the author had identified it.

256. "*Some Time-reactions Suitable for Lecture Experiments.*" By William Gerald Glendinning and Alfred Walter Stewart.

In concentrated solution, potassium iodide, potassium persulphate, and starch react practically instantaneously, producing starch-iodine blue. When sodium thiosulphate is also present, the appearance of the colour takes a longer or shorter time, according to the amount of thiosulphate added. When carried out in the way described below, the reaction forms a simple demonstration of induction periods.

The solutions required are M/5-potassium iodide, N/10-thiosulphate, a saturated solution of potassium persulphate, and some starch solution. A burette is filled with the thiosulphate solution, and fixed over a vessel into which are placed 10 cc. of the iodide solution, 5 cc. of the persulphate solution, and 5 cc. of the starch solution. The starch-iodine blue is formed immediately, and is exactly removed by the thiosulphate. If three extra drops of the thiosulphate are added, the blue colour will not return until a lapse of sixty-three seconds; and if six or nine drops be used, the period is correspondingly prolonged. In more dilute solutions, of course, much longer intervals are obtained.

In order to avoid error in timing, due to adding the thiosulphate drop by drop, the following device may be employed:—A T-piece is passed through a loosely-bored cork, which is clamped above the vessel used for the reaction in such a way that the T-piece lies horizontally. A second cork with a flat side cut on it is fixed firmly on the straight end of the T-piece. The requisite number of drops of thiosulphate solution are then dropped on to a microscope cover glass, which rests on the flat cork, and when it is necessary to add this to the solution, the T-piece is turned round in the bore of the cork so that the cover glass drops off the flat side into the reaction vessel. In this way the whole of the thiosulphate can be added at once. An ordinary square cover glass will retain ten drops easily if care is taken.

The quantities given above are sufficient to allow of the successive addition of three, six, and nine drops of thiosulphate solution without exhausting the other reagents to an undue extent.

Two modifications of the above reaction are as follows:—A solution of hydrogen peroxide may be substituted for the persulphate solution, the rest of the reagents remaining the same. In this case, if several titrations have to be carried out with the same solution, it is advisable to add some fresh starch each time the solution is rendered colourless, as otherwise a good tint is not obtained. Using 2 cc. of potassium iodide solution, 10 cc. of hydrogen peroxide solution (approximately 20 volumes), 8 cc. of starch solution, and 50 cc. of water, when three drops of thiosulphate solution are added the colour appears after about half a minute, the reaction being much more rapid than when potassium persulphate is used.

Instead of using hydrogen peroxide itself, a saturated solution of barium peroxide may be employed; but in this case certain modifications are necessary. The method of working is as follows:—The barium peroxide solution is placed in the reaction vessel, and to it some phenolphthalein is added. Sufficient hydrochloric acid to decolorise the phenolphthalein is poured in, and then the starch and potassium iodide are added. The starch-iodine blue is decolorised with thiosulphate as before, and a small excess of thiosulphate added. Should the liquid show any signs of becoming alkaline, as can be seen from the phenolphthalein tint reappearing, a few drops of hydrochloric acid are added. It is inadvisable to have a large excess of acid owing to its effect on the thiosulphate solution.

257. "*The Problem of Strong Electrolytes.*" (Preliminary Note). By James Kendall.

The dissociation formula $m^2/(1\ \ m)v = k + c\,.\,(1\ \ m)/m$ has been recently shown by the author from experimental results (*Trans.*, 1912, ci., 1275) to hold for all acids. The above formula may be arrived at theoretically by the assumption of the presence of complex ions of the type $(R_2)^{\cdot\cdot}$ or $(X_2)''$ in the aqueous solution of an electrolyte RX. This is already known to be the case for mercurous chloride, which ionises as $(Hg_2)^{\cdot\cdot}(Cl')_2$.

The equations for equilibrium, under the assumption of one complex ion, are of the form :—

$$RX \rightleftarrows R^{\cdot} + X' \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

$$2RX \rightleftarrows (R_2)^{\cdot\cdot} + 2X' \quad . \quad . \quad . \quad . \quad (2).$$

Let the undissociated ratio at dilution v be $1 - m$; of the total dissociated part m let n, in the case of one ion, be complex.

Then, applying the law of mass action to the balanced equations (1) and (2) above, we obtain :—

$$(m/v) \,.\, [(m - n)/v] = k \,.\, (1 - m)/v \quad . \quad . \quad (3),$$

$$(n/2v) \,.\, (m^2/v^2) = (c/2) \,.\, (1 - m)^2/v^2 \quad . \quad . \quad (4),$$

where k and $c/2$ are constants.

From Equation (4) we have $n = cv(1 - m)^2/m^2$; substituting for n in (3) we finally arrive at the equation—

$$m^2/(1 - m)v = k + c \,.\, (1 - m)/m \quad . \quad . \quad . \quad (5),$$

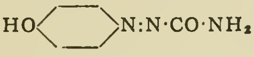
already found by experiment to hold in the case of all acids.

By the assumption that the ions form complexes of the above type in aqueous solution, the above dissociation formula, first obtained experimentally for acids only, may extended to cover all uni-univalent electrolytes.

258. "*Action of Semicarbazide Hydrochloride on the* p-*Quinones*." (Preliminary Note). By ISIDOR MORRIS HEILBRON and JAMES ALEXANDER RUSSELL HENDERSON.

Thiele and Barlow (*Annalen*, 1898, cccii., 315) and Borsche (*Annalen*, 1904, cccxxxiv., 143) have already examined the action of semicarbazide hydrochloride on *p*-benzoquinone and on some of its derivatives, and found that the compounds formed gave phenols on treatment with sodium hydroxide. They suggest that the condensation products exist in tautomeric forms as semicarbazones (I.) and *p*-hydroxyazoformamides (II.) :—

I.



II.

It seemed, however, to the authors that further evidence was necessary to decide the true constitution of the free condensation products. A spectrographic investigation has been made of the substances obtained by the action of semicarbazide hydrochloride on various *p*-quinones, as well as of the salts and esters of these products. The absorption curves of all the products are very similar, and practically identical in shape and position to those obtained by Tuck (*Trans.*, 1907, xci., 449) for the *p*-hydroxyazo-compounds.

The *p*-quinone condensation products with semicarbazide hydrochloride are therefore true hydroxyazo-compounds of the type (II.).

The investigation is at present being extended to other similar types of compounds.

259. "*The Interaction of Azoimide and Nitrous Acid*." (Preliminary Note). By EMIL ALPHONSE WERNER.

Whilst the decomposition of hydrazine by nitrous acid constitutes one of the numerous methods by which azoimide may be obtained, the further action of nitrous acid on azoimide does not appear to have been hitherto examined. When a solution containing sodium azide and sodium nitrite is treated with dilute sulphuric or acetic acid, interaction immediately takes place with brisk evolution of gas, consisting of nitrogen and nitrous oxide. The change takes place in accordance with the equation $N_3H + HNO_2 = N_2 + N_2O + H_2O$, and even with very dilute solutions the reaction is completed in a few minutes.

This interaction may be made the basis of a simple and rapid method for the analysis of azides, either by carrying out the decomposition in a nitrometer, and measuring the volume of evolved gas, or by titration of a dilute solution of the azide, previously acidulated with dilute sulphuric acid, with N/10-solution of sodium nitrite.

The following results were obtained with a sample of commercial sodium azide (Schuchardt) in a preliminary trial :—

I. 0·05 grm. of the azide and 0·06 grm. of sodium nitrite (95 per cent) dissolved in 1·5 cc. of water were introduced into a nitrometer, and 0·5 cc. of dilute sulphuric acid was added.

Gas evolved = 33·55 cc. (dry) at 0° and 760 mm.

0·05 grm. of pure sodium azide requires 34·46 cc.

Hence, 97·35 per cent of pure sodium azide was present in the sample.

II. A solution was prepared by dissolving 1 grm. of the sodium azide in 100 cc. of water.

Ten cc. diluted with 70 cc. of water, and 2 cc. of dilute sulphuric acid (1 : 7) added, were titrated with a N/10-solution of sodium nitrite (1 cc. = 0·0065 N_3Na) until a drop of the solution after being well stirred gave an immediate blue colour with starch and potassium iodide solution: 15 cc. of the sodium nitrite solution were required. Hence, 97·5 per cent of pure sodium azide was present in the sample.

The latter result is very probably the more accurate, as a small quantity of nitrous oxide is likely to remain in solution in the nitrometer method. It is intended to test the method more fully with some pure azides.

260. "*Benzylmethyl-, Benzylethyl-, and Allyl-ammonium Nitrites*." By PRAFULLA CHANDRA RAY and RASIK LAL DATTA.

Benzylmethylammonium nitrite has been obtained in solution only by the double decomposition between silver nitrite and the amine hydrochloride. During the process minute drops of an oily liquid make their appearance and float on the surface. After the end-point is carefully attained, the solution is left to remain, when within a short time the oil increases considerably, and settles down in globules at the bottom of the vessel. The oil was found to be a nitroso-compound, and analysis proved it to be *benzylmethylnitrosoamine*.

Found—C = 63·54 ; H = 6·79 ; N = 18·36. $C_8H_{10}ON_2$ requires C = 64·00 ; H = 6·66 ; N = 18·66 per cent.

The supernatant liquid was examined from time to time, and found to respond to the nitrite reaction. Evidently after the conversion of the greater portion of the nitrite into the nitroso-compound a process of equilibrium sets in, thus :—

$$C_7H_7{\cdot}NHMe,HNO_2 \rightleftarrows C_7H_7{\cdot}NMe{\cdot}NO + H_2O.$$

Benzylethylammonium nitrite has been obtained by the usual method as a pale yellow crystalline substance.

Found—C = 59·02 ; H = 7·83 ; N = 15·45. $C_9H_{14}O_2N_2$ requires C = 59·34 ; H = 7·69 ; N = 15·38 per cent.

The salt sublimes at 50—55° with simultaneous decomposition, although it begins to decompose slowly at the ordinary temperature (24°) in a vacuum. The sublimate consists of white glistening crystals. The products of decomposition are nitrogen, a nitroso-compound, and alcohols, according to the equations :—

$$C_9H_{14}O_2N_2 = C_7H_7{\cdot}OH + C_2H_5{\cdot}OH + N_2.$$

$$C_9H_{14}O_2N_2 = C_7H_7{\cdot}NEt{\cdot}NO + H_2O.$$

Allylammonium nitrite prepared similarly is a brown viscid liquid, having the characteristic odour of alkylammonium nitrites.

Found—C = 34·82 ; H = 8·05 ; N = 27·15. $C_3H_8O_2N_2$ requires C = 34·62 ; H = 7·69 ; N = 26·92 per cent.

The salt decomposes in a vacuum into nitrogen and allyl alcohol.

261. "*Note on the Action of Ethylene Oxide on Hydrazine Hydrate*." By EDWARD DE BARRY BARNETT.

When ethylene oxide is added to a large excess of well cooled hydrazine hydrate, a brisk reaction takes place with evolution of heat. After distilling off the excess of hydrazine, an oily residue remains, from which two substances can be separated by repeated fractionation in a vacuum.

β-Hydroxyethylhydrazine, $HO{\cdot}C_2H_4{\cdot}NH{\cdot}NH_2$, is the main product of the reaction, and forms a colourless very viscous oil, which boils at 119—120°/9 mm.:—

0·2628 gave 0·3034 CO_2 and 0·2560 H_2O. C = 31·5; H = 10·8.
0·1378 gave 44·0 cc. N_2 at 18° and 756 mm. N = 36·7.
$C_2H_8ON_2$ requires C = 31·6; H = 10·5; N = 36·9 per cent.

It at once combines with formaldehyde with evolution of heat to form a *compound*, $C_4H_8ON_2$, which crystallises from alcohol in colourless needles melting at 224°:—

0·2058 gave 0·3610 CO_2 and 0·1556 H_2O. C = 47·8; H = 8·4.
0·1010 gave 23·8 cc. N_2 at 15° and 762 mm. N = 27·7.
$C_4H_8ON_2$ requires C = 48·0; H = 8·0; N = 28·0 per cent.

Di-β-hydroxyethylhydrazine, $[HO{\cdot}C_2H_4{\cdot}NH{\cdot}]_2$ or $(HO{\cdot}C_2H_4)_2N{\cdot}NH_2$ (found, C = 39·7; H = 10·1; calculated, C = 40·0; H = 10·0 per cent) forms a colourless very viscous syrup, which boils at 171°/10 mm. It is probably identical with the *as*-di-β-hydroxyethylhydrazine described by Knorr and Brownsdon (*Ber.*, 1902, xxxv., 4474) as boiling at 188—190°/25 mm.

262. "*Note on the Hydrolysis of Acetic Anhydride.*" By JAMES CHARLES PHILIP.

In connection with Orton and Jones's paper on this subject (*Trans.*, 1912, ci., 1708), the results of some preliminary experiments made a few years ago in the author's laboratory were described.

The course of the reaction between acetic anhydride and water in glacial acetic acid solution was followed by determining the freezing-point from time to time. As the anhydride and water progressively combine, the freezing-point rises steadily until, when one or other of the two substances has disappeared, it reaches a constant value. If the acetic anhydride and water were taken in equivalent proportion, this final constant value would be the freezing-point of absolute acetic acid.

In reality, the depressions recorded at successive intervals are not strictly comparable, for as the reaction proceeds the quantity of solvent increases—by about 3 per cent from beginning to end in the actual experiments. It would be quite possible to allow for this in evaluating the velocity-coefficient, but, in view of the preliminary character of the work, no correction was applied.

When a mixture of acetic acid, acetic anhydride, and water had been prepared, portions were transferred to tubes of special resistance glass, which were then sealed up and immersed for different periods in a water-bath kept at a constant temperature. Each tube, on being taken out of the bath, was rapidly cooled, and the freezing-point of the contents was determined immediately.

The acetic acid used was obtained by repeatedly freezing out the pure commercial acid, and had a freezing-point of 16·42° (corr.). It still contained a trace of water, the amount of which was determined by adding a slight excess of acetic anhydride, and heating samples of the mixture in sealed tubes until no further change in freezing-point was observed; thus, in one estimation, 0·939 grm. of pure anhydride was added to 68·154 grms. of the acetic acid with freezing-point 16·42°; a sample of this mixture heated at 100° for fifteen hours, showed a rise of 0·39° in freezing-point; another sample, heated for thirty-two hours at 100°, showed a rise at 0·40°. Half the rise was due to the water, the amount of which was therefore 0·1 per cent.

The following table shows the results obtained in one case for the velocity of the reaction at 70·1°. The mixture made up contained 267·02 grms. of acetic acid, 6·23 grms. of anhydride, and 1·123 grms. of water. In calculating the velocity-coefficient by the formula $0{\cdot}4343\,k = \frac{1}{(a-b)t}\log\frac{b(a-x)}{a(b-x)}$, allowance has been made for the water present in the acetic acid.

t mins.	Freezing-point depression.	*k*.
0	1·550°	—
30	1·415	0·0033
60	1·290	0·0035
90	1·170	0·0037
160	0·970	0·0037
250	0·784	0·0038
360	0·653	0·0036
500	0·520	0·0037
600	0·446	0·0037
∞	0·115	—

In the experiment just recorded, water was in excess. Another similar experiment, carried out at the same temperature but with acetic anhydride in excess, gave the following values of *k* at somewhat similar intervals:—0·0032, 0·0034, 0·0034, 0·0035, 0·0035, 0·0036, 0·0037, 0·0037, 0·0037, 0·0036.

The mean value of *k* at 70·1° may therefore be taken as approximately 0·0036. From an experiment made at 80·5° a mean value of 0·0063 was obtained for *k*.

263. "*Condensation of Bromoacyl Haloids with Glucosamine.*" (Preliminary Note). By ARTHUR HOPWOOD and CHARLES WEIZMANN.

Bromoacyl haloids condense with glucosamine in cold alkaline solution, yielding bromoacylglucosamines.

α-Bromopropionylglucosamine,—

$$CH_3{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CH(CHO){\cdot}[CH(OH)]_3{\cdot}CH_2{\cdot}OH,$$

is prepared by adding α-bromopropionyl bromide (1 mol.) and N-sodium hydroxide (1 mol.) gradually, and alternately with frequent shaking to a cold solution of glucosamine hydrochloride (1 mol.) in N-sodium hydroxide (1 mol.). A colourless precipitate separates out, which, after addition of hydrochloric acid in slight excess, is collected, washed with a little cold water, and dried in air on a porous plate. The product crystallises from hot absolute alcohol in prismatic needles, melting and decomposing at 200—201° when gently heated, and at 210—211° when quickly heated. The crystals are readily soluble in water or dilute alcohol, but are only sparingly soluble in absolute alcohol. They dissolve instantly in cold ammonia or alkali hydroxides.

*α-Bromo*iso*hexoylglucosamine*,—

$$CHMe_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CH(CHO){\cdot}[CH(OH)]_3{\cdot}CH_2{\cdot}OH,$$

is prepared by the condensation of α-bromo*iso*hexoyl bromide (1 mol.) and glucosamine hydrochloride (1 mol.) in alkaline solution. It crystallises from absolute alcohol as a mixture of rhombic plates and prismatic needles, which melts when heated quickly at 178—181° with much decomposition. The crystals are moderately soluble in cold, and readily so in hot, water. They are sparingly soluble in cold, but readily so in hot, absolute alcohol. They dissolve slowly in cold ammonia or alkali hydroxides.

α-Bromolaurylglucosamine,—

$$C_{11}H_{22}Br{\cdot}CO{\cdot}NH{\cdot}CH(CHO){\cdot}[CH(OH)]_3{\cdot}CH_2{\cdot}OH,$$

is prepared by condensing α-bromolauryl chloride (1 mol.) and glucosamine hydrochloride (1 mol.) in a slightly alkaline solution. It crystallises from absolute alcohol in rhombic plates, which melt and decompose at 183—186°. The crystals are insoluble in hot or cold water, and moderately soluble in hot absolute alcohol. They do not dissolve in dilute hydrochloric acid, which shows that the amino-group, and not the hydroxy-groups in glucosamine, has been attacked during the condensation. The crystals are also almost insoluble in cold ammonia or alkali hydroxides.

The *bromoacylglucosamines* reduce alkaline copper solutions, yielding red cuprous oxide or ammonio-silver nitrate solution giving a silver mirror. On treatment with cold ammonium hydroxide and subsequent evaporation to dryness under diminished pressure, they yield colourless crystalline solids, probably *aminoacylglucosamine*.

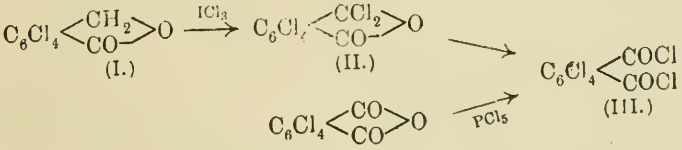
264. "*Note on the Formation of Tetrachlorophthalyl Chloride by Chlorination of Tetrachlorophthalide.*" By William Hobson Mills and Walter Henry Watson.

In view of the paper "On Symmetrical and Asymmetrical Dicarboxylic Acid Chlorides," by E. Ott, which appears in the current number of the *Annalen* (1912, cccxcii., 245), the authors communicated this note on some experiments on the chlorination of tetrachlorophthalide, undertaken on account of their possible bearing on the constitution of the chlorides of the 1 : 2-dicarboxylic acids.

Tetrachlorophthalide, as would be expected, is very resistant to chlorination, but the displacement of the two atoms of hydrogen was effected by heating the phthalide (5 grms.) with excess of iodine trichloride (10 grms.) in a sealed tube for five hours to 150°. Iodine and iodine chlorides were then removed by warming under diminished pressure, and the product was purified as far as possible by crystallising first from carbon tetrachloride and then repeatedly from light petroleum, when it melted at 132—134°. That it had been formed from the phthalide by the displacement of the two hydrogen atoms by two atoms of chlorine was shown by the fact that on warming with sodium carbonate solution it was hydrolysed with the formation of tetrachlorophthalic acid, as well as by the analysis. (Found: Reactive, $Cl = 20{\cdot}3$; $C_8O_2Cl_4(Cl_2)$ requires reactive $Cl = 20{\cdot}8$ per cent).

This product was identical with that obtained by the action of phosphorus pentachloride on tetrachlorophthalic anhydride, agreeing exactly in melting-point, general characters, and analysis. (The melting-point 118° given by Graebe, *Annalen*, 1887, ccxxxviii., 328, is accordingly too low if the compound is not dimorphic). In particular, the mixed melting-point showed no depression, and although a similar difficulty to that experienced by Ott (*loc. cit.*, p. 274) and by Brühl (*Annalen*, 1886, ccxxxv., 13) was met with in obtaining either product quite free from acid anhydride, there was no doubt as to their identity.

In the light of Ott's discoveries, it is clear that the obvious conclusion that tetrachlorophthalyl chloride possesses the asymmetrical structure (II.) (hexachlorophthalide) would not be legitimate :—



It must rather be assumed that at the temperature at which the chlorination takes place, hexachlorophthalide undergoes transformation, and that the product obtained in both reactions is the symmetrical acid chloride (III.).

265. "*Note on the Preparation and Properties of Sulphonic Esters.*" By John Ferns and Arthur Lapworth.

In a recent paper (*Trans.*, 1912, ci., 273) the authors described experiments showing that the reactions of sulphonic esters almost wholly depend on the nature of the alcohol from which the esters are derived. The behaviour of ethyl and methyl esters towards bases, and also towards sodium β-naphthoxide had been previously described, however (compare Ullmann and Werner, *Annalen*, 1903, cccxxvii., 120, and D.R.-P. 112177), a fact which the authors regret they had overlooked.

The list of available methods for preparing sulphonic esters given in that paper was intended to be complete, but did not include one by Ullmann (*Annalen*,, 1903, cccxxvii., 117), who showed that certain aromatic sulphonic acids may be converted into esters by treatment of their sodium salts with methyl sulphate.

In extension of the work described in the former paper, the authors heve found that *p*-toluenesulphonyl chloride, dissolved in pyridine, converts many alcohols directly and smoothly into the corresponding unsaturated hydrocarbons, sulphonic esters being doubtless intermediate products; by the same process glycerol may partly be converted into acrolein. It is hoped to extend the observarions to other hydroxy-compounds.

266. "*Electromotive Forces in Alcohol.* Part III. *Further Experiments with the Hydrogen Electrode in Dry and Moist Alcoholic Hydrogen Chloride.*" By Robert Taylor Hardman and Arthur Lapworth.

The electromotive forces of a series of concentration cells reversible to hydrions have been measured at 25°, and the corresponding values for the transport number of chloridion in absolute alcoholic hydrogen chloride were calculated with the aid of Nernst's equation. These values vary between 0·20 and 0·35, according to the concentration of hydrogen chloride, a result perhaps attributable to the inadequacy of the expression when applied to such electrolytes.

A re-examination of the influence of water on the potential of the hydrogen electrode in dilute alcoholic hydrogen chloride at 25° has been carried out with results similar to those recorded in Part II. (*Trans.*, 1911, xcix.. 2250). The temperature coefficients of the cells were also determined, and shown to be in fairly satisfactory agreement with the requirements of the solvate theory and with previous numerical data obtained from measurements on catalytic activity and availability.

267. "*Properties of α-Bromonaphthalene.*" By John Ickeringill Crabtree and Arthur Lapworth.

The authors have prepared α-bromonaphthalene in a fairly high state of purity. It appears to be dimorphous, the ordinary modification melting at 6·20° and the second between 0·2° and 0·7°, although it is uncertain whether the latter has been obtained quite free from the former.

Several of the more important physical constants of the substance have been re-determined.

268. "*Absorption Spectra of the Cobalto-derivatives of Primary Aliphatic Nitroamines.*" By Antoine Paul Nicolas Franchimont and Hilmar Johannes Backer.

The cobalto-derivatives of primary aliphatic nitroamines, $Co(NR{\cdot}NO_2)_2$, have, both in aqueous solution and in the anhydrous state, an intensely purple-violet colour, differing from that of solutions of ordinary cobalt salts.

The cobalt derivatives of ethylnitroamine and propylnitroamine combine with 2 molecules of water, forming respectively yellowish brown and bronze-green crystals; from methylnitroamine such a compound has not been obtained.

In order to gain objective data, the absorptive power for visible rays of the dissolved cobalt salts of methyl-, ethyl-, and propyl-nitroamine has been studied and compared with that of a cobalt nitrate solution.

The chief absorption band is found to be almost the same for the three cobaltonitroamines, but different from that shown by cobalt nitrate. In addition, cobaltomethylnitroamine shows an absorption for smaller wave-lengths.

The conclusion is drawn that in cobaltonitroamines the metal is attached to the nitrogen atom.

(To be continued)

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 4th, 1912.

Mr. Leonard Archbutt, President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Augustus Goodson, 19, Darnley Road, Hackney, N.E.; Frederick William Skevington, care of Messrs. G. H. Ogston and Moore, 87 and 89, Aldgate, E.; and John C. White, Tudor Lodge, St. James's Road, Upper Tooting.

Certificates were read for the second time in favour of Messrs. Stanley Elliott, Thomas Rigby Greenough, Harold Lowe, James P. Ogilvie, and John Algernon Lacy Sutcliffe.

The following papers were read and discussed:—

"*Value of the Guaiacum Test for Bloodstains.*" By Herbert S. Shrewsbury.

The author finds the guaiacum test the most useful of sorting tests for blood, when carried out correctly. In his opinion it is only characteristic when the following conditions are satisfied. The stain must give a red aqueous extract yielding no coloration to a straw-coloured solution of guaiacum in rectified spirits when applied by itself, but a blue coloration within one second on the further addition of hydrogen peroxide. The last two conditions are emphasised. Oxidisers, enzymes, &c., give a reaction with guaiacum solution alone, but this is not the case with blood. It is very necessary that the reaction should occur within one second, as even guaiacum solution and hydrogen peroxide by themselves will develop a faint colour on standing. Tested correctly, the author finds that none of the thirty substances mentioned by Sutherland in his monograph on bloodstains give a characteristic blood test. The majority took time for the development of colour, the time varying from five seconds to several minutes. Excluding the condition of a soluble red extract, out of the thirty substances only the following gave a correct reaction:—

1. Old bleaching powder.
2. Certain enzymes.
3. Ammonium chloride.
4. Sixteen per cent salt solution.
5. Dilute solutions of copper sulphate.

Weaker solutions of common salt than 14 per cent gave no colour; consequently there is no danger from the minute quantity of salt present in the liquids of the body. It is useful to remember that amongst commonly occurring enzymes those contained in maize or wheat flour satisfy these conditions, and if combined with a soluble red stain might be misleading. In two years' experience of the examination of a considerable number and variety of articles of clothing, the author has always found the guaiacum test to be confirmed by other reactions for blood. He points out that it is pre-eminently useful as a sorting test when much clothing has to be thoroughly examined, and though never to be relied on as proving blood, may be accepted as a perfectly satisfactory negative test, except under extraordinary circumstances. Although a great number and variety of vegetable stains occurred on the clothing examined by the author, there was never any complication on account of the reaction of enzymes. The author suggests that the guaiacum reacting property of the enzymes is eliminated during the drying of stains. Further experiments suggest that it is most difficult for a washed bloodstain to escape revelation by the guaiacum test, and that with washed bloodstains the test is highly specific, if not absolute proof of the presence of blood, though not of course characteristic of human blood.

"*Detection of Adulteration in Linseed Oil.*" By G. D. Elsdon and Herbert Hawley.

The authors describe a new method for detecting adulteration in linseed oil. The process consists in dropping 5 cc. of a 10 per cent solution of the oil in ether on to an Adam's milk coil, and, after the ether has evaporated, drying the coil for two hours in the steam-oven. The coil is then extracted with ether in the ordinary way and the extract, after drying, weighed. The weight of the extract, taken in conjunction with the iodine value, gives fairly conclusive evidence of the purity or otherwise of the oil.

"*Determination of Nitrates and Nitrites in Sewage Effluents.*" By Arnold Higginson.

The author shows that the nitrates in a sewage effluent may be easily converted into ammonia by submitting the sample, after boiling off the free ammonia in a retort, to the action of a copper-zinc couple in a strong solution of NaOH. The liquid is distilled and the ammonia estimated in the distillate. If a limited quantity of soda be used the ammonia is not obtained until the liquid is boiled down to a small volume. The process gives results which compare very well with those obtained by the phenolsulphonic acid method.

"*Estimation of Citric Acid in the Presence of certain other Acids.*" By L. Gowing-Scopes.

The paper deals with an examination of Beau's modification of Deniges's method for estimating citric acid. This method was found unreliable. An alternative method is proposed, using a reagent composed of mercuric nitrate, manganese nitrate, and nitric acid. Test results show a maximum error of +0·0003 and −0·0004. Accurate estimations can be made in the presence of all common acids other than malic, lactic, and hydrochloric.

"*Alcoholysis and the Composition of Cocoanut Oil.*" By G. D. Elsdon.

The author has used the method of Haller for determining the composition of cocoanut oil. He has found that the process is a useful qualitative test, but that it is only suitable for rough quantitative indications; the process is too long to be used as an ordinary laboratory test.

The composition of cocoanut oil has been found to be roughly as follows:—Caproic acid, 2 per cent; caprylic acid, 9 per cent; capric acid, 10 per cent; lauric acid, 45 per cent; myristic acid, 20 per cent; palmitic acid, 7 per cent; stearic acid, 5 per cent; and oleic acid, 2 per cent; no other fatty acids could be detected.

CORRESPONDENCE.

A SIMPLE APPARATUS FOR THE ESTIMATION OF CARBON DIOXIDE.

To the Editor of the Chemical News.

Sir,—As to Mr. Forbes's apparatus for estimation of carbon dioxide described in the Chemical News of December 13 (vol. cvi., p. 284), he seems to have omitted to say how he proposes to withdraw the residual CO_2 and to retain the moisture. Only one exit is figured, and it has no $CaCl_2$ tube attached. Mr. Forbes does not give his address, else I should have written him.—I am, &c.,

A Student.

Institute of Chemistry, December 13, 1912.

MEETINGS FOR THE WEEK.

Saturday, 28th,—Royal Institution, 3. (Christmas Lecture Epilogues, adapted to a juvenile auditory). "Alchemy," by Sir James Dewar, F.R.S., &c.

THE CHEMICAL NEWS.

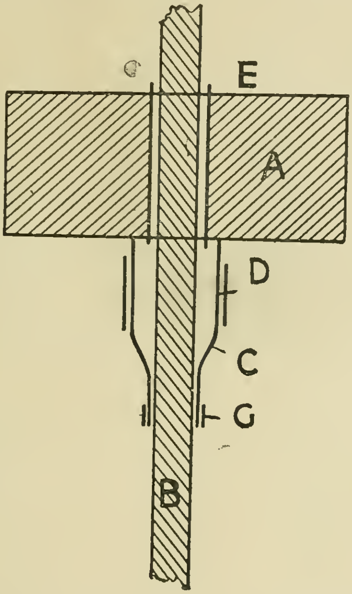
Vol. CVI., No. 2770.

A MERCURY SEAL FOR PHYSICO-CHEMICAL WORK.

By W. R. FORBES, B.Sc.

It is usual to place the mercury seal externally, but where circumstances permit of its internal position that has many advantages. The following piece of apparatus is the adaption of Findlay's form ("Practical Physical Chemistry") to internal use:—

Through the cork A a short length of glass tube passes, slightly larger than the stirrer B, which carries a glass tube C fastened to it with tubing at G to form a cup.



A carries the tube D, which is intermediate in diameter between B and C. The cup is filled with mercury.

In this form friction is reduced to a minimum. It is simple in construction, and the seal is difficult to force.

THE OXALATE-PERMANGANATE PROCESS FOR THE DETERMINATION OF COPPER ASSOCIATED WITH CADMIUM, ARSENIC, IRON, OR LEAD.*

By H. L. WARD.

(Concluded from p. 298).

The Separation of Copper from Iron as the Oxalate.

To secure the complete precipitation of copper in the presence of iron the first method tried was evaporated to dryness, carried out exactly as in the case of arsenic. No nitric acid was used on precipitation, and the residue was extracted with very dilute acid, after the addition in most cases of crystallised oxalic acid other than that used in the precipitation. The results of experiments appear in Table VI. It is plain that when only a moderate amount of iron is present the copper may be estimated with a fair degree of accuracy, but when the iron much exceeds 0·16 grm., the figures show, not an increase due to the inclusion of the oxalate of iron, as would be expected, but a loss in copper due to incomplete precipitation. The filtrate also gives a test for copper. The method therefore only gives satisfactory results when not more than 0·1 grm. of iron is present.

The effect of precipitation in a solution containing one-half its volume of glacial acetic acid is shown in Table VII.

It appears that when no nitric acid is present, the errors are positive, indicating that some of the iron comes down with the copper. When, however, the solution contains much free nitric acid, losses appear, and these losses increase with the amount of nitric acid present. It is evident, therefore, that the solution should not be strongly acid with both these acids at precipitation.

It appears, however, that when the precipitation is made in a solution just acid with acetic acid and a large excess of this acid is added after cooling to throw out the last traces of copper, the oxalate contains very little iron. The most successful procedure is to treat the solution with potassium hydroxide to faint alkalinity, then to make it just acid with acetic acid to precipitate at the boiling temperature with a large excess of oxalic acid. After cooling, about two volumes of acetic acid are added, and the oxalate allowed to settle over-night. Filtration and titration are made in the usual manner. Results of this procedure are given in Table VIII.

Should much free acid be present originally it should be removed by evaporation before neutralising the remainder with the potassium hydroxide, and if potassium oxalate crystallises out, as may happen if much potassium salt is present with the large amount of oxalic acid, it is best dissolved in a mixture of alcohol, water, and acetic acid in equal parts. When very large amounts of iron are present is is more satisfactory to increase the dilution on precipitation to 100 cc. It is necessary in all cases to have present a very large excess of oxalic acid to secure the complete insolubility of the copper.

Peters found that when potassium nitrate was present in the water solution of a copper salt, all the copper was not thrown down by oxalic acid. It becomes desirable therefore to ascertain whether copper oxalate is completely insoluble in the presence of commonly occurring salts, when one-half the solution consists of acetic acid. The results of experiments shown in Table IX. show clearly that the separation of the oxalate is complete even when very small amounts of oxalic acid are used. The potassium salts were chosen in preference to the sodium salts because potassium oxalate is much more soluble in water, and is therefore less likely to crystallise out in the course of an analysis. Ammonium salts may not be present, as a soluble double oxalate is formed, which is stable in the presence of a large amount of free acetic acid.

In the experiments detailed in the last division of the table concentrated hydrochloric acid was neutralised with potassium hydroxide, and acetic acid added before precipitation.

The Determination of Copper Associated with Lead.

The oxalate of lead, though fairly soluble in nitric acid, shows a tendency to be included in the precipitation of an oxalate which is insoluble in that acid. For this reason it was found impossible to separate copper from lead as oxalate, even in a solution very strongly acid with nitric acid. It has been shown in a previous paper (*Am. Journ. Sci.*, 1909, [4], xxvii., 448) that copper oxalate is insoluble in a 10 per cent solution of sulphuric acid containing one-half its volume of acetic acid and a large excess of oxalic acid. The method proposed, therefore, is to add to a solution of lead and copper as nitrates an equal volume of acetic acid, and then from 3 to 5 cc. of

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* From the *American Journal of Science*, xxxiii., p. 423.

TABLE VI.—*Separation of Copper from Iron by Desiccation and Extraction.*

Copper present.	Iron present.	Volume at precipitation.	Oxalic acid on precipitation.	Dilution on extraction.	Nitric acid on extraction.	Oxalic acid on extraction.	Copper found.	Error.
Grm.	Grm.	Cc.	Grms.	Cc.	Cc.	Grms.	Grm.	Grm.
0·0504	0·0393	50	1	50	2	2	0·0500	−0·0004
0·0504	0·0393	50	1	50	2	2	0·0501	−0·0003
0·0504	0·0393	50	1	50	2	2	0·0499	−0·0005
0·0504	0·0786	50	1	50	2	2	0·0499	−0·0005
0·0511	0·1000	50	1	50	5	3	0·0506	−0·0005
0·1533	0·1000	50	1	50	5	3	0·1527	−0·0006
0·0051	0·1572	50	2	50	5	2	0·0036	−0·0015
0·0504	0·1572	50	1	50	2	2	0·0597	−0·0007
0·0504	0·1572	50	1	50	2	2	0·0597	−0·0007
0·1542	0·1572	50	4	50	5	4	0·1524	−0·0018
0·0511	0·2000	50	1	50	5	3	0·0475	−0·0036
0·0511	0·2000	50	1	50	5	3	0·0475	−0·0036
0·0511	0·2000	50	3	50	5	3	0·0491	−0·0020
0·0511	0·3404	50	4	50	5	4	0·0482	−0·0029

TABLE VII.—*The Separation of Copper and Iron by Precipitation in a Solution containing large amounts of Acetic Acid.*

Copper present.	Iron present.	Volume at precipitation.	Oxalic acid.	Nitric acid.	Acetic acid.	Copper found.	Error.
Grm.	Grm.	Cc.	Grms.	Cc.	Cc.	Grm.	Grm.
0·0511	0·100	50	2	—	25	0·0524	+0·0013
0·0511	0·100	100	2	—	50	0·0524	+0·0013
0·0510	0·188	100	4	—	50	0·0514	+0·0004
0·0510	0·188	100	4	2	50	0·0511	+0·0001
0·0510	0·188	100	4	5	50	0·0499	−0·0011
0·0511	0·100	100	2	10	50	0·0475	−0·0036
0·0511	0·100	100	4	10	50	0·0489	−0·0022
0·0510	0·188	100	4	10	50	0·0487	−0·0023
0·0510	0·188	110	4	10	50	0·0468	−0·0042

TABLE VIII.—*Separation of Copper from Iron by Precipitation in nearly Neutral Water Solution with subsequent addition of Acetic Acid.*

Copper present.	Iron present.	Volume at precipitation.	Oxalic acid.	Acetic acid.	Copper found.	Error.
Grm.	Grm.	Cc.	Grms.	Cc.	Grm	Grm.
0·0051	0·31	50	6	100	0·0049	−0·0002
0·0051	0·45	50	6	100	0·0046	−0·0005
0·0543	0·15	50	6	100	0·0544	+0·0001
0·0543	0·21	50	6	100	0·0542	−0·0001
0·0543	0·31	50	6	100	0·0546	+0·0003
0·0543	0·45	100	12	200	0·0538	−0·0005
0·1629	0·45	50	6	100	0·1649	+0·0020
0·1629	0·45	100	12	200	0·1629	—

TABLE IX.—*Effect of Salts on the Precipitation of Copper Oxalate in the presence of Acetic Acid.*

Copper present.	Salt present.	Volume at precipitation.	Oxalic acid.	Acetic acid.	Copper found.	Error.
Grm.	Grms.	Cc.	Grm.	Cc.	Grm.	Grm.
			KNO_3 *present.*			
0·0501	1·0	100	1	50	0·0504	+0·0003
0·0501	3·0	100	1	50	0·0504	+0·0003
			K_2SO_4 *present.*			
0·0501	1·0	100	1	50	0·0500	−0·0001
			KCl *present.*			
0·0050	2·0	100	1	50	0·0045	−0·0005
0·0250	2·0	100	1	50	0·0246	−0·0004
0·0501	1·0	100	1	50	0·0501	—
0·0501	3·0	100	1	50	0·0501	—
			HCl *Neutralised with* KOH.			
	HCl (cc.).					
0·0511	1·0	100	1	50	0·0513	+0·0002
0·0511	2·0	100	1	50	0·0510	−0·0001
0·0511	3·0	100	1	50	0·0511	—
0·0511	5·0	100	1	50	0·0501	−0·0010
0·0511	3·0	100	1	50	0·0511	—
0·1002	5·0	150	1	100	0·1001	−0·0001

Table X.—*Separation of Copper and Lead. Both Determined.*

Copper present. Grm.	Lead present. Grm.	Sulphuric acid. Cc.	Acetic acid. Cc.	Volume at precipitation. Cc.	Oxalic acid. Grms.	Copper found. Grm.	Error, copper. Grm.	Lead found. Grm.	Error, lead. Grm.
0·0511	0·0500	3	50	110	2	0·0513	+0·0002	0·0499	−0·0001
0·0511	0·1000	5	50	100	2	0·0508	−0·0003	0·0996	−0·0004
0·0511	0·1000	5	50	100	2	0·0508	−0·0003	0·0997	−1·0003

Table XI.—*The Determination of Copper in presence of Lead. Lead not Determined.*

Copper present. Grm.	Lead present. Grm.	Sulphuric acid. Cc.	Acetic acid. Cc.	Dilution. Cc.	Oxalic acid. Grms.	Copper found. Grm.	Error. Grm.
0·0511	0·10	5	50	100	2	0·0508	−1·0003
0·1533	0·20	5	50	100	2	0·1527	−0·0006
0·1533	0·20	5	50	100	2	0·1530	−0·0003
0·0511	0·25	5	50	100	2	0·0511	—
0·1086	0·25	5	50	100	4	0·1081	−0·0005
0·0051	0·30	5	50	100	4	0·0052	+0·0001
0·0511	0·30	5	50	100	4	0·0508	−0·0003
0·0543	0·30	10	50	100	4	0·0537	−0·0006
0·1022	0·30	10	50	100	2	0·1018	−0·0004
0·0511	0·40	3	50	100	2	0·0509	−0·0002

sulphuric acid. Under these conditions the lead is completely precipitated as the sulphate, and may be filtered off and weighed as such. The filtrate is then evaporated somewhat, a little more acetic acid added, and the copper estimated as the oxalate in the usual manner. The results are shown in Table X.

Since the lead sulphate does not interfere with the permanganate titration, it is possible, as shown in Table XI., to estimate the copper as oxalate by precipitation and titration without first filtering off the sulphate of lead. In this case the sulphate is precipitated as before, the solution heated to boiling, and oxalic acid added. The sulphate and oxalate are then filtered off together, heated to boiling with dilute sulphuric acid, and the oxalate titrated with permanganate.

Summary.

It has been shown in this paper that copper may be estimated in the presence of cadmium by precipitation as oxalate, in the presence of nitric acid and subsequent evaporation to dryness, the residue then being extracted with nitric acid, and the oxalate filtered off and titrated with potassium permanganate. A still more accurate determination is obtained by precipitation of the oxalate in the presence of a large amount of free acetic acid and small amounts of free nitric acid.

Copper may be separated from arsenic in the higher condition by the same methods as are applicable in the presence of cadmium.

Copper may be separated from small amounts of iron by desiccation of the oxalate in the presence of nitric acid, and extraction with dilute nitric acid. A better method and one more universally applicable is to precipitate the copper by adding oxalic acid to the water solution of the salts of iron and copper, and adding two volumes of acetic acid to separate the small amount of copper remaining in solution.

Copper associated with lead may be estimated by first precipitating the latter metal with sulphuric acid in a solution containing a large amount of free acetic acid, and then throwing out the copper by oxalic acid (either before or after filtration), and determining the copper by titration in the usual manner.

Hydrolysis of Maltose by Dilute Acids.—Ladislas Kopaczewski.—The hydrolysing activity of acids towards maltose depends on their electrolytic dissociation, and increases very rapidly as the concentration rises above ¼-N. The hydrolysis of maltose by dilute acids is proportional to the temperature. The greater the concentration of the maltose the more rapid the hydrolysis; this is very noticeable when sulphuric acid is used.—*Bull. Soc. Chim.*, xi.—xii., Nos. 16—17.

SELENIUM GLASS.

Selenium, to the extent of about 11,000 lbs. annually, is produced by three American firms from the anode muds in electrolytic copper refining. The demand, which is not large, is practically limited to manufacturers of red glass and red enamelled ware; but while the use of selenium as a means of colouring glass was patented twenty-one years ago by F. Welz (*Ber.*, xxv., 819), very little has been published on selenium glass. It is for this reason that the paper by Fritz Kraze in *Sprechsaal*, 1912, xlv., No. 14, 214—No. 15, 227, is of great interest to the glass manufacturer; accordingly, it is abstracted at some length.

Welz used selenium or a compound of selenium and cadmium sulphide for the production of rose, red, and orange coloured glasses (see, in this connection, *Eng. Min. Journ.*, December 18, 1897, 731); but an inquiry in the "Fragekasten" of the *Sprechsaal* showed Kraze that these mixtures were not yet satisfactory. He gives us a good composition for coral-red corresponding to Kaiser-red glass (see *Sprechsaal*, 1911, 707): 100 kg. sand, 20 kg. soda, 8 kg. potash, 7 kg. lime, 0·5 kg. borax, 13 kg. cryolite, 300 grms. selenium, 700 grms. cadmium sulphide, and 230 grms. sulphur. Similarly, for a transparent yellow-red glass, 200-300 grms. selenium and 60 grms. uranium oxide with 100 kg. sand, 12 kg. soda, 16 kg. potash, 20 kg. minium, and 10 kg. limestone, are recommended. The use of selenium and uranium oxide in the manufacture of orange-yellow glass was patented in 1893. Uranium-selenium glass shows a green colour in reflected light, while it is yellow-red in transmitted light (*cf.* uranium glass).

Spitzer patented a process for the red coloration of glass by the use of selenites and selenates (*Ber.*, xxvii., 777). These compounds are more suitable than metallic selenium, since they are more stable in the heat of the furnace, and are in consequence less likely to become lost through volatilisation and oxidation. New shades of colour are obtained by the use of selenium and selenium compounds with gold (*Ber.*, xxviii., 195), or with silver, opacifying metallic oxides and certain minerals, such as cryolite, fluorspar, various phosphates, &c.

Even if elementary selenium is incorporated into the glass batch, it dissolves in the clear fusion without producing any coloration; doubtless it is oxidised and exists in the form of dioxide in a colloidal state. A reducing agent is necessary if a red selenium glass is to be obtained. Arsenic trioxide will effect the reduction of selenium compounds dissolved in glass, and the same reaction occurs with corresponding amounts of powdered charcoal or in fusion in a reducing atmosphere. With glasses fused with sodium selenate, Kraze always obtained a red coloration following an addition of arsenic trioxide corresponding to the reduction to selenium.

"All formulas including saltpetre for red selenium glass are absurd;" in fact, the use of saltpetre "does not seem to apply even in lead glass coloured with selenium" (*Sprechsaal*, 1911, 142), for there will always be an oxidation of the selenium present, giving rise to ineffective selenium (colourless dioxide) and occasioning considerable loss. Kraze failed to obtain a colour with a batch of the following composition: 100 kg. sand, 15 kg. potash, 15 kg. soda, 12 kg. marble, 6 kg. minium, 3 kg. saltpetre, and 125 kg. selenium.

Kraze concluded that if the red colour of selenium glass is due to the separation of red elementary selenium, then there must result an evolution of hydrogen upon treating the glass with concentrated hydrofluoric acid. Investigation showed a simultaneous formation of hydrogen selenide, which could only be attributed to the presence of a selenide in the glass examined, No. 1 of the experiments given below.

Glasses decolorised by means of selenium possess an unusual clearness and brilliancy. The use of selenium as a decolorising agent (sodium selenate is generally used) is claimed in German Patents 63,558, 78,565, and 88,615. Careful experiments have shown (see Miskowsky, *Keram. Rundschau*, xviii., 457) that the ratio of ferrous oxide to decolorising agent is 1 : 0·000208 for selenium, which acts as a decoloriser by producing a complementary colour which "covers" the green tint imparted to glass by iron oxides. (Selenium-manganese is now being marketed in the United States as a glass decoloriser.) Kraze found that the undesirable red tint, due to too much selenium in decolorised glasses, was removed when arsenic was added to the molten glass, which showed that arsenic acted as a reducing agent.

In the experiments made by Kraze, the following types of glass were placed in a Seger oven in chamotte crucibles and mixed with sodium selenate or selenium:—

I.	1·7	K_2O	CaO	9·8	SiO_2		
II.	1·7	Na_2O	CaO	9·8	SiO_2		
III.	1·18	Na_2O	CaO	6·94	SiO_2		
IV.	1·53	K_2O	CaO	5·4	SiO_2		
V.	1·53	K_2O	BaO	5·4	SiO_2		
VI.	1·53	Na_2O	BaO	5·4	SiO_2		
VII.	1·53	K_2O	ZnO	5·4	SiO_2		
VIII.	1·53	Na_2O	ZnO	5·4	SiO_2		
IX.	1·49	K_2O	CaO	9·8	SiO_2		
X.	1·49	K_2O	BaO	9·8	SiO_2		
XI.	1·49	K_2O	ZnO	9·8	SiO_2		
XII.	1·49	K_2O	PbO	9·8	SiO_2		
XIII.	1·49	K_2O	CaO	9·3	SiO_2	0·5	B_2O_3
XIV.	1·49	K_2O	CaO	9·47	SiO_2	0·33	P_2O_5
XV.	1·49	K_2O	CaO	9·3	SiO_2	0·5	SnO_2
XVI.	1·49	K_2O	CaF_2	0·3	Al_2O_3	9·8	SiO_2

According to the calculation of the mixtures of types I. to XVI., all contained 100 parts by weight of quartz, in order to measure the proportion of added selenium recommended by Schuster and Wilhelmy A.-G. for the production of rose-coloured glass. According to this firm, 300 to 350 grms. sodium selenate or 100 to 120 grms. elementary selenium are used with 100 kg. sand.

No. I. The crude mixture contained by weight: 100 quartz, 40 potash, 17 limestone. Of this mixture 157 grms. were fused with 0·3 grm. sodium selenate. On the first run, three hours after heating the Seger oven, the glass was still colourless. It was then treated with 0·5 grm. arsenic, and after thirty minutes another test was made. The result was a completely fused glass with a very faint red colour. This molten glass was next well-stirred, and one hour after the previous test was found to be coloured red. After another hour the colour remained unchanged. It was next mixed with 0·6 grm. more arsenic, which produced a deep red colour; and, in fifteen minutes, with the addition of another grm. of arsenic, the colour remained unchanged. This experiment showed that the red coloured selenium separated out under strong reducing influences, the colour increasing until the completion of reduction.

No. II. An equal molecular weight of soda was substituted for potash; and the mixture contained 100 grms. quartz, 31 grms. calcined soda, and 17 grms. lime. This time 0·5 grm. selenium was added. After two hours, the glass was colourless; the addition of arsenic an hour later gave no result, and the glass finally became greenish without any noticeable red tint. These experiments showed that the soda-lime glass was unsuited for selenium colouring; the formation of a coloured sodium selenide had not taken place. The green colour observed was traced to dissolved ferrous silicate, resulting from the iron rod employed in stirring.

No. III. This corresponded to a glass composition according to Tscheuschner and was selected in order to try a high-alkali glass: 100 grms. quartz, 30 grms. calcined soda, and 24 grms. calcium carbonate were fused with 0·3 grm. sodium selenate. After three hours, the glass was incompletely fused, very opaque, but clearly rose-coloured, being even stronger than No. I. before the addition of arsenic. The glass became slightly transparent thirty minutes later, but the red colour had disappeared; after another half-hour there still remained some unfused matter, but otherwise the glass was clear, although it possessed a greenish tint. An addition of 0·5 grm. arsenic was now made, and the result was a clouded and intensely green coloured glass; the green colour persisted until clear fusion. Another addition of 0·5 grm. arsenic gave a pale but still green glass. These fusions showed, as in the case of No. II., that soda-lime glass was hardly suited for selenium colouring, even though the greater lime content as compared to the soda present was somewhat favourable for colouring at first. The increase in depth of the green colour after the addition of arsenic was ascribed to a reduction of ferric silicate.

No. IV. 100 grms. quartz, 65 grms. potash, and 31 grms. calcium carbonate were fused with 0·5 grm. selenium. The iron oxide (from the rod) altered the red colour of the selenium. An addition of 0·5 grm. arsenic brightened the glass, and further additions served to produce ferrous oxide, the green colour of which, with the red colour of the selenium, produced the decolorisation. The cold glass was bright yellow-brown, although it had a rose tint.

No. V. The batch contained 100 grms. quartz, 65 grms. potash, and 60 grms. barium carbonate, making a glass which fused easily: 0·5 grm. selenium was added, and before fusion an addition of 1·5 grms. arsenic was made. After two hours, the glass was bright and possessed a coffee-brown colour and a rose shade. After thirty minutes, 1 grm. arsenic was added, whereupon the glass rapidly became colourless, with only a weak brown tint. Further additions of arsenic produced a green colour. The arsenic had finally caused a complete reduction of ferric oxide to ferrous oxide and consequently a green colour; the selenium had been volatilised, although probably barium selenide was formed to a certain extent.

No. VI. The batch contained 100 grms. quartz, 50 grms. calcined soda, 60 grms. barium carbonate, and 0·5 grm. selenium. The addition of arsenic was made as in No. V. The first result was an orange-brown, crystalline glass; after another addition of arsenic (1 grm.), it became colourless. The complementary effects of the colours entered in here, for on repeated additions of 1 grm. arsenic the glass became very green coloured.

No. VII. The fusion was made with 100 grms. quartz, 65 grms. potash, 25 grms. zinc oxide, and 0·5 grm. selenium. After two and a half hours, the glass was clear and of a deep brownish-yellow colour. The addition of arsenic failed to produce a change in colour after fifteen minutes; a second addition gave rise to a yellowish-grey tint; and a third addition caused no change but a slight brightening. Kraze was led to believe that zinc selenide was formed in this experiment.

No. VIII. 100 grms. quartz, 50 grms. calcined soda, 25 grms. zinc oxide, and 0·5 grm. selenium. The results obtained were similar to those in No. VII., except that the clarification occurred after three hours and the colour changes were different. After the first addition of arsenic, the colour change was to yellow, and further additions effected no change in colour and only a slight clarification. A red tint was never noticed.

The following tests were decidedly more acid than the preceding and the glasses were similar to potassium glasses of the type—

$$1{\cdot}49K_2O.RO.9{\cdot}8 \text{ acid.}$$

In the previous tests the acids entered into the composition solely as silica; in the following difficultly fusible acid glasses were experimented with for comparison.

No. IX. This was a composition for Bohemian crystal glass taken from Hohlbaum's "Zeitgemässe Herstellung, Bearbeitung und Verzierung des feineren Hohlglases." The batch of 100 grms. quartz, 35 grms. potash, and 17 grms. calcium carbonate was fused with only 0·1 grm. selenium. Three hours after heating the furnace, test 1 showed no unfused parts and was deep brown; two hours after, tests 2 and 3 possessed the same colour. The addition of 0·5 grm. arsenic, however, caused a change to a pretty red (test 4). The rose colour did not change after three-quarters of an hour (test 5), and even remained after repeated additions (2·5 grms.) of arsenic (test 6). Even after thirty minutes later, following an addition of arsenic (0·5 grm.), no change in colour was observed. The results of this experiment showed that the desired colour had been obtained with very small amounts of selenium (0·1 grm.). Hence the results agreed with those of No. I., for the measured addition of sodium selenate (40 per cent salt) used in the latter corresponded to 0·12 grm. selenium; but glass No. I., with less silica, did not assume a rose colour so rapidly as No. IX. Therefore, it seems that the acid content of the glass plays an important part in developing the red colour. Nevertheless, it must not be considered that sodium selenate requires more energetic reduction for red colouring than selenium.

Kraze also fused the batch of No. IX. with 0·2 grm. of selenium, with 1 grm. selenium, and again with double and five times the amount. What he expected did not occur; the red coloration did not become intensified from an increase in the selenium content, and the rose colour resulting from an addition of 0·1 grm. selenium could not be distinguished from that from 0·2 grm. selenium—in fact, both glasses were coloured even more strongly than when 0·5 grm. selenium was used.

No. X. In this experiment lime was substituted by barium oxide, but otherwise the glass was the same. The batch was: 100 grms. quartz, 35 grms. potash, 33 grms. barium carbonate, and 0·2 grm. selenium. The first test had hardly been fused before it showed a rose tint. Two hours after the gas oven was started, the glass was thoroughly fused, but the rose colour was brown tinted. Four hours later, tests showed that the product was somewhat brighter.

No. XI. A more acid zinc glass than No. VII. was obtained by substituting zinc oxide for barium oxide. The batch consisted of 100 grms. quartz, 35 grms. potash, 14 grms. zinc oxide, and 0·2 grm. selenium. Tests showed that at the beginning of the fusion there was a very weak rose tint, but the melt later became absolutely colourless; the addition of arsenic did not cause the least coloration.

No. XII. Composition: 100 grms. quartz, 35 grms. potash, 39 grms. minium, and 0·2 grm. selenium. After four hours fusion, the tests showed a yellow glass, but later brownish yellow, and finally a glass coloured a little more intensely.

The next three experiments were again with potassium—lime glasses, but boric acid, phosphoric acid, or stannic oxide was in part substituted. Replacement of part of the silicic by boric acid in the acid potash glasses diminished the red colour; and phosphoric acid and stannic oxide acted in a similar manner and to a greater extent. Replacement of the lime by fluorspar gave only a colourless glass, owing, no doubt, to the volatilisation of the selenium as fluoride during the fusion.

Kraze promises to investigate the existence of selenides in coloured selenium glasses.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 5th, 1912.

Sir Archibald Geikie, K.C.B., President, in the Chair.

The Secretaries made a preliminary statement on the identity of *Trypanosoma rhodesiense* with *T. brucei*, communicated by the Tropical Diseases Committee on behalf of Sir David Bruce.

Papers were read as follows:—

"*On a Gregarine*—Steinina rotundata, *nov. sp.—Present in the Mid-gut of Bird-fleas of the Genus* Ceratophyllus." By J. H. Ashworth, D.Sc., and Theodore Rettie, D.Sc.

"*Size of the Aorta in Warm-blooded Animals, and its Relationship to the Body-weight and to the Surface-area expressed in a Formula.*" By Georges Dreyer, William Ray, and E. W. Ainley Walker.

"*Size of the Trachea in Warm-blooded Animals, and its Relationship to the Body-weight, the Surface-area, the Blood-volume, and the Size of the Aorta.*" By Georges Dreyer, William Ray, and E. W. Ainley Walker.

"*Studies of the Processes Operative in Solutions*":—

XX. "*Conversion of Ammonic Cyanate into Urea, especially as Influenced by Alcohols.*" By E. E. Walker.

XXI. "*Hydrolysis of Cane-sugar by Dilute Acids.*" By F. P. Worley.

XXII. "*Hydrolysis of Cane-sugar by Sulphuric Acid, with a Note on Improvements in Polarimetric Apparatus.*" By F. P. Worley.

XXIII. "*Hydrolysis of Methylic Acetate by Acids.*" By F. P. Worley.

XXIV. "*Nature of Hydrolytic Process.*" By Dr. H. E. Armstrong, F.R.S., and F. P. Worley.

"*Direct Production of Characteristic Röntgen Radiations by Cathode Particles.*" By R. T. Beatty, D.Sc.

"*Penetrating Power of the γ-Rays from Radium C.*" By A. S. Russell, M.A.

Attempts have been made to detect a radiation from radium C possessing a greater penetrating power than ordinary γ-rays. A source of 300 millicuries of radium emanation was immersed in a tank of mercury at a distance of 20 cm. below the testing instrument, and sunk in the mercury till the leak in the testing instrument was no greater than the natural ionisation, It was found that the ionisation due to any radiation penetrating 25 cm. of mercury is less than 2×10^{-6} of that due to the unabsorbed γ-ray beam.

The absorption of the γ-rays was measured also for a great range of thickness of mercury. From 1 cm. to 22·5 cm. absorption took place strictly according to an exponential law. Over this range the intensity is diminished in the ratio of 360,000 to 1. The value of the absorption coefficient (cm.$^{-1}$ divided by the density) was found to be 0·0438, which is very nearly the same as that found by Soddy and Russell for lead, namely, 0·0437.

"*Photo-electric Behaviour of Iron in the Active and Passive State.*" By H. S. Allen, D.Sc.

"*Determination of the Radiation Constant.*" By H. B. Keene, B.Sc.

Previous determinations of the constant of the Stefan-Boltzmann law of radiation vary from 5·3 to 6·5. The law only applies to full radiators, and hitherto no investigator has used a full radiator to receive the radiation.

In this determination both emitter and receiver were close approximations to full radiators. The emitter consisted of a modified Heræus electric furnace at about 1000° C., the temperature of which was measured by a thermo-couple. The receiver consisted of a hollow spherical double wall thermometer bulb provided with a small aperture in its side whereby to admit the radiation to be measured. The space between the walls was filled with aniline which served as the thermometric substance, its expansion being observed in a capillary tube in the usual way. One mm. of the thermometer scale corresponded to a change of temperature of one two-thousandth of a degree Centigrade. In order to eliminate the effect of the variation of room temperature, two such thermometers were used differently, radiation being admitted into one of them, the differential effect giving a measure of the energy supply.

The interior of the thermometer bulb receiving the radiation was provided with an electric heating coil for the purpose of calibration.

The mean value obtained for the radiation constant equals $5{\cdot}89 \times 10^{-5}$ erg. cm.^{2} sec. deg.^{4} The paper contains the calculation of an exact expression for the energy exchange between two radiating coaxial circular apertures; the ordinary approximate expression which applies when the distance between the apertures is great being insufficiently exact in the present case.

"*Physiological Observations made on Pike's Peak, Colorado, with Special Reference to Adaptation to Low Barometric Pressures.*" By C. G. Douglas, J. S. Haldane, M.D., F.R.S., Y. Henderson, and E. C. Schneider.

"*Notes on the Life-history of* Trypanosoma gambiense, *with a Brief Reference to the Cycles of* Trypanosoma nanum *and* Trypanosoma pecorum *in* Glossina palpalis." By Muriel Robertson.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1912.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 305).

269. "*The Constituents of* Cluytia similis." By Frank Tutin and Hubert William Bentley Clewer.

Cluytia similis, Muell. Arg., which is identical with the plant referred to by Smith ("A Contribution to South African Materia Medica," Cape Town, 1895, p. 57) as a smaller variety of *Cluytia hirsuta*, is reputed in South Africa to be of value as an antidote for anthrax and for the disinfection of "milt-ziek," or anthrax-infected meat. The root of this plant is also stated to be eaten by natives as an antidote for snake-bite poisoning. The entire above-ground portions, and also the root, of *C. similis* have therefore been submitted to chemical examination, when, in addition to chrysophanol, fatty acids, and other known compounds, the following new substances were isolated:—(i.) *Cluytyl alcohol*, $C_{28}H_{58}O$ (m. p. 82·5°); (ii.) *cluytinic acid*, $C_{21}H_{42}O_2$ (m. p. 69°); (iii.) *cluytyl cluytinate*, $C_{49}H_{98}O_2$ (m. p. 76·5°); (iv.) *cluytiasterol*, $C_{27}H_{44}O$ (m. p. 159°); (v.) a new *acid*, $C_{10}H_{10}O_4$ (m. p. 159°); (vi.) *cluytianol*, $C_{23}H_{37}O(OH)_3$ (m. p. 300—305°). Cluytianol is isomeric with the dihydric alcohol, ipuranol, which it resembles in its general properties. *Triacetylcluytianol* melts at 160°, and the *tribenzoyl* compound at 192°.° The root also contained a quantity of inorganic matter, in which strontium was present.

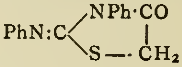
270. "*Constitution and Reactions of Thiocarbamides.*" By Augustus Edward Dixon and John Taylor.

A consideration of the synthetic methods for producing "thiocarbamide," or its substitution derivatives containing univalent radicles, and of the properties displayed by these substances, leads the authors to conclude that, when in the static condition, they are all constituted on the type $NH_2{\cdot}CS{\cdot}NH_2$.

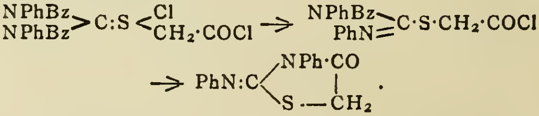
By reaction with halogen compounds, RX (X = haloid), thiocarbamides generally yield products containing the nucleus of iminothiocarbamic acid, $NH_2{\cdot}C(:NH){\cdot}SH$, or "thiourea"; it does not follow, however, that the parent substances have the configuration of the latter, or acquire it through tautomeric change of a thiocarbamide, prior to interaction. In the author's view, such phenomena are better explained as follows:—The primary product is an additive compound of the type $\begin{matrix}NH_2\\NH_2\end{matrix}\!>C{:}S<\!\begin{matrix}R\\X\end{matrix}$; when from this the elements of HX are withdrawn, the sulphur again becomes bivalent, the radicle, R, if alkyl, retaining its place with formation of $NH_2{\cdot}C(:NH){\cdot}SR$, but if acyl, moving to the unsaturated nitrogen atom, to give a substituted thiocarbamide, $RNH{\cdot}CS{\cdot}NH_2$.

When the radicle, R, itself contains halogen or hydroxyl, the secondary product may undergo further change, with loss of halogen acid, or of water; in the former case, if the thiocarbamide contains an acyl radicle, this is eliminated preferentially to hydrogen.

s-Dibenzoyldiphenylthiocarbamide yields with chloroacetyl chloride, diphenyl*iso*thiohydantoin,—



and benzoyl chloride, the explanation, on the above lines, being as follows:—



271. "*Effect of Heat on a Mixture of Benzaldehydecyanohydrin with* m-*Chloroaniline and with* m-*Toluidine.*" By Clement William Bailey and Hamilton McCombie.

The authors have extended the work described by Everest and McCombie (*Trans.*, 1911, xcix., 1752) by studying the effect of replacing aniline by substituted anilines.

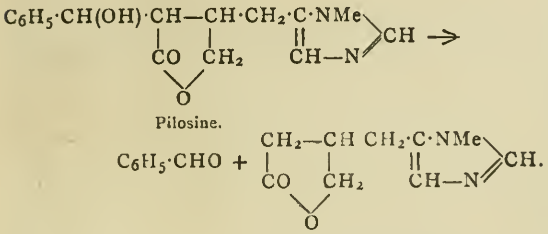
When benzaldehydecyanohydrin and *o*-chloroaniline are heated together, even for several days, no condensation product could be obtained. In the case of *m*-chloroaniline, the products obtained were exactly analogous to those described by Everest and McCombie in the case of aniline itself, namely, (1) m-*chloroanilinophenylacetonitrile*, $C_6H_4Cl{\cdot}NH{\cdot}CHPh{\cdot}CN$; (2) *dibenzoyldi*-m-*chloroanilinostilbene*, $C_6H_4Cl{\cdot}NBz{\cdot}CPh{:}CPh{\cdot}NBz{\cdot}C_6H_4Cl$; (3) 1 : 5-*diphenyl*-3-m-*chlorophenylglyoxaline*, $C_{27}H_{19}N_2Cl$, and (4) *a-keto-β*-m-*chloroanilino-aβ-diphenylethane*.

When *p*-chloroaniline was employed, the reaction took a different course. The product which was obtained gave figures in agreement with the formula $C_{35}H_{24}O_3N_2Cl_2$. The constitution to be assigned to this compound has not been determined, but it is hoped to return to this work later.

When the reaction was extended to the toluidines, results similar to those obtained in the case of the chloroanilines were obtained; thus, *o*-toluidine did not react with benzaldehydecyanohydrin, *m*-toluidine yielded products exactly analogous to those obtained in the case of aniline and *m*-chloroaniline, whilst *p*-toluidine gave a substance of the formula $C_{37}H_{30}O_3N_2$.

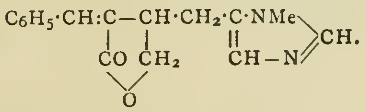
272. "*Pilosine: A new Alkaloid from* Pilocarpus microphyllus." By Frank Lee Pyman.

From the mother-liquors remaining after the separation of pilocarpine and *iso*pilocarpine from the total alkaloids of *Pilocarpus microphyllus*, a new alkaloid, *pilosine*, has been isolated in a yield amounting to 0·007 per cent of the leaves. Pilosine has the empirical formula $C_{16}H_{18}O_3N_2$, and is a monacid base. It melts at 187° (corr.), and has $[\alpha]_D +39{\cdot}9°$. It contains an N-methyl, but no methoxy-group. It also contains a lactonic grouping. On treatment with acetic anhydride it yields a new unsaturated base, *anhydropilosine*, $C_{16}H_{16}O_2N_2$, which melts at 133° to 134° (corr.), and has $[\alpha]_D +66{\cdot}2°$. Pilosine is decomposed on distillation with 20 per cent aqueous potassium hydroxide, benzaldehyde, and a new base, *pilosinine*, $C_9H_{12}O_2N_2$, being formed. The chemical and physiological properties, as well as the solubilities of the latter base, are very similar to those of pilocarpine and *iso*pilocarpine, and it seems probable that this base is a lower homologue of these alkaloids. Its formation from pilosine may then be represented as follows:—


Pilosine.

Pilosinine.

and anhydropilosine would then have the formula:—



The physiological action of the three alkaloids is similar to, but very much weaker than that of pilocarpine.

273. "*Note on the Alkaloids of* Pilocarpus racemosus." By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN.

The statements in the literature with regard to the amount and nature of the alkaloid contained in the leaves of *Pilocarpus racemosus* (Guadeloupe jaborandi) are conflicting.

Holmes (*Pharm. Journ.*, 1903, [4], xvii., 713) quoted the statement of G. Rocher, who examined the leaves in 1898-1899, that these contained 1 per cent of total alkaloids, of which two-thirds was pilocarpine, but mentioned that another sample examined in the laboratories of Messrs. Wright, Layman, and Umney, Ltd., contained only 0·34 per cent of total alkaloids.

Later, Holmes stated (*Pharm. Journ.*, 1904, xviii., 54) on the authority of A. J. Cownley, that the leaves of *P. racemosus* contained 0·6 per cent of total alkaloids, which gave about 50 per cent of a crystalline nitrate melting at 155°. Since pilocarpine nitrate melts at 178° and *iso*pilocarpine nitrate at 159°, he considered that this nitrate probably consisted largely of *iso*pilocarpine nitrate, or possibly of some other alkaloid.

Some time ago the authors examined a quantity of leaves of *P. racemosus* at the request of the Director of the Royal Gardens at Kew; on extracting the alkaloids and purifying them in the usual way, they obtained pure pilocarpine nitrate melting at 178° (corr.) in a yield amounting to 0·12 per cent of the leaves, but no other crystalline products. This result confirms Rocher's statement that the leaves contain pilocarpine.

The mother liquors after the removal of pilocarpine gave a red coloration with sodium diazobenzene-*p*-sulphonate, indicating the presence of a base containing a free imino-group, and contained a small amount of bases sparingly soluble in water. The latter did not yield pilosine (compare the preceding abstract) when seeded with this alkaloid, and the quantity was insufficient to admit of further purification.

274. "*Ignition of Electrolytic Gas by the Electric Discharge.*" By HUBERT FRANK COWARD, CHARLES COOPER, and CHRISTOPHER HENRY WARBURTON.

By suitable modifications in the usual apparatus for passing an electric discharge through a gaseous mixture, it has been found possible to ignite electrolytic gas ($2H_2+O_2$) at pressures much lower than any previously recorded. A flame which filled a globe of 570 cc. capacity has been produced at 5 mm. pressure, and one which travelled the whole length of a cylinder 2 metres long at 8 mm. In each case a small amount of gas remained uncombined. In two globes this residue varied in amount inversely as the original pressure of the gas, up to 70 mm. pressure.

275. "*Relation between Viscosity and Chemical Constitution.* Part V. *The Viscosity of Homologous Series.*" By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE.

Having had two long homologous series placed at their disposal by Dr. Pickard, the authors have examined the viscosities of the different members therein. They have compared the various physical properties which have been measured for these series, namely, rotatory power, density, refractive power, and viscosity, and find that the strongly constitutive properties of optical rotatory power and viscosity give similar curves when plotted against molecular weight. Linear relationships are afforded by density, boiling-point, refractive index, and log η. The rotatory powers and viscosities rise to the third or fourth member, and then proceed normally.

276. "*Relation between Viscosity and Chemical Constitution.* Part VI. *Viscosity and Additive Function.*" By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE.

Attention was drawn to the linear relationship afforded by log viscosity in any homologous series. Using the data of Gartenmeister and Thorpe and Rodger, it was shown that group constants of log η may be obtained, from which molecular values may be calculated in good agreement with those observed.

Using this method for ethyl acetoacetate, it is found that 6·7 per cent of the enolic form is present in the equilibrium mixture.

277. "*Relation between Viscosity and Chemical Constitution.* Part VII. *The Effect of the Relative Position of Two Unsaturated Groups on Viscosity.*" By ALBERT ERNEST DUNSTAN, THOMAS PERCY HILDITCH, and FERDINAND BERNARD THOLE.

The authors have examined the viscosities of a number of homologous series of compounds of the respective types $R{\cdot}[CH_2]_n{\cdot}R$ and $Ph{\cdot}[CH_2]_n{\cdot}R$, where R is a varying unsaturated radicle.

In both series the general order of the molecular viscosity rises when R is varied in the order Cl, CO_2Et, NH_2, and CN, and in addition the initial member, containing two chemically adjacent unsaturated groups, has been found to possess an exalted molecular viscosity, as calculated from the expression $\dfrac{\eta \times 10^6}{\text{Mol. vol.}}$.

In the symmetrical series $R{\cdot}[CH_2]_n{\cdot}R$, the members represented by $R{\cdot}CH_2{\cdot}CH_2{\cdot}R$ possess an enhanced value for this expression, but this is not the case in the phenyl group of compounds.

In the latter group the anomaly of the initial member is in general very pronounced, and is followed by an equally well-marked depression in the case of the second member, the values thereafter rising somewhat rapidly; the relative positions of the curves connecting the molecular viscosities of the members of each homologous series, the relative slopes of these curves, and the extent of the depression at the second term are in the ascending order R=H, Cl, CO_2Et, NH_2, CN, and OH.

The series examined afford undoubted evidence of the strong mutual influence of two unsaturated groups on viscosity, not only when the radicles concerned are adjacent in the molecule, but also when they may be supposed from common steric considerations to approach one another in space.

In addition, indications have been obtained of the varied influences exerted by combinations of two similar, and on the other hand of two dissimilar, radicles, the effects in the latter case depending to all appearance on the relative degree of unsaturation of the component radicles.

278. "*Contributions to the Chemistry of the Terpenes. Part XIV. The Oxidation of Pinene with Hydrogen Peroxide.*" By George Gerald Henderson and Maggie Millen Jeffs Sutherland.

When pinene is oxidised with 30 per cent aqueous hydrogen peroxide in presence of acetic acid, the chief product is α-terpineol, $C_{10}H_{17}\cdot OH$, partly free and partly as the acetate. The other neutral products of the reaction include borneol (as the acetate), a small quantity of dipentene, a trace of the aldehyde, $C_{10}H_{16}O$, formerly obtained by the oxidation of pinene with chromyl chloride, and some methane-1 : 4 : 8-triol (1 : 4 : 8-trioxyterpan), $C_{10}H_{17}(OH)_3$. The last compound has been obtained by oxidising $\Delta^{4(8)}$-menthenol-1 with dilute permanganate, but has not hitherto been directly produced from pinene. Neither pinene glycol, pinol, nor any ketone was detected among the oxidation products, and only a trace of an oily acid, or mixture of acids, was obtained.

It is obvious that the behaviour of pinene towards hydrogen peroxide differs very considerably from that of camphene under similar conditions (Henderson and Sutherland, *Trans.*, 1911, xcix., 1539), and that in this case, as in many others, the action of the reagent leads to disruption of the dimethyl*cyclo*butane ring in pinene, and to the formation of derivatives of isomeric terpenes.

279. "*Baly and Krulla's Hypothesis of Fluorescence.*" By Alexander Killen Macbeth.

To be of ordinary utility and find general acceptance, a theory of fluorescence must necessarily differentiate between absorbing substances which fluoresce and those which do not. It must also lay stress on the variation in wave-length and the increase in duration of the emission when the substance is in the solid state. The recent hypothesis of fluorescence put forward by Baly and Krulla (*Trans.*, 1912, ci., 1469) offers no explanation of these points.

The basis on which their hypothesis is built is the assumption of different degrees of binding up of the secondary valencies of the constituent atoms of the molecule; thus a substance is capable of existing, first, in a state 1, in which maximum condensation of the force field has occurred; after that in states 2, 3, 4, . . . &c., representing various stages of "opening up." The change 1 → 2 is brought about by the selective absorption of light of wave-length λ_2. By the influence of light of, say, wave-length λ_3 and a suitable solvent, the substance may be opened up into 3. Hence the reverse reaction 3 → 2 must be accompanied by an emission of light of wave-length λ_3. If the substances 1, 2, 3, . . . are present, the change 2 → 1 must involve disturbance of the system 3 → 2; that is, in the bringing about again of the state 1, which has been disturbed by the absorption of light λ_2, we must get the process 3 → 2, or emission of λ_3 also. Baly and Krulla further state that because of this, when 1 passes into 2 by the absorption of light of wave-length λ_2, the change 3 → 2 is produced with the emission of light of wave-length λ_3, the latter constituting the fluorescence. It does not seem reasonable to suppose such to be the case. If the substance can exist in the forms 1, 2, 3, . . ., it is justifiable, in the light of chemical theory, to assume that these forms are in the state of chemical equilibrium; thus, 1, 2, 3, . . . being intimately connected, the system can be represented as follows:—

$$1 \rightleftarrows 2 \rightleftarrows 3.$$

On Baly and Krulla's assumptions, the change 1 → 2 is accompanied by the absorption of light of wave-length λ_2; and the reverse change, 2 → 1, by an emission of the same light. Similarly, the changes 2 → 3 and 3 → 2 are accompanied respectively by absorption and emission of light of wave-length λ_3. It is thus evident that in equilibrium in solution there is a complete balance of light, as is seen on separating the two systems:—

$$\left.\begin{array}{l} 1 \xrightarrow{\text{Absorption of }\lambda_2.} 2 \\ 1 \xleftarrow[\text{Emission of }\lambda_2]{} 2 \end{array}\right\}\text{Balance} \qquad \left.\begin{array}{l} 2 \xrightarrow{\text{Absorption of }\lambda_2.} 3 \\ 2 \xleftarrow[\text{Emission of }\lambda_3.]{} 3 \end{array}\right\}\text{Balance}$$

If, now, the whole system is supposed to be disturbed by an exciting light of wave-length λ_2, effecting the change 1 → 2, according to the hypothesis, the equilibrium position will then be disturbed, and some of the process 2 → 3 will result. Later, equilibrium may be supposed to be again attained. The changes in this case are, first, an absorption of λ_2, and, secondly, an absorption of λ_3; and if equilibrium is then attained, there is a balance of light with, in addition, the preceding absorption effect. That is, the hypothesis leads to a further absorption of light, without any emission; thus, when the exciting light, λ_2, is cast on the substance, the changes may be represented as shown below:—

$$\left.\begin{array}{ll} (\alpha) & 1 \xrightarrow{\text{Absorption of }\lambda_2.} 2 \\ (\beta) & 2 \xrightarrow[\text{Absorption of }\lambda_3.]{} 3 \end{array} \quad (\gamma)\ 1 \rightleftarrows 2 \rightleftarrows 3 \right\}\text{Balance}$$

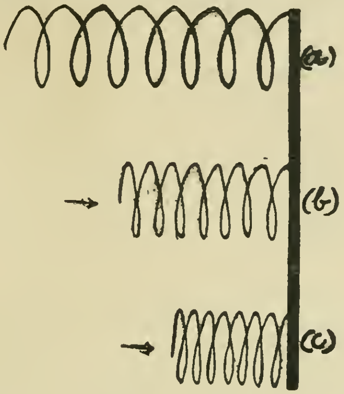
and the effect outstanding is clearly an absorption as of $\lambda_2 + \lambda_3$.

Further, if the exciting light γ_2 is withdrawn, it is most reasonable to suppose that under suitable conditions the reverse reaction will commence, and there will be an emission of the original wave-lengths which were absorbed, in agreement with Kirchhoff's law. This change may be represented thus:—First, the system 3, 2 is involved, giving the process 3 → 2, with its attendant emission of λ_3. This necessarily involves the process 2 → 1, giving emission of λ_2, and, later, equilibrium is established between 1, 2, and 3. . . . The effect may be summarised thus:—

$$\begin{array}{ll} 3 \rightarrow 2 & \text{Emission of } \lambda_3. \\ 2 \rightarrow 1 & \text{Emission of } \lambda_2. \\ 1 \rightleftarrows 2 \rightleftarrows 3 & \text{Balance.} \end{array}$$

Thus the application of the hypothesis would not explain fluorescence, and it seems more capable of explaining phosphorescence, since, whilst the light was acting, the reaction would be driven in the direction 1 → 2 → 3, the reverse change taking place under suitable conditions when the source of free energy is withdrawn. The system, in closing, would emit free energy in the form of light, and from the above considerations this light would be of a similar nature to that absorbed when the exciting source was in action. Examples in support of this are found in the cases of luminous paints and other phosphorescing substances. Moreover, it would appear from the behaviour of ammonium platinocyanide that the later stages may be isolated, as on cooling a crystal of this substance to the temperature of liquid hydrogen and exposing it to a strong light, no phosphorescence is noticed on removal to a dark room. On withdrawing the crystal from the chilled tube and allowing it to become warm, it presently emits light of great intensity. Fluorescence in this case is not shown until additional free energy enters the system in the form of heat, disturbing the molecular compound 3, 4 . . *n*, and resulting in the reformation of 1. A real difficulty, however, is met when one considers the case of substances which show no fluorescence at the ordinary temperature, and yet give strong emissions at low temperatures. At −180°, acetophenone, benzophenone, asparagine, hippuric, salicylic, and uric acids give brilliant fluorescence which they do not exhibit at the ordinary temperature. Here there are substances, at the ordinary temperature, containing free energy, and showing no fluorescence, which at low temperatures, when much of the free energy has been withdrawn, fluoresce strongly. This cannot be brought into agreement with the hypothesis of Baly and Krulla.

An analogy may be drawn between the hypothetical states 1, 2, 3 . . . *n*, and a spring fixed at one end. The first state 1 is denoted at (*a*), this being the state under ordinary conditions. When free energy is supplied to the spring (as light λ_2 is applied to the substance 1), there is absorption, and the spring is compressed to position (*b*), corresponding with the state 2. Further free energy will compress it to (*c*). corresponding with λ_3, giving 2 → 3. Now, the Baly-Krulla hypothesis states that 1 → 2, with absorption of λ_2, involves the change 3 → 2 with the emission of λ_3; yet there is no apparent reason why compression from (*a*) to (*b*) should necessitate the change from (*c*) to (*b*), the more so since the state (*c*) has not been reached. Similarly, on the basis of the hypothesis, if 2 is produced solely by the absorption of λ_2, then 3 cannot exist until 2 is passed; that is, until further absorption has taken place.



On these grounds it cannot be affirmed that an absorption of λ_2 develops an emission of λ_3. An idea of phosphorescence in such cases can, however, be formed by this means. At any degree of compression of the spring, withdrawal of the free energy supply (that is, pressure) is followed by an emission of the energy stored by the spring; and in the analogous case of light, this represents phosphorescence; but it cannot be taken as giving an account of the cases of acetophenone, &c., mentioned above.

Again, Nichols and Merritt (*Phys. Rev.*, 1904, June and July) have verified that the wave-length of the exciting light may vary over a very wide range, and still produce the same fluorescence spectrum. Applying this to the changes 1, 2, 3, &c., if the wave-length connecting the substances 1 and 2 can vary over a wide range, it seems most reasonable to deduce that the wave-lengths connecting 2 with 3 may also vary considerably. In other words, the fluorescence spectrum would vary widely, on the Baly-Krulla hypothesis, since this postulates that the latter wave-lengths constitute the fluorescence.

Moreover, Nichols and Merritt (*loc. cit.*) have shown, after careful investigation of the intensities of the fluorescence spectra of many substances, that even when the exciting source, λ_2, is made up of a band of spectra, slightly towards the red side of the point of most intense fluorescence, the emitted light is still of good intensity. In this case the exciting source (λ_2) has been varied, not only up to λ_3, but beyond this wave-length. The particular case $\lambda_2 = \lambda_3$ may be taken. On the Baly-Krulla hypothesis, this may be written :—

$$1 \xrightarrow{\text{Absorption of } \lambda_3} 2 \underset{\text{Emission of } \lambda_3}{\overset{\text{Absorption of } \lambda_3}{\rightleftarrows}} 3$$

and it is hard to see what, in such a case, causes an emission of λ_3.

The hypothesis can be regarded from yet another point of view. If it is true that an absorption of λ_2 takes place in the process 1 → 2, and a simultaneous emission of λ_3 in the process 3 → 2, the conclusion is inevitable that the amount of light absorbed differs when a substance is fluorescing and when it is in darkness. This is contrary to the facts observed and recorded by Wood (*Phil. Mag.*, 1908, [vi.], xvi., 940), who established the identical nature of the absorptions in these cases.

Seeing that the consideration of this hypothesis leads to no clear conception of the special cases of absorbing substances which show fluorescence, offers no explanation of the change of wave-length and duration of the emission when the substance is in the solid state, does not meet the case of substances exhibiting fluorescence as solids and yet showing no traces of the phenomenon when dissolved (for example, barium platinocyanide), and does not increase our knowledge of even the simplest facts in connection with the phenomenon, it cannot be regarded as a rational theory of fluorescence.

(We are indebted to the Chemical Society for permission to reproduce the accompanying illustration).

280. "*Hydrazoximes of Benzil and Diacetyl.*" By Martin Onslow Forster and Biman Bihari Dey.

Unsubstituted hydrazoximes do not appear to have been studied; accordingly, *benzilhydrazoxime*, $C_{14}H_{13}ON_3$, and *diacetylhydrazoxime*, $C_4H_9ON_3$, were prepared, together with their acyl derivatives and products of condensation with benzaldehyde and acetone.

281. "*The Relation between Constitution and Rotatory Power amongst Derivatives of Tetrahydroquinaldine.*" By William Jackson Pope and Thomas Field Winmill.

The authors have prepared a number of derivatives of *l*-tetrahydroquinaldine, and have shown that a close relation is observable between the molecular composition and constitution and the rotation constants of these substances,

282. "*The Dehydration of* iso-*β-Naphthol Sulphide.*" By Kenneth Ross and Samuel Smiles.

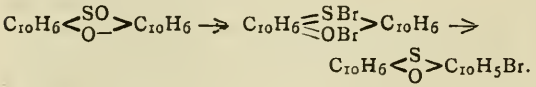
When heated with certain dehydrating agents the unstable sulphide of β-naphthol loses the elements of water, giving an *iso*naphthathioxin (m. p. 148°). It has already been shown that the stable or normal sulphide also yields a naphthathioxin (m. p. 166°) with these reagents. With nitric acid (D 1·4) the *iso*-derivative furnishes the oily nitrate of the sulphoxide, from which the solid base may be liberated by hydrolysis. This sulphoxide is attacked by warm hydrochloric acid, giving a mixture of chloro-derivatives of the naphthathioxin. If the reaction is carried out under suitable conditions, the chief constituent of the crude product is identical with the dichloro-derivative previously obtained (Christopher and Smiles, *Trans.*, 1912, ci., 710) by chlorinating the monochloronapthathioxin which is formed by the interaction of acetyl chloride and β-naphthasulphonium-quinone.

The naphthathioxin derived from the stable sulphide of β-naphthol undergoes a precisely similar series of changes; but the sulphoxide and chloro-derivatives are quite distinct from those of the *iso*-series.

The relations between these series are being examined, and will be discussed in connection with the nature of the two sulphides of β-naphthol.

283. "*Salts of Naphthathioxonium.*" (Preliminary Note.) By THOMAS JOSEPH NOLAN and SAMUEL SMILES.

Previous attempts to obtain the thioxonium chloride by interaction of hydrogen chloride and oxides of naphthathioxins have uniformly resulted (*Trans.*, 1912, ci., 710) in the immediate production of chloro derivatives of the nucleus, the thioxonium salt being apparently too unstable in presence of excess of this mineral acid to permit isolation. It has, however, been observed (*Trans.*, 1910, xcvii., 1112) that phenazothionium bromide reacts very sluggishly with hydrogen bromide, whereas the corresponding chloro-derivatives are very reactive. Taking advantage of this observation, it has been found that the thioxonium bromides may be obtained from the naphthathioxin oxides by treatment with luke-warm hydrobromic acid. They are slowly converted by the boiling reagent into the bromonaphthathioxins; the successive changes may be represented as follows:—



$$C_{10}H_6<\overset{SO}{\underset{O-}{}}>C_{10}H_6 \rightarrow C_{10}H_6\lessapprox\overset{SBr}{\underset{OBr}{}}>C_{10}H_6 \rightarrow C_{10}H_6<\overset{S}{\underset{O}{}}>C_{10}H_5Br.$$

These thioxonium bromides are more easily obtained by the interaction of bromine and β-naphthasulphonium-quinone in acetic anhydride or with the acetyl derivative of the unstable sulphide of β-naphthol in the same solvent.

284. "*Intramolecular Rearrangements of a-Sulphoxides of Diphenylamine.*" Part IV. By THOMAS PERCY HILDITCH and SAMUEL SMILES.

Previous experiments (*Trans.*, 1911, xcix., 145) have shown that the *o*-sulphoxide of diphenylmethane when treated with hydrogen chloride or hot glacial acetic acid yields thioxanthenyl chloride or thioxanthenol. Attempts have now been made to isolate similar derivatives from the products of rearrangement of the *o*-sulphoxides of diphenylamine; but they were not successful. It was shown, for example, that diphenylamine *o*-sulphoxide yields hydroxythiodiphenylamine when heated with acetic acid, whilst the tetrachloro-derivative furnished the phenazothionium hydroxide. Similar attempts to obtain the N-chloro-derivative from the tetra-nitro- and tetrachloro-sulphoxides were unsuccessful.

285. "*Diphenyl-2 : 3 : 2′ : 3′-tetracarboxylic Acid.*" (Preliminary Note). By JAMES KENNER.

Dimethyl 3-iodophthalate, $C_6H_3I(CO_2Me)_2$, forms prisms, m. p. 89°, and is converted by treatment with copper powder into *tetramethyl diphenyl-2 : 3 : 2′ : 3′-tetracarboxylate*, $C_{12}H_6(CO_2Me)_4$, which forms needles melting at 161°.

Diphenyl-2 : 3 : 2′ : 3′-tetracarboxylic acid, $C_{12}H_6(CO_2H)_4$, crystallises in plates melting at 265°, and is readily soluble in water.

The reactions of this compound are being investigated in connection with the author's studies on ring-formation from derivatives of 2 : 2′-ditolyl.

286. "*Reactions of Dibenzo*cyclo*heptadienone.*" (Preliminary Note). By JAMES KENNER and EMILY GERTRUDE TURNER.

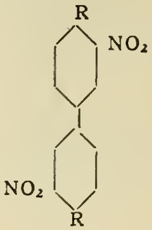
In connection with the authors' investigations of derivatives of 2 : 2′-ditolyl (*Trans.*, 1911, xcix., 2101), a comparison of the reactions of dibenzo*cyclo*heptadienone with those of β-hydrindone has been undertaken.

Unlike β-hydrindone, dibenzo*cyclo*heptadienone does not undergo condensation in the presence of alkali, and it yields a *dibenzylidene* derivative, m. p. 227°. Further, whilst β-hydrindone is known to yield a di*iso*nitroso-derivative (from which, by the action of formaldehyde and hydrochloric acid, the authors have prepared triketohydrindene hydrate), dibenzo*cyclo*heptadienone only gives rise to a *monoisonitroso*-derivative, m. p. 197°. With aniline, β-hydrindone yields the normal condensation product (leaflets, m. p. 97°), but the action of aniline on dibenzo*cyclo*heptadienone leads to the formation of phenylcarbylamine and a *compound*, golden-yellow prisms, m. p. 188°, the constitution of which has not yet been ascertained.

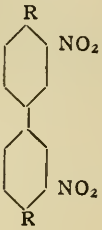
Other reactions of the two ketones are under investigation.

287. "*Studies in the Diphenyl Series.* Part II. *The Dinitrobenzidines; a New Form of Isomerism.*" By JOHN CANNELL CAIN, ALBERT COULTHARD, and FRANCES MARY GORE MICKLETHWAIT.

It has hitherto been assumed that the same *o*-dinitrobenzidine is obtained by the nitration of diacetyl- and diphthalyl-benzidine. It is now found that two different *o*-dinitrobenzidines are produced in these reactions. That from diacetylbenzidine melts at 275°, gives a diacetyl derivative melting at 310°, and a dinitrodiphenyl melting at 197—198° (Brunner and Witt, *Ber.*, 1887, xx., 1023), whilst that from diphthalylbenzidine melts at 233°, gives a diacetyl derivative melting at 222°, and a *dinitrodiphenyl* melting at 110°. It was suggested that the series of compounds of higher melting-points have the symmetrical (I.) and those of lower melting-points the unsymmetrical (II.) constitution (R = H, NH_2, or NHAc):—



I.



II.

Bandrowski's "*iso*dinitrobenzidine" (*Ber.*, 1884, xvii., 1181; *Monatsh*, 1887, viii., 472) has been found to be a mixture of 2 : 2′-dinitrobenzidine and 3 : 3′-dinitrobenzidine (m. p. 233) with a small amount of 3-nitrobenzidine.

288. "*Velocity of Reaction between Potassium Chloroacetate and some Aliphatic Amines.*" By TOM SIDNEY MOORE, DONALD BRADLEY SOMERVELL, and JOHN NEWTON DERRY.

The rates of reaction of potassium chloroacetate with ammonia, the three methylamines, the three ethylamines, and dipropylamine in aqueous solution at 25° have been measured, and the velocity constants calculated from the measurements have been compared with those found by Menschutkin for the reactions of the same bases with methyl, ethyl, propyl, and allyl bromides.

289. "*Absence of Optical Activity in the a- and β-2 : 5-Dimethylpiperazines.*" By WILLIAM JACKSON POPE and JOHN READ.

The authors have been unable to effect the resolution of either a- or β-2 : 5-dimethylpiperazine into optically active components by crystallisation with optically active acids or by condensation with *d*-oxymethylenecamphor.

INSTITUTE OF CHEMISTRY.

December 18th, 1912.

MR. W. J. A. BUTTERFIELD, M.A., F.I.C., delivered a lecture on "Chemistry in Gas Works," before the members and students of the Institute of Chemistry at University College, on Wednesday, December 18, 1912, Professor Raphael Meldola (President) in the chair.

Mr. Butterfield dealt first with the features of the gas industry which distinguishes it from other chemical industries, and especially with the variation which is permissible in the composition of the gas produced provided it conforms to the requirements of a public gas supply at the present day. These requirements he stated were: the gas should be that which conveyed the greatest number of heat units to the consumer at the lowest cost, but the gas also must have a strong smell, must give a flame having some, though not necessarily a high natural luminosity, and must not yield on normal combustion products which would be harmful to human beings or would damage the ordinary contents of interiors or the structural materials of rooms, plant, fittings, or other apparatus. He then referred to the growth and magnitude of the gas industry in this and other countries, and estimated the world's production of town gas in the year 1912 at 620,000 million cubic feet, in the manufacture of which about 60 million tons of coal would be consumed, while 30 million tons of gas coke would be sold for use off the gas works, and about 3 million tons of tar produced, together with ammoniacal products equivalent to about 550,000 tons of sulphate of ammonia. He gave the annual consumption of gas per head of the population in the world's chief capital cities, showing that London still headed the list with over 8000 cubic feet as compared with about 6000 cubic feet for Amsterdam, Berlin, New York, and Paris.

He discussed the extent to which gas was consumed for different uses, and showed by statistics and by a diagram of the quantity of gas sent out from a works each hour during twenty-four hours that the predominant use of gas at the present day was for heating purposes. Having regard to this and to the available raw materials and processes for gas manufacture, he stated that the most suitable gas for supply in this country now was characterised by (1) having a gross calorific power of 540 to 580 B.Th.U., (2) its having a specific gravity lying between 0·4 and 0·5, and (3) one volume of the gas requiring 1·0 to 1·1 volume of oxygen for its complete combustion. But the fluctuations in respect of each of these characteristics should be restricted within narrow limits so far as the gas supply to any one district is concerned.

He referred next to the early days of the gas industry, and in particular to the work of Accum, who was the "Practical chymist" on the board of the Gas Light and Coke Company when that company—the first gas company in the world—was founded in 1812. Comparison was made of carbonising methods and results in 1815 and 1912. The sequence of operations on a modern gas works was shown by reference to a diagrammatic plan of a gas works. Gas making processes were divided broadly into carbonising or coal-gas processes and carburetted water-gas processes. In 1910, carburetted water-gas formed 11·8 per cent of the gas supplied from gas works in the United Kingdom, the remainder being coal-gas. The manufacture of carburetted water-gas was briefly described.

Carbonising methods were dealt with more fully, especially in regard to the chemical aspects of modern processes of carbonising in fully charged horizontal retorts and in intermittent and continuous vertical retorts. The differences between the coke and tar produced in horizontal and vertical retorts were shown by means of samples derived from the carbonisation of the same kind of coal in each case:—(1) In horizontal and Dessau (intermittent), (2) in horizontal and Glover-West (continuous) vertical retorts, and (3) in horizontal and Woodall-Duckham (continuous) vertical retorts. The differences between settings of these types of vertical retorts were explained by aid of views thrown on the screen, and charging machinery for horizontal retorts was also referred to. The quality and value of coke, as affected by the process of carbonisation and the system of quenching, were considered. The condensation of coal-gas was discussed.

A demonstration of the action of naphthalene in causing obstructions of gas plant and service pipes was given during the lecture.

The second lecture, which will be given in January, will deal chiefly with the purification of gas, the valuation of by-products of gas manufacture, appliances for the use of gas, and the work of the analyst on gas works.

NOTICES OF BOOKS.

The Technology of Iron Enamelling and Tinning. By Julius Grünwald. Translated by Herbert H. Hodgson, M.A.(Camb.), B.Sc.(Lond.), Ph.D.(Heidelberg). London: Charles Griffin and Co., Ltd. 1912.

The author of this book has published many important communications upon the enamelling and tinning industries, and has done much to put our knowledge of the subjects upon a firm scientific basis; his papers and articles have, however, hitherto been somewhat inaccessible to the average student since they are scattered throughout a comparatively large number of journals and periodicals. Workers who are interested in the enamelling industry especially will be glad to be able to purchase a collection of the papers, and though the chapters in the book are unavoidably rather disjointed, many matters of both practical and theoretical interest are discussed. The articles deal with a variety of subjects, including the manufacture of enamels, the examination of cast-iron enamels, the technological history of tinning, the technological history of tinning, the recovery of tin from tinned waste and tin disease. The translation is accurate, and follows the German very literally.

The Physics and Chemistry of Mining. By T. H. Byron, F.I.C. Second Edition. London: Crosby Lockwood and Son. 1912.

In the second edition of this book the author has omitted the chapter on Magnetism and Electricity, and has thus made room for a rather fuller treatment of the application of the principles of heat and chemistry to the special case of coal mining. For students, mine managers, and foremen the book is a useful little practical guide from which they will learn a great deal more of the subjects which are of interest and importance to them than from very much larger and more comprehensive general works. Both physics and chemistry are treated from a very elementary point of view, but probably quite as fully as is necessary for the special purpose. A number of questions which have been set at the Colliery Managers' Examinations and at the Board of Education Examinations in Mining are given at the end of the book.

Analysis of Metallurgical and Engineering Materials. By Henry Wysor, B.S. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1912.

This book is intended to provide a complete guide to the analysis of all materials used in engineering and metallurgical chemistry, so that the student who uses it will need no other text-book even if at the outset he has no knowledge of quantitative analysis. No theory of analysis is included, though equations are usually given. The directions for the performance of the experiments are always clear and exact, and the average student should not have any difficulty in carrying them out. The book is interleaved with blank pages for notes and numerical results. The course opens with the quantitative analysis of limestone, cement, coke, and coal, and both gravimetric and volumetric work are included. Some gas analysis is described, as well as the calorimetry of gases, and a very short section deals with the microscopic examination of the structure of iron and steel.

The Journal of the Municipal School of Technology, Manchester. Vol. V. Published by the Education Committee. 1912.

This record of the investigations carried out by members of the teaching staff and students of the Manchester Municipal School of Technology during 1911 testifies to the great activity in research work exhibited at the school. Most of the papers have been reprinted from scientific periodicals, but a few of them do not appear to have been published before. They include some of considerable interest by Prof. Knecht, whose work on the estimation of tungsten and molybdenum and on cotton and cotton wax is already well known. An important paper by Mr. J. Prescott deals with the Rigidity of the Earth, and first appeared in the *Philosophical Magazine*. A list of Theses presented by candidates for the degree of M.Sc.Tech. and another of books written by members of the teaching staff are included, and the Record has been excellently printed by the Photographic and Printing Crafts Department of the School.

Chimie Légale. (" Forensic Chemistry "). By R. de Forcrand. Paris: H. Dunod and E. Pinat. 1912.

The text of this book is based upon a course of lectures on forensic chemistry which was delivered by the author at the University of Montpellier. Assuming that his readers possess a knowledge of the details of chemical analysis, the detection of adulterants, poisons, &c., he discusses the giving of evidence in courts of law and the drawing up of reports, and gives details of forms of procedure. The book will naturally be more valuable to French than to English chemists, since it is concerned with the French code only, and does not allude to the regulations and laws of other nations.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xi.—xii., Nos. 16—17, 1912.

Subfluoride of Silver.—M. Guntz.—Vanino and Paula Sachs have questioned the existence of silver subfluoride, and suggest that the supposed compound is a mixture of silver, silver fluoride, and silver hydroxide. The author believes that in their experiments they have not taken sufficient care in freeing their crystals from mother-liquor. When the subfluoride is treated with a neutral solution of sodium chloride it remains neutral or becomes only very slightly alkaline, whereas if a mixture of $AgF + Ag + AgOH$ was present, the reaction $AgF + AgOH + Ag + 2NaCl = NaOH + 2AgCl + Ag + NaF$ would occur, and the solution would become strongly alkaline.

Distribution of Manganese in the Organs of Animals.—Gabriel Bertrand and F. Medigreceanu.—The authors have detected manganese in all the animal organs and products they have examined, except in white of egg. There is no very great difference in the amount of manganese in corresponding organs of different individuals, and most of the organs or products of different species of the same class (mammalia, birds, or fishes) contain very similar amounts of manganese. Milk is very poor in manganese, though it contains rather more than blood.

Action of Uranium on Micro-organisms. — H. Agulhon and R. Sazerac.—The salts of uranyl seem to possess a special selective power towards certain cellules from an antiseptic point of view. Thus a proportion of 1 in 50,000 hinders alcoholic fermentation, while 1 grm. in 1000 of the same salts does not affect the development of Aspergillus or the acetic ferment. Moreover, uranium appears to have a remarkable power of increasing certain oxidation processes.

Determination of Chlorous Acid.—G. Lasègue—Chlorous acid can be determined by precipitating its lead salt as follows:—The chlorite in solution, which must not contain free alkali, is precipitated with an excess of a solution of lead nitrate. After shaking 6 volumes of alcohol at 85° are added, and it is allowed to stand for an hour. It is then filtered through a filter which has been weighed after drying *in vacuo*, and the precipitate is dried *in vacuo* over sulphuric acid and weighed. If the solution contains an excess of alkali it is treated with magnesium nitrate, which gives a precipitate of magnesia and the nitrate of the alkali; the estimation is then continued as before. The method can be used to determine chlorous acid in presence of all other oxygen acids, and even of small quantities of hydrochloric acid.

Determination of Tartaric Acid.—André Kling and D. Florentin.—The racemate method of determining tartaric acid is a general method applicable in estimating the acid in complex liquors as well as in metallic salts. The following solutions are required:—(A) A solution of diammonium citrate, containing 50 grms. per litre; (B) a solution of *l*-ammonium tartrate, absolutely free from the *d*-salt, containing 20 grms. per litre and 5 or 6 cc. of formol; (C) an acetic solution of lime obtained by dissolving 16 grms. of chalk in 120 cc. of acetic acid and making up to a litre; (D) a solution of HCl containing 40 grms. of acid (22° B.) per litre; (E) a solution containing 5 grms. of $CaCO_3$ dissolved in 20 grms. of acetic acid, and 100 grms. of sodium acetate per litre; (F) a solution of MnO_4K, containing about 16 grms. per litre, and titrated against a solution of tartaric acid of known strength. To determine the tartaric acid, 10 or 15 cc. of solution A are added to 150 cc. of the tartaric solution; then 25 cc. of B and 20 cc. of C. The mixture is shaken and allowed to stand for some hours. The precipitate is filtered off and dissolved in D, made up to 150 cc., and then treated with 40 to 50 cc. of E. The liquid is warmed to 80°, cooled, filtered, and the precipitate is dissolved by means of a cold 10 per cent solution of sulphuric acid. The solution is then titrated with F while boiling. The number obtained for the tartaric acid in the racemate when divided by 2 gives the amount of *d*-tartaric acid in the given solution.

Annales des Falsifications. No. 46, 1912.

Use of Sodium Hydrosulphite as Decolourising Agent in Wines, Sugars, &c.—A. Boris.—The use of sodium hydrosulphite, $Na_2S_2O_4$, has only a very slight advantage over that of alkaline disulphites. Even when just sufficient of it is employed it is never completely oxidised to sulphate, but it always gives rise to compounds of the thionic series, among which tetrathionic acid appears to predominate. When used in excess it yields a certain proportion of thiosulphate. All materials which have been treated with $Na_2S_2O_4$ contain compounds of the thionic series, especially tetrathionates and tetrathionic acid; if the treatment has not been carried out with great care they contain thiosulphates, and they may also contain aldehydic compounds of hydrosulphite capable of yielding combined hydrosulphite.

Use of Active Aluminium in the Determination of Arsenic.—E. Kohn-Abrest.—Aluminium rendered active by traces of mercury can be used in certain conditions in Marsh's apparatus to determine arsenic. It is best to use the metal in the form of foil or turnings, and the best degree of activity for the purpose is obtained by immersing it for three minutes in 1 per cent mercury dichloride. The quantity of water used for the generation of the hydrogen should be about 200 cc. to 3 to 5 grms. of metal. Aluminium should not be used when the amount of arsenic is less than 0·0005 grm.

MEETINGS FOR THE WEEK.

Tuesday, 31st.
Thursday, Jan. 2nd.
Saturday, " 4th.
Royal Institution, 3. (Christmas Lecture Epilogues, adapted to a juvenile auditory). "Atoms—Light—Clouds," by Sir James Dewar, F.R.S., &c.

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