THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Crenic and Apocrenic Acids, and on the Formation of Soil.

By Prof. Mulder.

THE author employed in his researches three different soils,—a black bog earth, *a*; a reddish, sandy, less fertile earth, *b*; and a brown and sandy earth from the diluvium, *c*.

On drying, *a* lost 27·74, *b* 32·18, *c* 33·60 per cent. From the undried earths boiling water dissolved of *a*, 0·424; of *b*, 2·771; of *c*, 1·540. The solution contained chloride of sodium, chloride of magnesium, chloride of potassium, chloride of ammonium, free formic acid, acetic, sulphuric, carbonic, crenic, apocrenic and humic acids, combined with potash, soda, lime and alumina. The soils exhausted with water were then extracted with boiling carbonate of soda, and the humine precipitated from the solution by sulphuric acid; *a* afforded 4·249, *b* 5·289, and *c* 8·667. The solutions, freed from humine, were supersaturated with potash, acidulated with acetic acid, and precipitated with acetate of copper. The washed and dried *apocrenate* of copper amounted in *a* to 1·865, in *b* to 1·228, in *c* to 0·701. The *crenate* of copper was thrown down from the filtered solution by careful addition of carbonate of ammonia; the crenate of copper purified by re-solution in a little acetic acid, precipitation by means of alcohol, washing with alcohol, excluding the presence of air, and drying *in vacuo* over chloride of calcium, amounted in *a* to 0·774, in *b* to 1·909, in *c* to 1·260.

The *apocrenate* of copper, as above obtained, still contains some silicic and phosphoric acids; it was desiccated in a dry current of air at 284° Fahr., at which temperature however the water is not always entirely expelled. This salt, abstracting from the above impurities, is a double salt of oxide of copper and ammonia, since the apocrenic acid (which is probably contained in the soil as apocrenate of lime and ammonia) by no means parts with all its ammonia on treatment with carbonate of soda. The salt contains 42·8 per cent. oxide of copper. The substance combined with the copper contains, according to the elementary analyses—

				Equiv.	Calculated.
Carbon	51·89	51·46	50·83 =	48	51·66
Hydrogen	3·75	3·79	4·16	21½	3·78
Nitrogen......	3·37		4·09	1½	3·74
Oxygen				29	40·82

$$= C^{48}\,H^{12}\,O^{24} + 1\tfrac{1}{2}\,NH^{3} + 5aq.$$

However, this ammonia compound has not always this composition; the author obtained from two garden earths a copper compound, the organic substance of which consisted of—

			Equiv.	Calculated.
Carbon..........	48·37	48·18	48	49·24
Hydrogen	3·90	4·04	23½	3·94
Nitrogen	1·11	1·48	½	1·19
Oxygen			31	45·63

$$= C^{48}\,H^{12}\,O^{24} + \tfrac{1}{2}\,NH^{3} + 10aq.$$

Humic acid likewise affords different ammonia compounds. Hermann and Liebig consider these to be perfectly distinct substances; but if the copper be separated and the residuous acid saturated with ammonia, the same compound is obtained in every case.

Apocrenic acid is likewise artificially produced by the action of nitric acid on organic substance and wood charcoal.

Nitrohumic acid, whose atomic weight = 6658, and whose composition of 55·1 C, 3·5 H, 2·9 N, and 38·5 O corresponds to the formula $C^{48}\,H^{17}\,NO^{26}$, is evidently only *apocrenate of ammonia* $= C^{48}\,H^{12}\,O^{24} + NH^{3} + 2aq$. Nitrohuminic acid is tetrabasic; Berzelius found the atomic weight of his nitrogenous apocrenic acid, which is likewise nothing further than an ammonia compound, to be 1667·5, *i. e.* = ¼ of 6558. The lead salt contains 4PbO, and $1NH^{3}$, and is therefore pentabasic. If nitrohuminic acid be saturated with ammonia, a combination is obtained, which, dried at 248°, is represented by $C^{48}\,H^{12}\,O^{24} + 3NH^{3} + 3aq$.

The *nitrophloretinic acid* of M. Stas is likewise nothing further than ⅖-apocrenate of ammonia; its true composition is not $C^{24}\,H^{10}\,NO^{12}$ (Stas), nor $C^{30}\,H^{12}\,NO^{15}$ (Liebig), but $C^{48}\,H^{12}\,O^{24} + 2NH^{3} + 2aq$ (53·39 C, 3·63 H, 5·15 N, 37·83 O). On treating phlorizine with nitric acid, phloretine and grape-sugar are first formed; this latter is then converted into humic acid, which renders the liquid black; and lastly, from the phloretine and humic acid is derived the apocrenate of ammonia, which renders the liquid again blue.

The author obtained *pure apocrenic acid* by converting humic acid from sugar by means of nitric acid into nitrohuminic acid, boiling this with potash, evaporating, dissolving the residue in water, supersaturating with sulphuric acid, adding some alcohol, removing the sulphate of potash by filtration, and precipitating the solution with acetate of copper. This salt of copper, dried at 212°, contained 24 per cent. oxide of copper (atomic weight 1548). The organic substance in it contained no nitrogen, 57·61 C and 3·09 H; the formula $C^{48} H^{13} O^{25}$ requires 57·95 C and 2·56 H. The copper salt is therefore undoubtedly $C^{48} H^{12} O^{24} + 4CuO + aq.$

The apocrenic acid, separated from it by sulphuretted hydrogen, and dried at 284°, contained 57·35 C, 3·36 H; $C^{48} H^{12} O^{24} + 2\,aq.$ requires 56·94 C, 2·71 H. A lead salt which was prepared proved to be anhydrous, for the organic substance in it contained 59·06 C, 2·87 H, and $C^{48} H^{12} O^{24}$ requires 59·00 C, 2·41 H.

Crenic Acid.—The crenate of copper above prepared likewise contains phosphoric acid; it is moreover very difficult to deprive it of water. Dried at 284°, it contained 74·12 per cent. oxide of copper and the organic substance contained in it:—

			Equiv.	Calculated.
Carbon	44·98	=	24	45·59
Hydrogen	5·50		17	5·27
Nitrogen..............	3·88		1	4·41
Oxygen			18	44·73

Consequently the atomic weight would be 4023·63; Berzelius found $1345{\cdot}9 = \frac{4037{\cdot}7}{3}$. The so-called crenic acid of the copper salt however is likewise an ammonia compound $= C^{24} H^{12} O^{16} + NH^{3} + 2\,aq.$ If the copper salt be again dissolved in acetic acid and precipitated by alcohol, the quantity of ammonia contained in it diminishes considerably. The organic substance contained, in one case, 45·77 C, 5·35 H, 1·94 N, which corresponds to the formula $2(C^{24}H^{12}O^{16}+HO) + NH^{4} O$; in a second, the amount of nitrogen was almost imperceptible, and the substance consisted of 46·87 C, 4·97 H; the formula $C^{24} H^{12} O^{16} + 3\,aq$ requires 46·78 C, 4·77 H.

Crenic acid is consequently $C^{24} H^{12} O^{16}$, but 2 equiv. crenic acid $+ O^{4}$ are apocrenic acid + 12 H O.

It is easy to observe that no other product is formed besides water, on the conversion of the moist crenate of copper into apocrenate in a glass filled with air and closed by mercury. The volume of air diminishes. If some potash be passed under the bell-glass, no further diminution takes place; the brown apocrenate, which has originated from the grass-green salt of the crenic acid, does not effervesce with acids.

Formation of Vegetable Mould.—From what has been stated, it follows that all the constituents of vegetable mould hitherto known (the geic, ulmic, humic, crenic and apocrenic acids) are non-nitrogenous bodies; they can combine with ammonia and other bases, and in part occur in combination with them. It is highly probable that no other peculiar stable products resulting from the decomposition of organic substances occur in the soil. The origin of these bodies cannot be demonstrated with certainty in all; apocrenic acid can and must originate from the crenic acid, and probably likewise from humic acid.

In what manner the crenic acid is formed is more difficult to determine; we find in it the same number of atoms of carbon as are present in cellulose, starch, gum and sugar. If the crenic acid in the soil is formed by the putrefactive decomposition of one of these substances, which is highly probable, it can only be effected by the assimilation of oxygen and the elimination of water.

In wood undergoing decay we find at the commencement of the process crenic, apocrenic and ulmic acids. The crenic acid disappears when the decaying substance is exposed to the free action of the atmosphere. In combination with bases, it has almost a greater tendency to pass into apocrenic acid; no crenic acid therefore occurs in the uppermost layers of the earth; it can only exist in the lower ones. If humic acid or humine originate from cellulose, ulmic acid and ulmine must be first formed; and these are then converted, by the oxidizing influence of the atmosphere, into humic acid and humine. Lastly, if geic acid is formed from humic acid, this must likewise result from oxidation. If cellulose is converted into ulmic acid, this can only be effected by the assimilation of oxygen and the elimination of carbonic acid and water.

We are only acquainted with seven substances, the fixed products of the decomposition of cellulose, one of the principal constituents of the vegetable kingdom; these are ulmine, humine, and their acids, geic, crenic and apocrenic acids. The analysis of entirely different kinds of vegetable mould has afforded none other. What becomes of the so-called encrusting substance of the cellulose is not known, any more than what becomes of the vegetable acids and vegetable bases, of the resins, colouring substances, and many other bodies of the vegetable kingdom. It is known that animal substances, at least all the proteine compounds, are converted into humic acid and ammonia, with absorption of oxygen. This is not known of gelatine, but it has been proved that ammonia may be produced from it. What becomes of the other elements on putrefactive fermentation is still unknown.

Now if we take the three substances first formed in the soil, and which always occur in it, and imagine them to be derived from cellulose, we have—

Ulmic acid	$C^{40}\ H^{14}\ O^{12}$
Crenic acid	$C^{24}\ H^{12}\ O^{16}$
Apocrenic acid	$C^{48}\ H^{12}\ O^{24}$
	$C^{112}\ H^{38}\ O^{52}$

If these three substances originate at the same time from cellulose, we see that with the formation of carbonic acid there remain 30 equiv. hydrogen:—

5 equiv. cellulose	C^{120}	H^{105}	O^{105}
Deduct 8 equiv. carbonic acid	C^{8}		O^{16}
	C^{112}	H^{105}	O^{89}
Ulmic, apocrenic and crenic acids..	C^{112}	H^{38}	O^{52}
		H^{67}	O^{37}
37 water........................		H^{37}	O^{37}
		H^{30}	

Now we know that in the putrefactive fermentation oxygen is absorbed without there being much carbonic acid given off; this oxygen serves to combine with the hydrogen to form water. In the conversion of pure cellulose into ulmic acid, we found that 8 equiv. carbonic acid were set free. No absorption of oxygen is necessary for the disengagement of this carbonic acid, just as little as in the vinous fermentation of sugar; but if ulmic acid has to be formed from the so-called encrusting substance, from a substance the quantity of which is far more considerable in woody plants than that of the true cellulose, the liberation of carbonic acid and the absorption of oxygen take place in a still unknown proportion. If the ulmic acid is probably converted into crenic acid, oxygen is requisite, and undoubtedly far more than there is disengaged of carbonic acid; here again there is an excess of hydrogen. In a word, in the putrefactive fermentation of the indifferent vegetable substances, as cellulose, starch, gum and sugar, and their conversion into humine, ulmine, ulmic, humic, crenic and apocrenic acids, hydrogen is constantly set free, and far more when all these substances being in a continual state of decomposition are converted with absorption of oxygen into carbonic acid.

The question now is whether the whole of the hydrogen combines with oxygen of the atmosphere to form water. According to Liebig, this must be answered in the affirmative; according to him, the whole of the hydrogen and carbon of vegetable substances are finally converted by the oxygen of the atmosphere into water and carbonic acid.

It is above all necessary to distinguish two relations in the process of putrefactive fermentation, perfect and imperfect access of air. When the first is the case, the carbon and the hydrogen of the organic substances become entirely oxidized to carbonic acid and water; and if the substance contains nitrogen, this is oxidized to nitric acid, ammonia having been first formed, as has been distinctly shown by Liebig. Putrefaction proceeds however quite differently when the access of oxygen is imperfect; in this case the so-called humic, ulmic, geic and crenic substances are first produced. The carbon not finding oxygen enough to become carbonic acid, forms carbonic oxide, and with the hydrogen carburetted hydrogens; the hydrogen combines with the nitrogen of the organic substances to form ammonia, but proceeds no further; and when sulphur and phosphorus are present, it forms with them sulphuretted and phosphuretted hydrogen.

In the soil the access of air is in part perfect, in part imperfect. The upper layers undergo quite a different change to what takes place with those situated inferiorly. In the former a perfect oxidation to carbonic acid, water and nitric acid (after previous formation of ammonia) results; in the inferior layers the oxidation also proceeds to a certain degree, but part of the products formed are identical with those which originate from organic substances in a confined space. No great quantity of carbonic acid can be produced in the inferior layers, no ammonia be oxidized to nitric acid; in them the soil is mixed with atmospheric air, but this is refreshed and renewed but very slowly; its oxygen is used for the oxidation of the carbon and hydrogen, the nitrogen remains.

It is known that organic bodies inclosed in a vessel with air and exposed to a certain temperature, generally decay and become mouldy much quicker than when the air can be renewed; the same prevails with respect to the soil. Hermann is inclined to admit, as proved by his experiments, that during decay, not only oxygen, but likewise nitrogen is condensed. These experiments themselves are not sufficiently accurate to admit of any conclusions being drawn from them; but we have sufficient experience, on a large scale, in the formation of nitre, to arrive at the conviction that nitrogen can be condensed from the atmosphere and become converted into nitric acid.

If we moreover add, that in the artificial formation of nitre ammonia is first formed, whether it be solely from the nitrogenous animal substances, or from these and the nitrogen of the atmosphere and the hydrogen of the putrifying bodies together, and that this ammonia is oxidized by the oxygen of the atmosphere to water and nitric acid, which Liebig and Kuhlmann have rendered highly probable, then a similar change must take place in the air confined in the soil. The oxygen, which is always liberated in the process of putrefaction, finds air in the soil with which to form ammonia, which subsequently becomes oxidized to nitric acid and water. All porous minerals contain ammonia, which is said to be condensed from the atmosphere; but if we consider that the air inclosed in cellars forms nitric acid, and is a product from the oxidation of the ammonia, the ammonia found in porous bodies is rather a product from a combination of the nitrogen of the atmosphere, just as in the nitre caves of Ceylon.

Whether any formation of nitre results in the soil from the oxidation of the ammonia cannot be determined with certainty; but it is highly probable that no such oxidation takes place, for there are always sufficient substances present liberating carbon, which combines with the oxygen of the atmosphere to form carbonic acid, and so prevent the oxidation of the ammonia to water and nitric acid. Otherwise the conditions in the soil are favourable to the formation of nitre, lime:—magnesia and potash, three bases which act so important a part in the nitrification, likewise occur in this.

That apocrenic acid can originate in this manner from humic acid, is highly probable from the action of nitric acid on humic acid. Humic acid and nitric acid form, for instance, $\frac{1}{5}$-apocrenate of ammonia, formic and oxalic acids, N and O^{44} being absorbed from the elements of the nitric acid. A true nitrification therefore cannot take place in the soil, since as soon as nitric acid is formed by the oxygen of the atmosphere from the ammonia combined with the humic acid, this instantly converts the humate of ammonia into apocrenate of ammonia, while at the same time carbonic acid is produced instead of formic and oxalic acids.

A higher oxidation of apocrenic acid converts this into crenic acid. Berzelius observed apocrenic acid to be quickly converted into crenic acid under the influence of nitric acid. In the uninterrupted action therefore of the oxygen of the atmosphere in a confined space, with the presence of decaying substances, it is probable that the ammonia inclined to the formation of nitre parts with its oxygen to the apocrenic acid to form crenic and carbonic acids.

That wood-charcoal, in which plants are able to grow, can likewise form ammonia in the same manner from water and the inclosed air, and thus give rise to the formation of apocrenic and crenic acids, is highly probable from the experiments of Berzelius, who prepared apocrenate of ammonia from nitric acid and wood-charcoal. This change must be assisted by the influence of vegetation. A small quantity of ammonia, arising from some organic substance, perhaps from the fallen cotyledons of the germinating plant, may first set this process going, which is then continued by the inclosed moist atmospheric air. This enables us to explain the origin of the 2 per cent. of humic extract which Büchner found in some vegetable charcoal which Lucas had employed for a year in the cultivation of plants. —*Journ. für Prakt. Chem.*, xxxii. p. 321.

*On the Action of Lead in Distilled and River-Water**.

By RICHARD PHILLIPS, Jun.

The author considers, from the action which is the subject of his paper, the following points of interest to arise:—1st, whether it is necessary that the lead should be exposed to the air, or whether the action would take place if it were below the surface of the water; 2nd, whether pure or distilled water, deprived of all atmospheric air, has any action on lead; 3rd, as to what is the nature of the white precipitate; 4th, if, besides this white precipitate, any soluble salt of lead is found; and 5th, as to which of the salts contained in river-water the non-formation of the white precipitate is due.

He proceeds to notice the remarks of Dr. Christison and Colonel Yorke on these subjects, and then gives his own experiments.

As to the first. In bottles containing distilled water were placed two pieces of lead of nearly equal size. In both a white precipitate occurred, but in that in which the lead had been exposed above the surface of the water, a far greater quantity than in the one where the lead had been covered with the water; and he concludes from this experiment, that although it is not necessary that the lead should be exposed above the surface of the water for the action to take place, still by offering a passage to the gases contained in the atmosphere it accelerates it.

The author observes, "I have before stated, Dr. Christison does not describe the method by which he performed his experiment on the non-solubility of lead in pure distilled water; and although I agree with him as to the fact, as I found some difficulty in ascertaining it, I will describe the process I followed. I found that on boiling pure distilled water so as to deprive it of all atmospheric air, that when it

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* Read before the Pharmaceutical Society, Dec. 11, 1844.

had regained its former temperature, and was placed in a well-stoppered bottle with a piece of lead, the bottle being perfectly full, although no action was apparent, and the lead remained almost as bright as when first placed in the bottle, yet if a little hydrosulphuric acid was added to the water, it instantly became of a brown colour, showing the presence of lead, the water having on cooling absorbed sufficient atmospheric air to act on the lead. If, on the contrary, the water was placed in the bottle when warm, and the lead immediately added, and the bottle stoppered, on cooling a vacuum was formed, which it was impossible to maintain, and the lead was acted upon. I therefore repeated the last experiment, but took the precaution, when the bottle was quite full and no vacuum had formed, to plunge the stopper under mercury, and to pour water above the mercury. The experiment was allowed to remain for some months; the lead retained its original brightness; and on breaking off the neck of the bottle, it being impossible on account of the vacuum to take out the stopper, not the slightest effect was produced on the liquid by hydrosulphuric acid, thus proving that pure water, without the presence of air, has no action on lead.

"From my experiments I am led to the same conclusion as Colonel Yorke, as to the manner of the formation of the white precipitate; in fact, I have obtained small masses of crystalline scales, which have formed on the surface of lead, which have dissolved without the slightest effervescence in acetic acid. I do not think, however, any fixed composition can be assigned to this substance, as on repeating his experiment of drying it under the air-pump upon two different specimens, one of which had been kept some years, and the other only a few weeks, in the former a much larger amount of carbonic acid was found than in the latter, showing that the precipitate had no definite composition, but that it depended, as to the quantity of carbonic acid, on the length of time it had been exposed in the solution.

"As to the existence of either of the salts of lead mentioned in a soluble state, I must confess that I differ with the two authorities I have named, and believe that what they consider to have dissolved is merely the hydrated oxide of lead held in a state of mechanical suspension, and for the following reasons:—I found that, in repeating an experiment of Colonel Yorke's, that of precipitating hydrated oxide of lead and washing it with warm distilled water, that the filtered liquor gave a brown precipitate with hydrosulphuric acid, after all the soluble salts formed had been washed away; but that on refiltering a portion of it through more than one filter, not the slightest discoloration was given to the liquor by the test; and as Colonel Yorke considered that the soluble salt was the hydrated oxide, a greater quantity of which would exist, as already shown, at the commencement of the action of the lead on the water, I placed a piece of lead in distilled water, and carefully tested the filtered liquor daily, for some weeks, with hydrosulphuric acid, but in no case could I find the slightest discoloration given to it. Now as the test is so delicate as to be capable of discovering, according to Pfaff, a 100,000th part of the metal in solution, if, as Colonel Yorke states, a 10,000th part of the oxide is held in solution, the test would of course have distinctly shown it.

"Dr. Christison considering that the action of the formation of a soluble salt of lead was due to the carbonate of lead becoming converted into bicarbonate by long exposure, I tested the liquid from one of the experiments I have before mentioned, when the lead in distilled water had been exposed to the action of the atmosphere for six years, and could not detect the slightest discoloration after the solution had been carefully filtered. I therefore conclude from these experiments, and I believe Dr. Thomson has previously arrived at the same result, that no soluble salt of lead is formed by the action of atmospheric air on lead in distilled water."

As to the last question, "to which of the salts contained in river-water the non-formation of the white precipitate is due," the author states that it is the sulphate of lime, and considers that the chloride of sodium, which has been generally supposed to be capable of exercising this preservative power, does not possess it, on account of its forming when decomposed a salt of lead partly soluble.

In conclusion, he remarks that the non-action of rain-water which had fallen after a long continuance of dry weather on lead, is probably due to the small amount of carbonate of ammonia which is contained in atmospheric air.

Examination of the Root of Rhubarb. By MM. SCHLOSSBERGER *and* DÖPPING.

An historical introduction leads the authors to the conclusion that our knowledge of the rhubarb root and of its active principles is by no means satisfactory, and consequently that fresh investigation is desirable. This investigation the authors made in the following manner:—

When alcohol of 0·912 to 0·863 spec. grav. is added to pulverized rhubarb, it becomes coloured of a deep brown yellow, from its extracting a considerable quantity of soluble constituents. When the spirituous extract is submitted, after one or two digestions, to strong pressure, and the residue digested afresh with spirit, it again becomes strongly coloured; on frequently repeating the operation of expression and extraction, the residue has only a faint yellowish colour, and no longer possesses the peculiar odour and taste of rhubarb, not even when warmed. Extraction with spirit is preferable to exhaustion with water or alkalies, as pectine, gum, and several salts, do not become dissolved.

The spirituous extract possesses the peculiar taste of rhubarb in a high degree, especially when the spirit has been expelled. The residue from the alcoholic extract thus obtained is yellowish-brown and of a syrupy consistence. It yields one portion to water; the other portion, which is principally a mixture of resins, remains undissolved.

I. *The portion of the spirituous extract insoluble in water* was evaporated in the water-bath to dryness, dissolved in the smallest quantity of alcohol of 0·863, and æther added to this solution as long as a precipitate formed. The latter had a grayish-brown colour and flocculent appearance; separated from the liquid by filtration, washed with æther, and pressed between blotting-paper, it acquired a yellowish-brown colour. Treated again with alcohol of 0·863, one portion was dissolved, and another portion was left behind; the residue was very sparingly soluble in hot alcohol, æther, cold and hot water, and readily soluble in ammonia and potash with a brown colour, from which it was precipitated by acids in brown flakes. The authors endeavoured to purify it by solution in potash, precipitation by sulphuric acid, and washing with water, until sulphuric acid could no longer be detected by barytes. Its composition agreeing with that of a resin from rhubarb, and its similarity to those substances comprised under the name of apothema, have induced them to call it *aporetine* of rhubarb. It is recognized by the above-mentioned properties, has when dry a black shining colour, is easily pulverized, and is decomposed when heated on platinum foil without melting. It consists of 58·89 C, 4·35 H, 36·76 O.

The portion *a* of the precipitate produced by æther, and separated by means of spirit from the aporetine, forms when dry and pulverized, a yellowish-brown powder, with the following properties:—It is extremely difficult of solution in water and æther, readily soluble in alcohol and alkalies, being re-precipitated from solutions of the latter by mineral acids with a yellow colour; it dissolves in acetic acid with a yellow colour. Its combinations with the alkalies are of a deep red brown; heated on platinum foil it melts with evolution of yellow vapours, diffusing a faint smell resembling rhubarb, and leaving behind scarcely any traces of ash. With respect to the yellow vapours which it gives off on being heated, they appear to indicate the presence of a peculiar acid, to be subsequently described; but all experiments to separate the latter had no result. Its taste did not resemble that of rhubarb. It dissolved in concentrated sulphuric acid, and was again precipitated from this solution by water in yellow flakes. The yellow colour which it possesses in its recently-precipitated moist state, led to its being confounded in many of the previous treatises with chrysophanic acid, the more so as it also partakes of the property with this latter of being coloured red by alkalies, which subsequently passes, it is true, into brown. On account of this last circumstance the authors call it the *brown resin* of the rhubarb (*phæoretine*). It consists of—

					Equiv.	Calculated.
Carbon	58·40	59·86	59·73	=	16	60·27
Hydrogen	4·97	5·15	5·15		8	4·95
Oxygen........					7	34·46

A lead compound, dried at 212°, contained 64·53 PbO, 20·4 C, 1·6 H; it does not therefore appear to be in chemical proportions.

When the *æthereal* solution of the resin from which the aporetine and phæoretine have been separated is freed by distillation from æther, the residue again evaporated to dryness, reduced to powder, dissolved in the smallest quantity possible of spirit, and again treated with æther as long as anything is precipitated from it, a quantity of resin, insoluble in æther but soluble in spirit, separates. This resin, however, is not distinct from the phæoretine.

The æthereal liquid, freed from this mixture of phæoretine and obtained pure by filtration, left, on distilling off the æther, a resinous residue, which was dried and pulverized, and again treated with æther as long as anything was removed. A blackish-brown granular substance remained, and the æther acquired a deep reddish-yellow colour. The granular residue deposited, on being treated with a small quantity of alcohol, the yellow body frequently mentioned above, and the mother-ley consisted for the greatest part of phæoretine. The light-coloured substance was purified by crystallization from adherent resin.

The æther was again partially removed from the deep reddish-yellow solution by distillation, and the residue left to itself in a porcelain basin which was accurately closed. After some days nearly the whole mass in the basin had congealed to a paste of crystals. With the addition of a little æther the crystals could be freed from the mother-ley by filtration; they were consequently frequently washed with it, being but sparingly soluble in it when isolated and free from resin. The filtered æthereal solution deposited on cooling more crystals.

When no more crystals separated from the æthereal mother-ley, it was evaporated to complete dryness. The substance obtained again presented all the properties of a resin. This resin, which is soluble in æther, forms with potash and ammonia brilliant purple-red combinations easily soluble in water, on which account the authors propose for it the name of *Erythroretine.* When pulverized it forms a yellow powder resembling that of rhubarb.

After desiccation the erythroretine dissolves with some difficulty in æther and acetic acid, not in hydrochloric and dilute sulphuric acids; it is readily soluble in alcohol, and is precipitated by acids from its alkaline combinations in yellow flakes, which soon aggregate. It dissolves in cold concentrated sulphuric acid with a brown-red colour, and is precipitated, on dilution with water, in yellow flakes. Like phæoretine, it dissolves in minute quantity in water, colouring it faintly yellow. Heated on platinum foil, it gives off yellow vapours, and yields a cinder which is difficult of consumption, but which leaves scarcely any ash behind. It has scarcely any taste. Dissolved in ammonia, it yields with basic acetate of lead a violet-red compound, insoluble in water; but on washing the precipitate so obtained, it is evidently changed by the carbonic acid of the atmosphere, becoming covered on its surface with a white coating of carbonate of lead.

Erythroretine consists of—

Carbon	63·08	62·94	19	63·96
Hydrogen	5·46	5·72	9	4·98
Oxygen			7	31·06

The lead compound contained 69·27 PbO, 16·8 C, 1·4 H; it allowed therefore no conclusion being made as to the constitution.

The *yellow granular crystalline body* which had separated from the æthereal solution of the resin, and which has already been described by several chemists under the different names of Rheine, Rheumine, Rhabarberic acid and Rhubarb yellow, &c. possessed in its perfectly pure state the following properties:—

It is a beautiful pure yellow substance, which crystallizes with difficulty, and generally separates in granular aggregations, is void of taste and smell, not easily soluble in æther even on boiling, although colouring it strongly, almost insoluble in cold, somewhat more soluble in boiling water, colouring it bright yellow; in hot alcohol of 0·863 spec. grav. it is tolerably soluble, very insoluble in acetic acid and dilute mineral acids; oil of vitriol dissolves it with a splendid red colour, but it is again precipitated on dilution with water in yellow flakes; alkalies dissolve it readily of the colour of the most beautiful red ink, and of such depth, that, as already observed by Brandes and Geiger, this colouring substance forms one of the most sensitive tests for alkalies. It is dissolved with a yellow colour by concentrated nitric acid, and on the application of heat is partially changed, as is rendered evident by the altered colour after supersaturating with ammonia. Contrary to the assertion of Jonas, the authors could not observe that sugar increased the solvent power of water for this substance. On evaporating the combination of the yellow body with potash to dryness, the red colour passes through violet into a beautiful blue, with deposition of an insoluble blue compound, which however on the addition of water again acquires its former red colour. Heated on platinum foil it volatilizes for the great part in yellow vapours, which are mostly deposited on cold objects as a yellow film; a quantity of the body however is always carbonified in this operation.

A spirituous solution of basic acetate of lead, added to a solution of the above body in alcohol, deposits a white powder, which disappears on boiling with water, while a carmine-red gelatinous mass separates.

All these reactions exhibit the greatest coincidence with those of the chrysophanic acid prepared by Rochleder and Heldt from *Parmelia**, and the analysis likewise afforded 68·69 C and 4·24 H. The great difference in Brandes and Leber's analyses of the so-called Rhabarberic acid probably arises from imperfect combustion.

Taking advantage of the properties of chrysophanic acid, and especially of the firmness with which its elements are combined, the authors have endeavoured to discover a shorter method for its immediate preparation, by carbonifying the finely-powdered rhubarb, as in the preparation of alizarine, with concentrated sulphuric acid, whose powerful action it withstands; the result however on the whole was very unsatisfactory. A considerable quantity of the yellow substance was obtained on extracting the coal with spirit and

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* See Chem. Gaz., vol. ii. p. 162.

then distilling it off; but it was always accompanied by a large amount of erythroretine, and, in the second place, it was extremely difficult to determine in advance the quantity of oil of vitriol requisite for the complete carbonization of the resins.

The authors also tried a third mode of preparation, viz. dry distillation; but such quantities of empyreumatic products accompanied the yellow vapours as to render it more difficult to obtain pure chrysophanic acid from the distillate than from the crude rhubarb.

II. *Examination of the Portion of the Spirituous Extract of Rhubarb soluble in Water.*—This forms a red liquid, which possesses in a high degree the bitter nauseous taste and smell of rhubarb. On treating it with an excess of sulphate of soda, it deposits a considerable quantity of resin, which, as is so frequently the case, had been dissolved in water through the medium of other matters. It was however impossible to obtain a perfect separation of the resin by sulphate of soda, for an addition of sulphuric acid always produced a flocculent sediment of resin. This resin, after separation from the sulphate of soda, did not differ from the above-described phæoretine except by a small amount of chrysophanic acid and resin soluble in æther (erythroretine). Perchloride of iron produced in the liquid, which had been shaken with the sulphate of soda, a considerable black precipitate, which, as it was still evident after digestion with animal membrane, which removed the whole of the *tannin*, proved the presence of *gallic* as well as tannic acid. If the solution which has been treated with sulphate of soda, after it has been separated from the salt and resin by filtration, be digested with calcined magnesia, evaporated to dryness and extracted with strong spirit, this acquires a deep red colour. The solution is free from tannic and gallic acids, and leaves on evaporation a reddish-brown, slightly-bitter *extract*, which however does not taste of rhubarb, dissolves entirely and with great ease in water, and, examined by Trommer's test, indicated the presence of sugar. In confirmation, a portion of the extract was dissolved in water and mixed with yeast, when a lively fermentation began, and a considerable disengagement of carbonic acid.

The authors did not find in their investigation any fat or wax, which are enumerated in several analyses; their presence however in small quantity is not at all improbable; perhaps they do not occur in all kinds of rhubarb. They found starch and pectine in considerable abundance, even in the best Russian rhubarb.

Since the organic acid in rhubarb, mentioned in all former analyses, is destroyed by reducing it to ash, the authors endeavoured to dissolve out its combination by treatment with dilute muriatic acid; the solution gave an abundant precipitate on neutralization with ammonia, which was digested with sulphuric acid after filtration and edulcoration; the filtered solution, neutralized with ammonia, deposited a considerable quantity of gypsum and some oxalate of lime, and gave an abundant precipitate with solution of sulphate of magnesia after repeated filtration. Malic acid, which is said to be a constituent of several species of rhubarb, could not be detected either in the muriatic solution from which the oxalate of lime had been separated by ammonia, or in the precipitate, or in the aqueous extract of the rhubarb.

When rhubarb is burnt, it yields a very considerable quantity of ash, of which but a small portion is dissolved by water; the aqueous solution proved to contain potash and soda; the portion insoluble in water dissolved entirely, with the exception of a little silica and sand, in dilute hydrochloric acid, with effervescence; it was found to contain traces of peroxide of iron, phosphate of lime and magnesia. The inorganic acids contained in the ash were the sulphuric, muriatic (chlorine), phosphoric and carbonic acids.—Liebig's *Annalen*, l. p. 496.

On the Atomic Weight of Zinc, according to M. A. ERDMANN.

In 1841 and 1843 Jacquelin obtained the number 414, recently M. Favre 412·5, for the atomic weight of zinc. The difference in these numbers induced the author to repeat the examination.

He employed zinc which had been distilled in a porcelain retort, and converted it into oxide with nitric acid, whence the number 410 resulted, in some experiments somewhat higher, in others somewhat lower. But the oxide of zinc so obtained was not free from oxide of lead, owing to commercial zinc containing lead; and the lead, although far less volatile than zinc, evaporates according to the laws of distillation of mixed bodies in the zinc vapour, and condenses with it, so that a perfect separation of these two metals cannot be effected by distillation.

He now prepared a perfectly pure oxide of zinc, mixed it with sugar, carbonized the sugar by gentle ignition of the mass in a covered crucible, conveyed the oxide thus mixed into a porcelain tube, exposed it to a very high temperature, and reduced it in a current of hydrogen. The pure zinc so obtained was oxidized, and the amount of oxygen taken up determined. It was found that the experiment could not be performed in a platinum crucible, since at the end of the experiment, when the oxide of zinc was removed, the platinum was observed to be coloured blue at all the places where it had been in contact with the oxide of zinc, arising from the formation of an alloy of zinc and platinum, which caused the atomic weight to turn out too high.

This source of error was avoided on performing the experiment in a porcelain crucible. Four experiments now gave for the atomic weight of zinc the numbers—

406·249 406·519 406·649 406·947

The mean of the decimals, whose fluctuations do not amount to more than what is called an unavoidable error of observation in all experiments, is 0·591. According to these experiments therefore the atomic weight of zinc is 406·591, only 3·365 higher than that formerly admitted (403·226) according to Gay-Lussac's determination.

In accordance with this, Erdmann calculates the composition of the oxide of zinc at—

		Old number.
Zinc	80·26	80·13
Oxygen	19·74	19·87
Of sulphuret of zinc at—		
Zinc	66·91	66·72
Sulphur	33·09	33·28
Of the sulphate of zinc at—		
Oxide of zinc	50·26	50·10
Sulphuric acid	49·74	49·90

Poggendorff's *Annalen*, lxii. p. 611.

Examination of Jalap Resin. By G. A. Kaiser.

Besides the ordinary *Jalapa tuberosa* or *ponderosa*, which occurs from the size of a nut to that of a fist, and which is derived from *Ipomæa Schiedeana*, Zuc., there is also met with at present another kind derived from *Ipomæa orizabensis*, which is paler, more fibrous, has a fainter smell and taste, and is known by the name of *Rad. Jalapæ fusiformis s. lævis* (*Stipites Jalapæ*). The resins from both agree, and are thereby distinguished from all other resins with which they might possibly be adulterated, in their being gradually dissolved by concentrated sulphuric acid, and depositing after some hours a brown smeary resin. Both are however essentially distinct. The resin from *Ipom. orizabensis* is simple and entirely soluble in æther; this was examined by Johnston, and found to be $C^{40} H^{34} O^{18}$; the author found $C^{42} H^{34} O^{18}$, and calls it *Pararhodeoretine*. The resin from *Ipom. Schiedeana* consists, on the contrary, of a soft resin soluble in æther and a resin insoluble in æther, which the author terms *Rhodeoretine*, which is identical with the Jalapine of Herberger and Buchner, but does not possess the properties of a base, but those of an acid, is decomposed by concentrated acids like salicine into grape-sugar and *Rhodeoretinole* = $C^{42} H^{35} O^{20}$, and gives an hydrate and various salts. This resin has likewise been examined by Cadet de Gassicourt and Gœbel.

Rhodeoretine: *Preparation.*—The root of *Ipom. Schiedeana* was treated with alcohol of 0·863 spec. grav., the extract mixed with water, and the alcohol removed by distillation; the dark brown resin was separated, boiled with water, and then washed with hot water as long as anything was removed, upon which it was again dissolved in alcohol of 0·863 spec. grav., and the solution digested two or three times with washed animal charcoal until it acquired a bright, faint, wine-yellow colour; the filtered alcoholic solution was then diluted with water and the alcohol distilled off. The resin obtained had a slight yellowish tint, and was of the consistence of Venetian turpentine, was boiled with distilled water, and treated several times with water, which takes up a considerable quantity of resin. Thus purified and evaporated to dryness in a water-bath, the resin formed a yellowish-white brittle mass, which possessed the well-known smell of jalap. The dry resin was boiled in a retort with æther as long as anything was removed. Finally, the resin was re-dissolved in a little alcohol, and then precipitated with æther. In this manner a colourless, perfectly transparent resin was obtained, a thin dry layer of which on a glass plate could scarcely be distinguished by the eye. The resin was then evaporated in a water-bath to dryness.

When pulverized it forms a nearly white powder, without smell or taste, insoluble in water and æther, but very readily soluble in alcohol. It is thrown down of a white colour from this alcoholic solution by water; the precipitate dissolves entirely in ammonia and acetic acid. The alcoholic solution has a faint acid reaction, dissolves but sparingly in cold potash, soda and the carbonate alkalies, but entirely on the application of heat. From these solutions acids do not precipitate it any longer; it dissolves entirely in cold concentrated ammonia with a light brownish colour; on expelling the excess of ammonia by heat a neutral solution is obtained, which may be mixed in all proportions with alcohol and water. The solution of this neutral salt of ammonia is not precipitated by nitrate of silver, neutral acetate of lead, chloride of barium or sulphate of copper; a flocculent precipitate is obtained only by means of basic acetate of lead. The solutions of the potash and soda salt behave towards these reagents just as the ammonia salt. Since the above method would not suffice to obtain a combination of the resin with earths and metallic oxides in the solid form, an alcoholic solution of the resin was boiled with hydrate of lime and magnesia; but none of the oxides could be detected in the filtered liquid. The resin was thrown down unaltered by water, nor was there in the residue any combination of the resin with the bases. Upon this an alcoholic solution was mixed with water till the resin began to separate; it was then boiled with oxide of lead, hydrate of lime and magnesia, but no salt could be obtained in a solid state even in this manner. If a solution of the ammonia salt is boiled with hydrate of lime until no more ammonia is given off, a lime salt is formed, soluble in water and alcohol, but from which no resin can be separated by muriatic acid. Treated in the same manner with hydrate of barytes, a salt readily soluble in water and alcohol is likewise obtained, but from which no resin could be separated by means of acids. Acetic acid dissolves the resin with ease; concentrated nitric acid dissolves it in the cold unaltered; when ammonia is added it again separates; cold dilute nitric acid does not dissolve it; on the application of heat it is dissolved with decomposition; it is insoluble in cold dilute, but is decomposed by concentrated sulphuric acid; moistened with it on a watch-glass, each particle becomes, in about ten minutes, of a beautiful carmine red, and dissolves; the liquid acquires a darker colour, and after some hours a brownish-black resinous body separates. Heated on platinum-foil, the resin first melts, and becomes brown, with evolution of a peculiar empyreumatic odour, and then burns with a bright, somewhat smoky flame, leaving behind a porous shining cinder, which at last disappears entirely. At 302° it melts to a bright yellow transparent mass, without however parting with any more water.

The pure resin was pulverized, dried at 212°, and burnt with chromate of lead. It furnished—

			Equiv.	Calculated.
Carbon	56·49	56·35	42	56·66
Hydrogen	7·94	7·89	35	7·78
Oxygen	35·57	35·76	20	35·56

Salt of Ammonia.—Some ammonia was poured over a quantity of the resin, and digested with it until it was entirely dissolved. The liquid, which had a somewhat brownish colour, was warmed until the excess of ammonia had been removed and the liquid had become perfectly neutral. On evaporation in the water-bath, the combination formed a brownish resinous mass, which was very readily soluble in alcohol and water; it possessed no odour, a bitter taste, and on treating it with potash it liberated ammonia.

Lead Salt.—A solution of the ammonia salt in water was mixed with some basic acetate of lead as long as any precipitate resulted, and the white flocculent deposit obtained carefully washed with water. Dried and pulverized it forms a powder.

Hydro-rhodeoretine.—To obtain the acid combined with the oxide of lead, the lead salt, carefully washed, was suspended in distilled water, and a current of sulphuretted hydrogen gas passed through it, frequently stirring, until it was entirely decomposed. The liquid filtered from the sulphuret of lead was transparent, and afforded on evaporation in the water-bath a slightly brownish resinous mass, possessing the following properties:—When dry it resembles externally the original resin, is quite as brittle and as easily pulverized; it dissolves readily in water and in alcohol, but is insoluble in æther, has no odour, but a tolerably strong, pure bitter taste. It melts on platinum foil, and then burns, giving off the same odour and the same bright, somewhat smoky flame, as rhodeoretine, leaving behind a porous cinder, which is consumed without residue. The aqueous solution has an acid reaction, and is neither rendered turbid by solutions of neutral metallic salts nor by those of the alkaline earths. The original lead salt is obtained only with basic acetate of lead, or with the neutral acetate and the addition of ammonia. It likewise dissolves in alkalies and carbonate alkalies, and forms the same salts as those obtained by dissolving the original resin in alkalies. It does not crystallize either from the alcoholic or from the aqueous solution; it dissolves in acetic acid and in cold nitric acid without decomposition. Water and ammonia do not again precipitate it. Like rhodeoretine it becomes coloured of a beautiful carmine red after a few minutes with concentrated sulphuric acid; and it likewise deposits after decomposition a brownish-black resinous mass, with the same peculiar odour; at 212° it cakes together; some few degrees above this temperature it melts to a yellow fluid. The pulverized acid, dried at 212°, was burnt with chromate of lead, and afforded—

Carbon	55·10	55·16	42	=	3185·8	55·54
Hydrogen	8·28	8·39	36		449·3	7·83
Oxygen	36·62	36·45	21		2100·0	36·63

Potash Salt.—For the preparation of this salt a quantity of rhodeoretine was conveyed into a boiling solution of carbonate of potash, in which it dissolved tolerably easy with a yellow colour. The solution was then evaporated to dryness in the water-bath, and the dry mass extracted with absolute alcohol. The potash compound dissolved in it, and the excess of carbonate of potash remained undissolved. The alcoholic solution was evaporated to dryness; the dry pulverized salt had a faint yellowish colour, and dissolved both in alcohol and readily in water; the aqueous solution had a bitter taste and an agreeable quince-like odour. Heated on platinum foil, it burnt with the same bright flame as rhodeoretine.

Barytes Salt.—A certain quantity of hydro-rhodeoretine was dissolved in water, a slight excess of barytes water added to the solution, and the whole then evaporated until the excess of barytes was converted into carbonate, and the liquid no longer had an alkaline reaction; it was then filtered and evaporated to dryness in the water-bath. Dry and pulverized, the salt forms an almost perfectly white powder, which is easily soluble in water and alcohol, but is precipitated from the aqueous solution by absolute alcohol. It has no odour, but a bitter taste; heated on platinum, it first melts, and then burns with a bright flame, diffusing the same odour as rhodeoretine. It melts at 221°. The analyses of the salts gave the following results:—

Lead Salt.

Carbon	36·95	37·31	42	= 3185·87	37·37
Hydrogen	5·32	5·40	36	449·3	5·27
Oxygen	25·29	24·85	21	2100·0	24·65
Oxide of lead..	32·44	32·44	2	2789·0	32·71
				8524·17	

Barytes Salt.

Carbon	51·11	50·94	84	= 6371·7	51·27
Hydrogen	7·55	7·54	72	898·6	7·23
Oxygen	33·71	33·89	42	4200·0	33·01
Barytes	7·63	7·63	1	956·9	7·69
				12427·2	

Potash Salt.

Carbon	53·49	53·37	126	= 9557·6	53·70
Hydrogen	7·78	7·66	108	1347·9	7·57
Oxygen	35·63	35·60	63	6300·0	35·42
Potash	3·37	3·37	1	589·9	3·31
				17795·4	

Decomposition of Rhodeoretine by Acids.—A quantity of rhodeoretine was dissolved in absolute alcohol, and dry hydrochloric acid gas passed through the solution as long as any was absorbed. In this operation it became of a dark reddish-yellow colour. The solution was corked and set aside for ten days, when it had become considerably darker and opake in mass. Mixed with water, a dark yellow oily liquid separated, which had an agreeable smell and dissolved in æther. The entire liquid was mixed with water, and then shaken with æther, which took up the oily liquid, acquiring a dark yellow colour; the remaining alcoholic solution continued of a dark yellow-red colour. The æthereal solution was washed with water, to separate the hydrochloric acid, and then exposed to the air. A dark brownish-yellow, thick, oily fluid separated on evaporation of the æther, which possessed a strong and not disagreeable odour. The neutral liquid volatilized with difficulty, but entirely, on exposure to heat, and burnt with a red flame. Boiled with solution of caustic potash, no action resulted; cold concentrated sulphuric acid was likewise without any effect upon it. The liquid was placed over sulphuric acid for some days, and then submitted to analysis, with the following results:—

Carbon	66·95	66·65	30	67·51
Hydrogen	10·67		23	8·53
Oxygen	22·38		8	23·96

The author has given the name of *Rhodeoretinol* to this body, from its origin and consistence.

The acid liquid separated from the rhodeoretinol was saturated with carbonate of lead, the filtered liquid evaporated to dryness in the water-bath, and extracted with absolute alcohol. A viscid transparent mass was obtained, which had a sweetish taste, dissolved in water and alcohol, burnt on platinum foil, giving off the well-known odour of burnt sugar; and when warmed with potash and sulphate of copper, exhibited the characteristic reaction of grape-sugar by the reduction of the oxide of copper, gave the characteristic crystals with common salt, and finally, on being dissolved in water and brought into contact with yeast, passed into vinous fermentation. It is evident from these reactions that this substance is identical with grape-sugar, &c.

The author made the same experiment with a solution of hydrorhodeoretine in absolute alcohol and hydrochloric acid gas, as with rhodeoretine. The solution acquired a dark yellow colour, and on mixing with water white flakes separated, which on being magnified exhibited the appearance of minute coherent drops of oil, and dissolved in æther. The æthereal solution, freed by washing with water from acid, gave on evaporation in the air a brown waxy mass, which possessed a similar odour to the rhodeoretinol. The acid solution, from which the substance had been removed by æther, likewise yielded, with excess of potash and sulphate of copper, the reaction of grape-sugar.

Resin soluble in Æther.—The æthereal extract of the resin, which was of a dark yellow colour, was evaporated by exposure to the air, when a clear brownish-yellow liquid mass separated, which on solution in alcohol was thrown down by water as a brownish oily mass, which also separated any remaining portions of rhodeoretine. The mass, purified by being again dissolved in alcohol and precipitated with water, possessed the following properties:—It was strongly acid towards blue litmus-paper, left a grease-spot on paper, possessed a very strong disagreeable smell, resembling that of the jalap-root, and an irritating taste, and was insoluble in hydrochloric, nitric and acetic acids even on warming. It dissolves in an aqueous solution of potash or soda, and is separated unaltered by muriatic acid. The alcoholic solution is precipitated by an alcoholic solution of acetate of lead with a yellow colour; it does not crystallize either from the æthereal or from the alcoholic solution, and remains, even after several months, still quite soft and smeary. Left in contact with water for some length of time, it is converted into a mass of prismatic acicular crystals, which adhere together, and even after several months form a smeary mass.

Pararhodeoretine.—A quantity of the accurately-determined root of *Ipomea orizabensis*, Pellet., was exhausted with alcohol, the extract mixed with water, and the alcohol removed by distillation; the resin so obtained was washed with hot water, again dissolved in alcohol and entirely decolorized by means of washed animal charcoal. The resin obtained by distilling off the alcohol, and boiling in water after desiccation in the water-bath, formed when pulverized a nearly white powder, which dissolved entirely in alcohol and æther to a transparent clear liquid. It is entirely dissolved by warm aqueous solutions of potash, soda, and the carbonate alkalies, and is separated by muriatic acid from these solutions in white flakes. Concentrated sulphuric acid dissolves it in the course of five to ten minutes with a beautiful purple-red colour; after some time a brown smeary resin separates. It melts when heated on platinum foil, and burns when ignited with a bright, somewhat smoky flame, leaving a porous coal, which can be entirely consumed. It possesses neither smell nor taste, is very brittle and easily pulverized. The resin obtained by evaporating the alcoholic solution in the water-bath, and dried at 212°, gave on combustion with chromate of lead the following result:—

Carbon ……	58·58	58·64	42	=	3185·9	58·88
Hydrogen ….	8·01	8·13	34		424·3	7·84
Oxygen ……	33·41	33·23	18		1800·0	33·28

According to Johnston, the resin of Scammony = $C^{40} H^{33} O^{20}$. The resins of the *Convolvulaceæ* abound therefore most in oxygen, and form by the soluble hydrorhodeoretine the transition from salicine and phloridzine. 7 equiv. starch ($C^{84} H^{70} O^{70}$) = 2 equiv. rhodeoretine + 30 O.—Liebig's *Annalen*, li. p. 81.

On Limone. *By* Dr. C. SCHMIDT.

This substance, which was discovered by Bernays in the pips of lemons and oranges, is probably contained in the seed of all the *Aurantiaceæ*. From the author's investigation it appears that it is not a base, and does not contain any nitrogen. It is obtained in the form of a white crystalline powder; its crystals belong to the rhombic system. This substance is very sparingly soluble in water, æther and ammonia, somewhat more in mineral acids, more easily in alcohol and acetic acid, but most readily in potash, from which solution it is precipitated unaltered by acids. Concentrated sulphuric acid dissolves it with a blood-red colour, from which water precipitates it, as well as from the alcoholic and acetic solutions, unchanged; it is carbonized by heat. When neutralized with carbonate of barytes, no barytes remains in the solution. It crystallizes readily from acetic acid; the crystals are free from chemically-combined acetic acid. The alcoholic solution has a neutral reaction; it neither affords precipitates with chloride of platinum nor with perchloride of mercury, with salts of lead nor with those of silver, potash, barytes and others (the latter must naturally be dissolved in alcohol, as otherwise the pure substance is precipitated by the water of the saline solution). It can be heated to 302° without undergoing change and without any remarkable loss in weight; at a higher temperature it suddenly becomes yellowish, and melts at 471° to a liquid of the same colour, which resembles a melting resin; it resolidifies to an amorphous mass, and even after several days does not present any trace of crystalline structure; it may however be dissolved in acetic acid by long digestion in the warmth, from which it crystallizes in the form and with the properties of the original unmelted substance.

The indifference of this substance towards oxidizing agents is remarkable; concentrated nitric acid dissolves it, especially with the assistance of a little heat; the solution is of a pale yellow, and even after long heating it is precipitated by water from the solution in an unaltered state. On boiling it with a concentrated solution of bichromate of potash it undergoes no change, nor with free chromic acid, *i. e.* sulphuric acid and chromate of potash, in which solution it floats unaltered even after boiling for several hours. The acetic solution has a strong bitter taste; however, it does not appear to produce any considerable physiological effects. 60 millegrammes, dissolved in acetic acid and taken early in the morning before breaking fast, produced no effect; nothing could be detected in the secretions. 25 millegrammes were given to a dog and 10 millegrammes to a bird, but likewise without any effect.

The elementary composition proved the perfect identity of the substance prepared from lemon and orange pips, and gave as the mean of several analyses, in 100 parts—

Carbon	66·09	42	66·17
Hydrogen	6·55	25	6·55
Oxygen	27·36	12	27·32

The formula is that of phloridzine, dried at 212° + 2 equiv. oxygen. Direct experiments with reducing agents, such as sulphurous acid, hydrochloric acid, sulphuretted hydrogen, hydrogen in *statu nascenti*, and the electric current, afforded however by their negative results the proof that this substance does not belong to the phloridzine series, especially as the characteristic decomposition of salicine by chromic acid was wanting. The combining weight could not be ascertained, since it was impossible to obtain combinations of this substance with other bodies.—*Göttinger gel. Anz.*, No. cxxi. 1844.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Adulteration of Cochineal. By M. LETELLIER *of Rouen.*

Two varieties of cochineal are found in commerce, the gray and the black. No satisfactory explanation has hitherto been given of this difference. Some think that it is owing to the different methods employed of killing the insect, others attribute it to a different mode of cultivation. MM. Fée, in his 'Cours d'Histoire Naturelle Pharmaceutique,' Bussy, in his 'Traité des Falsifications des Drogues simples,' and Boutron Charlard, in a note inserted in the 'Journal de Pharmacie,' vol. ii. tenth year, are of the same opinion; they think that these kinds of cochineal are only one and the same species, and the differences which are observed in them are owing to the custom of plunging the black cochineal into boiling water in order to kill it, which deprives it of the whitish powder with which it is naturally covered. The gray cochineal, on the contrary, which is killed by being exposed to the heat of an oven, preserves its proper colour. M. Guibourt, contrary to these gentlemen, thinks that black cochineal is a variety produced by cultivation, and still further removed from the savage state than the gray cochineal. Black cochineal is, according to this gentleman, richer in colouring matter and held in higher estimation. In confirmation of what he advances, he states that at Bordeaux persons are employed in converting, by a peculiar process, gray cochineal into black, at an expense of fifty centimes (five pence) per pound; he also agrees with M. Bussy, that if at the present time talc or white lead is added to cochineal, it is not black cochineal which undergoes this adulteration, but gray cochineal, with the sole view of increasing its weight. According to M. Fée, gray cochineal is generally more esteemed than black, because this latter has lost a little of its colouring principle by its immersion in boiling water at the time of gathering. He is not of the opinion of Boutron Charlard, who thinks that both are equal in quality. The latter person says, contrary to Guibourt, that black cochineal is transformed into gray, because this last is of more value.

The result of all these contrary opinions is, that it is perfectly impossible to judge of the goodness of a cochineal by its physical characters. In order to ascertain its value, we must have recourse to comparative experiments. We are indebted to MM. Robiquet and Anthon for two methods of determining the quality of cochineals according to the quantity of carmine they contain. The process of M. Robiquet consists in decolorizing equal volumes of decoction of different cochineals by chlorine. Using a graduated tube, the quality of the cochineal is judged of by the quantity of chlorine employed for decolorizing the decoction. The process of M. Anthon is founded on the property which the hydrate of alumina possesses, of precipitating the carmine from the decoction so as to decolorize it entirely. The first process, which is very good in the hands of a skilful chemist, does not appear to me to be a convenient method for the consumer; in the first place, it is difficult to procure perfectly identical solutions; in the next place, it is impossible to keep them a long time without alteration. We know that chlorine dissolved in water reacts, even in diffused light, on this liquid, decomposes it, appropriates its elements, and gives rise to some compounds which possess an action quite different from that of the chlorine solution in its primitive state. The second process seems to me to be preferable, as the proof liquor may be kept a long while without alteration. A graduated tube is also used; each division represents $\frac{1}{100}$th of the colouring matter. Thus, the quantity of proof liquor added exactly represents the quantity in hundredths of colouring matter contained in the decoction of cochineal which has been submitted to examination.

In my investigation I have not had recourse to chemical agents as did MM. Robiquet and Anthon; I had no hope of finding a better and more simple process than those proposed by them. I employ nearly the same course for cochineal as that followed by M. Girardin for annotto. In a word, it is by colorimetric essays that I judge of the quality of the cochineals of commerce. This method appears to me so simple and so convenient, that I think it right to make it known. It enables the consumer to judge of the value of a cochineal as well as the chemist.

As I have before said, two kinds of cochineal are found in commerce, gray and black. The gray cochineal may be separated into two very distinct varieties. The first is large, heavy, regular; the eleven rings which form it are distinctly seen. The insect has pretty nearly preserved its form, convex on one side, and concave on the other; its gray colour is owing to the whitish powder with which it is covered during its growth. The second variety is irregular and quite without form. The whitish coating which covers it is heaped in such great quantities in the concave part and between the rings of the insect, that it is in the form of small round masses, in which it is hard to distinguish any traces of the rings so well characterized in the first variety. This cochineal is in general the heaviest: it almost always contains, independent of the talc in which it has been rolled, some sand or metallic dust, which singularly increases its weight.

Black cochineal does not offer very distinct characteristics; it is sometimes like the gray cochineal, No. 1, heavy, concave on one side, convex on the other; at other times it is quite irregular, small and wrinkled in every direction; it is almost impossible to distinguish its first form and some traces of the rings which compose it. These latter characters belong especially to zacatillée cochineal.

Exhausted Black Cochineal.—Until 1840 the calico-printers, after having treated the cochineal at different intervals with water, threw it away as completely exhausted. M. Lemoine, a dyer of Rouen, was, I believe, the first whom the idea struck of ascertaining if this cochineal, which the cotton-printers threw away, was entirely deprived of its colouring principle. He found that it still contained from about 15 to 18 per cent. The dyer now buys this residue from the cotton-printer, at the price of from 1*s.* 6*d.* to 2*s.* 6*d.* the 2 lbs.; he dries it, spreads it in thin layers in a well-aired place, and preserves it in barrels for use. This cochineal having begun to undergo decomposition during its desiccation, always has a smell of putrified animal matter; it is black, quite without form, often agglomerated into more or less large masses.

Down of Cochineal.—We sometimes find a gray light substance in commerce, mixed with a great quantity of small black granules hard to the touch; this substance is known by the name of down, or cochineal siftings. MM. Fée, Boutron Charlard, Bussy and Guibourt, who have written on this insect, do not speak of this product. It contains about 20 per cent. of colouring matter.

These two products have lost much of the preference which dyers used to give them on account of the low price at which they were to be bought; because in order to obtain as beautiful a tint and as dark a one with them as that obtained with pure cochineal, three or four times as much matter is necessary, to which must always be added a small quantity of unexhausted cochineal; secondly, because this matter fills up the vats, and is very hard to detach from the tissue.

I owe to the kindness of the merchants of this town thirty specimens of cochineal, on which I have made experiments. In the houses which carry on a wholesale trade in this commodity, I have constantly found the same kinds of cochineal: the pure gray cochineal, No. 1, or gray cochineal of the Canaries, the blackish gray or zacatillée cochineal, No. 2, and the black or zacatillée cochineal, No. 3. This last is adulterated; merchants buy it as such. According to the information I gathered from these gentlemen, a great part of the cochineals which come to Bordeaux are converted into zacatillée cochineal. There are persons in this town whose sole occupation this is. This cochineal is offered to the merchants at from 6, 8 and 10 per cent. below the current price. Guibourt, as I before said, mentions this fraud as a certain proof that the black cochineal is superior to the gray.

By examining the zacatillée cochineals of commerce attentively, knowing moreover that they are always sold below the current price, I thought that only two kinds of adulteration were possible; the first might consist in rolling the cochineal, rendered moist, in a black heavy powder (manganese for example), to change the colour and increase the weight; the second, to deprive it of the whitish layer which covers it, by soaking it in boiling water, which at the same time must take a part of its colouring matter from it, which would be made use of. The first method hardly seems probable; a part of the black dust becoming detached by rubbing would always betray the adulteration. The irregular form of this cochineal, and the roseate lustre which it presents, lead me to think that the second kind of supposed adulteration is the most likely. I am therefore of opinion, according to my experiments, that gray cochineal is treated with warm water to extract a part of its colouring principle, that by this immersion the insect is in great part deprived of the white powder which covers it, and is transformed into black zacatillée cochineal. Whether it is this or any other method which is put in practice, it is certain that the zacatillée cochineal is less rich in colouring principle. It is sold as such in commerce; but it often happens that zacatillée is advertised at 6 per cent., and that it is 10, 12, and sometimes more. Up to the present time the buyer has not possessed an easy method of appreciating the different degrees of adulteration.

In the specimens which I procured from persons who retail cochineal, I found exactly the three qualities before mentioned, in addition the gray cochineal No. 2, which is frequently met with, and a cochineal which is quite black and contains a little sand. It is almost always in these last two that I found matters introduced to increase the weight.

When examined with a glass, the metallic powder that I obtained from four specimens only of cochineal out of twenty-three, presented all the physical characters of lead filings. Treated with nitric acid, it yielded a solution, which, when tested with chemical agents, showed all the characters peculiar to the salts of this metal.

The result from what precedes is, that the adulteration mentioned by M. Boutigny is but little spread in the wholesale trade; that this sophistication is, as I suspected, made in France and with the exhausted cochineals.

Colorimetric Tests.—I shall not describe the colorimeter, but shall refer for that to the memoir of M. Houton Labillardière, in the 'Bulletins de l'Académie Royale,' 1827, p. 73. The memoir of M. Girardin, inserted in the 'Bulletin de la Société Libre d'Emulation,' 1836, p. 149, may also be consulted.

The colouring matter of cochineal being soluble in water, I have used this solvent for exhausting the different kinds which I have submitted to examination in the colorimeter. I operated in the following manner:—I took a grain of each of the cochineals to be tried, dried at 122° F.; I submitted them five consecutive times to the action of 200 grains of distilled water at water-bath heat, each time for an hour; for every 200 grains of distilled water I added two drops of a concentrated solution of acid sulphate of alumina and of potash. This addition is necessary to obtain the decoctions of the different cochineals exactly of the same tint in order to be able to compare the intensity of the tints in the colorimeter*.

The purchaser now examines his cochineal by dyeing a sample of wool. The result obtained is compared with that of a cochineal

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* Care must be taken not to add to the water, which serves to extract the colouring matter from the different cochineals, more than the requisite quantity of acid sulphate of alumina and solution of potash, because a stronger dose would precipitate a part of the colouring matter in the state of lake.

whose tinctorial value is known to him; he operates at water-bath heat for two hours. Having begun this investigation in the hope of giving an easier and quicker process than those which have been used up to the present time, I have endeavoured to extract the colouring matter of the cochineal by a single treatment. I obtained this result: that five decigrammes of cochineal, treated at water-bath heat for an hour, with 1000 grs. of spring water, and the addition of ten drops of a solution of alum, were almost entirely exhausted. The liquor when cold was perfectly transparent, and gave in the colorimeter the same results which I obtained by the first process. The apparatus which I used is composed of two flasks of about a quart capacity, suspended by their necks to a small plank, the two extremities of which rest on the edge of a cylindrical vase which serves as a water-bath for them. Before applying heat, the weight of each flask containing the cochineal and the alum water in the indicated proportions should be separately taken. After an hour's boiling it is left to cool, each flask is again separately weighed, and to each of them is added the quantity of distilled water necessary to establish the primitive weight.

Some time ago M. Boutigny sent me four specimens of cochineal which he had received from M. Pimont of Bolbeck:—1, a cochineal from the Canaries; 2, a blackish-gray or zacatillée cochineal; 3, a black or zacatillée cochineal; 4, and lastly, a small blackish-gray cochineal, known by the name of rosette cochineal. Till then I had employed as basis for my experiments cochineal from the Canaries obtained from a merchant in this town.

The rosette cochineal gave me more colouring matter. The tinctorial value is to that of the gray cochineal as 105 or 110 are to 100.

In order to estimate a cochineal in the colorimeter, two solutions obtained, as described above, are taken; some of these solutions are introduced into the colorimetric tubes as far as zero of the scale, which is equivalent to 100 parts of the superior scale; these tubes are placed in the box, and the tint of the liquids enclosed is compared by looking at the two tubes through the eye-hole, the box being placed so that the light falls exactly on the extremity where the tubes are. If a difference of tint is observed between the two liquors, water is added to the darkest (which is always that of the cochineal taken as type) until the tubes appear of the same tint*. The number of parts of liquor which are contained in the tube to which water has been added is then read off; this number, compared with the volume of the liquor contained in the other tube, a volume which has not been changed and is equal to 100, indicates the relation between the colouring power and the relative quality of the two cochineals. And if, for example, 60 parts of water must be added to the liquor of the good cochineal to bring it to the same tint as the other, the relation of volume of the liquids contained in

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* For diluting the liquors the same water must always be used which has served to extract the colouring matter of the cochineals under examination, otherwise the darkest decoction would pass into violet as water was added to it to bring back the tint to the same degree of intensity as that of the decoction to which it is compared.

the tubes will be in this case as 160 is to 100, and the relative quality of the cochineals will be represented by the same relation, since the quality of the samples tried is in proportion to their colouring power.

Conclusion.

1. The adulteration of cochineal by a metallic substance menby M. Boutigny, is not of frequent occurrence in the trade, but it exists.

2. The value of the different cochineals tried may be separated into very distinct classes. The rosette cochineal and the gray cochineal, which I have always taken for comparison, appear to me to be the richest met with in the trade. In the second rank I will place the other gray cochineals, No. 1, which I have tried, and the zacatillée cochineals. Last come the gray cochineals, No. 2, and the zacatillée cochineals, which I think adulterated and in great measure exhausted.

3. A single treatment pretty well exhausts a sample of cochineal so as to give a just notion of its tinctorial value and of its trade price.

4. I am induced to think that the richness of the cochineals depends greatly on the mode of cultivation of this insect and on the district whence it is derived.—*Journ. de Pharm. et de Chim.*, Dec. 1844.

Cement for Glass and Porcelain.

M. Hänle recommends a mixture of 2 parts shell-lac and 1 part turpentine, which are fused together and formed into sticks. This may also be employed for cementing wood, &c., when dissolved in spirit and evaporated to the consistence of a syrup. Hensler grinds 3 parts litharge, 2 parts of recently burnt lime in powder, and 1 part white bole, to a mass with linseed-oil varnish. This cement is very tenacious when allowed to dry sufficiently long.—*Jahrb. für Prakt. Pharm.* ix. p. 23, and viii. p. 295.

PATENT.

Patent granted to James Overend, Liverpool, *for Improvements in Printing Fabrics with Metallic Matters.*

The invention consists,—first, of means of preparing materials for the purpose of printing on fabrics to be afterwards covered with metallic powder; and, secondly, in a mode of finishing fabrics.

The patentee first describes the materials and mode of combining them together for printing on cotton fabrics. He takes

One part of white lead.
One-eighth part of manganese.
One sixty-fourth part of litharge.
One-sixteenth part of sugar of lead.

These materials are to be then mixed with a gallon of clarified linseed oil, and reduced into a pasty state, and one gallon of gold size added; the whole is then boiled together by steam in earthenware vessels for half an hour, adding to it one-sixteenth part of yellow wax, one-forty-eighth part of dissolved gum, and one-sixteenth part of sugar-candy; it is then to be taken from the fire and passed through a sieve; a small quantity of yellow chromate is added to colour it. In some cases, when operating on woollen and other goods, a small quantity of turpentine or diluted muriatic acid is added; but when these materials are used, a small quantity of tallow, or other fatty matter, should be put into the mixture instead of the wax and gum. The colour being thus prepared is in a fit state for use, and is to be employed in the ordinary manner of block or other printing. After the fabric has been printed, and as it is drawn off the roller or block, the metallic powder is sifted on to the colour from a sieve, or by any convenient method; the fabric is to be then removed to a room heated by steam, or otherwise, to dry; when thoroughly dry, it is to be well-brushed until the whole of the powder is removed.

This invention may be employed in all descriptions of printing, and to any fabrics, and may be united with, and applied to printing in any colour. By this invention the metallic powder will bear the heat of the steam sufficiently long to allow of the colours with which the fabric is being printed to be fixed, and the goods may be dried in the air by preference to artificial heat. In the two cases above stated, either when printing with metallic powders, or with other colours, the fabrics must be passed under the cylinder according to the ordinary system; but in some cases, such as leather, where the fabric would be injured by the pressure of the ordinary cylinder, it is preferred to use a burnishing-stick with the hand. The fabrics are then subjected to pressure in order to give the metal a bright and burnished appearance; the fabric is then in a state to be subjected to the process of finishing, which is the second part of the invention, and which consists of submitting the fabric to the vapour of sulphur. The fabric that has been printed is wound on to a roller, and drawn over another roller covered with cloth; this roller is damped by water placed in a metal box in which it turns; the fabric is then passed over three other rollers, which are heated either by steam or any other convenient means. Underneath the fabric is placed a vessel about three feet long, in which is burnt charcoal and sulphur mixed with salt, the vapour from which mixes with the colour of the printed fabric as it passes over the rollers and finishes the process of printing; it also removes the disagreeable smell that it had imbibed from the oil in the previous processes. It is then to be dried by being again passed over the heated rollers as before. In preparing materials for printing on silk, these are varied by leaving out the sugar of lead, and by adding a small quantity of nitromuriatic acid sufficient to dissolve the wax used; and instead of using four ounces of yellow wax, eight ounces are employed, and four ounces of crystallized sugar; these materials are mixed together as before described. When using this preparation it is preferable to employ it in a warm state.—Sealed February 13, 1844.

THE CHEMICAL GAZETTE.

No. LIV.—January 15, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Lactic Acid. By M. J. Pelouze.

The memoir which I have the honour of presenting to the Academy may be considered as a continuation of the researches on lactic acid published by J. Gay-Lussac and myself in 1833. Since that period the history of this acid has been undoubtedly enriched by several important observations; but most of the investigations have been almost exclusively directed towards its natural state and the means of producing it artificially. The examination of its chemical properties has, on the contrary, been very much neglected. Nevertheless lactic acid is one of the substances the most widely distributed in the animal œconomy and among vegetables, where it appears frequently to act a very important part. It exists naturally in milk, and is formed in abundance during the spontaneous acidification of this fluid. MM. Bernard and Barreswil have recently confirmed its existence in the gastric juice. It moreover results, from some yet unpublished observations of M. Gobley, that it likewise occurs in a free state in the yolk of egg. It is found in all vegetable juices the vinous fermentation of which has not followed a regular course, in the spoiled and fermented flours of all the Cerealia, in the liquors of the tanner which have undergone spontaneous fermentation, and in the waste liquors of the starch-makers; it is formed in abundance when a sugar, of any class whatsoever, is placed in contact with an earthy alkaline carbonate and a ferment, especially with the caseous matter of milk, at a temperature of from 68° to 86° Fahr.

Butyric fermentation, which immediately succeeds the lactic fermentation of sugars, gums and starch, has added to the interest which lactic acid deserves in a chemical and physiological point of view.

Lactic acid is a colourless liquid, soluble in every proportion in water and alcohol, of a pure acid taste, so strong and biting as to be almost insupportable. Its composition, which is very simple, was ascertained at the same period (1833) by MM. Mitscherlich and Liebig, and by Gay-Lussac and myself. Its formula is $C^6 H^6 O^6 = C^6 H^5 O^5 + HO$*. These numbers express 1 equiv. of monohydrated acid.

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* $C = 75$; $H = 12{\cdot}5$; $O = 100$.

The action of heat on lactic acid is highly remarkable. At a temperature approaching to 266° Fahr., but which may be raised higher without any inconvenience, a colourless liquid distils over, which is nothing but water holding in solution a small quantity of lactic acid. After the lapse of a very long time, when no more water is disengaged, the operation is complete; the residue has acquired a yellowish tint, has become solid, easily fusible, of an excessive bitter taste, almost insoluble in water, but very soluble in alcohol and æther. Not a trace of any gas is liberated in this action, which consists in a simple dehydration of the lactic acid.

The composition and properties of the above solid residue leave no doubt as to its true nature. It is anhydrous lactic acid, such as it exists in the lactates. It is, in fact, formed of 6 equiv. carbon, 5 of hydrogen, and 5 of oxygen. Long-continued ebullition with water, or long contact with this liquid in the cold, or exposure to moist air, convert it into ordinary lactic acid. This transformation is, as it were, spontaneous under the influence of soluble bases. Milk of lime gives with insoluble lactic acid the ordinary salt, with its 6 equiv. of water. I determined its capacity of saturation, and extracted the monohydrated acid from it. Lactic acid must therefore be added to the somewhat limited number of acids which part at an elevated temperature with their saline water, *i.e.* that proportion of water which they exchange for bases in forming salts. Twelve years ago I pointed out this property in the malic and paramalic acids; and I subsequently met with it, conjointly with M. Liebig, in œnanthic acid.

The dehydration of lactic acid is effected, however, much more slowly than that of the preceding acids; and it is undoubtedly owing to this circumstance that it had hitherto been overlooked. I may moreover add that this phænomenon is manifested at a temperature which is almost always employed without hesitation in drying most organic substances; and this observation shows what caution should be observed in such experiments.

Anhydrous lactic acid submitted to the action of dry ammoniacal gas absorbs 1 equivalent, and forms a peculiar combination ($C^6H^5O^5$, H^3N), in which the ammonia has not ceased to be affected by those reagents which are generally employed to detect its presence.

I have found that anhydrous œnanthic acid forms a combination of the same class, which should perhaps be assimilated to the amidogen salts.

Lactic acid, or rather the anhydrous lactic acid just mentioned, resists the further action of heat until about 482° Fahr. At this temperature some gases are liberated; these consist of carbonic oxide, mixed with only 4 to 5 hundredths of its volume of carbonic acid; the proportion of this latter gas gradually increases, and towards the end of the experiment attains to about half that of the carbonic oxide. No carburetted hydrogen appears to be formed.

Several volatile substances make their appearance at the same time as the gases, and are condensed in the receiver. I shall first speak of a beautiful crystalline body, which Gay-Lussac and I described under the name of *anhydrous lactic acid*, an inappropriate name, which I propose applying to the body described above, and which presents in fact the composition of the organic matter of the driest lactates. This crystalline substance, which I shall hereafter call *lactide*, a name already proposed for it by M. Gerhardt, has acted an important part in several discussions relative to the constitution of organic acids. As it is without analogy in chemistry, and is very curious in several respects, I have repeated our former analyses, and have again verified its conversion into ordinary lactic acid. Lactide is represented by the formula $C^6 H^4 O^4$, that is, it is lactic acid minus 2 equiv. of water; and this composition explains both its formation in the dry distillation of this acid, and its metamorphosis into lactic acid under the influence of water or hydrated bases.

There exist therefore two neutral substances, $C^6H^5O^5$ and $C^6H^4O^4$, which are not lactic acid, but which originate from it by the loss of 1 or 2 equiv. water in dry distillation, and which are capable of regenerating it, either directly or indirectly, by absorbing the 1 or 2 equiv. of water requisite for this purpose. The hydrated acid produced by the action of water or moist air on lactide is limpid, quite colourless, and perfectly pure.

The peculiar composition of lactide led me to expect that by acting on it with ammonia gas, it would give rise to a body belonging to the amide series; for these, analytically speaking, are nothing further than anhydrous ammoniacal salts, from which the elements of 1 equiv. of water have been eliminated. The result answered my expectation.

When the body $C^6 H^4 O^4$ is exposed to the action of gaseous ammonia, it gradually becomes fluid, and absorbs this gas with disengagement of heat. A new substance, *lactamide*, results, the composition of which has been established by analysis and synthesis. It is formed of 1 equiv. of lactide, $C^6 H^4 O^4$, and of 1 equiv. ammonia; but this ammonia exists in it in the latent state, as in the bodies belonging to the amidogen series. Aqueous acids and the alkalies only liberate it with the assistance of heat, and very slowly; it dissolves in water without undergoing any alteration, and it is only under a pressure corresponding to a temperature higher than 212° that it is converted into lactate of ammonia. Milk of lime decomposes it, gradually disengaging the ammonia, and oxalic acid separates ordinary lactic acid from the lime salt.

Lactamide does not appear capable of combining either with bases or acids; it is without any action on coloured tests. Alcohol dissolves it in considerable quantity, and deposits it on concentration or on cooling in beautiful white transparent crystals, whose primitive form is a right rectangular prism.

Besides lactide, lactic acid yields on its decomposition by heat another substance, which I propose to name *lactone*, from its appearing to bear the same relation to lactic acid as acetone does to acetic acid. It is obtained pure by submitting the products of distillation of lactic acid to a gentle heat. When the temperature has reached 266° the distillation is discontinued; the distilled liquid is washed with small quantities of water, in which one portion dissolves while another floats on the surface; it is removed, and placed in contact for several days with chloride of calcium, and is finally submitted to fresh distillation.

Lactone derived from the decomposition of lactic acid is hydrated; its formula is $C^{10} H^8 O^4, HO$; this is not surprising, for it is formed in the presence of a large quantity of water. It has so great an affinity for this liquid that it may be rectified several times over chloride of calcium without being obtained dry. I have already stated, that to obtain it anhydrous it must be left for several days over this substance.

Anhydrous lactone forms a colourless or slightly yellowish liquid, the colour of which becomes gradually darker in contact with the atmosphere. It has a hot burning taste and a peculiar aromatic odour. It is much lighter than water, in which it dissolves in perceptible quantity. It burns readily with a beautiful broad blue flame, without any deposition of carbon. It boils at about 198°. Its formula is $C^{10} H^8 O^4$, which represents 2 equiv. lactic acid which have been deprived of 2 equiv. carbonic acid and 2 equiv. water ($C^{12} H^{10} O^{10} = C^{10} H^8 O^4 + 2CO^2 + 2HO$), or 2 equiv. lactide $= C^{12} H^8 O^8$ deprived of 2 equiv. carbonic acid. Its formation in the distillation of free lactic acid has nothing extraordinary, for Prof. Liebig and I long since showed that acetic acid afforded considerable quantities of acetone by the sole action of heat; and this is a further relation between acetone and lactone.

Among the gaseous or volatile products of the dry distillation of lactic acid I have already mentioned carbonic oxide, carbonic acid, water, a small quantity of lactic acid, lactide and lactone. There is moreover formed a small quantity of acetone, and an odorous liquid insoluble in water, the nature of which I am still ignorant of. The distillation, begun at about 482°, is not terminated before 572°. At this term there only remains in the retort a coal of difficult incineration, representing in weight about one-twentieth of the acid employed. In one experiment, which lasted 8 hours, 80 grms. of monohydrated lactic acid, distilled at a temperature between 482° and 572°, afforded 48 grms of liquid products*, 5·5 coal, and 26·5 gas, in which carbonic oxide preponderated.

A peculiar circumstance, which it may perhaps not be useless to mention, led me to the discovery of a very interesting property of lactic acid. M. Gélis furnished me with a quantity of this acid, which he had obtained from lactate of lime, produced by the fermentation of glucose in the presence of chalk and caseum. This

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* These liquid products deposit on cooling variable quantities of lactide. When this is mixed with the products of decomposition of the lactic acid, it appears to change into acid on exposure to moist atmosphere much quicker than when pure. At the end of a few days nearly the whole of the distilled liquids dissolves in water; only a small quantity of solid matter, almost entirely formed of anhydrous lactic acid, is precipitated. The filtered liquid contains, so to say, nothing but ordinary lactic acid.

The hydration of the lactide is far more easy than that of the anhydrous lactic acid. This explains why it yields but very little of this latter body.

acid decomposed at a less elevated temperature than the acid produced under similar circumstances with milk-sugar; and, what was more remarkable, yielded carbonic oxide entirely free from any admixture of carbonic acid, as it did not produce the slightest opacity in lime-water; and only after having disengaged considerable quantities of the former of these gases did it yield towards the end a little carbonic acid. I believed for a long time in the existence of two lactic acids, but I subsequently ascertained that this difference in the products was owing to the presence of a small quantity of sulphuric acid in the acid prepared by M. Gélis, who had decomposed the lactate of lime with a slight excess of sulphuric acid, and evaporated and extracted the residue with alcohol to remove the sulphate of lime.

This fact once established, I was able constantly to reproduce pure carbonic oxide from lactic acid, and lactates derived from any source whatsoever.

When lactic acid or a lactate, for instance lactate of iron, is mixed with from 5 to 6 times its weight of concentrated sulphuric acid, and the mixture exposed to a gentle heat, a lively effervescence soon ensues, owing to an abundant disengagement of pure carbonic oxide. The mixture acquires a dark brown colour; treated with water, when the evolution of gas has ceased, it deposits a black substance, which resembles in appearance ulmic acid. The reaction is so precise and easy that I do not hesitate to propose it as one of the best methods of preparing pure carbonic oxide.

6 grms. of crystallized lactate of iron, representing 3·775 monohydrated acid, yield very approximatively 1 litre of carbonic oxide. This proportion corresponds nearly to one-third of the lactic acid; the black substance constitutes about another third; and without asserting it as positive, I believe that water is the third substance which is formed in the action of sulphuric on lactic acid.

To ascertain whether the formation of carbonic oxide should be attributed to the decomposition by the sulphuric acid of a certain quantity of formic acid produced in the disintegration of the lactic acid, I diluted the sulphuric acid with so much water that it could no longer act on formic acid; but in no case have I been able to detect the presence of this body.

It would undoubtedly be very difficult to find a satisfactory explanation of this singular mode of alteration of lactic acid; but the fact is not the less interesting and worthy the attention of chemists.

Lactates.

I have little to add to the history of the lactates. The salts of iron, magnesia and zinc contain 3 equiv. water of crystallization, are sparingly soluble, and without doubt isomorphous; however, I dare not advance this latter assertion in a positive manner, as the crystals of all three salts are very small, and it is difficult to measure their angles.

Lactate of lime contains 6 equiv. of water, and is very sparingly soluble in this liquid; but it dissolves in considerable proportion in alcohol, from which it is precipitated by æther in the form of a white crystalline powder. The alcoholic solution of lactate of lime is thrown down by phosphoric acid, while in an aqueous solution the lactic acid displaces the phosphoric acid from phosphate of lime.

Lactate of ammonia is deliquescent, and does not crystallize.

With oxide of copper lactic acid forms a beautiful blue salt, the primitive form of which is a right rectangular prism. It crystallizes with ease, and contains 2 equiv. of water, which it parts with at 248°. When subjected to the action of heat it disengages a mixture of carbonic oxide and carbonic acid; the copper is soon reduced to the metallic state; the substance in the retort melts, and is decomposed into the same products as free lactic acid. When the last third of the distilled products is mixed with water, it sometimes happens that they suddenly become solid, and deposit a substance which is nothing but lactide. This lactide is very soluble in lactone, and to this circumstance should be attributed the small quantity of crystalline substance frequently found in the products of distillation of free lactic acid or of the lactate of copper.

Lactate of copper, previously deprived of its 2 equiv. water of crystallization, afforded on dry distillation 41·0 liquid substances, holding in solution a large amount of lactide, 29·5 metallic copper, 3·3 coal, and 26·2 of gas (CO and CO^2).

Lactate of copper presents a peculiarity worthy of attention; it crystallizes sometimes in large dark green prisms, which do not differ either in form or composition from the blue salt; re-dissolved in water they change into the blue crystals, and both have the formula $CuO, C^6 H^5 O^5, 2HO$.

When a solution of caustic potash is added in excess to lactate of copper, it yields a deep blue liquid; a portion of the oxide of copper is precipitated by lime, while another remains in solution even in presence of a considerable excess of the latter. Under similar conditions acetate of copper is always precipitated entirely, and the liquid after the reaction is perfectly colourless. This character furnishes a ready and precise means of distinguishing lactic from acetic acid in secretions where these two acids do not exist simultaneously.

Tartaric acid, which, like the sugars and lactic acid, prevents the precipitation of the oxide of copper by caustic potash, presents no obstacle to the entire precipitation of this same oxide by milk of lime. The same is the case with paratartaric and citric acids; the salts of copper are completely precipitated by the hydrate of lime, notwithstanding the presence of these acids. Lactic acid, and the sugars whence it is derived, are the sole bodies among those mentioned in whose presence the oxide of copper is not precipitated, or is thrown down but incompletely by the lime. With the others the precipitation is always complete. I draw attention to these circumstances, because they will allow of our distinguishing lactic acid from some of the bodies which frequently accompany it. When it is question of a substance so important as lactic acid, no observation, if well-made, can appear void of interest; it may be imagined, for instance, how useful properties of the kind I have enumerated will be for confirming strictly the presence of lactic acid in a secretion like the gastric juice, where it exists in but a minute proportion and mixed with many other substances.

I may add, without fear of being contradicted, that it is to be regretted that the numerous analyses which have been made of the organs and secretions of animals have not always been preceded by a more profound examination of their principal constituents. At a period when the characteristic properties of lactic acid were not satisfactorily known, its presence has been pointed out and denied by turns in the gastric juice. With the assistance of some of the experiments related in this article, and of some others, MM. Bernard and Barreswil have most satisfactorily demonstrated lactic acid to be the true cause of the acidity of the gastric juice.—*Comptes Rendus*, Dec. 9, 1844.

On two new Metals, Pelopium *and* Niobium, *discovered in the Bavarian Tantalites. By* Prof. H. Rose.

I have discovered in the tantalite of Bavaria two new metals, in the present memoir however I shall only treat of one: the oxide of the second metal, to which I have for the present assigned the name of *oxide of pelopium*, greatly resembles tantalic acid, although I am fully persuaded that it is distinct. I shall however institute a series of experiments to determine their precise difference.

For more than four years I have been engaged in investigating the tantalites from various localities, and the tantalic acids derived from them. An observation of my brother engaged me to undertake these researches. He found that the tantalites of Bodenmais in Bavaria, and those of North America, have the same crystalline form as Wolfram. I had also noticed that the tantalites from the same or from different localities, having the same form of crystal and the same chemical composition, differed from each other by their specific gravity.

The analysis of these different tantalites was executed according to Berzelius's method, by fusing the mineral reduced to a very fine powder with bisulphate of potash in a platinum crucible.

To obtain an accurate idea of the composition of the tantalites of Bavaria and of North America, it was requisite to submit the tantalic acid obtained from them to a very strict examination. On comparing the amount of oxygen of the tantalic acid, derived from these localities, with the amount of oxygen of the bases, protoxide of iron and protoxide of manganese, the relation existing between them is found not to be simple. This relation is, on the other hand, perfectly simple in the tantalites from Finland, viz. as 3 : 1. The tantalic acid derived from the tantalites of Finland only is pure. Its characters have been described by Berzelius, and it alone will retain the name of tantalic acid. The acid obtained from the tantalites of Bavaria is composed of two acids, one of which greatly resembles the tantalic acid procured from the Finland tantalites, and will form the subject of a future communication. The other likewise resembles tantalic acid, but differs from it in many essential points: it is the oxide of a metal which differs from all known metals. I have called it *Niobium,* and its acid *niobic acid,* from Niobe, daughter of Tantalus, a name which calls to mind the resemblance between the two metals and their oxides.

Tantalic and niobic acids bear most resemblance in their properties to titanic acid and the binoxide of tin: all four have probably the same composition. Both of them, when calcined in the hydrated state, present the same luminous phænomenon. Both are white before and after calcination. When tantalic acid is heated, it acquires a faint yellow colour; niobic acid, on the contrary, a deep yellow; both became colourless on cooling. Tantalic acid forms on cooling a white dull powder; niobic acid, fragments possessed of great lustre, similar to that presented by titanic acid precipitated by ammonia and calcined; with this difference,—that the titanic acid exhibits a brownish tint, while the niobic acid remains colourless.

Tantalic and niobic acids readily combine with the alkalies. When fused with carbonated alkalies, they expel the carbonic acid. These combinations are soluble in water, and also in an excess of a solution of caustic or carbonated potash, but with difficulty in an excess of caustic or carbonate of soda. The niobate of soda indeed is almost insoluble in an excess of a solution of soda. Acids precipitate the tantalic and niobic acids from these solutions. Sulphuric acid precipitates both completely on the application of heat; but in the cold the tantalic acid is only partially thrown down by it, while the niobic acid is entirely precipitated. Hydrochloric acid in the cold only produces a turbidness in a solution of tantalate of soda; an excess of acid even causes this to disappear; with the assistance of heat it precipitates the tantalic acid, but not completely. In a solution of niobate of soda it produces a considerable turbidness in the cold, without precipitating the whole of the niobic acid, which it effects however with the assistance of heat. Oxalic acid has no effect on either of the alkaline solutions, while acetic acid produces precipitates. Hydrochlorate of ammonia forms precipitates.

When an infusion of galls is added to a solution of tantalate of soda, rendered slightly acid with hydrochloric or sulphuric acid, it produces a bright yellow precipitate. In a solution of niobate of soda it gives rise to a deep orange-yellow precipitate, which has some resemblance to the precipitate formed under similar circumstances in a solution of titanic acid. Both the precipitates dissolve in caustic alkalies.

The tincture of galls is the best test for small quantities of tantalic or niobic acids in acid solutions; but it should be observed that the presence of oxalic acid, or of any other non-volatile organic acid, prevents the formation of the precipitate.

The yellow ferrocyanide of potassium produces in a solution of tantalate of soda, rendered acid with a few drops of sulphuric acid, a yellow flocculent precipitate, which is slightly soluble in a large excess of hydrochloric acid. It gives rise to a decided red precipitate in a solution of niobate of soda, resembling that produced in the same solution by tincture of galls. The red ferrocyanide of potassium forms a white flocculent precipitate in a solution of tantalate of soda, a deep yellow one in a solution of niobate of soda.

If a blade of zinc be immersed in a solution of tantalate of soda rendered slightly acid, it produces no effect at first; butafter some time a white deposit is formed consisting of tantalic acid, which is thrown down when the excess of acid begins to dissolve the oxide of zinc formed. In a similar solution of niobate of soda the zinc produces a blue precipitate, which in the course of time becomes brown.

Perchloride of tantalum, prepared from tantalic acid by means of charcoal and chlorine, is yellow, very fusible and volatile. Perchloride of niobium prepared in the same manner is colourless, nonfusible, and but very slightly volatile.

When dry ammonia is passed over perchloride of tantalum, the gas is absorbed, but very slowly, and the perchloride becomes less heated than is the case with the other liquid and volatile metallic chlorides placed under the same circumstances. This is not owing to the perchloride not possessing great affinity for the ammonia; but the new combination formed envelopes the perchloride of tantalum, and prevents the reaction from extending further. If this new compound be heated, metallic tantalum is obtained, and hydrochlorate of ammonia disengaged. The whole of the hydrochlorate of ammonia is removed by washing with water. On heating the metal with access of air, it is converted into tantalic acid with evolution of light. The reduction of tantalum requires a much higher temperature than that of titanium under similar circumstances. Metallic tantalum presents the appearance of black crusts. Water has no action on it.

Perchloride of niobium submitted to the action of dry ammonia becomes yellow, with considerable evolution of heat, because from its being infusible it offers a greater surface to the action of the ammonia. On applying heat to the new compound it immediately becomes black, with disengagement of hydrochlorate of ammonia. The reduction is effected at a much lower temperature than that of the tantalum. On washing it with water to free it from hydrochlorate of ammonia, the water passes clear as long as it contains any of that salt; but when the metal is nearly pure the water becomes turbid. This inconvenience is avoided by adding a few drops of alcohol to the water. When heated in the air the metal burns with evolution of light into white niobic acid. Nitric acid and *aqua regia* are without action on it even on boiling; but it is attacked, with disengagement of red vapours, by a mixture of nitric and hydrofluoric acids. Tantalum behaves in the same manner towards these acids.

If the same atomic composition be admitted for tantalic and niobic acids, the weight of niobium will be higher than that of the tantalum.—*Comptes Rendus*, Dec. 9, 1844.

On the Condensation of Nitrogen by Vegetable Mould, and on the Nutritive Power of the Soil. By Prof. MULDER.

Mulder does not admit with Liebig, that the whole of the nitrogen of unmanured soil can be derived from the ammonia contained in the atmosphere. Even supposing, what has not been proved, that 1 lb. of rain-water contained $\frac{1}{4}$ gr. of ammonia, this quantity could never occur except at the commencement of a rain, and the water subsequently falling could contain scarcely any or no ammonia. The author, in his researches on the constituents of mould, has been led to quite a different mode of accounting for the nitrogen of the soil, as will be seen from the memoir in our last number. From that it is evident that ammonia is probably first formed, out of this nitric acid, and from the latter, under the influence of the hydrogen liberated at the formation of humous substances, ammonia, which remains in combination with the humic acid. The possibility of a condensation of the free nitrogen of the atmosphere to ammonia results from the following experiments:—

When clean, fresh iron filings are placed in a flask moistened with a little water and red litmus-paper suspended in it, the paper in the closed flask becomes in a few days blue*.

On the 10th of May some freshly-ignited powdered charcoal was conveyed into a glass flask with hot distilled water, so that about seven-eighths of the flask remained filled with atmospheric air. On the 1st of August the charcoal was examined; it was distilled with pure caustic potash, and gave perceptible traces of ammonia. The water with which the charcoal was washed remained perfectly colourless.

Humic acid, prepared from sugar, was moistened with a little water (both free from ammonia), and left for six months in a closed flask; upon being then treated with potash, the substance disengaged a considerable quantity of ammonia.

Well-ignited charcoal was conveyed, on the 10th of May, while hot, into a glass flask with ground stopper, sprinkled with potato-starch and moistened with water. It was examined on the 1st of August; a disengagement of gas had commenced, for on touching the stopper it was thrown out of the neck. The mixture had a very distinct smell of cheese. A portion, distilled with potash, gave abundant proofs of ammonia, far more than the charcoal alone. Washed with water, the liquid passed colourless through the filter.

Gum arabic, mixed in the same manner with charcoal, gave the same result, as did likewise pure cane- and milk-sugar. The quantity of ammonia disengaged from the latter was considerable.

On the 10th of May a solution of pure milk-sugar in distilled water was placed in a glass-stoppered bottle, so that seven-eighths of the bottle remained filled with atmospheric air. A similar experiment was made with pure cane-sugar. Both exhibited, after a few

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* According to Berzelius this results from the decomposition of the colouring substance, azolitmine, when kept in a moist state. *Report* for 1844, p. 53.—ED. *Chem. Gaz.*

days, mould plants, which increased rapidly, especially in the milk-sugar. On the 1st of August they were removed from the solution, submitted to dry distillation, and the distillate tested for ammonia; it was found to contain a considerable quantity.

Now, since the circumstances in which the soil is placed are perfectly identical with those to which, in the above experiments, the charcoal (and humic acid) was exposed, there must actually take place in the soil an incessant formation of ammonia from the nitrogen of the atmosphere.

The form of the mould plants from milk-sugar (few are developed from cane-sugar) is closely allied to that of *Mycoderma Vini*. These plants are said to make place for others; and if the experiment be carried on sufficiently long, one generation follows the other. The organization of plants of the simplest kind consists in the formation of cellulose on the one hand, and in proteine on the other. These two substances are absolutely necessary for the formation of the simplest cell plants. Exhausted with acetic acid, the plant developed from milk-sugar yields a liquid, in which proteine may be distinctly proved by means of ferrocyanide of potassium. The solution of the milk-sugar had remained perfectly clear in this experiment, and the plants formed in this clear solution in great number. No gases were disengaged. The cellulose therefore necessarily originates from the milk-sugar by mere separation of water.

The origin of the proteine combined with the cellulose cannot be clearly proved.

These experiments may be multiplied in the most simple manner. All vegetable acids, and many of the indifferent substances, afford mould plants in larger or smaller quantity. Starch, above all, deserves attention in this respect. Arrowroot starch, preserved in pure water in a closed flask with air, very soon becomes turbid and opake, and forms a white precipitate. Mulder never observed during two months and a half mould form *at the top*, but in quantity *in* the mass itself, and then likewise on the surface. According to De Saussure, there originates from starch which has been exposed to the air or preserved in some bottles with air, after a few months, a mixture of sugar, gum, &c., and what in the present case deserves especial attention, a substance which he calls *ligneux amylacè*. This *ligneux amylacè* is cellulose combined with a little proteine, that is, a mould plant. De Saussure found from 4·4 to 10·53 per cent. in the starch employed. *Ligneux amylacè*, or mould plants, which afforded very considerable traces of ammonia, were likewise obtained from potato-flour that had been preserved in a close flask with pure water and pure atmospheric air for two months.

The influence of other bodies on the condensation of nitrogen to ammonia in the soil is of great importance. The nascent hydrogen which is set free from the decomposed organic substances binds the nitrogen of the atmosphere, just as iron filings and water form ammonia with the nitrogen of the atmosphere. A mixture of powdered charcoal with $\frac{1}{100}$ wood ashes was placed in two glass vessels, and ulmic acid, prepared from sugar, conveyed into one; both were exposed to an atmosphere free from ammonia. Brown beans were placed in the first, and white beans in the other; they were then sprinkled with distilled water, perfectly free from ammonia, and kept moist. The development and growth of the plants were extremely different in the two vessels; those in the ulmic acid vegetated powerfully, the others remained far behind. After twenty-four days they were taken out, the roots carefully freed from the charcoal with water, then dried and weighed. The residuary charcoal and the charcoal mixed with humic acid afforded, on distillation with potash, a considerable quantity of ammonia.

Three white beans, dried at 212°, weighed 1·465; three brown beans, 1·277; three plants of the brown beans, which had grown in charcoal and ash only, dried at 212°, weighed 1·772; three of the white beans, which had grown in charcoal, ash and ulmic acid, 4·167. This experiment, therefore (and we shall return to it presently), proves the nutritive power of the ulmic acid for the plants. The three white and the three brown beans were filed to a powder, and the plants of both treated in the same manner. The amount of ash was as follows:—

0·488 white beans, dried at 212°, yielded 0·023 ash.
0·633 of the white bean plants, 0·043.
0·403 of brown beans, 0·015.
0·605 of the plants of the latter, 0·055.

The amount of nitrogen, on the contrary, was—

	White beans.	Nitrogen.	Brown beans.	Nitrogen.
Beans	1·465	50 CbC	1·277	27 CbC
Plants	4·167	160 CbC	1·772	54 CbC

Three white beans, therefore, in becoming plants in charcoal, ulmic acid and ash, had taken up more than thrice the amount of nitrogen; three brown beans in charcoal exactly twice the quantity.

It is a difficult matter to ascertain whether the organic constituents of the soil are absorbed as such by the plants. This difficulty arises principally from the circumstance of its being impossible to present the same quantity of nutriment to the plants submitted to examination; and with too large or too small a quantity results are obtained between which no comparison can be made.

Several glasses of the same size were arranged side by side in an uninhabited room, exposed to no exhalations; some coarse well-washed sand was placed in the first five, and into all the other series of five a mixture of the same sand with 1 per cent. of common wood-ashes; and moreover, in the second five, 5 per cent. of a mixture of different constituents of the soil, or of substances which it was interesting to examine. The substances were sprinkled with pure distilled water and kept moist.

In each series of five were planted,—1st, small brown beans; 2nd, white beans; 3rd, green peas; 4th, barley; 5th, oats.

After a month, from the 16th of May to the 16th of June, the following was the result of the development of the above seed:—

1. *Sand and Rain-water.*—Seed came up very sparingly, the plants scarcely a hand's span high, nearly all faded.

2. *Sand, Ashes and Rain-water.*—1st, did not germinate; 2nd,

very sparingly; 3rd, tolerably well developed; 4th, very poor; 5th, somewhat better, but still very weak.

3. *Sand, Ashes, Ulmic Acid from Sugar, and distilled Water.*—1st, poorly; 2nd, tolerably well; 3rd, very well; 4th, did not come up; 5th, very well.

4. *Sand, Ashes, Apocrenate of Ammonia prepared from Sugar, and distilled Water.*—None succeeded except No. 5, and this but very badly.

5. *Sand, Ashes, Humate of Ammonia from Garden Earth (Ammoniacal Extract of Humus), distilled Water.*—None came up.

6. *Sand, Ashes, Humic Acid from Garden Earth, and distilled Water.*—1st, very beautifully developed; 2nd, none came up; 3rd, imperfectly developed; 4th, none came up; 5th, tolerably well developed.

7. *Sand, Ashes, Aqueous Extract of Humus, and distilled Water.*—1st, 2nd, 3rd and 5th, none came up; 4th, imperfectly.

8. *Sand, Ashes, Ulmate of Ammonia prepared from Sugar, and distilled Water.*—1st, 2nd, 3rd and 5th, very beautifully developed; 4th, imperfectly.

9. *Sand, Ashes, Humate of Ammonia from Bog Earth, and distilled Water.*—1st, 2nd, 3rd and 5th, very beautifully developed; 4th, did not come up.

10. *Ordinary Soil and distilled Water.*—Results perfectly identical with those of the preceding experiment.

11. *Ignited Charcoal reduced to a coarse Powder, Ashes, and distilled Water.*—All came up, but were far less developed than in the last three experiments.

If we glance at the results of these experiments, and leave out of question those substances which from some cause or other were injurious to germination (experiments 4 and 5), it appears,—*a*, that rain-water and atmospheric air do not afford sufficient nutriment to plants; the inorganic substances are wanting; *b*, that rain-water, ashes and atmospheric air do likewise not suffice; *c*, that the aqueous extract of humus contains too little organic substance to yield to the plants what they require; *d*, that ulmic acid prepared from sugar is actually advantageous to the growth of plants, although it contains no nitrogen; *e*, that the humic acid from garden earth is extremely advantageous to the growth of plants; *f*, that the ammonia compound of this latter, as well as the acid from bog earth, produce a luxuriant development; *g*, that lastly, plants do not succeed so well in wood-charcoal and ash, as in ordinary soil, or in the substances mentioned in *e* and *f*.—*Journ. für Prakt. Chem.*, xxxii. p. 344.

On the Chemical Phænomena of Digestion. By MM. C. BERNARD *and* C. BARRESWIL.

The constant acid reaction exhibited by the gastric juice constitutes one of its essential properties. It is known, in fact, that when it is neutralized by an alkali or by a carbonated alkali, it loses altogether its digestive powers, which however may be restored to it by re-establishing the acid reaction. On the other hand, it is certain that the acidity is not the sole agent of the activity of the gastric juice; for on exposing the pure fluid to a temperature near to boiling, it equally loses its digestive power, not by the absence of the acid reaction, which remains the same, but because we then act on another of its constituents, which is essentially modified by heat.

According to these two principal facts, we admit that the gastric juice owes its properties to the union of two principles inseparable in their action, viz. 1st, to a substance with an acid reaction; 2nd, a peculiar organic matter destructible by heat. In the present memoir we shall treat solely of the cause of the acid reaction of the gastric juice.

Two opinions prevail at the present time respecting the cause of this acidity. In the one it is said to be owing to the presence of biphosphate of lime; in the other it is attributed to an acid existing in a free state in the gastric juice. The principal fact which has been adduced to prove the non-existence of free acid and merely the presence of biphosphate of lime is, that it may be treated with carbonate of lime in excess without giving rise to the disengagement of carbonic acid. Our experiments have shown us that this happens solely from the excessive dilution of the acid in the gastric juice, which allows of the small quantities of carbonic acid produced being dissolved in proportion as they are formed. We have found that when the gastric juice was previously concentrated, a considerable effervescence was obtained with chalk. We have moreover observed that the gastric juice dissolves the neutral phosphate of lime, and have convinced ourselves that this salt is entirely insoluble in the biphosphate of the same base. From these experiments we have concluded that the gastric juice owes its acidity to the presence of a free acid, and not to the biphosphate of lime.

Those authors who have admitted the presence of a free acid in the gastric juice differ in opinion concerning its nature; some consider it acetic acid, others phosphoric, the majority hydrochloric, and lastly some lactic. We have successively endeavoured to detect these different acids. Before, however, describing the course we followed in our experiments, we will observe that they were made with very pure gastric juice taken from several healthy dogs.

Acetic acid being a volatile acid, we submitted the gastric juice to distillation at a gentle heat, with the suitable precautions to avoid any of the liquid being mechanically carried over; the first products, collected and tested with litmus-paper, did not offer any acid reaction. Gastric juice, to which a trace of acetic acid or even of acetate of soda had been added, on being submitted to distillation afforded a product which was evidently acid. These and other experiments seem to prove that the gastric juice contains no free acetic acid nor acetates.

On reflecting that the first products of the distillation of the gastric juice never exhibited any acid reaction, we were tempted to reject likewise the presence of free hydrochloric acid, because according to received notions this acid should have passed over in the first part of the process.

We should however have fallen into error, as will be seen from the following experiment. In fact, when water slightly acidulated with hydrochloric acid is submitted to distillation, nothing but pure water is found to pass over at first, and the acid is not disengaged until towards the end of the operation. This unsuspected fact induced us to distil a fresh portion of pure gastric juice to dryness. At first, and during nearly the whole duration of the experiment, a neutral limpid liquor passes over, which does not precipitate nitrate of silver; the gastric juice being evaporated to about four-fifths, the distilled liquor is perceptibly acid, but produces no turbidness in salts of silver; only towards the end, when but a few drops of gastric juice are left in the retort, the acid liquid which passes over yields with salts of silver an evident precipitate, which does not disappear on treatment with concentrated nitric acid. There was not the least doubt that this latter product was hydrochloric acid; but it remained to be ascertained whether it existed in the gastric juice, or whether it was not produced by the decomposition of a chloride in the course of the operation.

When the *least trace* of oxalic acid is added to gastric juice, which as is known contains some lime, a turbidness results from the formation of oxalate of lime insoluble in the gastric juice, while an equal quantity of the same reagent produces no turbidness in water containing two-thousandths of hydrochloric acid to which some chloride of calcium has been added. This experiment clearly demonstrates that the hydrochloric acid exists as a chloride, and not in a free state in the gastric juice. This will subsequently be confirmed by other experiments.

Phosphoric acid being a fixed acid, we had to look for it in the juice concentrated by distillation. This residue had acquired an excessively acid reaction, producing effervescence with chalk; but it never entirely lost its acid reaction, notwithstanding the presence of an excess of carbonate of lime. This character, added to those which have been described by various authors, positively indicates the presence of phosphoric acid. We then saturated some gastric juice with lime and with oxide of zinc; the filtered solutions were neutral, and presented all the characters of those of lime and zinc, proving that phosphoric acid is not the only free acid in the gastric juice; for had it been so, we should have found, from the insolubility of the two phosphates, neither lime nor zinc in the filtered liquid. We ascertained by experiment that the other principles of the gastric juice, such as chloride of sodium, did not at all hide or affect this reaction.

To determine at present the nature of the acid which afforded the soluble salts of lime and zinc, it should be borne in mind that it is an acid which passes over towards the end of the distillation, and does not precipitate the salts of silver. Such characters are presented by lactic acid. We submitted to distillation some water acidulated with lactic acid, and we found in this operation a striking analogy with the phænomena produced in the distillation of the gastric juice, viz. at first nothing but pure water passed over, towards the end an acid liquor, and a liquid residue strongly acid is left, which produces effervescence with carbonates. On distilling water acidulated with lactic acid, to which a little chloride of sodium has been added, we obtained a still more complete analogy; the operation presented three distinct periods, exactly as with the gastric juice; first only pure water passed over, then an acid which did not precipitate salts of silver, and the last drops of the liquid carried with them hydrochloric acid.

This experiment explains the presence of hydrochloric acid in the ulterior products of the distillation of the gastric juice; this acid is, in fact, derived from the decomposition of the chlorides by the lactic acid in the concentrated liquors. Should this fact not suffice to prove that the gastric juice contains no free hydrochloric acid, the following experiments will remove all doubt on the subject. If some starch be boiled in hydrochloric acid, it soon loses the property of being rendered blue by iodine, while lactic acid does not in the least modify it even after prolonged ebullition. On the other hand, if some starch be boiled with hydrochloric acid to which an excess of a soluble lactate has been added, the starch remains unaltered, as if it had been boiled solely in lactic acid. This experiment clearly proves that hydrochloric acid cannot exist in a free state in presence of an excess of a lactate. By similar proofs it may be demonstrated that the existence of hydrochloric acid is inadmissible in presence of an excess of a phosphate or of an acetate.

On summing up, we find that the lactic acid and the acid of the gastric juice have in common the characters of being non-volatile, are carried over during distillation by the vapour of water, and expel hydrochloric acid from chlorides. Following up the comparison between these two acids, we have observed in the acid from the gastric juice all the characters pointed out by M. Pelouze for lactic acid; these two acids, in fact, give salts of lime, barytes, zinc and copper, soluble in water; a salt of copper, which forms with lime a soluble double salt, the colour of which is much deeper than that of the simple salt; a salt of lime soluble in alcohol, and which is precipitated from the alcoholic solution by æther. From the characters enumerated, the existence of this acid appears to us to be at present incontrovertible. Lactic acid had been previously pointed out in the gastric juice by M. Chevreul and MM. Leuret and Lassaigne.

Conclusions.—From the facts contained in this memoir, we may safely state that the acid reaction of the gastric juice is not owing to biphosphate of lime; but that it results, on the contrary, from the presence of an acid in a free state. We have never been able to confirm the existence of free hydrochloric and acetic acids, as has been asserted.

We have constantly found the well-marked characters of lactic acid in combination with a small proportion of phosphoric acid*.

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* This phosphoric acid should be regarded as a secondary product from a reaction of the lactic acid on the phosphates contained in the gastric juice.

In our opinion the lactic acid should be regarded as a constant physiological production of the organism. In fact, to whatever conditions of alimentation we have subjected animals, we have never observed the nature of the acid principle of the gastric fluid to vary. Thus after an exclusively vegetable or animal diet continued for several days, or even longer, we have always found free lactic acid.

In advancing that lactic acid is the constant cause of the acidity of the gastric juice, we do not wish to be understood as considering that this acid is from its nature gifted with certain special properties, which render it indispensable to the process of digestion. On the contrary, it results from the experiments of M. Blondlot and our own, that if an acid reaction is indispensable in order that the dissolving property of the gastric juice be manifested, the kind of acid producing this reaction is indifferent.

Thus we have been able to saturate gastric juice with neutral phosphate of lime, or to add a large excess of acetic or phosphoric acid, and even of hydrochloric acid, in such quantity as to be really *in a free state* in the liquid, and the gastric juice always retained its digestive properties. This equivalence of acids with respect to the activity of the gastric juice appears necessary; for at each moment, from the very fact of alimentation, the most different salts are introduced into the stomach at the moment of the formation of the gastric juice. It may be conceived that, if among these salts there should be one whose acid could be displaced by the lactic acid, the digestive functions would infallibly be disturbed if the new acid set at liberty could not replace the normal acid.—*Comptes Rendus*, Dec. 9, 1844.

Cement for Stone Ware, Earthen Ware, &c.

Is best obtained by melting together 3 parts sulphur, 2 parts white resin, 1 half part shell-lac, 1 part elemi, and 1 part mastic, with 3 parts brickdust. This cement is spread on the previously warmed surfaces.

On the Composition of the Protocarbonate of Iron.

By M. Witstein.

The carbonate of the protoxide of iron, precipitated by powdered crystallized carbonate of soda from a boiling solution of recently-prepared protosulphate of iron, washed by decantation, well-pressed in linen and dried, contains, according to Wittstein, protoxide of iron, water and carbonic acid, in the proportion of 46·7 : 13·6 : 28·7, which corresponds to the formula $FeO\,CO^2, HO$. Moreover, a variable quantity of hydrated peroxide of iron is always mixed with it. The salt becomes heated in the air, disengages carbonic acid, and passes into hydrated peroxide, losing nearly 23 per cent. in weight. The residuous reddish-brown powder, which is free from carbonic acid, yields on ignition 22 per cent. water, which would correspond to the formula $3Fe^2O^3 + 8HO$. On ignition the protocarbonate of iron leaves 59·48–60 per cent. anhydrous peroxide of iron.—Buchn. *Repert.*, xxv. p. 65.

On the Preparation of pure Caustic Potash and Soda. By M. Bizio.

The best method of rendering potash and soda caustic is, according to the author, to mix a solution of 1 part of the dry carbonate salt with 1 part freshly-prepared dry hydrate of lime, and allowing it to stand in a closed vessel for 24 hours at a temperature of 68° to 78° Fahr., frequently shaking it. The potash salt should be dissolved in 12 to 15, the soda salt in 7 to 15 parts water; the carbonate of lime separates in a granular state, and the clear caustic ley may be decanted. A weaker ley may be obtained from the residue by fresh treatment with water*.—Berzelius, *Jahresbericht*, xxiv. p. 104.

Preparation of Pyrophorus from Alum. By M. Elsner.

An intimate mixture of 3 parts roasted alum and 1 of flour is conveyed into a phial, which is placed in a Hessian crucible filled up to the neck with sand; the crucible is then heated in a wind-furnace till the glass nearly melts. The phial is then stopped up and allowed to cool. A pyrophorus made from 5 parts alum and 1 part powdered charcoal, is also very good, and never fails if a sufficient heat has been employed in its preparation.—*Journ. für Prakt. Chem.* xxxiii. p. 27.

ANALYTICAL CHEMISTRY.

On the Detection of Prussic Acid in Cases of Poisoning. By M. Witting.

The method recommended by the author in suspected cases of poisoning by prussic acid, is to mix the mass with one-sixth alcohol, and to distil off one-fourth. If it contain prussic acid, the distilled product generally evolves the peculiar smell. To this product a little caustic potash is added, and then a mixed acid solution of protochloride and perchloride of iron, when prussian blue is formed.

If it be suspected that the poisoning was effected with cyanide of potassium, cyanide of zinc, &c., some hydrochloric acid should be added along with the alcohol previous to distillation.—Berzelius's *Jahresbericht*, xxiv. p. 269.

Description of an improved Method of detecting Arsenic in Cases of Poisoning. By M. Berzelius.

The scientific committee appointed by the Prussian government to examine the various methods proposed for the detection of this

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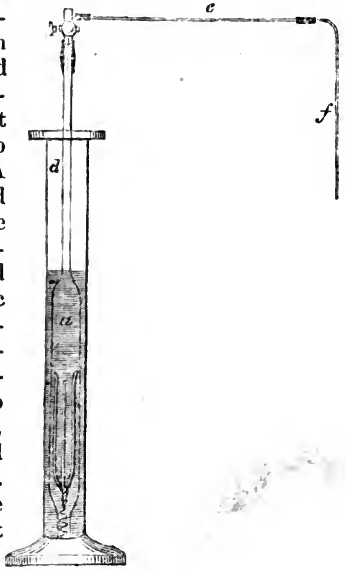
* We have found this method to present on trial no advantage over that of the Pharmacopœia, in which half the quantity of lime is used with boiling water.—Ed. *Chem. Gaz.*

poison, and to ascertain the safest and most expedient, have suggested an improvement in Marsh's apparatus, which surpasses, in my opinion, all the other modifications from the certainty and distinctness of the result. The annexed figure shows the simple arrangement of the apparatus:—*a* is a wide glass tube, or a narrow cylinder of about 1¼ inch in width and 10 inches in length, contracted at the lower extremity to an aperture ½ an inch in diameter. It should be of thick glass, so as to possess the requisite strength. A glass tube, *d*, 2 lines in width and 10 inches long, is joined to the upper end, which is likewise contracted. A brass stop-cock is fixed by means of a short caoutchouc tube air-tight to the upper extremity of this tube, closed at the summit, and provided with a short lateral tube, at a right angle with it, to which a narrow straight glass tube, 8 inches in length, *e*, is connected air-tight by means of caoutchouc. To the other extremity of the tube *e* a second descending tube, *f*, bent at right angles, is affixed.



Some strips of zinc, ascertained to be free from arsenic, are inserted in the tube *a* through the inferior aperture; they should be of such length as to reach to two-thirds of the tube, in which they are maintained by a spirally-wound copper wire, which is likewise inserted through the inferior aperture.. The tube, thus arranged, is placed in a glass cylinder, whose inner diameter is slightly greater than requisite to admit easily the tube *a*, and of from 16 to 18 inches high. The acid liquid to be tested for arsenic is poured into this cylinder to such a height, that when the tube *a* is filled with it, it stands 1 or 2 lines above the connection of *a* with *d*. The cock is then opened, so that the liquid may enter and fill the tube, when it is again closed. The zinc now dissolves, and the liquid is forced back again through the inferior aperture of *a* into the cylinder. If any froth is formed in the operation, as is usually the case, the apparatus is shaken gently, that the zinc strips may destroy the froth and cause it to subside.

In the mean time the tube *e* is heated in the centre, or somewhat nearer to the cock, over an Argand spirit-lamp, to redness, the open extremity of the tube *f* immersed beneath the surface of some water contained in a small vessel; and when *e* is perfectly red-hot, the cock is opened sufficiently to admit of the gas passing in slowly successive bubbles through the tube *f* into the water. It must not be allowed to proceed faster if the whole of the arsenic is to be deposited from the gas on its passage over the incandescent part. As soon as the tube *a* is again filled with liquid, the cock is closed, and not opened until the whole of the liquid has been expelled. The experiment is continued in this manner until a quantity of arsenic has been deposited sufficient to apply the necessary tests. To collect gradually the whole of the arsenic which has been deposited near the incandescent spot, the flame is advanced by degrees as far as the centre of the tube, when the whole of the arsenic will be contained in the half nearest to *f*. When the cock is closed the tube is filled with hydrogen gas, and we are able to test by sublimation whether the deposited body has the volatility of arsenic, that is whether it sublimes at a gentle heat; to ascertain, therefore, whether it is pure arsenic, or is accompanied by other less volatile bodies, for instance antimony. The arsenic is then collected, so as to form a ring in the interior of the tube; which, when it has become cold, is removed, and a fresh one substituted for it, and the arsenic collected in this manner in fresh tubes as long as the liquid affords any gas.

The glass tube which has been removed is cut with a file near the place where the arsenic is collected, and this placed in a small glass containing fuming nitric acid, in which the arsenic is dissolved with the assistance of heat. The solution obtained is then evaporated over a water-bath on a watch-glass to dryness, to drive off the nitric acid. Arsenic acid is soluble in water, while antimonic acid or oxide of antimony is insoluble. The arsenic acid affords, when mixed with neutral nitrate of silver, a tile-red precipitate of arseniate of silver. The arsenic collected in another tube is not employed, but sealed at both ends; and the sample of arsenic preserved in the hermetically-closed tube presented in evidence on the trial.

A third tube should be somewhat broader, in order that after the arsenic has been collected in it and the hydrogen gas expelled by air, the arsenic may be oxidized in it and sublimed as arsenious acid, when the ordinary octahedral form of the sublimed crystals may be recognised with a magnifying glass. The arsenious acid may be then washed out with a little water containing some ammonia, to test it with nitrate of silver. The behaviour of antimony differs with respect to this test decidedly from that of arsenic.

The zinc and sulphuric acid employed in these experiments are previously submitted to a similar examination in the same apparatus, when it is easily ascertained whether they are free from arsenic or not.

The great advantage of this apparatus is, that none of the arsenic is lost, as the experimenter has it in his power to regulate the passage of the gas through the heated tube as slowly as he chooses, and the disengagement of gas may be stopped at pleasure, if any circumstance should necessitate a delay.—Berzelius's *Jahresbericht*, xxiv. p. 262.

THE CHEMICAL GAZETTE.

No. LV.—February 1, 1845.

Account of the new Metal Ruthenium, *discovered in the Platinum Residues. By* Prof. Claus.

The author describes his discovery in a letter to M. Hess as follows:—At last, after two years' continued work, I have succeeded in obtaining in a pure state the new metal announced by me some time back, and of extracting it in a very simple manner from the platinum residues. I have hitherto only been able to obtain the metal as a blackish-gray powder, which is considerably lighter than iridium. It belongs to the interesting group of the platina metals and its chlorides, and double chlorides resemble greatly those of iridium. The similarity of the potassio-chloride of iridium to the corresponding salt of the new metal is so great, that Berzelius, to whom I forwarded a sample, announced to me in a letter that it was a salt of iridium; eight days later, however, I again received a letter from him, in which he retracts his former view, and looks upon it as the salt of an unknown metal. The metal, however, has such marked and peculiar characters, that no doubt can remain as to its distinctness; its highest chloride is of a beautiful orange-yellow colour, and affords a precipitate of black oxide when thrown down from its aqueous solution by ammonia, while the solutions of the chlorides of the other platina metals are not all precipitated by ammonia at the ordinary temperature. The solution of this chloride is only effected by sulphuretted hydrogen after long-continued action; at first a brown sulphuret, which subsequently becomes black, is thrown down, and the solution acquires a splendid azure-blue colour. This phænomenon is owing to the sulphuretted hydrogen converting the chloride, with deposition of some sulphuret, into a blue protochloride, which is not in the least affected by sulphuretted hydrogen. If a slip of zinc be inserted in a solution of the orange-coloured chloride, rendered acid with muriatic acid, a black metallic powder is deposited after some time, and the liquid acquires a dark indigo-blue colour; subsequently the whole of the metal is precipitated, and the solution becomes colourless.

The metal, as well as all its compounds, yields, when ignited with nitre, a blackish-green mass, which dissolves in distilled water to a beautiful orange-coloured liquid, which consists of a combination of the metallic acid with potash. This solution blackens organic substances, and is decomposed by alcohol, by the action of acids, &c., with deposition of a velvety black combination of the oxide with potash, which dissolves entirely in boiling muriatic acid to a solution of the orange-yellow chloride. The chloride is very easily decomposed, especially in the aqueous solution; with loss of chlorine it becomes dark brown, almost black, sometimes cherry-red, and deposits a black insoluble powder. In this decomposed state it has an entirely inconceivable tinctorial power; a fiftieth of a grain of the chloride suffices to render half a pound of water almost opake. If the chloride be thrown down with ammonia, the black precipitate dissolved in muriatic acid and evaporated to dryness, a dirty green residue is obtained, which dissolved in much water affords an opake black liquid with a slight tint of cherry-red, which on evaporation and the addition of a little nitric acid, exhibits the most beautiful play of colours. First it is violet, then azure blue, red, yellow, and finally, on evaporation to dryness, green. This latter property the salt possesses in common with the sesquichloride of iridium; but the other characters, the behaviour towards nitre and sulphuretted hydrogen, are so characteristic, that the distinctness of this metal is immediately evident. The power of the metal of combining with alkalies is so great, that on fusion with caustic potash it dissolves entirely in it, and yields an orange-coloured liquid, which is rutheniate of potash. It is for this reason that the metal cannot be reduced in the same way as the other platinum metals from their chlorides, by mixing them with soda and igniting. On mixing the chloride of the metal, or its combination, with potassium with soda and igniting, the greater portion of the mass dissolves in water with an orange-yellow colour.

I shall call this metal *Ruthenium*, because it occurs in small quantity in the white body described by Osann, which consists principally of silica, titanic acid, peroxide of iron and zircona, and was regarded by Osann as a peculiar metallic oxide, which he called oxide of ruthenium. The discovery of the new metal escaped Osann, because he extracted his crude oxide of ruthenium repeatedly with muriatic acid, and did not examine the solution, but regarded the insoluble residue as the new oxide. In my researches on the platinum residues I have likewise obtained Osann's ruthenium, possessed of all the properties described by that chemist. From this oxide I have extracted with muriatic acid a considerable quantity of my oxide of ruthenium, together with some peroxide of iron.

After having made myself acquainted with the properties of the metal on small quantities, I found it very easy to prepare it from the platinum residues. Before, however, I had become more accurately acquainted with the ruthenium, I had fused the whole of my stock of platinum-residue with nitre (decomposing large quantities with chlorine is very troublesome, and requires too much time); from the fused mass I prepared the various combinations of the platinum metals contained in it, and obtained from 15 lbs. of residue near upon 4 oz. of metallic osmium. In this operation I became acquainted sooner than Fremy with the osmite of potash, prepared however in a different manner from his. It is a very beautiful salt, crystallizing in regular octahedrons of black, garnet or rose-red colour, which depends on the greater or less rapidity of its formation. If they have time to form large regular crystals from a not too saturated solution on gradual cooling they are black, and transparent at the margins with a garnet-red colour. If they separate quickly from a saturated solution, they are garnet-red; and if the separation of the salt is assisted by stirring, the crystals are pulverulent and are of a rose-red colour. The salt is almost white when reduced to a powder; it is $KO + OsO^3 + 2Aq$. It now dissolves slowly in water with the colour of the manganate of potash; on evaporation the solution is partially decomposed, free osmic acid, OsO^4, escapes, and black oxide of osmium, $OsO^2 + aq$, is precipitated, the solution becomes strongly alkaline, and a portion of the salt separates undecomposed. This decomposition may be prevented by adding to the solution of the salt a large quantity of free potash. Acids decompose the solution immediately into oxide of osmium and osmic acid, $2(OsO^3)$ becomes $OsO^2 + OsO^4$: this fact I likewise noticed earlier than Fremy. The oxide on being heated in a glass tube has the remarkable property of being decomposed with a slight detonation into metallic osmium and osmic acid; $2(OsO^3)$ give rise to $Os + OsO^4$. I have prepared the entire series of the osmium compounds; osmite of barytes, $BaO + OsO^3 + aq$, forms beautiful black crystals, possessing a diamond lustre, when the solution of the osmic acid is mixed with an excess of barytic water; the yellow liquid deposits the salt in the course of four weeks.

I further prepared from these extracts of the first fusion with nitre, a considerable amount of iridium salts; among other things I obtained 3 oz. of an iridium salt, possessing properties very different from the ordinary salt, which however I looked upon as iridium, and added to the other potassio-chloride of iridium. I was then not sufficiently acquainted with the properties of the salt of ruthenium; at present I know that it was potassio-chloride of ruthenium. Nothing now remained but to endeavour to prepare ruthenium from the residue, which had been fused once with nitre and extracted with water and acids, and which I had set aside for further investigation. I was so fortunate as to obtain from this nearly-exhausted residue near upon 1½ oz. of the potassio-chloride of ruthenium. I mixed equal parts of the residue with nitre, and kept them at a white heat in a Hessian crucible for two hours. The mass was taken out while still red-hot with an iron spatula, and after cooling was reduced to a coarse powder, which was extracted with distilled water, leaving it to stand with it until it became clear; the perfectly clear liquid, which is of a dark yellow colour, is then decanted. The liquid cannot be filtered, because it is decomposed by the action of the filter and stops it up. It contains rutheniate, chromate and silicate of potash, not a trace of rhodium or iridium, and only a very minute trace of osmiate of potash. Nitric acid is cautiously added to this solution until the alkaline reaction of the liquid has disappeared; by this, oxide of ruthenium and potash and some silicic acid are precipitated as a velvet-black powder, while chromate of potash remains dissolved. After edulcoration the oxide of ruthenium and potash is dissolved in muriatic acid, and the solution evaporated until the silica separates as a gelatinous mass; it is then diluted with water and filtered. It must not be evaporated to dryness for the more complete separation of the silica, because the chloride of ruthenium is thereby decomposed into an insoluble protochloride. The filtered solution, which is of a beautiful orange-yellow colour, is evaporated down to a very small volume, and mixed with a concentrated solution of chloride of potassium, when the salt $KoCl^2 + RuCl^4$ separates in reddish-brown crystals. Still more salt is obtained on evaporating the liquid decanted from the crystals. The salt may be further purified by recrystallization.—*Bullet. de la Classe Physico-math. de l'Acad. de St. Pétersb.* t. iii. p. 311–316.

On the Products resulting from the Destructive Distillation of the Butyrate of Lime. By G. CHANCEL.

In my researches on butyrone*, I pointed out the difference in the results which are obtained according to whether only a small portion or a considerable quantity of anhydrous butyrate of lime be submitted to destructive distillation. In the first case, by regulating carefully the temperature, the butyrate is decomposed into carbonate of lime and butyrone, which distils over nearly pure. But the reaction is no longer so simple when considerable quantities are operated upon; the residue of carbonate of lime is always impurified by a somewhat large deposit of carbon, and the liquid products obtained are highly coloured, and possess a disagreeable compound odour, in which it is impossible to recognize that peculiar to pure butyrone.

This liquid, which is formed at least of three different substances, begins boiling at about 203° Fahr., but the temperature gradually increases up to 392°, and above.

To isolate the butyrone and the products accompanying it, I am not acquainted at present with any other means than fractioned distillation, turning to account the difference of volatility of the various substances. In this manner three distinct products are finally obtained:—

1. A limpid colourless liquid, distilling entirely at 203°.
2. A limpid colourless liquid, boiling at 291°, at which temperature it distils over completely. This second product is nothing but butyrone.
3. A liquid somewhat less limpid than the preceding, always coloured slightly yellow, and which I have not yet succeeded in purifying sufficiently for investigation. I have however every reason to believe that it is a hydrocarbon, for a piece of potassium preserves its metallic lustre in it. The boiling point of this substance is between 437° and 446°.

In organic chemistry there exists a class of combinations the type of which is formed by aldehyde. These compounds have the most varied properties, and differ from one another as well by their reactions as by the nature of the products which they give rise to under

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* See Chem. Gaz., vol. ii. p. 340 and 367.

the influence of various agents; but they all possess a fundamental character which ranges them in one group. The composition of these bodies is in fact represented by that of the free acid whence they are derived minus 2 atoms of oxygen, and when placed under peculiar circumstances of oxidation they absorb oxygen to regenerate their acid.

The body which I am about to describe should be arranged in this group; it exhibits in fact the same relation towards butyric acid as aldehyde does to acetic acid; and when submitted to the influence of certain oxidizing agents, it absorbs 2 atoms oxygen without parting with any hydrogen, and is converted into monohydrated butyric acid.

Butyral, the name which I have assigned to this substance (abbreviated from butyraldehyde), is a perfectly colourless limpid liquid of great mobility; it has a burning taste, a sharp penetrating odour, boils at 203°, and when pure distils over entirely at this temperature. Its density at 71°·5 is 0·821; it dissolves a small portion of water, and is itself slightly soluble in this medium, to which it communicates its odour; alcohol, æther, pyroligneous æther and potato-oil, dissolve it in every proportion. It is very inflammable, and burns with a luminous flame slightly margined with blue. Placed in contact with crystals of chromic acid, it instantly ignites with a kind of explosion.

Submitted to the cold produced by a mixture of æther and solid carbonic acid, butyral preserves all its fluidity; butyrone, on the contrary, almost instantly congeals, and crystallizes in large colourless transparent laminæ. Exposed to the contact of pure oxygen in a hermetically-closed flask, it does not acquire any colour, but after a certain time becomes strongly acid; if mixed now with a little water, the greater portion dissolves, communicating to it its acidity, while the unaltered butyral collects on the surface. The presence of platinum-black very much accelerates this absorption of oxygen; the peculiar odour of butyral disappears almost entirely, and is replaced by that of butyric acid; diluted with water, it decomposes carbonate of lime with effervescence, and the filtered solution contains butyrate of lime.

Butyral heated with water and oxide of silver reduces this latter with great facility without any disengagement of gas; the liquid retains in solution a salt of silver, which is no butyrate, but probably a combination of a new acid (butyrous acid?), containing without doubt less oxygen than the butyric acid, and which would correspond by its composition to acetous or aldehydic acid. I am now engaged in a series of experiments, which will I hope decide this important question. By treating the liquids containing the butyric aldehyde by the method described by M. Liebig for the aldehyde of acetic acid, a deposit of metallic silver is always obtained; it suffices in fact to make an aqueous solution of butyral, to add to it a few drops of caustic ammonia, and subsequently a quantity of nitrate of silver sufficient to cause the alkaline reaction to disappear. On heating this liquid slightly, the sides of the vessel become coated with a reflecting layer of silver of great regularity; on employing a mixture in suitable proportions, the reaction takes place with great precision.

M. Liebig considers the reduction of the salts of silver by acetic aldehyde as one of the distinctive properties of this substance; it ought certainly to be admitted as a generic character of all the bodies of this class. The layer of metallic silver which forms under the influence of these compounds presents, in this case, so perfect a uniformity and continuity, that there is room to hope that this property may one day be applied to the arts. Preserved from contact with the air in flasks, butyral does not seem to undergo any change; at least after more than six months I found that it retained exactly all the characters which it possessed at the moment of its preparation.

Chlorine and bromine attack it violently, giving rise to an abundant disengagement of hydrochloric and hydrobromic acids, and to some peculiar compounds containing chlorine and bromine. Nitric acid, of every degree of concentration, attacks it, with disengagement of red vapours. Butyral does not form any definite combination with dry ammonia; caustic ammonia does not appear to alter it; however, I have not yet studied the action of the alkalies on this substance.

Composition.—Having described the properties which characterize butyral, I now proceed to establish its composition. I have made numerous analyses of this substance and of the products gathered at different periods of distillation; they all gave me numbers very nearly alike, leading to the rough formula $C^8 H^8 O^2$.

The density of the vapour became an important means of controlling the preceding formula, and at the same time of fixing the true nature of the butyraldehyde; several determinations always gave me satisfactory results, although generally somewhat too high.

One experiment gave for the weight of the litre of vapour at 32° F. and $0^{m}{\cdot}76$ of pressure .... 3·398 grs.
Density.................................... 2·061 grs.

The calculation gives

8 volumes of carbon	6·742
16 volumes of hydrogen	1·101
2 volumes of oxygen	2·205
	10·048

$$\text{Density} = \frac{10{\cdot}05}{4} = 2{\cdot}512.$$

The preceding experiment places beyond doubt the composition of butyral, and moreover shows that the formula $C^8 H^8 O^2$ expresses 4 volumes of vapour, and that in this respect this substance presents the same molecular grouping as butyric acid, to which it is related.

I have made some experiments with a view to convert the butyral into butyric acid under the influence of oxidizing agents; I shall, however, here only mention the results obtained with sulphuric acid, having been prevented from completing these researches by want of materials.

When fuming sulphuric acid is added in small portions to twice its weight of butyral, at the same time carefully agitating the mixture, it dissolves with an elevation of temperature, the liquid becoming of a very deep red. The action is assisted by heating to 212°, which occasions a slight disengagement of sulphurous acid; the mixture becomes brown but not black. On treating the liquid, diluted with water, with an excess of carbonate of barytes, removing the sulphate of barytes by filtration, and evaporating to crystallization, a small quantity of a white salt, slightly tinged with yellow, is obtained, which evolves in a high degree the peculiar odour of butyric acid. This salt contains not a trace of sulphur; dropped into water it dissolves, giving rise to gyratory movements which characterize the soluble butyrates; it possesses, in fact, all the characters of the butyrate of barytes. I have several times repeated this experiment, and always with the same result. To remove all doubt, I made four analyses of samples from three different preparations; they furnished numbers varying between 48 and 49 per cent. barytes; 100 parts of the anhydrous butyrate contain, according to theory, 49·22 per cent. barytes.

The butyrate of barytes obtained under these circumstances had crystallized from a hot solution, it contained 2 equiv. of water of crystallization. Two experiments gave 10·5 and 10·07 per cent. water; the formula $BaO, C^8 H^7 O^3 + 2HO$ requires 10·37. The salt, which crystallizes on spontaneous evaporation, contains, according to MM. Pelouze and Gelis, 18·83 per cent. water of crystallization, which corresponds to 4 atoms. The salt with 2 atoms of water does not melt in this water at 212° like that with 4 equiv., to which this property appears exclusively to belong. This circumstance removes an objection made by M. Lerch in his researches on the volatile acids of butter*, who states that the butyrate of barytes is not fusible at 212°, as asserted by Chevreul and Pelouze and Gelis.

In no case was any trace formed of a compound acid, containing the elements of butyral united to an oxygenized compound of sulphur; I believe I may affirm that butyric and sulphurous acids are the sole products which result; the reaction may therefore be expressed by the equation—

$$\underbrace{C^8 H^8 O^2}_{\text{Butyraldehyde.}} + 2SO^3 = \underbrace{C^8 H^8 O^4}_{\substack{\text{Monohydrated} \\ \text{butyric acid.}}} + 2SO^2$$

Thus the sulphuric acid acts simply in this case as an oxidizing agent.

The facts above detailed place beyond doubt the elementary composition of butyral, and I trust they equally show that this substance is the true aldehyde of butyric acid.

There still remained two important questions to be solved, viz.—

1. What is the rational formula for this compound? Should it be considered as the hydrate of an organic oxide, and the formula $C^8 H^7 O, HO = C^8 H^8 O^2$ assigned to it? or should it be regarded

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* See this Journal, vol. ii. p. 377.

as a substance analogous to the oil of bitter almonds? I have made some experiments to decide this question, but the results obtained were not satisfactory.

2. In what manner should the formation of butyral be interpreted? What is the action which gives rise to it in the destructive distillation of the butyrates? On this question, as on the preceding, I possess at present but very imperfect notions. I may, however, observe that this simple elimination of oxygen from butyric acid is not the sole example of its kind. M. Boussingault, to whom we owe the discovery of suberone, which is formed under similar circumstances, has shown that this substance is represented by the formula $C^8 H^7 O$, and consequently only differs from crystallized suberic acid, $C^8 H^7 O^4$ by 3 atoms of oxygen. He also found that suberone exposed to the air absorbs oxygen, and is converted into suberic acid; nitric acid, and other oxidizing agents, effect the same transformation. These properties would tend to range this substance in the class of the aldehydes, from which however it is removed by its composition. Dr. Sacc, moreover, has obtained the true suberic aldehyde by the distillation of linseed oil; the author expresses the composition of this substance by the formula $C^8 H^7 O^2$; it is a compound of great stability, and resists for a long time the action of nitric acid, which however finally converts it entirely into suberic acid.—*Comptes Rendus*, Sept. 30, 1844.

On the Liquefaction of Gases. By Professor FARADAY.

The author, in a letter to M. Dumas, gives the following account of his mode of experimenting:—

I sought in the first place to obtain a very low temperature, and employed for this purpose Thilorier's bath of solid carbonic acid and æther, placing it however under the recipient of an air-pump. By maintaining a constant vacuum, I lowered the temperature to such a degree, that the carbonic acid of the bath was not more volatile than water at the temperature of 86°, for the barometer of the air-pump stood at 28·2 inches, the external barometer being at 29·4.

This arrangement made, I joined together, by means of corks and stop-cocks, some small glass and copper tubes, so that with the aid of two pumps I was able to subject various gases to a pressure of 40 atmospheres, and at the same time to submit them to the intense cold obtained under the air-pump, and to examine the resulting effects. As I expected, the cold produced several results which pressure alone would never have done, and principally in the solidification of bodies ordinarily gaseous. The following is a sketch of the various results:—

Olefiant gas was condensed to a beautiful colourless transparent liquid, but it did not solidify; it dissolves the resinous, bituminous and oily bodies.

Pure *hydriodic acid* may be obtained either in the solid or liquid state. Solid hydriodic acid is very clear, colourless and transparent; generally several fissures traverse the mass; it greatly resembles ice.

Hydrobromic acid may also be obtained either as a limpid and colourless liquid, or as a clear transparent solid.

Both these acids require a very careful distillation in closed vessels and under great pressure, to be obtained pure and colourless.

Fluosilicic acid was condensed to the liquid state, but it is requisite to operate at the lowest temperature. It is extremely liquid and mobile, like hot æther; it then produces a pressure of about 9 atmospheres, and gives no sign of solidification. It is transparent and colourless.

Fluoboric acid and *phosphuretted hydrogen* presented some results of condensation.

Hydrochloric acid liquefies readily at less than 1 atmosphere of pressure, but it does not solidify.

Sulphurous acid freezes immediately, as was to be expected.

Sulphuretted hydrogen becomes solid, and then forms a white, transparent, crystalline mass, bearing greater resemblance to solid nitrate of ammonia or to camphor, than to ice.

Carbonic acid, when it passes from the liquid to the solid state without being dispersed in the form of snow, constitutes a very beautiful substance, transparent like crystal, so that for some time I doubted whether the tube which contained it was empty or full; and I was even obliged, in order to ascertain the presence of the solid body, to melt a portion of it. Solid carbonic acid exerts a pressure of 6 atmospheres, which proves how readily liquid carbonic acid ought to become solid when allowed to escape into the free air.

Oxide of chlorine is a beautiful, orange-red, very friable, crystalline substance. It exhibits no trace of explosive power.

Protoxide of nitrogen is one of the gases which I had formerly condensed. I have seen in the journals that M. Natterer has repeated my experiments with a compression-pump, and that he has obtained the liquid in the open air. I have likewise condensed it to a liquid by means of my pump, but I have moreover solidified it by means of the cold bath. It then forms a beautiful transparent or colourless crystalline body, but in this state the pressure of its vapour does not amount to that of 1 atmosphere; and this result is confirmed by another experiment, in which, having opened a vessel containing this liquid, a portion evaporated, cooled the remainder, but did not solidify it. The cold produced by this evaporation is very intense, which was proved by placing the tube and its contents in a bath of solid carbonic acid and æther in the air. This bath, which instantly freezes mercury, behaved like a vessel filled with hot liquor, and immediately caused the protoxide of nitrogen to boil violently. It is therefore my intention to employ the liquid protoxide of nitrogen for some new experiments on hydrogen, oxygen and nitrogen; for on placing a bath of this liquid protoxide in the receiver of an air-pump, and expelling the air and the gas, we are able to place the bath of the protoxide relatively to that of the carbonic acid *in vacuo*, in the same relation that the two baths observe in the air.

Cyanogen freezes, as was already proved by Bussy.

Perfectly pure and dry *ammonia* may be obtained as a transparent, crystalline white substance, heavier than liquid ammonia, and diffusing very little odour, from the weak tension of its vapour at this temperature.

Arseniuretted hydrogen and *chlorine* do not pass from the liquid to the solid state.

Alcohol becomes thick like cold oil, but does not crystallize any more than *caoutchene, camphene* and *oil of turpentine*, but these bodies become viscid.

Binoxide of nitrogen and *oxide of carbon* did not exhibit the least sign of liquefaction at the lowest temperature, and at a pressure of 30 to 35 atmospheres.

While making these general observations, I have determined several numbers relative to the point of fusion of these various gases and their tension at different temperatures. The numbers will be given in the memoir which I am preparing on this subject, and in which I hope to have something new to say respecting the state which oxygen, nitrogen or hydrogen may affect in passing to the liquid state. Will this latter body present itself in the metallic form, as you think? Will nitrogen prove to be a metal, or retain its place among the non-metallic bodies? This, experience will show.—*Ann. de Chim. et de Phys.*, Jan. 1845.

On the Organic Acids of Lactuca virosa *and* sativa.

By M. KÖHNKE.

Numerous doubts have been raised against the distinctness of the so-called lactucic acid of Pfaff; the author has endeavoured to settle these, and has found that the fresh plant contains no oxalic acid, but *malic* and *succinic* acids; that, on the contrary, no succinic but oxalic acid occurs in the lactucarium. The author's experiments are as follows:—

Fresh entire plants of *Lactuca virosa* were cut into pieces, digested for several hours in warm water, boiled for a time, expressed and filtered, the solution precipitated with basic acetate of lead, the precipitate collected, washed, suspended while still moist in distilled water, and decomposed by sulphuretted hydrogen. The coloured acid liquid obtained was evaporated at a moderate heat; it finally congealed to a thick jelly. It had been ascertained by previous experiment that the acid was soluble in spirit, the gelatinous substance insoluble; the mass was therefore treated with strong alcohol and warmed, when the latter substance separated in whitish lumps. This substance, after removal, dissolved with difficulty in water, very readily in dilute muriatic acid, from which solution it was thrown down as a voluminous precipitate on saturating the acid with caustic ammonia. It had a horny appearance when dried, a dirty yellowish colour, and was now perfectly insoluble in water, and very sparingly soluble in dilute muriatic acid.

The acid spirituous solution, which still appeared much coloured, and but little of which colour could be removed by treatment with purified animal charcoal, was mixed with water, the alcohol distilled off at a very gentle heat, and more water added to the residue, which was then saturated with carbonate of ammonia, which considerably decolorized the liquid and removed some carbonate of lime; on filtration and evaporation an acid crystalline salt of ammonia was obtained, which was procured in very white masses by frequent recrystallization with addition of caustic ammonia.

The salt was dissolved in water, again precipitated with basic acetate of lead, the precipitate collected, edulcorated and decomposed with sulphuretted hydrogen, upon which the clear acid was evaporated to a certain degree, and then exposed to the heat of summer. In the course of 14 days numerous crystals had formed, which in 14 days more, during which time the solution had evaporated down to about half, increased considerably in quantity and size, and after careful collection and washing with a little cold water appeared as prismatic trilateral columns with obtuse terminations; those, on the contrary, which were applied to the side of the basin resembled butterflies' wings; the latter crystals, dissolved in spirit and crystallized, then dissolved in water and recrystallized, formed colourless, regular, prismatic, tabular crystals.

The residuous acid liquid was mixed with water and with sulphuret of barium, and finally saturated with some carbonate of barytes, the soluble salt of barytes carefully decomposed with dilute sulphuric acid, and the acid obtained evaporated. It could not be obtained in a crystalline state, but when dried for several weeks at a moderate heat formed a white efflorescent salt. This dried acid, heated in a glass tube, was decomposed with effervescence and evolution of irritating acid vapours, which were partly deposited on the cold sides of the tube in the form of a sublimate (maleic acid) and the residue consisted of a white acid crust (fumaric acid). It was consequently *malic acid*. For further confirmation the acid was dissolved in water, and chloride of potassium added to the solution, and to another sample, lime-water; both, however, without producing any change. A solution of acetate of lead immediately formed a caseous precipitate, which melted like a resin in boiling water.

The precipitate obtained by saturating with sulphuret of barium and carbonate of barytes was collected and treated with dilute sulphuric acid, filtered, an excess of milk of lime added to the acid fluid, and filtered boiling. On evaporating the filtered solution some small crystals separated, characterized by their being decomposed when heated in a glass tube with evolution of vapours, which excited coughing, and with the deposition of an acid sublimate. The residue from the treatment with milk of lime behaved therefore like citrate of lime, from which moreover a small quantity of pure citric acid was obtained in a crystalline state. For this purpose the lime salt was carefully decomposed with sulphuric acid, the filtered solution having however been previously examined for tartaric and oxalic acids. Chloride of calcium and chloride of ammonium added to a portion saturated with caustic ammonia produced no turbidness; a portion to which a slight excess of caustic ammonia had been added, and then a solution of gypsum, exhibited, even after a long time, no change; a sample rendered neutral, and boiled with chloride of calcium and caustic ammonia, immediately afforded a white pulverulent precipitate.

The acid first obtained in prismatic tabular crystals was now submitted to a more accurate examination, and accordingly heated in a glass tube; it was entirely volatile, with evolution of abundant vapours, which excited coughing, and deposition of a sublimate resembling that of the lime salt already mentioned; treated with chlorine and nitric acid, the crystals again afforded the same acid.

The acid required 2 parts alcohol, 3 parts hot and 24 parts cold water, for solution.

A sample was now dissolved in water, and tested with the reagents mentioned by Pfaff. It immediately caused a considerable brownish turbidness in neutral protosulphate of iron; a solution of acetate of magnesia produced no change, which was likewise the case with sulphate or acetate of copper, which however were precipitated of a light blue colour, when the acid was neutralized with caustic ammonia. The acid, dissolved in water and neutralized with caustic ammonia, was employed for the following reactions:—Acetate of barytes and solution of lime, as well as solution of gypsum, produced no change; acetate of lead, a precipitate which was soluble in the free acid, in dilute nitric acid, and in an excess of the precipitant; nitrate of silver, a pulverulent precipitate soluble in caustic ammonia and nitric acid; solution of corrosive sublimate, no change; but with solution of the protonitrate of mercury, an abundant caseous precipitate; perchloride of iron, a dark brown voluminous precipitate; and acetate of zinc, a white precipitate, which was soluble in much hot water.

From these preliminary tests, there can be scarcely any doubt that the peculiar acid of the plant is *succinic acid*.

Lactuca sativa was treated in the same manner as *Lactuca virosa*, and curiously enough yielded the same results, except as to the amount of succinic and malic acids. 100 lbs. of the fresh *Lactuca sativa* gave 122 grs. of succinic acid and 11 drms. of dried malic acid; 50 lbs. of fresh *Lactuca virosa* yielded 28 grs. pure crystallized succinic acid and 3 drms. of dried malic acid.

An *Extractum Lactucæ virosæ* afforded, when treated in a similar manner, on an average 1 gr. of succinic acid per ounce. In this examination the tests for oxalic acid were likewise repeated, but with a negative result.

According to the most recent analysis, an oxalate is constantly contained in lactucarium; the author convinced himself of its presence in some *Lactucarium anglicum*, procured in commerce, which on extraction with boiling water, treating the solution with basic acetate of lead, and decomposing the lead salt with sulphuretted hydrogen, yielded the acid in considerable quantity and in beautiful prismatic needles, and likewise citric and malic acids; no succinic acid however could be detected in the lactucarium, of which two ounces were employed.

To ascertain, moreover, whether the oxalic acid probably existed in the *Lactuca* as oxalate of lime, and could consequently not be extracted by water, the following experiments were made on some pounds of the dried plant *Lactuca sativa,* collected in the flowering season. The plant, cut into small pieces, was treated with warm water containing nitric acid, then expressed, filtered, and the acid saturated with carbonate of ammonia, then boiled, filtered, precipitated with basic acetate of lead, the precipitate washed and decomposed with sulphuretted hydrogen, which operation was again repeated; finally, the colourless solution was evaporated and set aside in a warm place. After a considerable length of time a crystalline mixture was obtained in a syrupy fluid, which collected carefully, brought on to bibulous paper and recrystallized, gave prismatic crystals.

A portion of the acid, saturated with caustic ammonia, did not afford any oxalic acid, but only succinic and citric acids, which yielded, on separation by means of lime-milk and decomposition of the lime salts, pure crystallized succinic and citric acids. The quantity of succinic acid which was obtained this time was considerably greater than previously.—*Archiv der Pharm.*, xxxix. p. 153.

On the Preparation and Composition of neutral and basic Perchloride of Iron. By C. WITTSTEIN.

According to the following method the neutral crystallized perchloride of iron is always obtained of constant composition:—4 parts of pure hydrochloric acid of 1·130 spec. grav. are gradually added to 1 part pure iron-filings or turnings contained in a spacious glass flask, heat applied, and when no longer any action is evident, the whole is brought on a filter, and the iron on the filter washed with some distilled water, dried, and its weight determined. We thus learn the quantity of the *iron in solution.* The clear bright green solution is poured back into the previously cleansed flask; 2 parts of hydrochloric acid of 1·130, and $1\frac{1}{3}$ part nitric acid of 1·20 spec. grav., added to it, and heat applied as long as yellowish-brown vapours are given off; the yellow solution is then emptied into a previously-weighed porcelain dish and evaporated, constantly stirring with a glass rod, until a sample solidifies on becoming cold, and the dish weighs still 4 times more than the dissolved iron. The dish is now placed on a plate, in a cool place, covered with a bell-glass, and the plate where the margin of the bell-glass touches it smeared with fat to keep off the moisture of the atmosphere. In a few days the syrupy solution is entirely converted into a dry crystalline mass consisting of small rhombic tablets, which may easily be removed by warming the dish for a moment; they should be immediately reduced to powder and preserved in a well-closed vessel.

The analysis of this salt gave—

Fe....................	25·25	2	25·34
Cl....................	50·21	3	49·55
Aq....................	24·54	6	25·11

On the further application of heat the salt yields hydrochloric acid and water, and leaves 50 per cent. of a dark reddish-brown deliquescent residue, which disengages on ignition chlorine and chloride of iron, and leaves pure oxide of iron, which is only partially soluble in water, the same in spirits, and contains, according to analysis,—

$Fe^2 Cl^3$	47·41	1	49·21
$Fe^2 O^3$	49·86	2	48·04
Aq	2·73	1	2·75

It is undoubtedly a mixture of perchloride, peroxide and hydrated peroxide of iron.

A constant basic combination is formed, on the contrary, when a solution of protochloride of iron is exposed in water to the atmosphere. A yellowish-brown powder is gradually deposited, which is decomposed on washing with water, and finally consists solely of the hydrated peroxide; but when pressed between paper and dried at 133°, consists of—

$Fe^2 Cl^3$	23·76	1	22·58
$Fe^2 O^3$	64·12	6	66·06
Aq	12·12	9	11·36

The liquid filtered from the combination still contains protochloride, for on long exposure to the air it becomes turbid and forms a fresh deposit.—Buchn. *Rep.*, xxxvi. p. 30–39.

ANALYTICAL CHEMISTRY.

On the Quantitative Separation of Tin from Antimony.

By M. A. Levol.

The basis of every chemical analysis resting essentially on opposite properties in the elements which are to be separated, it results that nearly related compounds are on this account those whose analysis presents the greatest difficulties.

Antimony and tin offer this peculiarity in their combinations in the highest degree. No method has been pointed out, at least as far as I am aware, for effecting their quantitative separation, and the processes in use for enabling us to ascertain their proportions, still leave much to be desired, since they only admit of the antimony being obtained separately, and never the tin.

Both the amount of tin, as well as that of antimony, may be obtained in the following manner:—I suppose any alloy to be taken; after having reduced it to a thin plate, a certain quantity (2 grms. suffice) is heated with hydrochloric acid; after some minutes boiling, a saturated aqueous solution of chlorate of potash is added in small quantities at a time, until the alloy entirely disappears; the two metals are then thrown down together by means of a bar of distilled zinc; the bar having been separated from the precipitate with proper care, that no loss may be incurred, some concentrated hydrochloric acid, in quantity about equal to what was employed at first, is added to dissolve the alloy, and the whole boiled in order to redissolve the tin, without previously removing the chloride of zinc. When the action is terminated, that is when nothing remains but the antimony, which is always the case after an hour's boiling, this metal then forms a very fine blackish powder; it is collected on a weighed filter, and the tin may now be immediately obtained from the liquors by sulphuretted hydrogen.

M. Chaudet's process is likewise by means of hydrochloric acid; but by acting as he does, on the alloy of the two metals, an addition of tin is necessary, according to his experience, in order that the *setting out* may be exact, each time that the antimony is in a greater proportion than 1 to 20 of tin, which happens very often, and moreover supposes that an approximative analysis has been previously made. By operating, on the contrary, in the manner above described, no longer on an alloy, but upon a simple mechanical mixture formed of recently-precipitated incoherent particles, it is easy to obtain the same result without any addition, which is opposed to the positive determination of the tin forming part of the alloy.

If, instead of having to analyse an alloy, as I have just supposed, we had to determine the amount of antimony and tin contained in the state of salts in the same liquor, the operation would be exactly the same after the entire precipitation by zinc; but I ought not to omit insisting on a precaution which it is important to use in this latter case, and which consists in completely destroying by hydrochloric acid and evaporation the nitric acid which the solvent might contain, so as not to have, on the determination of the antimony, the uncertainty which the production of *aqua regia* would cause in the subsequent treatment; I have, in fact, observed that the perchloride of tin is susceptible, like the perchloride of antimony, and I might also add that of iron, of reacting on metallic antimony, which they dissolve, being reduced to protosalts; from the presence of nitromuriatic acid serious errors might result, although it could not act directly on the precipitated antimony, This circumstance led me to suppress the use of nitric acid in the method which I have just described, and to substitute for it chlorate of potash.

This reaction of the perchlorides on the antimony has however its advantage, if we profit by it, of dissolving the alloy more quickly; and it is with this view, for effecting the solution, that I do not add the chlorate until some protochloride of tin is already formed; this salt being thus converted into perchloride, immediately reacts on the antimony, and a fresh addition of chlorate alternately reproduces the same series of reactions; whilst by employing it at the outset, the greater part of it would be destroyed by the hydrochloric acid.—*Ann. de Chim. et de Phys.*, Jan. 1845.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Silvering of Steel by Galvanic Action.

By M. Desbordeaux.

Hitherto it has been found impossible to obtain a very adherent deposit of silver on steel until after having covered the latter metal with a layer of copper, and it is necessary to effect the coppering with the double cyanide of copper and potassium; that which is obtained by the immersion of steel in the sulphate of copper, even on employing, as recommended, the contact of zinc by means of a metallic conductor, does not suffice, owing in this case to a slight oxidation always taking place at the surface of the steel, which prevents the layer of copper adhering firmly.

It will be well to remark, that although in galvanoplastic operations iron and steel appear to have been assimilated to each other in as far as the plating is concerned, there is in this respect a decided difference between them, for the iron may be plated without any previous coppering; and this difference seems to be owing solely to the presence of the carbon in the steel, since even when it has been tempered it is equally impossible to make the silver adhere to it.

The previous coppering of the metal being effected, another difficulty presents itself, and this is, that the layer of copper frequently dissolves, either wholly or in part, in the bath of cyanide of silver in which the piece is afterwards immersed. The result is, that in all the places where the copper has disappeared no silver is deposited, or at least it comes off upon the slightest rubbing. This cause of failure happens the more surely the thinner the layer of copper, so that, in order to avoid it, it is indispensable to prolong the operation of coppering; great care must also be taken, in this first operation, not to use the red copper of commerce for the anode, as this metal contains zinc, which, however small the proportion may be, is sure to injure the solidity of the coppering.

Struck with these difficulties, and with those which all the processes of coppering steel present, I have endeavoured to find a new method, and I think that that which I am about to make known leaves little to be desired.

This method consists in immersing the steel for several minutes in an extremely weak solution of double nitrate of silver and mercury, to which a few drops of nitric acid have been added. To make this solution, it suffices to dissolve separately 1 grm. of nitrate of silver in 60 grms. of water, and 1 grm. of nitrate of mercury in an equal quantity of the same liquid. The two solutions are then mixed, and 4 grms. of nitric acid of 1·357 spec. grav. added to them. These proportions need not be strictly exact, but the addition of nitric acid is absolutely essential. Water which contains hydrochlorate of lime, or any organic matter, should be avoided, for it inevitably decomposes in part the nitrate of silver; distilled water must be used as far as it is possible. It is not to be expected that the nitrate of mercury should wholly dissolve in the water, for we know that it is transformed in this medium into subnitrate and into acid nitrate, which remains in solution, whilst the subnitrate is precipitated as a greenish-yellow powder; this deposit should be left in the solution to be used for plating. It is not necessary that the nitrate of silver should be pure; that obtained by dissolving silver alloyed with a tenth of copper in nitric acid produces exactly the same effect.

When the steel has been immersed in the solution of double nitrate of mercury and silver, it is almost instantaneously covered with a slight blackish deposit, which easily comes off by passing a piece of linen over its surface. The steel is then perfectly bright, and at the same time clothed with an extremely thin pellicle of silver, but which adheres very firmly. The blackish deposit which is formed appeared to me to be almost exclusively carbon,—a body, whose presence, as I have before remarked, prevents the deposition of the silver on the steel. After this quick and simple preparation, the piece of steel is quite prepared to receive the layer of silver, which forms with the greatest facility, and adheres so firmly, that not only does it bear burnishing for a long while, but will even resist red heat without losing any of its solidity.

It should however be borne in mind, that the layer of silver, the deposition of which is effected by means of the pile, ought, in the new method, as in that with previous coppering, to attain a certain thickness, in order that the steel may be preserved from oxidation. A very simple mode of ascertaining whether the coating of silver is sufficiently thick, consists in immersing for a certain time a small portion of the plated piece in an acid solution of sulphate of copper. As long as the silver acquires a yellow colour, it is a certain index that the layer of silver is insufficient; it is still permeable, since it allows the steel to exercise its action on the sulphate of copper. Recourse should not be had to this experiment but when it is nearly certain that the coating is sufficiently thick, for silver cannot be coppered, even slightly, without risk of its adhesion; and in all cases it is more advantageous to go a little beyond what is strictly necessary. The thicker the coating of silver, the less danger is there of oxidation.—*Comptes Rendus,* Dec. 30, 1844.

PATENT.

Patent granted to Alfred Vincent Newton, London, *for Improvements in the Manufacture of Cyanogen and its Compounds, particularly the Prussiates of Potash and Soda.*

This invention consists in the application of nitrogen gas, which is obtained by the decomposition of atmospheric air or from the waste gases of sulphuric acid chambers, to the manufacture of cyanogen and the cyanides. It is stated that, by the means adopted by the inventor, the difficulties of carrying into practical and œconomical use the grand principle of employing nitrogen obtained from the surrounding atmosphere have been surmounted.

The different materials which are employed in the process, according to the peculiar circumstances of the case, are as follows:—1. Whatever may be the source whence the nitrogen is obtained, it may always be employed, provided it is not accompanied by oxidating substances. It is not necessary that the nitrogen should be perfectly pure; it may be mixed with carbonic oxide, hydrogen, carburetted hydrogen, and other gases; but the presence of oxygen must be carefully avoided, as well as all matters capable of affording it, as they would tend to destroy the cyanogen as fast as it is formed. This essential point is effected and obtained in an œconomical manner by using atmospheric air, taking the precaution to convert the oxygen contained therein into carbonic oxide, before it is permitted to come into contact with the cyanides already formed. The means by which this is accomplished will be hereafter explained. Another source of nitrogen is the waste gases of sulphuric acid chambers, after being washed in a solution of sulphate of iron and of milk of lime, so as to deprive them of sulphurous and nitrous vapour. The nitrogen so obtained is employed in the same manner as if obtained directly from atmospheric air. 2. The nature of the carbonaceous material which is employed in the process is not of much consequence; satisfactory results have been obtained with wood-charcoal, coke, pit-coal, peat, spent-bark, wood, and other similar substances; but as regards œconomy, produce and convenience, wood-charcoal in pieces of the size of a hazel-nut is preferable to any other. 3. With respect to the potash and soda, the carbonates are preferred; but any other salt capable of being resolved ultimately into carbonate, oxide or metal, may be employed. Although the choice of the materials is not of much consequence, it is not so with regard to the mode in which they are employed; thus, the more or less intimate mixture of the charcoal with the alkali, and the proportions of the two, have a great influence. If the alkaline salt is easily fusible, it may be previously fritted with the charcoal, or the two substances may be carefully mixed. It is however in general preferable to soak or steep the charcoal in a concentrated alkaline solution, and to dry the mixture before using it; but whatever be the way of mixing the matters, it is of the greatest importance that they should be perfectly dry before they are placed in the retorts. The proportions of alkali and charcoal may be varied to a certain extent, but there are limits which should not be passed; an excess of alkali renders the chemical decompositions incomplete, and a too small proportion is not œconomical; but, according to the difference in the density of the charcoal, it may vary from 25 to 100 parts of alkaline salt to 100 parts of charcoal. With hard wood charcoal, the proportions which have been found to answer best are from 30 to 50 parts carbonate of potash to 100 parts of charcoal, according to the intensity of heat in the retort. As regards the quantity of nitrogen gas, it must be used in excess to hasten the operations; still, a too rapid current of gas must be avoided, because it would carry off with it a part of the cyanides already formed, and also a greater or less proportion of unreduced alkali, and deposit them beyond the sphere of action. The combination of the nitrogen is effected most rapidly and completely when the gas is forced through a long column of alkalized charcoal, at a high degree of heat, and under a certain pressure, and when it experiences obstacles and considerable friction in penetrating through the pores of the charcoal and interstices between the pieces; all these conditions are combined in the most effective manner in the apparatus hereafter described.

After having considered these general questions, it remains to determine the most advantageous mode of constructing and working the apparatus. The points most worthy of attention are the following:—1st, heating the mixture of charcoal and alkali to the highest possible degree and in the most uniform manner, and taking the proper precautions to recover the vapours of potassium, sodium, and other alkaline and saline combinations that may be carried off with the waste gases; 2nd, to force through the pores and interstices of the alkalized charcoal a steady current of air or nitrogen gas; 3rd, to protect the mass of cyanized carbon from all contact with oxygen during the whole period of heating and cooling; 4th, a continuous operation, which is generally so advantageous in manufacturing processes, becomes here a necessity, or at least a most important consideration; because, setting aside the waste of fuel, labour and time, the dilatations and contractions caused by interruptions of the work, occasion a speedy destruction of the apparatus; on this account a perfect steadiness of firing and uninterrupted operations are peculiarly desirable.

The apparatus for carrying out these requisites may be varied in dimensions and form, and may be modified to suit different carbonaceous matters; but without confining the invention to the arrangement of parts herein set forth, two applications are described. The first and simplest form consists of one retort, which is of fire-clay or other suitable material capable of supporting a white heat; it is slightly conical, tapering downward, and open at top and bottom; the best form in the transverse section is elliptic. This is placed vertically in a furnace, heated intensely, and as regularly as possible; its lower end rests upon the flange of a second retort, or refrigerator of cast iron, and of a similar shape, having at the bottom an extractor, mounted on suitable bearings, which is worked periodically by an attendant, to convey the cyanized charcoal into an extinguisher or dip-pipe, the mouth of the latter being plunged into a saline solution, which acts as a hydraulic valve. From the side of the dip-pipe, at a short distance below the extractor, is the waste gas-pipe, which conducts the gases and vapours into the hydraulic main; the end of this pipe is turned downward, and plunged into water or a solution of a salt of iron. By another pipe the incondensible gases are drawn off from the main by a pump, or other convenient aspirating machine.

In the other form of the apparatus there are ten retorts working with one air-pump and one hydraulic main, besides contrivances for drying alkalized charcoal, and a method of working the feeding and extracting apparatus by machinery. The pans or under-backs, which receive the cyanized charcoal as it drops from the extractor, are kept constantly charged with a protosalt of iron, or with hydrated protoxide of iron diffused in the liquor, for the purpose of converting the simple cyanides into ferrocyanides the moment they fall into the liquor. If thought desirable, a fire may be lighted beneath these pans to warm the liquor. The management of the furnace-fire requires much attention, to prevent variations of temperature, and coke is preferred to bituminous coal.

The working of the apparatus will be easily understood. The retort is kept constantly full of alkalized charcoal, and the air-pump set to draw a steady current of air through the materials in the retort. The gas drawn through may be either burned air, common atmospheric air, or hot air, as supplied to ordinary blast furnaces.

The time required for reducing the alkali, and converting it into cyanide, is in direct ratio to the intensity of the heat; with a good white heat, two or three hours are sufficient to convert almost the whole of the alkali into cyanide. Whether the retorts are fed by machinery or otherwise, care must be taken to keep them constantly full, according to the working of the extractor, which, as before mentioned, delivers the cyanized charcoal into the dip-pipe, where it drops into the saline solution below; but previous to this it may be cooled in the iron retort, by surrounding a part of that vessel with a cold water-chamber.

The liquor in the under-back should always contain *a slight* excess of iron or ferrosalts, or the alkaline cyanides will be decomposed into formiates of potash and soda and carbonate of ammonia. It is easy to ascertain when sufficient iron is present: by taking out a small quantity of the clear liquor, and dropping into it a little weak solution of protosulphate, or any other protosalt of iron, a white precipitate will fall without any tinge of red; but when, on the contrary, the liquor gives a brown red precipitate, or a mixture of red and white, it wants iron. When it is certain that the liquor contains a slight excess of iron, the charcoal is taken out and thrown into vats or cisterns, and washed, either with cold or warm water, until the salt is completely extracted; the weak liquors are passed successively through new charcoal, by which they are easily brought to 20° Beaumé's hydrometer. At this strength the liquors may be thrown into evaporating pans, and be boiled until the sulphate of potash falls down; this is separated as usual, and drained. The remainder of the liquor is then drawn off into other vessels to crystallize; or, instead of drawing it off, the evaporation may be carried still further, until the prussiate also falls down and separates in a similar manner. The potash mother-liquors serve for fresh operations. The first rough crystals are washed and crystallized a second time, as usual.—Sealed Dec. 13, 1843.

THE CHEMICAL GAZETTE.

No. LVI.—February 15, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Nature of Yeast. By Prof. MULDER.

WHEN sugar ferments at a moderate temperature (from 59° to 77° Fahrenheit), alcohol and carbonic acid always result; many saccharine juices, such as those of ripe fruit, of the beet-root, of the carrot, and of the onion, behave in the same manner; but if they are allowed to ferment at from 95° to 105°, entirely different products are formed. The albumen and gluten of the juices are destroyed, and the entire amount of nitrogen is contained in the liquid as ammonia; while under this altered influence of heat, lactic acid, mannite, and a substance resembling gum, originate from the sugar, instead of the carbonic acid and alcohol: there is at the same time a disengagement of gas. It is evident therefore that the metamorphosis of the sugar depends entirely on the state of the gluten and albumen of the vegetable juices, both of which in alcoholic fermentation are converted into the principal constituent of the ferment, which, when it undergoes a decomposition other than the usual one, yields entirely new products, having not the least resemblance with those resulting from alcoholic fermentation. It evidently results from this that the general notion of a motion of the molecules does not suffice to explain the formation of carbonic acid and alcohol from sugar, but that the motion must be a peculiar one, in fact one which communicates itself to the molecules in one direction and no other.

The most simple alteration of the ferment is alone sufficient to produce vinous fermentation. This consists, in the first place, in the formation of acetic acid, followed by a subsequent disengagement of carbonic acid, and probably cotemporaneous formation of ammonia. If anything is opposed to that change, the ferment no longer possesses the power of causing fermentation or of supporting it. High drying, corrosive sublimate, nitrate of silver, creosote, &c. destroy it. Yeast is indeed only capable of producing fermentation, or at least of exciting it, in the presence of oxygen or atmospheric air; when these are wholly excluded no fermentation takes place.

A variety of strange ideas have been entertained respecting the nature of yeast; recent experiments have convinced me that it undoubtedly is a cellular plant consisting of isolated cells. The plants are vesicles of a substance which approximates in its properties and composition to cellulose, but differs from it in many respects. Its composition is $C^{12} H^{20} O^{10}$. It is insoluble in cold and boiling water, yields no xyloidine with nitric acid, is rapidly converted by muriatic acid into humic acid, and dissolves readily in a concentrated solution of caustic potash in the cold. Its composition can by no means be reduced to that of cellulose $= C^{24} H^{42} O^{21}$.

Each vesicle incloses a proteine body, which is insoluble in boiling alcohol, is consequently not gluten, is very readily dissolved by acetic acid, consequently is not albumen, and which is so easily altered by boiling water that it may be regarded as a superoxide of proteine, $C^{40} H^{74} N^{10} O^{26} = C^{40} H^{62} N^{10} O^{12} + O^{8} + 6H^{2} O$.

The proteine is moreover contained in such a state in the vesicles, that its composition approaches to that of fibrine, albumen and caseine. Extracted with acetic acid and precipitated with carbonate of ammonia, it has an analogous composition to the above bodies, viz. 54·35 C, 7·04 H, 16·03 N, 22·58 O.

These vesicles, consisting of substance resembling that of cells, do not contribute in the least to the fermentation, but are exosmotically penetrated during fermentation by the proteine compound; they become smaller, contract, and remain at the close of the operation in the state of shrivelled globules. The proteine compound, which has made its way out, and is characterized by being most readily decomposed at a certain temperature, immediately undergoes decomposition, and leaves nothing behind but ammonia and a small quantity of an extractive substance not yet accurately examined:—

	C.	H.	N.	O.
Proteine	40	62	10	12
Ammonia		30	10	
	C^{40}	H^{32}		O^{12}

The first cause of the phænomenon of fermentation is therefore due to heat. Just as several bodies, for instance the hydrated oxide of copper, are decomposed at a certain temperature under water, there is likewise for the proteine compound of yeast,—a very complex substance,—a temperature at which it can no longer exist in solution. The decomposition extends to the sugar, which is converted into carbonic acid and alcohol. During this process, especially at the commencement, a small quantity of oxygen is absorbed; this absorption, however, is by no means the *cause*, but rather the *first consequence* of the decomposition of the proteine compound.

What has been said respecting the principal constituent of yeast is likewise applicable to the yeast itself, only that the cellular membranes of the yeast-globules have no influence at all on the fermentation, but are rather mere bearers of the proteine compound, and after fermentation remain behind as insoluble substances.—Mulder, *Versuch einer allgem. physiologischen Chemie*, 1844, p. 48.

Observations on Asarone (the Camphor of Asarum). *By* Dr. Schmidt.

The volatile substance contained in the roots of *Asarum europæum* forms, according to the author, rhombic prisms with several different combinations. The analysis of the crystals yielded 69·5 per cent. C, 7·68 H, and 22·82 O, a result which differs somewhat from that obtained by Blanchet and Sell. The author therefore heated them to boiling with strong alcohol, in order to purify them by re-crystallization. This had scarcely lasted ten minutes when a very interesting phænomenon occurred; the mass became gradually yellow, reddish and red; only a portion crystallized after having been left to stand for a night; the remainder spontaneously evaporated under a bell-glass, formed a red, amorphous, resinous mass, which redissolved in alcohol again dried to an amorphous mass, but was precipitated by water from this solution in minute globules, which strongly refracted light, and exhibited a lively molecular motion, and carbonified when heated between two watch-glasses without subliming, consequently had nearly lost its former properties. Nevertheless the analysis yielded the same composition for the crystals as for the amorphous modification:—

	Crystalline.	Amorphous modification.
Carbon	69·37	69·11
Hydrogen	7·66	7·65
Oxygen	22·97	23·24

The red substance appears to be a product of oxidation, which is formed in very small quantity, as is confirmed directly by subsequent experiments with nitric and chromic acids, and other oxidizing agents; the most essential part of this process, however, is probably to be sought in a similar transposition of the elements as occurs among other bodies in opianic acid. If, for instance, the crystals be kept for a greater or less length of time at a temperature slightly exceeding 248°, they solidify more slowly in proportion to the time and degree of temperature; but if both have been carried too high they no longer solidify; a proof, that in this case the alteration in the position of the minutest particles towards each other does not occur suddenly, but gradually, with numerous gradations. The author confirms the statement of his predecessors, that the boiling point of this substance rises from 536° to 572°, when decomposition results, although this appears paradoxical at first sight, since the crystals are readily and entirely volatile between watch-glasses. This however results from the gradual transition of the crystalline into the amorphous modification, as the author convinced himself in an unsuccessful determination of the density of vapour, in which, for instance at a temperature of a metallic bath of 554°, unfortunately only the smallest portion of the substance escaped in the form of vapour, while the remainder solidified partially after four days, and evidently consisted of a mixture of the two modifications.

The crystals dissolved readily in nitric acid, the amorphous modification with more difficulty, with formation at the commencement of the previously mentioned red resin; both yielded oxalic acid, without any intermediate crystalline product. The formation of the same red resin, which is not further altered, takes place with chromate of potash and sulphuric acid, the chromic acid being reduced; sulphuric acid and hyperoxide of manganese afford the same product, while peroxide of lead with acids is without any action.

The red resin is not altered by being melted in sulphurous acid or hydrochloric acid gas, nor are the pure crystals.

The action of chlorine was very violent; the instant it was added on the sides of the vessel the whole melted with so violent an action that it appeared to boil; after the first action had subsided absorption took place more quietly; the mass, which at first had become red, changed to green, and the author terminated the operation when 3·114 grs. of unemployed substance had absorbed 1·440. Had the whole of the hydrogen been substituted by chlorine, the analysis of this green product should have given 47·4 per cent. C and 4·3 H; but if the chlorine had been absorbed without the elimination of an equivalent quantity of hydrogen, 47·4 C and 5·2 H should have been obtained; the experiment gave 47·22 C and 4·41 H, consequently the first case had occurred.

The author however does not consider the violent reaction at the commencement of the operation to have arisen *solely* from this elimination of the hydrogen in the form of hydrochloric acid, since this was given off for a couple of hours to the same extent, but quietly; it rather appears to be owing to an alteration in the position of the elementary particles towards each other in their passage from the crystallized to the amorphous state, such as we see result during the process of transmutation in aldehyde, chloral, the cyanic acids, &c. Direct experiment fully confirmed this supposition; the preparation of the analogous crystalline combinations with chlorine did not succeed, as no action of the chlorine resulted with the application of cold. The amorphous combinations with chlorine were all of them non-volatile, resembling green resins; and when some of the alcoholic solution was dropped into water, it exhibited numerous globules from $\frac{1}{400}$th to $\frac{1}{800}$th of a line in diameter, which refracted light strongly, and presented a lively molecular motion; they did not exhibit any crystalline structure, even after some weeks. These combinations with chlorine yielded on destructive distillation hydrochloric acid, various gaseous products, a green thick oil containing chlorine, and a carbonaceous residue. The portion of this oil which passed over on redistillation between 428° and 435° yielded on analysis—

Carbon	49·48
Hydrogen	4·87
Chlorine	28·80
Oxygen	16·85

The action of concentrated sulphuric acid and of anhydrous sulphuric acid gave more complicated products, having all the colours of the rainbow, but in the further investigation of which the author was stopped from want of material. Since this substance is related in the crystalline state to the camphor of the *Laurineæ*, and on the other hand in the amorphous state to the resins, the author thinks he is justified in advancing a formula with 20 equiv. carbon as base; the formula $C^{20}H^{13}O^{5}$ answers completely to the numbers found, and agrees with the chlorine compound, the analysis of which corresponds to the formula $C^{20}H^{11}Cl^{2}O^{5}$.

The substance would accordingly contain the elements of 2 atoms of the so-called anhydrous camphoric acid *minus* 1 equiv. HO, or its formula may be deduced empirically from that of several resins $= C^{20}H^{16}O^{2}$, by supposing 3 equiv. H to be replaced by 3O, whether rationally or not the author does not decide, since direct experiments made with this view failed; but he considers it improbable for that very reason.—*Journ. für Prakt. Chem.*, xxxiii. p. 221.

Notice respecting Veratrine.

According to M. Versmann, the veratrine of commerce frequently contains lime, resulting from the employment of lime in its preparation. A small quantity of lime moreover facilitates the drying, and renders the preparation more beautiful. It is easily detected on incineration, and is best removed by dissolving the veratrine in spirit, precipitating with sulphuric acid, filtration, driving off the alcohol, and precipitating the veratrine with ammonia.—Buchn. *Rept.*, vol. xxxv. p. 101.

On Idryle and Idrialine. By M. Bödeker.

One of the products obtained in the working of the bituminous mercurial ores in Idria is the so-called *Stupp*, a soft black mass mixed with globules of mercury. It was supposed to contain idrialine, but in its stead another hydrocarbon was found, idryle $C^{3}H$, and a more accurate examination has proved that idrialine contains oxygen, and is an oxide of idryle.

The idryle was obtained from the stupp by extracting it repeatedly with boiling alcohol, and dissolving the soft brown mass remaining after distilling off the alcohol in concentrated boiling acetic acid, from which it crystallizes on cooling. It is obtained perfectly pure by recrystallization from alcohol.

Idryle forms a very loose glittering mass, consisting of minute crystalline laminæ, which are not quite colourless, but always exhibit a yellowish-green iridescence. It has scarcely any perceptible odour or taste. It melts at 187° to a clear pale yellow liquid, and solidifies at 174° to a concentrically-radiate, opake, almost colourless mass. Heated further, it sublimes readily and entirely in the form of an extremely minute and loose dust, consisting of delicate laminæ, which are most beautifully iridescent. It dissolves very sparingly in alcohol, æther, oil of turpentine and acetic acid, at the ordinary temperature, but so readily on boiling that the saturated solutions of the first three solidify on cooling. A very small quantity suffices to impart to the solution a beautiful blue iridescence, similar to that of an acid solution of sulphate of quinine. Concentrated sulphuric acid is coloured of a golden yellow by it already at the ordinary temperature; when warmed it dissolves it in large quantity to a deep greenish-yellow liquid, which forms a clear solution with water; only after being strongly heated is any sulphurous acid disengaged. These solutions have likewise a strong blue iridescence. This behaviour towards sulphuric acid, and its lower melting point, essentially distinguish idryle from idrialine, which is dissolved by sulphuric acid with an intense blue colour, and the melting point of which is even above 313°; it is therefore not fusible in hot oil of turpentine like idryle, nor can idrialine be sublimed undecomposed even in a current of carbonic acid; a small portion only escapes decomposition. Idryle differs just as much from chrysene, which has a yellow colour, melts at 446°, and is wholly insoluble in alcohol. It was found to contain—

	Found.	Equiv.	Calculated.
Carbon	94·568	3	94·75
Hydrogen	5·459	1	5·25

$C^3 H$, however, is curiously enough the relative composition in equivalents which Dumas has assigned to idrialine, and has also been ascertained by Laurent to be that of chrysene. This induced the author to submit idrialine in the first place to a fresh analysis, the more so as Dumas himself doubts the correctness of the single analysis made by him.

For this purpose the idrialine was prepared according to Dumas's method from idrialite, and purified by recrystallization, partly from pure oil of turpentine, partly from a mixture of oil of turpentine with alcohol, and partly from acetone. It formed after pressure a beautiful mass, with a mother-of-pearl lustre, and free from mercury.

The following composition was obtained as the mean of four closely-agreeing analyses:—

Carbon	91·828	42	91·990
Hydrogen	5·299	14	5·094
Oxygen	2·873	1	2·916

Idrialine is consequently not a mere hydrocarbon, but undoubtedly contains oxygen. Carbon and hydrogen however exist in it in the same relative proportion as in idryle; and if it be correct to consider idryle as the radical of the idrialine, the composition of idryle must be expressed by the formula $C^{42} H^{14}$. Some experiments to prepare idryle from idrialine did not give the expected result; it is however beyond a doubt that the idryle contained in the stupp has originated from the idrialine, for it is not to be found in the mercurial ores.

Unfortunately, from want of material, I was unable to determine the density of its vapours, and to pursue further its behaviour towards chlorine and sulphuric acid. It combines with both; with the latter it forms a compound acid, which affords soluble salts with barytes and oxide of lead, and is probably identical with the idrialino-sulphuric acid discovered by Schrötter.

The stupp contains, besides idryle, another decidedly distinct crystalline body, which however could not be obtained in sufficient quantity for closer examination. It was deposited from the alcohol with which the stupp had been boiled immediately on cooling, while the idryle remained dissolved. It formed minute pale yellow laminæ, was far less soluble than idryle in alcohol and acetic acid; its melting point was above 212°, but it sublimed before melting, and was dissolved only by warm concentrated sulphuric acid with a brownish-red colour. An analysis which could only be made with 0·140 grm. yielded 93·654 carbon and 5·666 hydrogen.—*Journ. für Prakt. Chem.*, xxxiii. p. 249.

Preparation of Hippuric Acid from Human Urine.

An anonymous correspondent of the 'Lancet' recommends evaporating the urine until the salts are deposited, then adding strong alcohol and applying heat, when the urea, lactates and hippurates, are dissolved, while the uric acid, &c. remains. The clear solution is then poured off, evaporated nearly to dryness, the residue redissolved in hot water, the urea decomposed by passing a current of chlorine through the solution, and then by the addition of a small quantity of a mineral acid and concentration the hippuric acid obtained in the crystalline state.

Observations on Creosote. By M. DEVILLE.

According to the author, the following rule may be applied to several of the resins, viz. that on their destructive distillation they yield the same oil (or at least one isomeric) as that from which they originated. The body formed on the distillation of guaiacum resin, $C^{14}H^{16}O^{4}$, called by the author hydruret of guaiacyle, resembles in every respect creosote ($C^{14}H^{16}O^{2}$), and may be considered as its oxide. Creosote colours salts of iron blue, guaiacum oil brown; both give with bromine crystalline compounds in which substitution occurs. Creosote may be regarded as the alcohol of the benzoyle series; both yield, when treated with sulphuric acid and chromate of potash, a peculiar salt of chrome; neither of them become coloured by exposure to the air if in the *pure* state. Creosote would therefore range in the class of essential oils which are regenerated by distillation; and this would explain why it is not obtained from all woods, and likewise why it appears to have a different composition according to its origin.—*Ann. der Chim. et der Phys.*, xii. p. 228.

ANALYTICAL CHEMISTRY.

On the Decomposition of the Phosphate of Lime by Alkaline Carbonates. By M. WACKENRODER.

PHOSPHATE of lime obtained in the moist way is decomposed to a very considerable extent by boiling with carbonate of potash or soda.

Bone-earth, which, as is evident from the behaviour of a solution of freshly-burnt bones in nitric acid towards nitrate of silver, is not a bibasic but a tribasic phosphate of lime, is not attacked by carbonated alkalies in the moist way, but readily on fusion with them; a fact of some importance in analyses of the ashes of plants. On fusing 2 parts pure carbonate of potash with 1 part bone-ash, the mixture either cakes together or fuses with a strong heat. The melted mass appears on cooling on the surface of cleavage dense and vesiculous, on the surface scaly crystalline, and it almost seems as if the mass were a double salt. Cold water poured over the powdered *caked mass* immediately extracts a large quantity of tribasic phosphate of potash, for ammonio-nitrate of silver produces in the acidulated liquid a considerable yellow precipitate. The *fused mass*, on the contrary, also in the state of powder, is a long time before it is attacked and decomposed by cold water. Hot water, however, immediately extracts a large quantity of tribasic phosphate of potash from it. It might be supposed that in the phosphate of lime of the bones, the relation between base and acid remained the same, a portion of the phosphoric being replaced by carbonic acid. The vesiculous nature of the fused mass, however, proves the evolution of carbonic acid. The phosphate of lime in the bones must therefore either be converted into a more basic salt, or if it were originally $= 8CaO + 3PO^5$, be at least changed into $3CaO + PO^5$.

If the ashes of the cones of *Pinus sylvestris*, from which the seed had been removed, and which contain much potash and a tolerable quantity of alumina, are treated with cold water, not a trace of any phosphates are extracted even after 24 hours' action. On boiling the water, and even on merely warming it, a large quantity of tribasic phosphate of potash is formed. This may probably be produced from the phosphate of the peroxide of iron contained in the ashes, but the phosphate of lime must also have some share in it. I was astonished to find, that on again heating the ashes to faint redness, in order to make a complete analysis of them, a large quantity of tribasic phosphate of potash was now extracted, just as from bone-earth which had been ignited with carbonate of potash. If the ash be entirely deprived of its soluble constituents with hot water, a very considerable portion of the phosphoric acid is found combined with potash in the liquid; but this amount of phosphoric acid can only be accounted for as phosphate of lime, *i. e.* as bone-earth in the constituents of this ash so abounding in lime.—*Ann. der Chem. und Pharm.*, li. p. 163.

On the Reduction of Chloride of Silver. By J. Deck *of Leamington.*

In the determination of chlorides and chloride of sodium, in the analysis of the various saline springs of Leamington, I have obtained large quantities of chloride of silver, and find that the easiest and quickest method of reducing it to its pure metallic state, is to mix it with one-third its weight of black resin and one-twelfth nitre; heat it to a cherry-red in a Hessian crucible for ten minutes, then quickly raise it to a white heat for about twenty minutes, when it may either be poured out into an ingot, or remain till cold at the bottom of the crucible.

I have reduced several ounces by this method, and find it preferable to any other; that of Prof. Gregory, by caustic potash, leaves a portion undecomposed, and that of M. Ricker, by deflagrating with charcoal and nitre, effects its partial combustion and loss.

In the number of the *Archiv de Pharmacie* which has just reached us, Dr. Meurer also states that he has not found Prof. Gregory's process to answer. The experiment proved perfectly successful in a test-tube, but on attempting to decompose some ounces of chloride of silver freshly precipitated it failed, even after four or five boilings with fresh solution of caustic potash.

The process recommended by Gmelin in the new edition of his excellent *Handbuch*, is to fill a crucible almost to the top with an intimate mixture of 3 parts chloride of silver and 1 of colophony; it is then exposed to a gentle heat, when the resin burns with a green flame, owing to the muriatic acid generated from the chlorine of the chloride and the hydrogen of the resin; a stronger heat is then given to fuse the silver, a little borax added, and the crucible tapped gently once or twice to facilitate the union of the silver. This process was first proposed by M. Mohr.—Ed. *Chem. Gaz.*

PHARMACOLOGY.

Essay on the Purple Foxglove (Digitalis purpurea).

By M. Homolle.

The author commences this treatise, which obtained the prize offered by the Société de Pharmacie, with a general account of the several memoirs hitherto published on this subject, and then describes some preliminary experiments, previously to arriving at the following process for eliminating the principle digitaline in a pure and crystalline state.

2 lbs. of the dried leaves of *Digitalis*, coarsely powdered and previously moistened, are conveyed into a displacement apparatus, and treated with water. The mixed liquors obtained are immediately precipitated with a slight excess of subacetate of lead, and thrown on a filter. They pass limpid and nearly free from colour, preserving all their bitterness, and presenting a slightly acid reaction. Some dissolved carbonate of soda is added until no further precipitate is formed. The liquid is filtered anew and freed from lime which it still retains by oxalate of ammonia, and afterwards from salts of magnesia by ammoniacal phosphate of soda.

The filtered liquor presents an alkaline reaction, is clear, of a yellow brown tint, and excessively bitter; a slight excess of a solution of tannin is added to it, and the precipitate formed collected on a filter and dried between folds of blotting-paper, and then mixed whilst still moist with one-fifth of its weight of powdered oxide of lead. The soft paste which results is thrown on a filter to drain, pressed between blotting-paper, and finally dried in a warm chamber. It is then powdered and extracted with strong alcohol.

The alcoholic solution, sufficiently evaporated at a gentle heat, leaves as residue, in the form of a yellowish granulous mass, with a small quantity of supernatant mother-ley, the bitter principle still retaining some traces of oil, salts and extractive substances.

This mass is washed with a little distilled water, which removes any deliquescent salts, without perceptibly dissolving the bitter principle. It is left to drain, and again dissolved in boiling alcohol with the addition of a sufficient quantity of charcoal washed with hydrochloric acid; it is then boiled and thrown on a filter. The liquid passes colourless; left to spontaneous evaporation in a warm chamber, the substance is partly deposited on the sides of the dish in the form of thin, light, semi-transparent layers, and partly at the bottom of the vessel in the form of agglomerated whitish granular flakes.

The perfectly dried product is reduced to powder and treated with rectified æther. It is left 24 hours in contact, then boiled and filtered. This æthereal solution, on spontaneous evaporation, leaves a slight crystalline white layer, consisting of a certain proportion of the bitter principle, a trace of green oleo-resinous matter, a substance whose odour calls to mind that of *Digitalis*, and of a substance crystallized in beautiful white needles, without smell, of an acrid and rather sharp taste, insoluble in water and alcohol, fusible at about 302° Fahr., and upon cooling forming a yellow radiated crystalline mass. The small quantity we have been able to isolate has not permitted us to ascertain its other properties. We shall pursue the investigation of it as soon as we obtain a sufficient quantity.

An experiment made on 250 grs. of aqueous extract of digitalis, prepared with care, which was redissolved successively in alcohol and water, did not enable us to obtain the bitter principle solid and completely isolated. We thence concluded that the heat required for preparing the extract, altered this matter still combined with the bodies which accompany it in the plant.

Another experiment, made on 2 quarts of juice of fresh digitalis, yielded a beautiful product; but the very small proportion seemed an objection to this method of preparation, independent of the very great inconvenience of only being able to employ this process at a certain period of the year.

The fermentation which the presence of a small quantity of sugar in the plant caused in the liquors, however little the temperature was raised or the operation prolonged, the result of which was always the precipitation of a small proportion of altered bitter matter, induced us at first to add to the water with which the digitalis was exhausted one-tenth in volume of alcohol; we also hoped by this means to avoid the solution of a part of the salts of lime and of magnesia. We have had to abandon this addition, which rendered the process more expensive without affording better results. In general it is best to carry on each operation rapidly, and to avoid a temperature exceeding 50° or 54° Fahr.

We pass on to the study of the physical and chemical properties of the principle which we have isolated, leaving it the name of digitaline, which former chemists have assigned to it by anticipation. Digitaline is white, colourless, difficult to crystallize, and assuming most frequently the form of porous warty masses or of small laminæ. It is so intensely bitter that the 15th part of a grain suffices to communicate a decided bitterness to 2 quarts of water). The taste of solid digitaline is however slow in developing itself, owing to its sparing solubility in water.

It causes violent sneezing when it is powdered or agitated carelessly, even in small quantities.

Digitaline dissolved in water or alcohol is without action on red or blue litmus-paper; it is therefore a neutral substance.

A sample of this substance, purified with great care by alternate solutions and washings, without the use of charcoal, for fear of introducing foreign matters, was employed in ascertaining the following properties:—

Exposed in a tube to the action of heat of an oil-bath, it began at 356° to become slightly coloured; at 392° it had become brown; and towards 400° it began to soften to a sort of paste, which swelled, appearing to acquire a lighter tint from the interposition of gaseous bubbles. The temperature having been carried by degrees to 428°, the substance diminished in volume, re-acquiring the brown tint which it had at 392°. When tasted after this experiment, it had lost a great part of its bitterness, and had acquired an acid, astringent taste.

Another portion, heated in the air on a slip of platina, became at first soft, then took fire and burnt briskly, but with a somewhat dull and smoky flame. No visible residue is left; but on moistening the spot with a little distilled water it becomes alkaline. The same phænomenon has been observed to a certain extent upon burning a small quantity of perfectly pure crystallized morphine. If the digitaline is not in a pure state, it burns, forming a very high porous mass, which disappears entirely if calcination be continued.

A portion burnt in a glass tube diffuses acid vapours. If it be heated with a fragment of potash, the vapours are alkaline; but as this occurred when experimenting for comparison on some pure salicine, we considered that it was due to a phænomenon similar to that described by MM. Faraday, Reiset and Gerhardt, and that the nitrogen here disengaged in the form of ammonia did not originate from the digitaline.

We were desirous of verifying the presence or absence of nitrogen by M. Lassaigne's process*, and experimented comparatively on digitaline, salicine and morphine. In the first two cases we only obtained a faint greenish-yellow tint, which we attributed to the persalt of iron, and with the morphine a slightly bluish emerald-green tint. Although these last results were not as decided as we had expected, for with morphine, a nitrogenous substance, we ought to have obtained a beautiful dark blue tint, yet as they were constantly the same in several experiments, we regarded them as con-

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* See Chemical Gazette, vol. i. p. 429.

firmatory of our first conclusion, namely, that digitaline is not a nitrogenous compound.

Cold water dissolves a little more than $\frac{1}{2000}$th, boiling water about $\frac{1}{5000}$th; no opacity results on cooling. During the evaporation of the two solutions a part of the matter separated in the form of white flakes, and on the sides of the vessel some yellowish stripes formed, probably arising from an incipient decomposition of the digitaline by the heat employed for the evaporation. The best solvent for digitaline is alcohol. It takes up a large portion in the cold, and still more when heat is applied. The boiling solution, however, does not form any deposit on cooling. When digitaline has been purified by æther, it appears to dissolve with rather less facility in alcohol. The alcoholic solution, left to spontaneous evaporation, deposits the digitaline partly in a pulverulent, partly in a crystalline state. Towards the end of the evaporation the liquid often forms a kind of hydrated mass, which, after entire desiccation, takes the form of warty crusts. Concentrated æther dissolves so much the less of this bitter principle, the lower its density.

Action of Acids.—We have not been able to form any combination of digitaline with acids. This result was probable from the neutrality of this principle.

Digitaline becomes black directly it is placed in contact with concentrated sulphuric acid, and soon forms a solution which appears blackish-brown when examined in a thin layer; after some time this colour passes successively into reddish-brown, smoky-amethyst, pure amethyst, and finally to a beautiful crimson. If during this interval a portion of the solution is added to a small quantity of water, a clear beautiful green solution results. Concentrated hydrochloric acid quickly dissolves it, communicating to the liquid a yellow tint, which after a few instants changes to a beautiful emerald-green, and becomes darker and darker until it is of a dark green. In about an hour's time the liquor becomes turbid, and the matter at first dissolved is precipitated in the form of green flakes floating in a greenish-yellow liquid. In the course of two days the flakes have become of a blackish-green colour.

Digitaline does not dissolve in phosphoric acid, but merely acquires a slightly greenish tint after two or three days.

In pure concentrated nitric acid digitaline readily dissolves, with disengagement of reddish vapours, and forming a beautiful orange-yellow solution. The following days the solution changes to a golden yellow colour, and so remains.

In all the above reactions the digitaline is more or less immediately destroyed.

Acetic acid dissolves digitaline without colouring or changing it, at least as quickly as the concentrated mineral acids.

Action of Potash.—A little potash added to an aqueous solution of digitaline causes the bitter flavour to disappear slowly; but if the mixture be evaporated to dryness, the bitter taste gives place to an astringent one.

The singular property which alkalies possess of destroying the bitter taste of certain bodies had already been noticed by M. Bouchardat, with respect to cynisine and lactucine; but we should add, that digitaline, submitted to the action of liquid ammonia for more than 10 days, did not appear to undergo any alteration.

We have not found any salt which was precipitated by an aqueous solution of digitaline. A solution of tannin renders the liquid opake white in mass, and opal only if a drop be examined; the precipitate does not begin to form till after 24 hours.

Amongst the different properties of digitaline which we have passed in review, there is one which seems especially characteristic, and which belongs, as far as we are aware, to no other substance; it is that of forming a beautiful emerald-green solution with concentrated hydrochloric acid. This reaction is the more valuable, as a particle of this substance placed in a tube with 2 or 3 drops of hydrochloric acid is sufficient to develope the green colour after a few instants; and we think that this character ought to form the proper criterion for discovering digitaline in medico-legal or analytical researches; afterwards will come the action of sulphuric acid and that of acetic acid.

The conversion of digitaline into an acid astringent principle, on the one hand by the influence of heat, and on the other by potash, joined to the slight alteration which we observed during the evaporation of the aqueous solution, indicate in a practical point of view that the employment of heat must be very unfavourable in making the pharmaceutical preparations which have digitalis for basis, and that care must be taken not to add alkaline salts to them.

We have seen that pure digitaline is scarcely soluble in water; we must not, however, conclude from this that this agent is unfit to dissolve the active principle of the plant. In the *Digitalis* it occurs in combination with saline and extractive matters, which favour its solubility in this medium.

Digitaline which has not been purified by æther retains, as above stated, a green matter, an odoriferous substance and a crystallizable principle, and is known by its peculiar odour, calling to mind that of *Digitalis*. It dissolves but imperfectly in hydrochloric acid, so that the liquor remains turbid, but presents the same intense green colour. It moreover leaves some light flakes on solution in acetic acid.

The author has not submitted the digitaline to elementary analysis, not having been able to obtain it perfectly pure in sufficient quantity, the amount in the plant being extremely minute.

Physiological and Therapeutical Action of the bitter Principle of Digitalis.

M. Homolle exhibited the bitter principle to a rabbit, introducing 5 centigrms. into the cellular tissue of the thigh; it produced anxiety, trembling, and reduction of the pulse from 148 to 124; 10 centigrms. reduced it from 108 to 102, it subsequently rose to 144. 15, 20 and 30 centigrms. were afterwards given, and reduced the action of the heart 24 to 30 beats. During these experiments there was no vomiting; the state of the urine could not be satisfactorily ascertained. It was found that a fifth part of the quantity, which when taken into the stomach acted as a poison, produced the same effect when inserted beneath the skin. 5 centigrms. given to a dog had no effect upon the pulse, but produced vomiting. A similar dose, repeated also, produced vomiting, a bloody stool, and increase of the pulse from 148 to 154. 5 centigrms. inserted beneath the skin caused staggering, hiccough and trembling, and raised the pulse to 184, the action of the heart becoming irregular and tumultuous. 1 centigrm. applied to a blistered surface on the author's arm, in one instance reduced the frequency of the pulse, in another increased it, with occasional intermission, producing headache, dimness of sight and lassitude; the urine was diminished in quantity. 2 centigrms. produced analogous effects.

The author remarks that 1 centigrm., endermically applied, is sufficient to produce all the poisonous effects, as headache, dimness of sight, general debility, shivering, diminished urinary secretion, irregularity and intermittence of the pulse, without alteration in its frequency. 5 milligrms. taken internally produced very similar symptoms, slight diminution of the frequency of the pulse, debility and dimness of sight, normal quantity of urine, sometimes vomiting, increased frequency of pulse on assuming the erect posture; after the exhibition of the medicine was withheld, the quantity of urine was much increased.

In a severe case of pleurisy and pericarditis, complicated with anasarca, deficiency of urine, which was bloody, orthopnœa, tumultuous action of the heart, with a pulse which could not be counted, digitaline in the dose of 2 milligrms. repeated three times, was followed by the evacuation of 3 pints of limpid urine, and the pulse was reduced to 120 and regular. Four pills of 4 milligrms. were given during the next day, the urine continued abundant, the pulse was 96, occasionally intermittent; by the continuance of the medicine the pulse was finally reduced to 54, with occasional interruptions; the patient was afterwards completely cured. In a case of simple pleuritic effusion, digitaline appeared to hasten the absorption of the fluid. Its diuretic action was also well-marked in a case of nervous palpitation.

M. Solon not only has confirmed the experiments of the author, but has even found the digitaline more active than he did. He always observed that in the dose of 1 to 3 milligrms. in the day, its action on the circulation was marked, and reduced the pulse from 72 to 55 in the minute; the poisonous effects were always observed when the dose of the substance amounted to 1 centigrm. per diem. The diuretic action observed in some of the above experiments has not been confirmed. M. Solon concludes from his observations, that the dose of the digitaline should be from 1 milligrm. to 1 centigrm*.

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* As the therapeutic actions of medicinal substances do not come within our limits, we have been obliged to curtail these experiments considerably.—Ed. *Chem. Gaz.*

PROCEEDINGS OF SOCIETIES.

Meeting of the Royal Society.

Thursday, Jan. 23, 1845.

(Sir J. W. Lubbock, V.P. and Treas., in the Chair.) "An Account of the artificial formation of a Vegeto-alkali," by George Fownes, Esq.

The substance which is the subject of investigation in this paper is a volatile oil, obtained by distillation from a mixture of bran, sulphuric acid and water, and is designated by the author by the name of *furfurol.* Its chemical composition is expressed by the formula $C^{15} H^{6} O^{6}$, and its properties are the following:—When free from water and freshly rectified, it is nearly colourless; but after a few hours, it acquires a brownish tint, which eventually deepens almost to blackness. When in contact with water, or when not properly rendered anhydrous, it is less subject to change, and merely assumes a yellow colour. Its odour resembles that of a mixture of bitter almond oil and oil of cassia, but has less fragrance. Its specific gravity at 60° Fahr. is 1·168; it boils at 323° Fahr., and distils at that temperature without alteration. It dissolves to a large extent in cold water and also in alcohol. Its solution in concentrated sulphuric acid has a magnificent purple colour, and is decomposed by water. Nitric acid, with the aid of heat, attacks the oil with prodigious violence, evolving copious red fumes, and generating oxalic acid, which appears to be the only product. It dissolves in a solution of caustic potash, forming a deep brown liquid, from which ashes precipitate a resinous matter. With a slight heat, it explodes when acted upon by metallic potassium.

When placed in contact with 5 or 6 times its bulk of *Liquor ammoniæ,* it is gradually converted into a solid, yellowish-white, and somewhat crystalline mass, which is very bulky, perfectly soluble in cold water, and easily obtained in a state of dryness under a vacuum. The formula expressing the chemical constitution of this substance, or of *furfuroamide,* as the author calls it, is $C^{15} H^{6} N O^{3}$, and it is classed by him with the *amides.* The oil itself appears to be identical with the substance described by Dr. Stenhouse under the name of *artificial oil of ants.* Another substance, isomeric with the amides, and of which the formula is $C^{30} H^{12} N^{2} O^{6}$, was obtained by the author, and termed by him *furfurine,* and found to have the properties of a vegeto-alkali, and to form saline compounds with various acids.

Chemical Society of London.

Nov. 4th, 1844. (The President in the Chair.) The following communications were read:—

"Examination of a Specimen of diseased Wheat," by Mr. J. Carty.

The author's attention was lately directed by Mr. Briggs, of Overton, near Wakefield in Yorkshire, to a kind of disease which he considers to be burnt ear, and analogous to smut, which had attacked some wheat growing on his land. The stalk of the wheat was of the usual height and strength, and the ears seemed externally healthy; but on breaking into the grain it was found to be filled with a black powder, instead of the white, thick juicy substance found in healthy wheat at the same period of growth. It was a thick-set red wheat, sown in December on a light and good turnip soil, to which an unusually large quantity of guano (4 cwt. per acre) had been applied as a manure. About one-tenth of the whole quantity was diseased, while several other kinds of wheat, sown in the same field, but to which no guano had been applied, were perfectly sound.

The ears had a much greener appearance than the same kind of wheat in a healthy condition, and emitted a very disagreeable smell, which is not easily described.

On close examination the grains were found filled with a black unctuous powder in place of the milky pulp of the healthy seed. This powder was separated in quantity by bruising the ears in a mortar and sifting through fine muslin, and submitted to chemical examination. It had the same disagreeable smell as the ears, but stronger; it was oily to the touch, and heavier than alcohol and water. When heated in the air it burned with a bright flame, leaving a residue of charcoal, and eventually a trace of white ash. When heated in a tube, it gave off water, empyreumatic and oily matters, and a little ammonia. It was insoluble in a solution of potash and in hydrochloric acid; nitric acid made it yellow, and hot sulphuric acid dissolved it with purplish-red colour. Boiled with water, it yielded merely a little gum and bitter brown extractive matter, the greater part remaining undissolved. Alcohol extracted a fat oil, and a waxy or resinous matter; the undissolved portion appeared to consist of lignine mixed with charcoal. The black powder greedily absorbed oxygen from the air when in a moistened condition, giving rise to carbonic acid.

A carefully conducted proximate analysis of the substance led to the following results:—

Wax or resin with fixed oil	7·0
Gum and extractive matter, &c.	7·8
Lignine and charcoal	82·7
Ashes	2·5
	100·0

The ash consisted chiefly of earthy phosphates and silicate of potash.

Dec. 11*th*, 1844. (Thomas Graham, Vice-President, in the Chair.)

"Analysis of the Bonnington Water, near Leith, Scotland," by Edward G. Schweitzer, M.D.

The author commences this elaborate and valuable communication by detailing the source from which the spring rises, the strata through which it passes, the characters of the water, its specific gravity, temperature, and the volume emitted. The qualitative testing is then minutely given, and this is succeeded by a most instructive essay on the quantitative analysis of this highly complicated mineral water; the contents of which in the pint of 34·659 cubic inches are,—sulphate of potash, 2·46554; sulphate of soda, 1·51227; sulphate of lime, 6·28166; iodide of sodium, 0·00728; bromide of sodium, 0·07886; chloride of ammonium, 9·49939; chloride of sodium, 3·82963; chloride of magnesium, 3·12017; nitrate of soda, 2·02154; carbonate of magnesia, 1·70443; protocarbonate of iron, 0·05807, or at the spring, 0·69973; protocarbonate of manganese, 0·01535; ammonia united to organic matter, 0·42285; alumina, 0·02245; silica, 0·18651 = 31·22600 grs.

The author recommends the following as an excellent test for nitric acid, when accompanied either by iodine or bromine, or both. It is known that the presence of nitric acid is easily indicated, when, to the concentrated fluid to be examined, pure sulphuric acid is added, and to this mixture a concentrated solution of the protosulphate of iron. The smallest trace of nitric acid, even the $\frac{1}{4000}$th or $\frac{1}{3000}$th part, is evidenced by the appearance of a pink colour, more or less intense. A large amount of nitric acid is indicated by a black colour, a combination of the oxide of nitrogen with the protoxide of iron; however, here we have only to consider minute proportions. The salts of iodine and bromine, when treated with the same test, tinge the fluid with their own peculiar colour, but a greater addition of the solution of the protosulphate of iron destroys the colouring, which is not the case with nitric acid. If the quantity of nitric acid be very small, and that of iodine predominates, it is necessary for comparison to make a standard fluid, from which not only the presence of nitric acid may be inferred with certainty, but even its approximate quantity. For that purpose 50 grs. of distilled water are employed, in which half a grain of iodide of potassium is dissolved; to this 50 grs. of sulphuric acid is gradually added, and afterwards 50 grs. of a concentrated solution of protosulphate of iron. The sulphuric acid precipitates the iodine, which is redissolved by the addition of the iron solution—forming an iodide of iron—whereby the fluid assumes a yellowish tinge, resembling the colour of a solution of chromate of potash; the smallest proportion of nitric acid, however, should it even amount to $\frac{1}{3000}$th part, will in this diluted state be manifested by a brownish tinge, which becomes much darker in proportion as the quantity of nitric acid increases. If a bromide be present instead of an iodide, the nitric acid can be ascertained with equal facility, from its imparting a greenish tinge to the fluid. 50 grs. of distilled water, containing half a grain of an alkaline bromide to which 50 grs. of sulphuric acid have been added, will indicate $\frac{1}{2000}$th part of nitric acid, by developing a brownish tinge, whereas a similar mixture without the nitric acid will remain colourless. This is obvious, as in the first instance, by the addition of the sulphuric acid, hydrobromic acid is formed, which is colourless, but becomes again decomposed by the presence of free nitric acid, whereby the fluid contracts a brownish tinge. The presence of both bromides and iodides does not interfere with the delicacy of this test for nitric acid; the reaction is the same as if an iodide only were present. However sure and delicate this test is, the presence of organic matter makes it complicated, and where the organic matter cannot be perfectly separated, the presence of nitric acid is easily overlooked, which indeed happened in this analysis at the first examination. In such cases I find the test with indigo preferable; yet, where the quantity of nitric acid is very small, it is best to submit the concentrated fluid to distillation with sulphuric acid.

"Description of a Chemical Lamp-Furnace," by Edward Solly, Esq., F.R.S.

The exhibition at the recent meeting of the British Association of a hydrogen lamp-furnace constructed by the Rev. V. Harcourt, by the aid of which a crucible could, with great convenience and expedition, be raised to a very high temperature in a short time, and maintained in that state at pleasure, suggested to the author the idea of attempting to substitute for the hydrogen the cheaper material of coal-gas, mixed with such a quantity of air as to ensure complete combustion without deposition of carbon.

Mr. Solly's lamp-furnace consists of two parts, viz. a ring-burner about an inch in diameter, having on its upper side six small apertures, and a second ring of metal tube, rather more than 3 inches in diameter, pierced in its inner side by twelve small holes at regular intervals, and supported at a height of about 2 inches above the smaller ring. By this arrangement eighteen small converging jets of flame are directed against the bottom and sides of the crucible, which is supported within the upper ring by a triangle of stout platinum wire. The mixture of air and gas burned in this lamp is made by injecting by a bellows, or otherwise, a sufficient quantity of air into the pipe which supplies the coal-gas. To prevent the current of the latter from being stopped or driven backwards by the greater pressure of the air, the gas is admitted by an inner tube placed in the centre of that conveying the air, so that both currents flow in the same direction. The proportions of air and gas are regulated by stop-cocks. The heat obtained by this lamp is sufficient to ignite to bright redness in a very short space of time a platinum crucible of considerable size, and to effect the perfect and rapid decomposition of siliceous minerals by fusion with an alkaline carbonate. A small piece of silver, placed in a thin porcelain crucible, and put into the platinum crucible before mentioned, may be melted in a few minutes. Mr. Solly suggests that this lamp might also prove useful for blowing or bending large and thick glass tubes.

"Notice of a new hydrated Phosphate of Lime," by John Percy, M.D.

When fresh precipitated phosphate of lime is dissolved in carbonic acid gas, and the solution allowed to remain for a few days exposed to the air, it deposits minute scales of phosphate of lime. These crystals are microscopic modified rhomboidal plates of a brilliant white, and have the formula $2CaO + PO^5 + 6HO$. The rational formula will doubtless be $HO, 2CaO + PO^5 + 5HO$, 1 equiv. of water being basic and 5 constitutional. On heating at 134° to 148° Cent.

another hydrate results, having the formula $HO, 2CaO + PO^5 + 2HO$.

"On a curious Change in the Composition of Bones taken from the Guano Deposits," by Robert Warington, Esq.

The subject which formed the basis of this communication had been put into the author's hands by Mr. Edwin Quekett for chemical investigation, and was found to be composed of sulphuric acid, potash and ammonia, with a little uric acid. This saline matter had entirely replaced the substance of the bone, and presented a radiated texture; muscular fibre in a dried state was still adherent to the surface of this pseudo-morphous bone.

REVIEW.

A Thermometrical Table, on the Scales of Fahrenheit, Centigrade and Reaumur, comprising the most remarkable Phænomena connected with Temperature in relation to Climatology, Physical Geography, Chemistry and Physiology. By ALFRED S. TAYLOR, Lecturer on Chemistry at Guy's Hospital.

THIS Table exhibits an enlarged representation of a thermometer, graduated according to the scales of Fahrenheit, Reaumur and Celsius; on the sides of which, and opposite the degrees, are enumerated a large number of the most interesting points connected with temperature in relation to the subjects just mentioned. We certainly have here an immense number of facts condensed into a very small space, and in some respects we doubt not it will be found of great utility. There can be no chemist who has not occasionally found the reduction of the thermometric degrees of one of the continental scales to his own, or *vice versâ*, troublesome and annoying; and it is a great pity that this is not avoided by adopting some uniform standard. However, the table having the corresponding degrees of the different scales arranged opposite each other, this difficulty vanishes, and we avoid any calculation. Another great use of it consists in its indicating the melting points of metals, and the boiling points of saturated saline solutions; so that if a bath of any given temperature is required, by referring to the degree we find opposite it a liquid which boils at that temperature. But although this table contains an immense number of facts relating to temperature (in truth there is hardly a chemical one at all required which is not there), we believe we have stated the whole of its practical utility; for the reason that there is no guide to direct us; to find what we require, we are obliged to wade through hundreds of words (so small and crowded as to be beyond the sight of many, and to endanger that of the rest) before we find the one sought. In short, it may be stated, that in all cases where we wish to find out what phænomena occur at any *known* temperature, by reference to this table we shall at once obtain that knowledge; but where we require to know at what temperature any particular phænomenon occurs, unless we know nearly what it is, we must wade through the whole contents of the table. We are sorry to see so valuable and laborious a collection of most interesting matter arranged in such a useless form. Had the facts been collected under different heads, separating the chemical from the physiological, &c., or even the whole been arranged alphabetically, they would indeed have formed a valuable table both to the chemist and physician. It would also have been better if some of the least useful facts had been omitted, especially for the tabular form, as it requires the use of such extreme abbreviation as in some cases to be almost unintelligible. A small pamphlet, containing a mere enumeration of its contents, accompanies the table.

PATENT.

Patent granted to W. T. Cookson, Newcastle on Tyne, *for Improvements in Apparatus for burning Sulphur.*

THIS invention has for its object the so arranging apparatus for burning sulphur when manufacturing sulphuric acid, that the heat generated in the operation may be employed in obtaining the steam requisite for the process of making sulphuric acid, and for other purposes, as the heat resulting is more than is required for generating steam sufficient for the manufacture of sulphuric acid from the sulphur burned, and therefore may be employed in evaporating and concentrating other fluids.

The apparatus consists of a steam-boiler with three flues, having doors similar to those ordinarily used, with regulators to regulate the passage of air to the burning sulphur. The burner-plates are flat, and are placed within the flues, and there is an open space beneath each plate to admit air, such air not being allowed to pass beyond the end of the burner-plate. The nitre-pans are placed in the "stalk," or may be introduced into the flues. The gases pass from the flues into the "stalk" or chamber, and thence are conveyed into the sulphuric acid chamber, to which also steam is conveyed from the boiler by a pipe in the ordinary way; and as there will be more steam generated than will be required for the gases from the quantity of sulphur burned, the remainder of the steam is employed for any useful purpose, amongst others for obtaining a draught for the sulphuric acid chamber. In starting to use this apparatus, charcoal or other fuel in a suitable holder is applied under the boiler to heat the water, so as to get sufficient heat for the sulphur; and when the apparatus is at work, the space under the boiler and flue thereto may be kept closed.

As the burner-plates are in contact with the metal of the flues, the heat is conducted off to the water, which prevents sublimation and irregularity in the burning of the sulphur.—Sealed Sept. 20, 1844.

THE CHEMICAL GAZETTE.

No. LVII.—March 1, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Athamantine. By MM. WINCKLER *and* SCHNEDERMANN.

FROM the author's experiments on this substance, it results that athamantine is related by its properties to the fats, being decomposed by the action of various reagents, especially by the alkalies, into valerianic acid, and another body which appears to take the place of the glycerine in the ordinary fats.

Athamantine is obtained most advantageously from the dried roots of *Athamanta Oreoselinum*[*], by extracting them with hot alcohol of 0·863 sp. gr., distilling off the alcohol and water from the filtered extract, and treating the residue with 6 to 8 times its weight of æther, which dissolves out the pure athamantine. The æthereal solution is digested with animal charcoal, the æther removed by distillation, and the residue dissolved in alcohol of 0·912 to 0·901 at a gentle heat. On placing this solution in a cold spot, white, flexible, slender, acicular crystals, frequently several inches in length, gradually separate in radiating groups; the entire liquid soon becomes filled with them; they are mixed with some brownish oily drops, which are removed as much as possible from the crystals, and these entirely freed by repeated solution and crystallization.

The product so obtained is a very loose, light, brilliant, white, satiny tissue of flexible, very minute crystals, resembling asbestos. The authors looked upon it for a long time as pure athamantine, and most of their experiments were performed with it as such until they found that athamantine was capable of forming large solid crystals, which differ from the tissue of minute crystals by a somewhat different composition and lower melting-point; it appears therefore that the latter, notwithstanding its pure homogeneous appearance, is still mixed with a fatty substance. They could not succeed in producing the large crystals at will. They obtained them most beautifully from some athamantine separated in an oily form from alcohol, when this had stood at a summer temperature for some time with the supernatant alcohol; the oily mass had then become partly

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[*] The discovery of this substance was noticed at p. 113 of the first volume of this Journal.—ED.

converted into these crystals, which however could not again be obtained under apparently the same circumstances. Sometimes they were obtained immediately from alcohol with the usual form of crystal, but always in small quantity. The crystals were nearly an inch in length, perfectly colourless, generally four-sided rectangular prisms with truncate ends.

Athamantine has a peculiar rancid, soapy smell, which is especially perceptible when warm, and a rank, bitter, subsequently somewhat irritating taste. It is insoluble in water, readily soluble in alcohol, æther, oil of turpentine and the fat oils. From an alcoholic solution, saturated with the assistance of heat, it separates on cooling in oily drops, which generally remain for a long time soft, and then solidify to a crystalline mass. It melts on the application of heat to a yellowish oily liquid, which sinks to the bottom in water, and on cooling forms a clear turpentine-like mass, which after a considerable length of time resolidifies, some radiate crystals resembling wavellite being first formed, and into which the entire mass is gradually converted. The melting-point of the pure athamantine is very near 174°; the minute crystals, on the contrary, melt already at 138° to 140°. Athamantine cannot be volatilized without decomposition; it supports, however, a tolerably high temperature. On destructive distillation it yields, along with other products, a considerable quantity of valerianic acid. It contains no nitrogen; the analysis made with the solid crystals led to the formula $C^{24} H^{15} O^{7}$, which was confirmed by subsequent observation.

The athamantine in minute crystals afforded in the analyses constantly varying results. From the mean of these it contains 1·9 per cent. carbon and 0·5 per cent. hydrogen more than the large crystals.

When dry muriatic gas is passed over athamantine at the ordinary temperature, it absorbs it, soon cakes together, and gradually melts, without becoming warm, to a clear yellowish-brown oily liquid, which soon begins to solidify, some minute, white, acicular crystals, in radiate groups, being formed in it. This solidification begins even while a portion of the athamantine is still unmelted and unaltered, and the reaction of the gas on it is thereby prevented or rendered difficult; on which account, to render it as perfect as possible, the gas should be passed in a rapid current, and as soon as the substance begins to melt, the vessel turned round and agitated as much as possible, in order to spread it over the sides. On the application of a gentle heat to the liquid mass, gas bubbles are evolved from it, which become more frequent the higher the temperature is carried, and at 212° produce boiling; at the same time a clear colourless liquid distils over, which is hydrated valerianic acid; the mass becomes thick, and gradually opake, from the separation of a solid body; it finally becomes quite stiff and dry, and is entirely converted into this body. It is this body which replaces the glycerine in the athamantine. The authors propose for it the name of *Oroselon*.

If the liquid mass be allowed to solidify, and then heated to 212°, it again changes into a thickish liquid, rendered opake by the separation of oroselon, exhibiting the same evolution of gas and separation of valerianic acid, and being likewise converted, after sufficient heating, entirely into oroselon.

Oroselon is left as an amorphous porous mass, of grayish-white colour. It is purified by solution in alcohol and crystallization, which however is attended with some difficulty. It does not dissolve readily in alcohol, even on the application of heat; the solution is of a yellow colour. On the cooling of the boiling saturated solution, it separates in warty masses, which adhere to the sides of the vessel, and consist of concentric aggregations of minute acicular crystals. It is freed from any adherent athamantine by a little alcohol, when it becomes whiter; but it always retains a faint yellowish colour, of which it could not be deprived, although it is undoubtedly perfectly white in the pure state; this appears to arise partly from the imperfect purity of the athamantine employed, and partly from its undergoing a change during the evaporation of its solution, thus acquiring a greenish-brown colour, which gradually becomes reddish-brown. Oroselon is void of taste and smell, insoluble in water, and soluble in æther, to about the same extent as in alcohol, with a yellow colour. Dilute potash or ammonia added to it colours it yellow, and dissolves a small portion of it with a lively yellow colour; concentrated solution of caustic potash dissolves it with the application of heat in considerable quantity with a reddish-brown colour. Acids produce in these solutions a yellowish-white precipitate. At about 374° it melts to a clear yellow fluid, which solidifies on cooling to an amber-coloured non-crystalline mass, which is carbonified and destroyed by further heat. It undergoes no perceptible loss in weight by this melting, but is so changed that it no longer crystallizes on the evaporation of its solutions, but separates in perfectly amorphous yellow drops. Oroselon contains no chlorine. The authors adopt the formula $C^{14}H^{5}O^{3}$, the only one which satisfactorily explains the decomposition of the athamantine. The analysis gave—

C....	74·70	74·88	74·79	14	=	1051·7	74·37
H ..	4·57	4·56	4·63	5		62·4	4·41
O ..	20·73	20·56	20·58	3		300·0	21·22

The liquid which distilled over on the decomposition of the athamantine by muriatic acid agrees altogether with valerianic acid in odour, taste, and other properties; its identity was moreover confirmed by analysis.

The gas which is given off on heating the athamantine which has been liquefied by treatment with muriatic acid gas, appears from experiment to consist solely of muriatic acid. The athamantine therefore is decomposed in this operation simply into hydrated valerianic acid and oroselon. According to theory, 100 parts athamantine should yield 52·7 parts oroselon. The authors attempted in one experiment to determine the quantity of the latter, and obtained 56·2 per cent.

Athamantine undergoes the same decomposition when it is heated immediately to 212° and exposed to the action of muriatic gas, or when heated with concentrated muriatic acid. None of the products formed contain chlorine, and it has quite the appearance as if the action of the muriatic acid was catalytic, since it apparently exerts no kind of chemical action whatever; nevertheless this is the case,—the muriatic acid forms, according to the experiments of the authors, a combination with the athamantine, which is however decomposed on the application of heat, and even at the ordinary temperature, into muriatic acid, hydrated valerianic acid and oroselon. They regard the liquid mass into which the athamantine is converted on treatment with muriatic gas, and which soon begins to solidify, as this compound. In the solid state it consists, at those places where it covers the sides of the vessel in a thin layer, of minute white needles in stellate groups; the chief mass, however, presents an amorphous appearance, a gray colour, and is thoroughly moist, and smells strongly of valerianic acid. On opening the vessel, after being closed for some time, vapours of muriatic acid are given off, even when carbonic acid had been previously passed for a considerable length of time through it. The authors consider this to be owing to the muriatic compound of the athamantine being readily decomposed, and that even during solidification it separates into muriatic acid, valerianic acid and oroselon. They once succeeded in obtaining it tolerably pure by treating the solidified mass with æther, which dissolved the greater portion, but left a part behind as a white crystalline powder; it was separated by filtration and washed with a little æther. Examined under the microscope, it appeared perfectly homogeneous, and consisted of small tabular crystals with mother-of-pearl lustre. Alcohol and æther dissolved it readily, and left on evaporation some acicular crystals and a mass of amorphous appearance, the latter in greater proportion or exclusively when the evaporation was effected by heat. It melted below 212° to an oily fluid, but which very soon became opake-whitish, with evolution of bubbles of gas, and then solidified, being converted into oroselon; boiled with water, it likewise melted to oily drops, which gradually disappeared and seemed to be entirely dissolved; on cooling a crystalline body separated from the water, which will be described hereafter. An analysis of this substance yielded a result agreing closely with the formula $C^{24} H^{30} O^{7} + H Cl$; the amount of chlorine found was 13·32 per cent. It appears therefore beyond a doubt that in the action of muriatic acid upon athamantine 1 atom of the latter combines with 1 equiv. of the former, and that the valerianic acid and oroselon are products resulting from the decomposition of this combination.

In subsequent experiments the authors could not succeed in obtaining this body in any quantity; mere traces of it, in an impure state, sometimes remained on agitation with æther. The whole of the congealed mass dissolved with the greatest ease in alcohol and æther, proving that at least a great portion of it does not consist of oroselon, this being but sparingly soluble. On spontaneous evaporation this liquid acquires a strong agreeable fruity odour, which perfectly resembles that of valerianic æther, and leaves a crystalline mass, which contains only traces of chlorine, and consists principally of oroselon. On evaporation with the assistance of heat, the same fruity odour is perceptible, and the oroselon separates in cauliflower-like masses, which however, as was evident on analysis, were still mixed with some of the muriatic compound. The combination of athamantine with muriatic acid is accordingly decomposed by alcohol, more or less completely, into muriatic acid, valerianic æther and oroselon. The same decomposition results when muriatic gas is passed into the alcoholic or æthereal solution of athamantine.

It was stated above, that the muriatic compound of athamantine dissolved in boiling water, and that on the cooling of the solution a crystalline body separated. The authors obtained this body (which they designate by a) in too small a quantity to examine it accurately and completely. The greatest anomalies occur with reference to its formation; sometimes they obtained it by boiling the crude mass treated with muriatic gas; in other cases none of it was formed, but only oroselon. It separates from the boiling aqueous solution on cooling in minute needles, which appear under the microscope as long prismatic crystals. When dry it forms a loose white silky mass; it dissolves in considerable quantity in boiling water, but very sparingly in cold. Alcohol and æther dissolve it readily, and it is left on evaporation in fine needles or scales. It dissolves in dilute caustic potash with a beautiful yellow colour; acids precipitate it in minute needles, while the solution at the same time loses the yellow colour. Ammonia likewise dissolves it in small quantity and with a yellow colour; this solution gives with acetate of lead a beautiful yellow precipitate; it contains no chlorine. The analysis made by the authors (69·15 per cent. C, 5·01 H, 25·84 O) seems to indicate that it originates from the oroselon by the absorption of 1 atom of water, or that it is the body which is in combination with anhydrous valerianic acid in the athamantine. Its composition is the same as that of hydrated benzoic acid, from which however it is distinguished both by the yellow colour of its alkaline solutions and by its not subliming without apparent decomposition.

Sulphurous acid acts upon athamantine exactly like muriatic acid; in this case a combination of athamantine with sulphurous acid is formed, which is very readily decomposed into sulphurous acid, hydrated valerianic acid and oroselon. The athamantine takes up 14·63 per cent. SO^2, 1 at. = 14·91.

Athamantine dissolves in pure concentrated *sulphuric acid*, with evolution of heat, to a clear brownish liquid, giving off at the same time a powerful smell of valerian. If the acid is previously diluted with a little water and cooled with ice, the solution is nearly colourless; on mixing it with water, a considerable yellowish-white precipitate results, which forms, after washing and drying, a yellowish or grayish-white powder. This body contains no sulphur; it is oroselon, more or less changed by the action of the sulphuric acid, and gave no constant results on analysis. It dissolves like oroselon in alcohol and in potash with a yellow colour, but differs from it in being quite amorphous and not at all crystalline.

The clear colourless liquid filtered from this body yields, on distillation, a product having a strong odour of valerianic acid, and which is rendered turbid by a white flocculent substance floating in it; the quantity however is very small. Separated by filtration and dried, it forms a light white crystalline mass, which dissolves readily in æther and alcohol, and is left on evaporation in minute needles. It melts at above 212°, and solidifies on cooling to a crystalline mass. The authors leave it undetermined whether this body be identical with the substance *a*.

The liquid filtered from this substance was neutralized with alkali, concentrated by evaporation, and then mixed with nitrate of silver. A considerable white precipitate resulted, which dissolved on boiling, and separated on cooling in fine laminæ, with a silver lustre, and which agreed entirely in its properties and composition with the valerianate of silver (55·55 per cent. AgO, 28·75 C, 4·56 H).

Athamantine is likewise completely decomposed by *caustic alkalies*, with separation of valerianic acid, a relation which indicates its affinity to the known fatty bodies. When heated with caustic potash, it dissolves in it with a red-brown colour; if the solution of potash is very concentrated, it dissolves without the application of heat. On acidulating the clear red solution with sulphuric acid, it acquires a strong odour of valerian, and a yellowish-white precipitate separates in considerable quantity, which may easily be filtered from the clear and colourless liquid. After washing and drying, this body (*b*) varies in different preparations, owing to the authors employing for its preparation the athamantine in fine crystals, which was then considered to be pure; and likewise to a change which this body undergoes by the influence of alkalies. In its purest state it forms a yellowish-white mass of earthy appearance, but usually it had after drying a brownish dirty colour. On ignition it constantly left a small quantity of ash. In its purest state it is almost insoluble in water, and but very sparingly soluble in alcohol; the solution has a yellow colour, and on evaporation leaves the body as a yellowish-white amorphous powder. On analysis the results varied with products of different preparations; they seemed however to indicate that it was formed from the oroselon by the absorption of water, the latter however appearing to amount to less than 1 atom. This results from the analysis of the precipitate which acids produce in alkaline solutions of oroselon. This precipitate agrees with the body *b* in its properties, but exhibits on the evaporation of its alcoholic solution an indistinctly crystalline appearance.

The body *b*, in its recently precipitated state, dissolves in ammonia with a yellow colour; the solution, which is somewhat turbid and opake, and cannot be obtained clear by filtration, gives with acetate of lead an abundant flocculent precipitate of a beautiful yellow colour, but which is not easily obtained of constant composition; it is probably composed, according to the experiments of the authors, according to the formula $2Pb + C^{14} H^{5} O^{3}$ (61·27–66·54 PbO, 24·59–28·240 C, 1·62–2·08 H).

Under the influence of alkalies the body *b* undergoes a change, in consequence of which it acquires a brownish colour and becomes far more soluble in alcohol; at the same time its composition is altered, the amount of carbon decreases, while that of the hydrogen increases. This change occurs especially when the action of the alkali is assisted by heat. The precipitate from the alkaline solution of oroselon undergoes the same change.

On distillation of the liquid filtered from the body *b*, valerianic acid passes over, rendered turbid by the same flocculent body which results from the action of sulphuric acid on athamantine, but the quantity of which is here much smaller.

Athamantine undergoes the same change by boiling with milk of lime or barytic water as by potash. Liquid or gaseous ammonia has no perceptible action on it.

The authors suspected that the essential oil of *A. Oreoselinum* might stand in some relation to valerianic acid, or that this might perhaps be formed from it, and were thus led to make some experiments on the subject, which did not however confirm their supposition. The oil was prepared from the fresh herb by distillation with water; it had a strong aromatic juniper-like odour, boiled at 325°, and its specific gravity was 0·843. It was distilled alone, and the first and last portions collected separately and analysed; the first portion was free from oxygen, and composed according to the formula $C^5 H^4$ (88·4 C, 11·8 H). The last portion contained 0·71 per cent. oxygen. According to this the oil of athamantine is identical in composition with the oil of turpentine, and contains only a very small quantity of an oxygenated oil, which probably owes its origin to the action of the air.

Muriatic acid gas is absorbed by the rectified oil, which passed over at the commencement in considerable quantity and with evolution of much heat. It was saturated with the gas, being kept at 5° during the operation; it acquired a dark brown colour, and deposited a small quantity of are sinous matter, but nothing crystalline. The product obtained, washed with carbonate of soda and distilled with water, formed a clear colourless liquid, which gradually acquired a brownish colour, a strong turpentine odour, boiled at about 374°, and floated on water. According to the authors' analyses, it is composed after the formula $C^{20} H^{16} + H Cl$, therefore like turpentine camphor.—*Göttinger gelehrte Anzeigen*, No. 121.

Experiments on the passage of Medicinal Substances into the Urine. By MM. Laveran *and* Millon.

The authors ascertained from several experiments, that when the potassio-tartrate of soda passes off in the urine, it is always found in the state of carbonate; but that it only escapes by this outlet when given in repeated small doses, by which the motions are not increased. But if the salt be exhibited in doses of 7 drms. to 1½ oz., it generally acts as a purgative, and the urine is acid instead of being alkaline. The constitution also must undoubtedly have some influence in the production of one or the other effect. In four cases sulphur neither appeared in the urine, nor was the quantity of sulphates increased. In fifteen experiments sulphate of soda was found to act the same as the potassio-tartrate of soda; when given in small doses and in strong subjects it passes into the urine, but in large quantities and in debilitated patients it was entirely separated by the bowels. In ten cases, in which salicine had been taken, salicylous and salicylic acids were detected in the urine, at least the violet-colour, on the addition of salts of iron, appeared in the natural urine, the distilled liquid, and the alcoholic and æthereal extracts.—*Ann. de Chim. et de Phys.*

Examination of the Seeds of Phytelephas macrocarpa *and* microcarpa. *By* M. von BAUMHAUER.

M. Baumhauer has submitted the seeds of the above tree*, which have been for some time brought from Peru into the European market, to a chemical examination. On account of their hardness and snow-white colour, for which they have been applied in various ways to turning, they have been called vegetable ivory. In the unripe state, Ruiz and Pavon state that they are eaten by the Peruvians. The juicy stone-fruits are crowded together on a common stalk; they are angular, containing four seeds; each seed is surrounded with horny albumen. The walls of the cells are composed of a hard rind, which is generally still attached to the fruit as it occurs in commerce.

Payen, in his memoir on cellulose†, has already analysed the seed-coats of the *Phytelephas*, after treating them with æther, alcohol, ammonia, acetic acid and water. He found the composition as follows:—

Carbon	44·14
Hydrogen	6·30
Oxygen	49·56

He, moreover, found that they were converted into dextrine by sulphuric acid; into xyloidine, without the production of any colour, by nitric acid: thus they consisted of pure cellulose, containing traces merely of silica.

Baumhauer concludes from his experiments, that the perisperm of the above nuts is not, as Payen supposes, pure cellulose mixed with albumen, two nitrogenous bodies, two fatty matters, silica and salts, but that another substance is still present, which has a somewhat different composition to that of cellulose. He proceeded in his experiments in a manner similar to that of Payen. The seed-coats were separated from the brown rind by a file, then powdered by using a finer file and sifting, and exhausted by æther, alcohol and boiling water. The remaining powder, which contained neither nitrogen nor ash, yielded in three analyses—

	I.	II.	III.
Carbon	44·28	44·44	44·39
Hydrogen	6·32	6·13	6·22
Oxygen	49·40	49·43	49·39

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* Mr. Connell's examination of these seeds will be found at p. 104, vol. xxiv. of the *Philosophical Magazine.*—Ed.

† Chem. Gaz., vol. ii. p. 509.

It was now repeatedly boiled with strong acetic acid, washed with hot water and alcohol, dried at a temperature of 284°–302°, and again analysed. It gave—

Carbon	43·57
Hydrogen	6·27
Oxygen	50·16.

The powder obtained in the first experiment yielded to ammonia a brown matter, precipitable by acetate of lead; the residue, after repeatedly washing with water, acetic acid and alcohol, was of a yellow colour. It was dried at 284°–302°, and burnt with oxide of copper (I.). Two other portions were treated for a considerable length of time with dilute solution of soda, and after washing, &c., also analysed (II. III.); they yielded—

	I.	II.	III.
Carbon	43·65	45·73	45·59
Hydrogen	6·31	6·32	6·57
Oxygen	50·04	57·95	47·84

After partial evaporation, acetic acid threw down brown flocks from the soda solution. Ammonia and acetate of lead caused a whitish-yellow precipitate in the solution.

To separate the two substances, Baumhauer digested the powder of the seed-shells for several days in cold concentrated solution of potash; after dilution with water, the powder was separated by filtration, washed with hot water, and the whole operation repeated as long as the potash dissolved anything. The residue was finally exhausted with hot concentrated acetic acid, alcohol and æther.

The ingredient in solution was separated by saturating the alcoholic solution with acetic acid, washing with cold water, and treating with hot acetic acid, alcohol and æther. By digestion with cold concentrated solution of potash, no decomposition takes place, inasmuch as the residuary powder and the dissolved ingredient are both obtained of a snow-white colour. The powder which remains after treating the seed-coats of *Phytelephas*, when dried at 302°, Baumhauer found to possess the following composition:—

Carbon	43·63	24	43·71
Hydrogen	6·30	42	6·24
Oxygen	50·07	21	50·05

The substance soluble in potash, which the author intends examining more accurately, yields the same composition as starch, from which however, as from inuline, it differs in properties. By decomposing the salt of lead with sulphuretted hydrogen, evaporation, and washing the residue with the solvents mentioned above, it is obtained in a state of purity.—*Ann. der Chem. und Pharm.* xlviii. p. 356.

On the Preparation and Properties of the Hyperoxide of Silver.

By M. Fischer.

It is only possible to obtain this oxide in the galvanic way, and solely from the sulphate or nitrate of silver. It is difficult to procure large quantities, because, in the first place, the reduced silver, which is deposited at the negative pole in the same proportion as the hyperoxide at the positive, extends so easily, from its peculiar crystallization, that it reaches the hyperoxide, which is thus not only contaminated with metallic silver, but is likewise reduced; and because, secondly, the nitric or sulphuric acid liberated at both poles redissolves the hyperoxide. To avoid the latter, the decomposed acid silver solution should be changed from time to time for a fresh neutral one. To avoid the first inconvenience, the arrangement must be such that the reduced silver may separate in granular and not fibrous crystals, which is effected by employing a concentrated solution of silver, or by causing the negative pole to act as a large metallic surface on the solution of silver. But the most sure method, when the dendritic silver increases so as to threaten to come within the sphere of the positive pole, is to shake it off the negative one.

A clay cylinder, such as is employed for Grove's batteries, is placed in a platinum basin on a plate of glass. The silver solution is poured into both to a certain height, and a thick platinum wire held in the silver solution in the cylinder so that it touches neither the bottom nor the sides; the platinum dish and the wire are connected with the two poles of a galvanic battery, and according to whether it be desired to obtain the hyperoxide in large or in small pulverulent crystals, the wire or the basin is placed in contact with the positive pole. The same takes place with the reduction of the silver at the negative pole; beautiful large crystals are formed on the wire, small ones on the basin. Now since in the first case the crystals soon increase so that they attain the sides of the porous cell, penetrate it, and so reach the hyperoxide in the basin, they must be frequently knocked off the negative wire. It is evident that the power of the galvanic battery is of great influence in the preparation of this body, as well as the concentration of the solution; for the quantity of hyperoxide of silver separating within a certain time increases with the force of the battery; but it is not advantageous to employ a very powerful battery nor a very saturated solution of the nitrate, since the reduced silver separates in precisely the same proportion, and the dendritic crystals consequently reach towards the positive pole, and also from the increasing quantity of free acid, it is to be feared that some of the prepared hyperoxide may again be dissolved. From 1 to 2 grms .of this hyperoxide were obtained in less than an hour with a Bunsen's carbon and zinc battery of four elements, and a solution of 1 part nitrate of silver in 8 to 10 of water. With sulphate of silver, the product, on the contrary, was very small, owing to the saturated solution containing only $\frac{1}{150}$th of the salt, and the hyperoxide which separates being very readily soluble in the free sulphuric acid.

The hyperoxide obtained must be washed; but since by continued washing the compound is decomposed, it is difficult to indicate the point when all mechanically-adherent salt has been removed.

The compound has the same *properties* whether it be prepared from the sulphate or nitrate. It forms regular octahedrons of a steel-gray colour, with metallic lustre. Dried at 59° to 68° Fahr., it parts at 212° with 2·45 to 2·5 per cent. water, loses its lustre and becomes darker. The salt dried in the air decrepitates on the application of heat. At 302° and above, the excess of oxygen is expelled, without the nitrate or sulphate of silver present being affected. It gives off pure oxygen gas, and muriatic acid no longer yields chlorine with the residue. At a higher temperature, far above 572°, perfect decomposition results, and there is finally left a residue of *pure* metallic silver.

The continued action of water acts in such manner that nitrate and sulphate of silver, and at the same time, with corresponding evolution of oxygen, oxide of silver pass constantly into solution, so that the residue always contains some hyperoxide, with nitrate and sulphate; at least the author could not succeed with cold water in removing in this manner the whole of the sulphate and nitrate. The author thence concludes that the octahedrons are chemical combinations of the hyperoxide with the sulphate or the nitrate; and although he does not deny the possibility that Walquist* may have obtained and analysed the hyperoxide free from those salts, which however is not proved, he considers it more probable that the body analysed by Walquist was not the octahedral compound itself, but only a product of its decomposition.

The author has only analysed the combination with nitric acid; he first determined the entire amount of silver, as chloride, by precipitating the nitric solution of the body; expelling the water of crystallization by exposure to 212°; then, by heating the compound dried at 212° to 302°–392°, the loss in oxygen of the hyperoxide; finally, the nitrate of silver, by dissolving the compound in dilute sulphuric acid, adding an excess of barytic water to the solution, when sulphate of barytes and oxide of silver were precipitated; the precipitate was rapidly filtered, the liquid evaporated, and from the weight of the sulphate of barytes thrown down the amount of nitric acid calculated. The first experiment gave 78·9 silver, the second 2·5 water of crystallization, the third 4·5 to 4·7 oxygen, the fourth 7·9 nitric acid. This corresponds, according to the author, to the formula $4Ag\,O^2 + Ag\,O, NO^5 + 2HO$. He adopts a similar composition for the combination with sulphuric acid.—*Journ. für Prakt. Chem.*, xxxiii. p. 237–246.

On a new Character of the Salts of Lime and Magnesia.

M. Marchand remarks, that all treatises on chemistry agree in stating that the salts of lime and magnesia are not precipitated by the ferrocyanide of potassium. The ferrocyanides of calcium and magnesium being very soluble in water, also induced the belief that the characters stated by authors were correct; this however is not the case, for when ferrocyanide of potassium is added to even weak solutions of salts of lime or magnesia, an abundant precipitate of a slightly yellowish-white colour soon begins to deposit, and it adheres

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* Chem. Gaz. vol. ii. p. 323.

strongly to the sides of the vessel. The only precaution to be taken in producing the effect, is to take care that the solutions are perfectly neutral, because the precipitate is soluble even in weak acid. When heat is employed the precipitation takes place immediately.

The ferrocyanides of calcium and magnesium being, as already stated, very soluble in water, it became important to determine the nature of the precipitated salts; for this purpose a portion of the lime precipitate, which had been dried at 158° F., was treated with nitric acid and boiled in it till no trace of prussian blue remained; the liquor, being evaporated to dryness and the residue analysed in the usual way, gave as results that the salt of lime was composed of

One atom of	protocyanide of iron..	669·12 or	27·75
One ...	cyanide of calcium ..	585·93 ...	24·25
One ...	cyanide of potassium .	819·83 ...	34
Three ...	water	337·44 ...	14
		2412·32	100·

It results from this composition, that this salt is represented by the formula $(\mathrm{Fe\,Cy^2,\ Ca\,Cy^2,\ K\,Cy^2 + 3H^2O})$, and may be considered as a double ferrocyanide of potassium and calcium, or as a hydrated triple cyanide of iron, calcium and potassium; the salt is remarkable on account of the cyanogen being combined in equal proportions, with equivalent quantities of potassium, calcium and iron, and with a quantity of water sufficient to convert the cyanides into hydrocyanates.—*Journ. de Chim. Médicale,* Octobre 1844, and *Phil. Mag.*

ANALYTICAL CHEMISTRY.

On the Action of Solutions of the Neutral Phosphates of the Alkalies upon the Carbonate of Lime and some other insoluble Carbonates.

By J. Lawrence Smith, M.D.

It is a fact, that notwithstanding the advanced state of the science of chemistry, we are ignorant of some of the laws that govern the relative affinities of acids for bases, and the action of neutral salts upon each other. It is true, such and such acids are ranked according to what is termed their strength, and such bases are said to be more powerful than others; still from time to time facts are developing themselves that contradict these established rules. The decomposition of the sulphate of lead by certain neutral alkaline salts, I thought could be explained upon a known law, that when there existed two acids and two bases in solution (the sulphate of lead being dissolved by the salts used), the stronger acid sought the stronger base, and the feebler acid had to combine with the feebler base, notwithstanding being originally in combination with an alkali. But how are we to explain the fact about to be mentioned, which so far as my information goes has not been previously observed? it is that the weakest solution of the *neutral phosphate of soda or potash* will decompose the *carbonate of lime* in the cold, giving rise to carbonate of soda and phosphate of lime.

This fact was first observed while analysing the ashes of a plant which was fused with carbonate of soda for the purpose of estimating the phosphoric acid. The fused mass was thrown into about 4 oz. of water, and digested at about 180° Fahr. for a couple of hours; the insoluble portion was separated, and treated with an acid, when to my astonishment it dissolved with but a *very slight* effervescence, in fact with the escape of only a bubble or two of gas, the carbonate of lime expected not being present. It was known that this circumstance could not arise from a want of decomposition of the original matter, as it was kept fused for half an hour with 4 times its weight of carbonate of soda; therefore the only rational conclusion was, that the phosphate of lime was in the first case decomposed by the soda, but was subsequently re-formed upon treating the fused mass with water. This has been verified by direct experiment.

12 grs. of neutral phosphate of soda and 6 of carbonate of lime were digested for 2 hours in 4 oz. of water at 180° Fahr., when the carbonate of lime was found almost completely decomposed, and the clear solution upon evaporation furnished carbonate of soda.

6 grs. of precipitated carbonate of lime added to a solution of 20 grs. of phosphate of soda (equivalent proportions of each) in 1 oz. of water were kept in a vial for one month, the temperature never exceeding 65° Fahr. At the expiration of this time the insoluble portion contained 3½ grs. of phosphate of lime, corresponding to a decomposition of about 2½ grs. of the carbonate of lime; the soluble portion indicated a corresponding portion of carbonate of soda.

Other insoluble carbonates were experimented with, as the carbonates of magnesia, strontia, baryta and lead; the results were the same, differing only in degree. Even hydrated alumina decomposes slightly the phosphate of soda when boiled with it for a length of time.

I tried two other neutral salts, the acids of which produce insoluble salts with lime, to see if they would act in the same way. The chromate and the tartrate of potash were digested a length of time upon the carbonate of lime, but no decomposition ensued.

I shall not attempt to seek for an explanation of this at present, but shall go on collecting facts of a similar character, to endeavour to find out some general principle that may operate in this and in other cases. This fact itself would not be published at the present time, if it were not of the greatest importance to put analytical chemists upon their guard; for but a few days ago an individual wrote to me, that he was estimating the phosphate of lime in a certain class of bodies by fusing them with carbonate of soda, which will certainly be productive of some error; and although it is to be regretted that our methods of arriving at phosphoric acid in analysis may be diminished by this fact, still it will only stimulate us to find out some other to solve this, one of the most difficult and annoying problems in analytical chemistry.—Silliman's *Journal*, Jan. 1845.

On the Separation of the Oxide of Cobalt from the Oxide of Manganese. *By* M. Clöz.

This process, which may be employed with advantage in separating a small quantity of oxide of cobalt contained in certain oxides of manganese, consists in treating the perfectly neutral metallic solution with an excess of the persulphuret of calcium or potassium. The sulphuret of cobalt dissolves entirely in the reagent; the sulphuret of manganese, on the contrary, is entirely insoluble.—*Journ. de Pharm.*, Feb. 1845.

On a new Test for Bile and Sugar. *By* Dr. M. Pettenkofer.

The phænomena about to be described, and of which an abstract was given in a former Number of this Journal (vol. ii. p. 468), were discovered by the author in studying the products of decomposition of the bile; the accuracy of this test depending upon several collateral circumstances relating to the purity of the reagents and use of proper proportions, we have deemed it necessary to notice these at greater length.

The author remarked that when ox-gall had been treated with sugar, and concentrated sulphuric acid was added until the precipitated choleic acid had begun to redissolve, the mixture became considerably heated, and the liquid assumed a deep violet tint, similar to that of hypermanganate of potash. It was at first considered that this remarkable alteration might depend upon the decomposition of the biliary colouring matter; but it was found equally to occur, nay even more evidently, with the bile which had been decolorized, and with pure biline obtained by Berzelius's method. All the attempts to separate the new product in an isolated state have hitherto completely failed. The author consequently confines his observations to the application of this phænomenon as a test (*a*) for bile (choleic acid), and (*b*) for sugar. The following is the method of proceeding:—A small quantity of the liquid supposed to contain the bile (if the substance be solid it must be treated with alcohol, and the solution evaporated) is poured into a test-tube, and two-thirds of the volume of sulphuric acid added by drops. The heat of the mixture must be kept below 144° Fahr., otherwise the choleic acid will be decomposed. From 2 to 5 drops of a solution of 1 part of cane-sugar to 4–5 of water are now added, and the mixture shaken. If choleic acid be present, the violet-red colour will appear more or less distinctly according to the quantity present. The following precautions are however requisite to be attended to:—1st, the temperature must not exceed that mentioned to any extent, otherwise the colour, although formed, will be again destroyed; 2nd, the quantity of sugar must not be too large, because the colour of the sulphuric solution will become dark brown, and sulphurous acid will be formed, whereby the violet-red colour may be concealed or destroyed; 3rd, the sulphuric acid must be free from sulphurous acid; 4th, if the fluid contain albumen, it is best to coagulate this previously, since albuminous solutions, although only when very concentrated and when heated with sugar and sulphuric acid, produce a similar colour. It could not be produced with mucous, nor with dilute albuminous solutions, which were always altered to a brown colour; 5th, a great excess of chlorides, although such is rarely found in animal bodies, converted the colour to a brownish red; 6th, if the bile be in very small quantity, the fluid should be carefully concentrated on the water-bath, extracted with alcohol, this also evaporated to a small volume, and the test applied to the cold solution. Sometimes an interval of several minutes is required for the production of the colour, especially when the sulphuric acid is added very slowly, and consequently a lower temperature is generated. In liquids, where the bile is in very small quantity, as in urine, secretions, &c., the author has found it requisite to make a spirituous extract, to evaporate this nearly to dryness on the water-bath, and then to transfer the moist residue into a watch-glass. When quite cold, sulphuric acid and a very small quantity of syrup are added, so that the temperature of the solution remains low. In the course of a few minutes, if the most minute trace of bile is present, the colour is produced. In this reaction, the grape-sugar, starch, or in fact any substance which is convertible into grape-sugâr by sulphuric acid, may be substituted for the cane-sugar. The same result was obtained with the bile of man, the fox, dog, ox, pig, fowl, frog and carp. The author concludes from this, that the bile of all the Vertebrata agrees chemically in containing choleic acid combined with soda.

By means of this test the author detected bile in the urine of a patient afflicted with pneumonia. The fæces of a healthy man, when extracted with spirit and treated as above, did not yield the slightest reaction, whilst on adding a little bile previously to the fæces it was perfectly developed. In the stools produced by calomel, several observers have remarked that the green or yellowish-green colour is converted into red by treating them with mineral acids; by applying the sugar and acid, the same phænomena are produced. In all cases of diarrhœa, bile is found in the stools. The author imagines that the alterative effects of purgatives might be thus explained, by their carrying off the bile as fast as it is secreted, consequently preventing its absorption.

Concentrated muriatic acid heated with bile and sugar likewise produces a red colour, but this is much lighter and less beautiful than with sulphuric acid.

This test may also be adopted for the detection of sugar. If sugar be suspected in a liquid, urine for instance, an aqueous solution of ordinary ox-gall is gradually treated with sulphuric acid, until the precipitated choleic acid is again redissolved; the suspected urine is then added, whereupon the violet-red colour is produced. As the quantity of sugar present is usually small, it is best previously to concentrate it. To detect bile in blood, the albumen is first separated by ebullition with spirit, and the concentrated fluid treated as above. If this test is used for sugar, the absence of starch must be previously proved by iodine.

The author thinks his test better than Trommer's in the examination of blood and urine, both because it acts more rapidly and delicately, and because its action is uninterrupted by the ammoniacal salts of the urine, the free ammonia of which retains the proto- and peroxides of copper in solution until it is completely expelled by boiling, whereby the reduction of the oxide of copper may be readily effected by other substances. Pure manna and gall, when treated as above described, afford no trace of the peculiar reaction. It is thus easy to detect grape-sugar in manna.—*Ann. der Chem. und Pharm.*, Oct. 1844.

On Pettenkofer's new Test for Bile. By Dr. W. J. Griffith.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,

Should you consider the following remarks on M. Pettenkofer's test sufficiently interesting, you will oblige me by inserting them.

Your obedient Servant,
J. W. Griffith, M.D.

The test proposed by M. Pettenkofer is an exceedingly valuable one, and when applied in conjunction with that of the well-known reaction of acids on the colouring matter, will serve to supply what has hitherto been a desideratum, viz. a ready means of recognising the peculiar biliary and the colouring matters in animal fluids. In a case of jaundice, which I had an opportunity of examining, the urine was of a golden-yellow colour, slightly albuminous, and not containing more than the ordinary proportion of other ingredients; on the addition of nitric acid, the green and red tints were well-marked, the former exceedingly intense; but on applying the sulphuric acid and syrup as recommended, and adopting the requisite precautions, not the slightest evidence of the presence of the choleic acid could be obtained, nor on analysis by the ordinary methods was I more successful; I therefore consider this a well-marked example (and I have since found another) wherein the biliary colouring matter only was separated with the urine. In examining a number of healthy urines, with a view to test the validity of this purple colour with the acid syrup, I was occasionally much perplexed by finding, on the addition of the acid alone, that the urine assumed a reddish-purple colour, closely resembling the characteristic one, and the subsequent addition of the syrup produced no alteration, thus rendering the test apparently inapplicable. This alteration arises from the action of the acid on the colouring matter of the urine, and may always be distinguished from the true test-colour by allowing the mixture to repose; the choleic purple is permanent, whilst the other is gradually changed to a brown colour. The experimenter will find that where the bile is in very small quantity, a considerable excess of acid will frequently detect it when a smaller quantity will not; the syrup however must be added in very small quantity.

On the Detection of the Constituents of the Bile in Urine.
By M. Schwertfeger.

The author recommends precipitating the urine with basic acetate of lead, as the reaction with nitric acid, when small quantities only are present, is not perceptible. When bile is present, a yellow precipitate is formed with the basic acetate of lead, from which a green solution is obtained with alcohol containing some sulphuric acid, and from which pure alcohol extracts, with the assistance of heat, bilate of lead. It is impossible to conclude, as to the presence of bile, from the colour of the urine, since similar colours may likewise originate from other causes.—*Jahrb. für Prakt. Pharm.*, ix. p. 375.

CHEMICAL PREPARATIONS.

Acetate of Iron as a Remedy for Arsenical Preparations.

The hydrated peroxide of iron is of admitted efficacy in cases of poisoning with uncombined arsenious or arsenic acid; but according to the experiments of Duflos, it is quite ineffectual when these acids are combined with bases, as for example, Fowler's solution, or arsenite of potash, or arseniate of potash, which last is frequently employed in calico-printing, and is consequently easily procured.

In the uncertainty in which the practitioner may be placed as to whether the arsenical poison be free or combined, it is very important to administer the oxide of iron in such a form as to produce a favourable result: to this end it is convenient to employ the peracetate of iron.

This compound may be prepared by adding to the hydrated peroxide of iron obtained from the decomposition of four parts of liquid perchloride of iron, three parts of acetic acid of density 1·06, and sufficient water to make up 16 parts.

This liquid, which is a solution of peracetate of iron with excess of base, precipitates arsenious and arsenic acid from all their solutions, either free, or combined with any base; 500 grains of it are sufficient to decompose 1880 grains of Fowler's solution.

This result demonstrates that liquid peracetate of iron merits preference in cases of poisoning by arsenical compounds. It should be remembered that its power is more rapid in proportion as it is more diluted with water; besides which, large dilution prevents all irritating action of the acetic acid set free.—*Journ. de Ch. Méd.*, Novembre 1844, as inserted in the *Philosophical Magazine.*

[The mode of preparing the above compound is not very clearly stated, for the strength of the liquid perchloride of iron is not given. It may be presumed that peracetate of iron mixed with peroxide is to be employed; the degree of excess of the latter is of little consequence, and the strength of the peracetate is limited by the employment of four parts of acetic acid of 1·06 made up to 16 parts with water, and this, it appears, is to be largely diluted before exhibition. —Ed. *Phil. Mag.*]

On Officinal Sulphur præcipitatum. *By* Dr. Otto *of Brunswick.*

The officinal precipitated sulphur varies much in external appearance; sometimes it is of a pure yellowish-white, sometimes of a more or less dirty grayish or even brownish-white. It could not be accounted for why the former colour was peculiar to the preparation obtained from the sulphuret of calcium, and the latter to that prepared from the ordinary sulphuret of potassium. From some experiments which have been made in my laboratory, it has resulted that the dirty-coloured appearance of the latter preparation is owing to certain impurities, especially to an amount of sulphuret of copper. Ordinary potash (always or nearly so) contains copper; this passes into the purified potash, and from this into the sulphuret of potassium, which on saturation with acids deposits sulphuret of copper. Carbonate of potash prepared from tartar yields a yellowish-white *sulphur præcipitatum*, like the sulphuret of calcium. A preparation thrown down from ordinary sulphuret of potassium retains its dirty colour even when fused with pure carbonate of potash, and again precipitated with acids, but the dirty colour disappears immediately on pouring chlorine water on it (in the dry state, for when recently precipitated it is converted by it entirely into sulphuric acid), and the copper may be detected without difficulty in the solution, and likewise in the residue left on incineration. If some pure carbonate of potash, prepared from tartar, be fused with sulphur, with the addition of some oxide of copper, a sulphuret is obtained, from which acids throw down a more or less brownish-white precipitate. Sulphuret of iron likewise appears to occur constantly in the preparation obtained from ordinary sulphuret of potassium. It appears therefore absolutely requisite that in future the sulphur præcipitatum be prepared solely from the sulphuret of calcium.—*Pharmaceut. Central Blatt*, Jan. 1, 1845.

On the Purification of commercial Nitric Acid.
By M. C. Barreswil.

Commercial nitric acid almost always contains hydrochloric acid, which it is frequently important to separate. The usual method for effecting this consists in adding a slight excess of nitrate of silver to the nitric acid, and distilling. However convenient this process may be, it is always employed with regret; for although the loss in silver is theoretically naught, it practically amounts to a pretty considerable quantity in a laboratory in which much pure acid is employed. For this reason I thought it might be useful to indicate a very simple method for obtaining pure nitric acid without the employment of nitrate of silver. It consists in distilling the commercial acid, and setting aside the first portions, amounting to from one-fourth to one-eighth, according to the quality of the acid employed. This first product is very impure, and may be turned into nitro-muriatic acid; that which passes over subsequently is absolutely pure.—*Journ. de Pharm.*, Feb. 1845.

On the Adulteration of the Sulphate of Quinine. By M. PELLETIER.

The sulphate of quinine is easily adulterated with salicine, although it does not crystallize in the same form. When the sulphate of quinine is mixed with one-half or only one-fourth of salicine, the reaction of concentrated sulphuric acid is sufficiently decisive to enable one to conclude as to the sophistication; but if there be but one-tenth in the mixture, the sulphuric acid does not acquire the bright red colour which characterizes pure salicine; in this case the liquid resembles sulphuric acid coloured by some particles of carbonized vegetable matter. To be able to pronounce positively, it is therefore requisite to isolate the salicine, and to obtain the above reaction in all its force.

I added 12 decigrms. of concentrated sulphuric acid to 2 decigrms. of sulphate of quinine sophisticated with one-tenth of salicine; the salt was dissolved and coloured brown. I then added 25 grms. of distilled water, when the brown colour disappeared, and the salicine remained white and suspended in the liquid. The salicine is not dissolved by this acid solution of sulphate of quinine. I then filtered and collected on a watch-glass a very bitter white powder, which gave the bright red reaction with cold concentrated sulphuric acid.

If from 50 to 60 grms. of water be added the liquid remains opake, apparently without any precipitate resulting; but after some time one is observed to form with the gelatinous appearance of a precipitate of hydrate of alumina, which it is far more difficult to collect. It is consequently important to add the water in small portions, and to cease when it is seen that the precipitate separates with facility.—*Journ. Chim. Med.*

Decomposition of the Tincture of Iodine.

M. Herzog draws attention to the fact, that tincture of iodine should not be kept very long, and that more attention should be paid to its condition, since owing to the action of the iodine on the alcohol it is decomposed, with formation of hydriodic acid, iodic æther, and probably some other products. Tincture of iodine is very easily tested, by shaking it with an excess of pure copper filings until it is entirely decolorized. The copper collected on a filter indicates directly by its increase in weight the quantity of iodine; but the solution contains, notwithstanding free acid, no copper, and the decomposition which has taken place is evident from the æthereal smell and the acid reaction. Perchloride of mercury produces in it a yellowish-white precipitate, which subsequently becomes red; and nitrate of ammonia and silver, a yellow flocculent precipitate, which becomes gray in water at 212°. On evaporating the filtered solution, red acrid vapours are given off; if it be saturated with potash, evaporated, and the residue heated to a faint red heat, a vapour of a peculiar odour is disengaged, some carbon separated, and the residue effervesces with acids.—*Archiv der Pharm.*, xc. p. 37.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Dec. 2, 1844. (Robert Porrett, Esq., Treasurer, in the Chair.)

"On a means of detecting Quinic Acid," by John Stenhouse, Ph.D.

As it is a point of considerable importance to be able to distinguish the true Cinchona barks from the spurious, Dr. Stenhouse offers, in the present communication, a means of effecting this through the medium of the quinic acid, which is always present in the genuine Cinchonas. The process proposed consists in converting the acid into quinone by means of sulphuric acid and peroxide of manganese, and submitting the mixture to distillation, when the quinone, with its strongly-marked characteristic properties, passes over. Less than ¼ oz. of the sample of bark is sufficient for the trial. In operating on spurious barks, the alburnum of the *Pinus sylvestris*, the latter being stated, on the authority of Berzelius, to contain a ½ per cent. of quinate of lime, and also in cases when quinic acid is said to be associated with gallic acid,—the author could not trace its presence, even when operating on 1½ lb. of the material, although on adding 2 grs. of quinate of lime the quinone was immediately traceable. The author also states that the presence of an alkaloid may be readily detected by macerating the bark in dilute sulphuric acid, treating the precipitate thrown down by carbonate of soda with caustic soda or potash, and distilling; quinoiline will pass over, which is easily recognised by its peculiar characters and properties. The exact nature of the alkaloid is to be subsequently ascertained.

"Remarks upon Chloranil," by Dr. Augustus William Hofmann, Assistant in the Giessen Laboratory.

Chloranil was first obtained by Erdmann when studying the action of chlorine upon indigo. He represents it by the formula $C^6 Cl^2 O^2$. Laurent considers that its equivalent should be $C^{12} Cl^4 O^4$.

Erdmann obtained chloranil by passing a stream of chlorine through an alcoholic solution of chlorisatine or bichlorisatine; but this process is circuitous, and yields very little chloranil, other products resulting and in larger quantity. Fritzsche formed chloranil by the continued action of chlorate of potash and hydrochloric acid upon aniline. Dr. Hofmann confirmed his statements, and observing the relation between the aniline and the phenyle series, endeavoured to obtain chloranil from the latter group of bodies, and with success, chloranil being often formed as one of the last results of decomposition of organic substances under the united influence of chlorine and oxygen. By means of hydrochloric acid and chlorate of potash Dr. Hofmann first obtained chloranil from hydrate of phenyle; and he found an aqueous solution or a watery extract of coal-gas naphtha, which contains both aniline and hydrate of phenyle, preferable to a solution in alcohol.

To purify chloranil, it must be washed with water and crystallized from alcohol. Alcohol dissolves it when hot, and deposits it on cooling; it is more soluble in hot æther, but separates from either of these solvents in golden-yellow scales; volatile at 302° F., but subliming completely at 410° to 428° F. The identity of the substance obtained from the hydrate of phenyle with Erdmann's chloranil was proved by the results of several analyses.

In the action of hydrochloric acid and chlorate of potash upon hydrate of phenyle, other substances are formed before chloranil. On interrupting the decomposition, and examining these bodies, they proved to be chlorophenussic and chlorophenissic acids. These acids are convertible into chloranil. Moreover, Laurent's nitrophenessic and nitrophenissic (carbazotic) acids are in the same way converted into chloranil.

Chrysolepinic acid of Schunck is also transformed into chloranil by the same agency; and it was found that several bodies in the salicyle series, as salicylous acid, salicylic acid and nitrosalicylic acid (indigotic acid or anilic acid), under the influence of hydrochloric acid and chlorate of potash, decompose and yield chloranil.

Benzoic acid, although identical in composition with salicylous acid, does not yield chloranil; nor do nitrobenzoic acid, benzine, nitrobenzide, binitrobenzide or hydruret of benzyle.

Salicine (the basis of the salicyle series), being soluble in water, seems to be the fittest substance for yielding large quantities of chloranil. Salicine and chlorate of potash must be dissolved in boiling water, and small quantities of hydrochloric acid added at intervals; one of the results of the ensuing decomposition is chloranil.

In conclusion, Dr. Hofmann calls the attention of chemists to the chlorate of potash as an oxidizing agent applicable to organic chemistry; he has heated *quinone* with it and hydrochloric acid, and found it readily convertible into chloranil. Dr. Hofmann proposes to pursue the subject, and to trace the relations of quinone and aniline.

"On the Decomposition of Oxides and Salts by Chlorine," by Alexander W. Williamson.

Mr. Williamson states the views of the nature of these compounds entertained by Berzelius, Serullas, Balard, Millon and Gay-Lussac. He then relates some experiments he made in order to become better acquainted with hypochlorous acid. The first point he endeavoured to ascertain was the quantity of chlorine with which a base is capable of combining; he found the average of three experiments made upon barytes gave 9·57 barytes, 8·22 chlorine, or nearly 2 equiv. The result of further experiments appeared to prove that the 2 equiv. of chlorine were combined, one equivalent with the barium, the other with the oxygen, forming a mixture of chloride of barium and hypochlorous acid. Upon endeavouring to purify this mixture from all free chlorine, he observed a remarkable decomposition of the hypochlorous acid, which takes place on exposure to daylight, and more rapidly in sunshine, and still more in a water-bath, in which chlorine is given off and chlorate of barytes is formed. Having found that, on heating barytes with chlorine, the decomposition takes place in so simple a manner, he next tried the alkalies; the average of two experiments with potash gave 590 potash, 677 chlorine, or 2 equiv. of potash to 3 of chlorine. Mr. Williamson considers the cause of the potash combining with a smaller quantity of chlorine than the barytes to arise from the stronger affinity of potash for chloric acid, which causes a decomposition of the hypochlorous acid, by which chloric acid is formed and chlorine set free.

Upon treating carbonate of potash with chlorine in a similar manner, he obtained a mixture of hypochlorous acid and chloride of potassium, which upon heating converted part of the chloride of potassium into chlorate of potash. He then obtained the same result by treating a solution of chloride of potassium with hypochlorous acid, and heating them over a water-bath.

An aqueous solution of hypochlorous acid has a great tendency when heated to form chloric acid, setting free chlorine. When chloride of potassium is present, this chloric acid, in the moment of its formation, decomposes the chloride, setting free its chlorine, the metal oxidating itself at the expense of the hypochlorous acid. It appears that by treating carbonates with chlorine, hypochlorous acid may be obtained in a free state and be quietly distilled over, and therefore might be available for obtaining this acid for use. Mr. Williamson recommends in preference to use carbonate of lime suspended in water as the most available for this purpose.

Mr. Williamson then tried the action of chlorine and different other salts with stronger acids, with nearly similar results as to decomposition. The salts tried were tribasic phosphate of soda, common phosphate and bibasic pyrophosphate of soda, sulphate of soda, sulphate of peroxide of iron, sulphate of zinc, manganese and lead, chromate of potash, alum, borate of soda, nitrate of potash and acetate of lead. Concluding from analogy that similar decomposition might be produced by cyanogen, he treated tribasic and common phosphate of soda with this gas; both were decomposed.

He concludes the paper by directing the attention of the manufacturers of chloride of lime to the production of an aqueous solution of hypochlorous acid on a large scale, which might be most œconomically prepared by acting upon sulphate of soda with chlorine, and distilling off the acid of a strength to contain in a given weight more bleaching power than the well-known lime compounds.

"On some of the Substances which reduce Oxide of Silver and precipitate it on Glass in the form of a Metallic Mirror," by John Stenhouse, Ph.D.

Aldehyde, the saccharic, salicylic and pyromeconic acids have been for some time known to precipitate metallic silver from its ammonio-nitrate solution with the assistance of heat, the metal forming a brilliant coating of various shades on the inner surface of the containing vessel. Since Mr. Drayton's patent process has been laid before the public, Dr. Stenhouse has experimented on this subject, and finds that a great number of substances will produce the same effect as the alcoholic solutions of the oils of cloves and cassia; the acid oil of pimento in a few minutes, and grape-sugar slowly in the cold; and if assisted by heat, cane-sugur, gum-arabic, starch, phloridzine, salicine; and if the solutions be very concentrated, oils of laurel, turpentine, and the resin of guaiacum. The following substances produce no effect:—the neutral portion of the oil of pimento, oil of rhodium, cinnamic, benzoic, meconic, komenic, tannic and pyrogallic acids; gum elemi, benzoin and olibanum, and glycerine.

Dr. Stenhouse states, that ingenious as Mr. Drayton's patent process certainly is, it labours under a very serious inconvenience. In the course of a few weeks the surface of the mirrors formed by his process becomes dotted over with small brownish-red spots, which greatly injures their appearance. The cause of the spots seems to be this—that the metallic silver while being deposited on the surface of the glass carries down with it mechanically small quantities of a resinous matter, resulting most probably from the oxidation of the oil. This resinous matter, which is interposed between the glass and the silver, in the course of time begins to act on the metallic surface with which it is in contact, and to produce the small brown spots already mentioned. If an excess of the essential oils is employed to precipitate the silver, the metallic mirror is much darker, and gets sooner discoloured than usual. No doubt the alcohol present in the solution keeps up much of the resinous matter; still a little of it is almost always deposited on the silvered surface, and acts in the injurious way described *.

"On the Decomposition of Salts of Ammonia at ordinary Temperatures," by Dr. Henry Bence Jones.

The author's attention was first drawn to the subject by observing that blue litmus-paper dipped into urine which was decidedly alkaline became distinctly red upon drying in the air, and that a similar effect could be produced at pleasure with healthy urine, to which ammonia in great excess had been added. The change of colour of the litmus was ultimately traced to a slight decomposition undergone by all ammoniacal salts, when their solutions are allowed to evaporate either into the air or into a vacuum. The acetate, oxalate, hippurate, benzoate, nitrate, sulphate, hydrochlorate, hydrosulphate, phosphate and carbonate, dissolved in water and mixed with excess of caustic ammonia, became very distinctly acid during evaporation. It is probable however that the actual amount of decomposition undergone is exceedingly small, the effect ceasing as soon as a very small portion of acid has become free.

Dec. 16*th*, 1844. (The President in the Chair.) "On some Specimens of the Green Glass of Commerce," by Robert Warington, Esq.

The principal subject of this communication was a green glass which has lately appeared as an article of commerce in the form of

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* It is stated by Mr. Drayton in the 'Pharmaceutical Journal,' that the brown spots noticed by Dr. Stenhouse occur only when the oil employed is old and unfit for use. It is also necessary to protect the back surface of the silver with a varnish, which by effectually excluding the air, or any other agent, which might act upon the metal, preserves it in its original brilliant state.—Ed. *Chem. Gaz.*

wine bottles. These are offered to the consumer, the wine merchant, at a lower price, and with the tempting recommendation that they will cause port wine to deposit its crust sooner and firmer than the bottles usually employed. On examination this property was found to arise from an excess of lime having been used in its manufacture, which had rendered the glass to a certain extent soluble in weak acids. Dilute sulphuric acid acted to such an extent as to form a crystalline deposit of sulphate of lime in the interior of a quarter of an inch in thickness, and this in its crystallization had burst the bottles in all directions.

"New ways in which Aniline is formed," by Drs. J. S. Muspratt and A. W. Hofmann.

It is well known that notwithstanding the progress made within the last few years in organic chemistry, the kind of decomposition which an organic body shall undergo when subjected to the action of powerful chemical agents can seldom or never be predicted beforehand. This arises from the great ignorance which yet prevails concerning the true constitution of these bodies. One very important fact, almost amounting to a general law, has however been observed, namely, that bodies possessing the *same composition*, but *very different constitution*, under the influence of powerful chemical agents, frequently give rise to *similar products*. Illustrations are readily found; thus the *draconic acid* of Laurent, when distilled with barytes, divides into carbonic acid and a pyrogen product, *dracole*; exactly the same change happens with an isomeric body of totally different constitution, *salicylate of methyle*; and experiments made by the authors in the laboratory of Giessen tend to the same point.

The *anthranilic acid* of Fritzsche, when distilled *per se* or with lime, gives carbonic acid and *aniline*; *salicylamide*, produced by the action of ammonia on salicylate of methyle, and a compound called *protonitrobenzoene*, generated by the action of nitric acid on a hydrocarbon extracted by M. Deville from tolu-balsam, are both isomeric with anthranilic acid. MM. Muspratt and Hofmann accordingly prepared both salicylamide and protonitrobenzoene, and submitted them to distillation with quicklime; the first yielded, among other products, a small quantity of aniline, the presence of which was demonstrated by its peculiar reaction with hypochlorite of lime; the second afforded the same substance, but in much larger quantity. These phænomena offer great interest, and promise by their extended study to lead to general conclusions of great value.

Jan. 6th, 1845. (Thomas Graham, Vice-President, in the Chair.) "Observations on the Decomposition of Metallic Salts by an Electric Current," by James Napier.

After alluding to his former paper on this subject, the author states that he has found, by observation of his every-day occupation in electro-plating, that the results are contradictory to the present received theory, "that there can be no irregularity of force in any part of a voltaic current, and that the decompositions dependent upon the current are always in definite proportions." Indeed there is no law which appears to him more definite than "that if a large positive and small negative electrode be used, there will be more dissolved from the former than is deposited upon the latter, and the converse." A series of observations and experiments are then detailed in proof of this position. Mr. Napier concludes by remarking, that from the details given it is evident that when electrodes are used which combine with the elements set free, the amount liberated at or combined with one electrode is but a measure of that liberated at or combined with the opposite electrode; but the element liberated at the negative is a proper measure of the amount of electricity passing through the electrolyte if it be composed of single equivalents, all electrolytes being decomposed as if they were constituted of two elements; again, that the stronger the solution or menstruum employed is, so comparatively is there more dissolved from the positive electrode; this may result from its solubility in the menstruum, but he considers that the electricity influences this action. Whether this arises from an exalted affinity excited between the metal and the negative element of the electrolyte he does not venture to assert, but it favours the argument that chemical action is the result of electricity rather than the converse.

Jan. 20th, 1845. (The President in the Chair.) "On the distilled Waters of the Pharmacopœia," by Robert Warington, Esq.

This paper consists of an examination of the medicated waters of the Pharmacopœias of this country, prepared either by distillation or through the medium of carbonate of magnesia, and was commenced in consequence of a fact noticed by the author, that water containing a very small quantity of spirit became acid by long exposure to the air. On experiment it was found that many of the distilled waters underwent the same change, and evidently from the small quantity of spirit ordered to be introduced, as other portions of the same waters, to which no spirit had been added, did not in any case undergo this change. Many of the foreign Pharmacopœias also direct the simple distillation of the material with water without any spirit. In the instances where carbonate of magnesia is employed, the author proves that its action is only mechanical, to subdivide the oily particles, and thus expose a greatly extended surface to the solvent action of the water. It is also shown experimentally, that of all substances carbonate of magnesia is about the worst that can be employed; and this arises not from its forming soluble compounds with the oily acids, as is generally supposed, but from its being dissolved to an injurious extent in the distilled water employed: he therefore proposes the substitution of the Cornish porcelain clay, finely powdered silica, glass or pumice stone, as a medium for the mechanical subdivision of the essential oil.

PATENTS.

Patent granted to Charles Low, Kingsland, Middlesex, *for certain Improvements in the making or manufacturing of Iron and Steel.*

These improvements consist in the use of the following materials in the manufacture of malleable iron and steel, viz. oxide of manganese, plumbago, charcoal, and nitrate of potash, soda or lime (preference being given to the ordinary saltpetre of commerce).

The above materials are mixed in the proportion of 42 lbs. of oxide of manganese, 8 lbs. of plumbago, 14 lbs. of wood charcoal, and 2 lbs. of saltpetre; and 66 lbs. of this mixture are thrown into the blast furnace with each charge of ore likely to produce 480 lbs. of metal. It may be introduced with equal advantage into the puddling furnace when the pig iron is in a fused state, by throwing a few pounds of it upon the surface of the metal every few minutes, and thoroughly incorporating it therewith by stirring, until the 66 lbs. have been used, or until the metal begins to thicken, or "come to nature;" it is then balled, &c. as usual. The mixture may also be employed, in like proportions, for improving the quality of iron in the cupola or other furnace used by founders.

Another part of this invention consists in the application of the mixture to the manufacture of cast steel from malleable iron, which has been made by the above processes. For this purpose 2 or 3 lbs. of the mixture are added to every 30 lbs. of steel, when in the melting-pots, during its conversion into casts teel. Or the object may be more immediately effected by adding the ingredients (in the same relative proportions as for steel) to the malleable iron, made as above; and then the application of a moderate heat will fuse the iron in contact with the mixture, and immediately convert it into cast steel.

The mixture should be ground previous to use; for the puddling furnace, it should be brought to a moderately fine powder, and the patentee prefers to introduce it at the top of the furnace through a hopper or tube, which will spread it more evenly than if distributed by hand through the furnace door; for the blast furnace and cupola the powder may be in a coarser state.—Sealed May 25, 1844.

Patent granted to Charles Watterson, Manchester, Lancaster, *for Improvements in the Manufacture of Soap.*

These improvements in the manufacture of soap consist chiefly in the peculiar method or process of mixing or combining the oil or fatty matters employed with caustic soda, and in subsequently adding water, for the purpose of converting such mixture or produce into soap. By means of this invention, it is stated that the soap is rendered of a purer and more efficient nature, and also that a considerable œconomy of time is effected in the operation, the soap being sufficiently hard for sale or use in the course of a few hours, instead of several days, as is the case under the ordinary process of manufacturing. The ingredients employed are nearly the same as in common use, namely,—1st, all animal and vegetable oils, either mixed or separately; 2nd, liquid caustic soda, of the strength of 22 per cent.; 3rd, water as free from earthy salts or metallic oxides as can be obtained.

The improved process of manufacture is as follows:—To make half a ton of soap, put in a pan 7 feet in diameter and about 2 feet deep, 784 lbs., say, of raw palm oil; as soon as the same has become fluid add gradually 407 lbs., more or less (according to the quality of soap required), of liquid caustic soda, of the strength above specified, taking care to mix the ingredients thoroughly by an instrument adapted to the purpose. The heat must then be increased, and the mixture constantly moved about, to prevent it from caking on the bottom of the pan. After continuing the operation, and at the end of 3 or 4 hours, the mixture assumes a whitish appearance, and by continuing the heat the whole of the aqueous part is entirely evaporated, and the mass reduced to a perfectly dry state. The heat is now increased, and in a short time the mass becomes again of a liquid form, and changes to a brownish colour, which indicates that the combination of the oil with the alkali is effected. The fire is then speedily withdrawn, and the stirring is continued so long as any fear of scorching is apprehended. When this is over, the first part or day's operation is concluded, and the pan may be locked up, for the purpose of cooling, or for the night, by the excise-officer. The second part of the operation consists in breaking up or grinding the product, now in a solid form, into a state of powder. To this add 45 gallons of pure water (or slightly more or less), and thoroughly agitate the mixture for about half an hour. The heat is then applied, and the contents of the pan raised to the boiling-point, and kept so for about 3 hours, during which time the stirring and agitation must be continued. So soon as the evaporation has been carried to the desired extent, and the soap appears of a proper consistency, it is allowed to cool gradually. The whole contents of the pan (no leys or waste accruing from the operation), while yet in a liquid state, are now put into the ordinary frames and left to cool. The day following, the contents of the frame will be found hard enough for cutting in the usual way; and as soon as cut up the soap is in a fit state for sale and use.—Sealed May 8, 1844.

Patent granted to Benjamin Brunton Blackwell, Newcastle-upon-Tyne, *and* William Norris, Exeter, *for an Improvement in coating Iron Nails, Screws, Nuts, Bolts, and other Articles made of Iron, with certain other Metals.*

In coating iron with copper by electro-deposition, it is found that the iron is liable to be corroded, and that frequently, either during the operation or afterwards, an oxide of iron is formed upon the article beneath the copper coating. To prevent the articles from being thus injured is the object of the present invention, which consists in case-hardening, or coating with lead or an alloy of lead, nails, screws, nuts, bolts and other articles, made of iron, previous to coating them with copper by electro-deposition.

The case-hardening may be performed by any of the ordinary methods; the mode adopted by the patentees consists in removing from the surface of the articles any scale that may adhere thereto, and then placing them, with some parings of hoof or horn or bone-dust, in a crucible or iron box, well luted, and subjecting them to a red heat; the articles being removed as soon as a very thin film of case-hardened surface is obtained.

The iron articles may be coated with lead, or an alloy thereof, by first cleaning their surface, and then dipping them into the molten metal, in the same manner as is practised for coating iron with tin. The alloys of lead preferred by the patentees are two in number; the first is formed by the addition, to any given quantity of lead, of from one-fifth to one-tenth of tin; and the second consists of 15 parts of lead, 2 of tin and 1 of antimony.

After receiving this first coating, the articles are ready to be placed in a solution of copper, and in the circuit of a galvanic battery; this should be done while the articles are yet hot from the first operation, and the battery should be kept at a temperature between 80° and 100° Fahr.—Sealed Feb. 21, 1843.

Patent granted to Andrew Kurtz, Liverpool, Lancaster, *for certain Improvements in Apparatus to be employed for drying, evaporating, distilling, torrefying and calcining.*

This invention of improvements in apparatus to be employed for evaporating, distilling, torrefying and calcining, consists in the application and employment of metallic pipes or tubes, for the passage of fire and transmission of heat over the upper surface of the pan or vessel in which the substance or liquid submitted to such or similar operations is contained. These metallic pipes or tubes are to be placed side by side, in a range or series, over the top of the evaporating pan or vessel; and as the flame and heat are conducted into and passed through them, instead of acting directly on the surface of the substances under operation, as commonly done, the several operations of drying, evaporating, distilling, torrefying and calcining, may be performed in a much more perfect and œconomical manner. The pipes or tubes employed for this purpose are preferred to be of cast iron, and, for operations where great heat is required, of a circular or oval form (the heat for such operations should never exceed 1200° Fahr.); but the pipes may be made of other metals and forms if found practicable.—Sealed Feb. 14, 1844.

THE CHEMICAL GAZETTE.

No. LVIII.—March 15, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Combinations of Bismuth, with Observations on its Atomic Weight. By M. Heintz.

It is well known that the oxide of bismuth was first considered to be composed of 1 atom of metal and 1 of oxygen; subsequently, on account of the specific heat of the metal, it was considered to consist of 2 atoms of metal to 3 of oxygen; this view prevailed until Stromeyer's analysis of the superoxide of bismuth, when the former view of the composition of the oxide, of 1 atom of metal to 1 of oxygen was again generally admitted. The recent experiments of Werther on a new sulphuret of bismuth*, and especially those of Arppe, communicated by Berzelius, again speak in favour of $Bi^2 O^3$. The author has prepared Werther's sulphuret of bismuth, and found it to contain 13·72 S, 86·20 Bi, which agrees exactly with Werther's statement. In a memoir contained in the Proceedings of the Glasgow Philosophical Society for 1842, Dr. Thompson has admitted, besides the oxide, a suboxide, $Bi^2 O$, and an acid, $Bi^2 O^5$. The suboxide, which is said to be obtained by fusing the metal for some time exposed to the air and agitating, is however only a mixture of metal and oxide; for if bismuth be separated as a fine powder by zinc in the moist way, this combines with far more oxygen from the atmosphere, even below the fusing-point, than required by the above formula. The acid Thompson prepared by means of hypochlorate of soda, and washed it with acetic acid; he ignited the dried acid, and considered the loss as oxygen; the author has convinced himself that acetic acid remains in the substance prepared in this manner. He has succeeded in proving, by the preparation and analysis of the superoxide of bismuth, by the composition and behaviour of several of the salts, that the oxide is $Bi^2 O^3$, and the equivalent of the metal consequently 1330·377.

Suboxide and Protochloride.—When oxalate of bismuth is heated to 392°, carbonic acid escapes, and the residue is merely a mixture of metallic bismuth and carbonate of bismuth. It is just as impossible to obtain a protochloride of bismuth; the dry chloride does not act, even at a red heat, on metallic bismuth; heated in a current

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* Chem. Gaz. vol. i. p. 204.

of hydrogen, it sublimes unaltered, and only when the gas is not free from air or sulphuretted hydrogen, is some basic chloride or sulphuret of bismuth formed. Metallic bismuth is scarcely attacked by dry muriatic acid gas; Werther's sulphuret of bismuth yields a mixture of chloride of bismuth with some sulphuret, &c.

Superoxide of Bismuth (bismuthic acid).—According to Berzelius's Manual, Arppe prepared this combination in the following manner:—Nitrate of bismuth is dropped into a solution of caustic potash, when a very finely-divided hydrated oxide of bismuth is precipitated, which when the precipitation has terminated is boiled with the excess of potash, well-washed, and then while still moist boiled with a solution of hydrate of potash so concentrated that on cooling it deposits crystals. Into this warm mixture a current of chlorine is passed, which is immediately absorbed with evolution of heat; if the gas is passed in rapidly, a blood-red mass of a beautiful colour is obtained in a very short time. The clear liquid is likewise of a red colour. The undissolved red mass is freed by edulcoration from the mother-ley; but it is impossible to wash out the entire amount of alkali, for even when the washing was continued for a week what passed through was still alkaline. The red body moreover contains chlorous acid. If it be digested gently with dilute nitric acid chlorous acid is disengaged, while the potash combines with the nitric acid. The insoluble body is of a dark red colour, and consists of oxide of bismuth combined with bismuthic acid. If it be washed, and then digested further with nitric acid sufficiently strong to dissolve bismuth, the oxide is extracted and the acid left behind, which is then washed and dried, and so forms hydrated bismuthic acid.

M. Heintz could never obtain a red colour, however often he passed chlorine through a concentrated solution of potash, in which oxide of bismuth was suspended; the pale yellow colour of the oxide passed either into a dirty gray or into an ochre colour, according as the solution of potash was more or less concentrated, and the clear liquid always remained colourless. The gray precipitate was difficult to free from chlorous acid by washing, and only imperfectly; the ochre yellow, on the contrary, entirely, although it required time. It is therefore necessary, in the preparation of the superoxide of bismuth, to employ the solution of caustic potash so concentrated, that even after being mixed with the moist oxide of bismuth it solidifies on cooling. The chlorine should not be passed through the solution of potash until it is no longer alkaline. In this case an ochre-yellow powder is always obtained, which is easily purified from all chlorine by washing with distilled water, presupposing the hydrate of potash employed to have been pure.

In the washing of this ochre-yellow powder, it almost always happens that when the caustic potash is nearly removed, the precipitate becomes so minute that it is a long time before it is wholly deposited, and very easily passes through the filter. In such cases it is best to let it quietly subside for some days, to pour off the still turbid supernatant liquor, and then to bring it on to a filter and wash it further.

The ochre-yellow powder thus obtained contained potash, water, oxide and superoxide of bismuth. The absence of any compound of chlorine, and also of chlorous acid, was ascertained by fusing a portion with pure carbonate of soda, boiling the melted mass, and adding some nitrate of silver to the fluid previously acidulated with nitric acid. When it is treated with nitric acid of 1·15 spec. grav. no hypochlorous acid is disengaged; and if it is not warmed no evolution of gas is perceptible. If the precipitate (which however should be perfectly washed, because any amount of chloride of potassium would give rise, on the addition of nitric acid, to the formation of hydrochloric acid, and would consequently cause the peroxide of bismuth to be decomposed) is digested very gently and repeatedly with nitric acid, it is possible to dissolve the whole of the potash and the oxide of bismuth, while the peroxide remains behind. In the washing it is well not to employ pure water, but at first a dilute acid, to which gradually more water is added, and then pure water, to prevent the precipitation of the basic nitrate of bismuth.

The superoxide obtained in this manner is of a dark brown-red in the moist state, but when dry forms a very minute woolly powder of the colour of the hydrated peroxide of iron. Muriatic acid dissolves it instantly, with considerable disengagement of chlorine. If the acid is dilute, basic chloride of bismuth immediately separates. Concentrated sulphuric acid likewise disengages oxygen, even without the assistance of heat. Dilute sulphuric acid dissolves it, but only after long boiling. By long boiling with nitric acid of 1·20, it is dissolved with evolution of oxygen; it dissolves immediately in cold nitric acid, when to the mixture a solution of sulphurous acid in alcohol is added. To test it for chlorine, it may be dissolved in nitric acid by means of this solution.

The method of analysis was as follows:—The powder, dried at 212°, was placed on a glass boat in a tube open at both extremities, and heated in a current of atmospheric air. The water contained in it was collected in a chloride of calcium tube and weighed. The glass boat with the remaining oxide was likewise weighed, and its loss, after subtracting that of the water, calculated as oxygen. The oxide of bismuth thus obtained was then heated to redness in the same tube in a current of hydrogen, and the oxygen determined by the water formed, which was collected in a chloride of calcium tube. To check the result the residuous metal was weighed, and finally examined for potash, but in vain, at least in the samples which had been washed with nitric acid:—

Bismuth ..	86·25	86·77	86·69	86·42	1	=	1330·377	86·93
Oxygen ..	13·75	13·23	13·31	13·38	2		200·000	13·07
							1530·377	

The ochre-yellow powder obtained on passing chlorine through a highly-concentrated solution of potash in which oxide of bismuth is suspended, consists of a mixture of oxide of bismuth with a compound containing superoxide, potash and water. The examination was made in the following manner:—The water and the oxygen constituting the superoxide were determined by igniting the substance in a current of atmospheric air free from carbonic acid. From this it was possible to calculate the quantity of the superoxide. The residue in the boat was dissolved in nitric acid, the oxide of bismuth precipitated with ammonia, and the potash contained in the filtered liquid determined as sulphate. Two quantities of this substance, prepared at different times, gave the following results:—

	I.	Oxygen.	II.	Oxygen.
Superoxide of bismuth......	72·54	9·48	85·70	11·20
Potash	7·23	1·23	8·30	1·41
Water	4·57	4·06	5·47	4·86
Oxide of bismuth..........	15·66		0·53	

Oxide of Bismuth.—For the preparation of the superoxide of bismuth, the author employed the yellow oxide which had been prepared by boiling nitrate of bismuth with hydrate of potash; when bismuth is precipitated with ammonia, the oxide obtained is, as is well known, white; this is the hydrate which does not lose its water by boiling, but if some caustic potash be added, and the whole evaporated, this precipitate likewise becomes yellow, a phænomenon long since known. Fremy gives a correct explanation of it, viz. that the hydrated oxide is deprived of its water by boiling with potash, just like the hydrated oxide of copper.

Chloride of Bismuth is obtained in the moist way when oxide of bismuth is dissolved in muriatic acid and evaporated to crystallization. But the crystals so obtained cannot be separated from the mother-ley sufficiently to render them fit for analysis. The author therefore passed dry chlorine over metallic bismuth, contained in a tube open at both ends, and applied heat when it had become filled with chlorine. The chloride of bismuth was collected at one place with the assistance of a spirit-lamp, the gas contained in the tube after cooling expelled by a current of air, and the tube then sealed both behind and in front of this place. It was now weighed, the chloride of bismuth washed out with water, and then the empty tube weighed, so that in this manner the quantity of the substance employed in the experiment could be determined. In the analysis the author evaporated the salt with pure caustic potash to within a small volume, filtered the separated oxide of bismuth, and precipitated the chlorine acidulated with nitric acid by nitrate of silver; but previously to applying this method to the quantitative separation of bismuth from chlorine, he convinced himself of its accuracy by previously boiling basic chloride of bismuth with potash, filtering and edulcorating the precipitate. As soon as the water passed off free from chlorine, the precipitate on the filter was tested for chlorine, of which it proved to be perfectly free. The results obtained were—

Bismuth	66·13	66·83	2	66·71
Chlorine	33·47	33·28	3	33·29

Chloride of Bismuth with Oxide of Bismuth.—The author analysed the basic salt precipitated from the dry chloride of bismuth by water, as well as that from a solution of oxide of bismuth in muriatic acid by dilution, and likewise that from a solution of nitrate of bismuth in nitric acid thrown down with a solution of common salt. All three possessed the same composition.

In the first analysis the substance was dissolved in nitric acid, the bismuth precipitated with sulphuretted hydrogen, the excess of which was removed by sulphate of copper, and the chloride then thrown down with nitrate of silver. In the other analyses the chlorine was determined by fusing the salt with carbonate of soda, extracting with water, and precipitating the liquid faintly acidulated with nitric acid. The oxide of bismuth was thrown down from the nitric solution by sulphuretted hydrogen, the sulphuret of bismuth obtained redissolved in nitric acid, and the oxide precipitated with carbonate of ammonia. The author also attempted to determine the quantity of water in some separate experiments, by ignition of the substance with oxide of lead. It is necessary, in this case, not to apply too great a heat, as otherwise some chloride of lead might readily be volatilized. The analyses agree with those of Jaquelain:—

Bismuth	79·64	79·31	79·89	6	79·64
Chlorine	12·25	13·24	13·28	3	13·25
Oxygen				6	5·99
Water		1·34	1·05	1	1·12

An anhydrous basic chloride of bismuth was likewise obtained in the dry way on subliming dry chloride of bismuth in a current of hydrogen, caused without doubt by a slight impurification of hydrogen gas with air. It consisted of—

Bismuth	80·33	6	80·55
Chlorine	13·48	3	13·40
Oxygen......................	6·19	6	6·05

Iodide of Bismuth.—When a mixture of finely-pulverized metallic bismuth is exposed with iodine in a current of carbonic acid to a high temperature, iodine at first sublimes, the glass tube becoming filled with the peculiar violet vapours. As soon as the excess of iodine has been expelled, a red-brown gas is obtained on the application of a higher temperature, which is deposited in the colder parts of the tube in the form of dark green spangles with metallic lustre; they may be readily freed from any admixture of iodine by a gentle heat. The salt is not altered by exposure to the air, and is dissolved by muriatic acid with a yellow colour; nitric acid likewise dissolves it, the liquid acquiring a dark colour from the separated iodine. On mixing it with water, hydriodic acid is extracted, and a basic tile-red salt remains undissolved. This most probably is the same which is formed when oxide of bismuth is thrown down from a solution by iodide of potassium and the addition of much water; a precipitate resembling in colour exactly the sublimed iodide of bismuth in the pulverized state is obtained, which acquires by washing with much water, and especially on boiling, a tile-red colour.

The iodide of bismuth was decomposed by boiling with hydrate of potash; it was, however, requisite to evaporate it to within a small volume, in order to combine the whole of the iodine with the potassium. Its composition was—

Bismuth	36·55	36·00	2	35·98
Iodine	63·94	63·13	3	64·02

Sulphate of Bismuth.—If oxide of bismuth be dissolved in sulphuric acid and evaporated to dryness, there appears at no time any hope of obtaining a constant combination. When the mass is strongly ignited, it becomes yellow, and then ceases to evolve sulphuric acid in large quantity; on cooling it becomes perfectly white. At a higher temperature it gradually loses more and more sulphuric acid, and the temperature at which it is formed is not far distant from that at which it again parts with sulphuric acid. The salt is however characterized as a peculiar combination by the property it possesses of becoming yellow when heated. To obtain it therefore of constant composition, it is requisite to expose the evaporated solution of bismuth in sulphuric acid to as gentle a heat as possible until the mass has become yellow. This salt is insoluble in water, but is dissolved by nitric and sulphuric acids. In the analysis the nitric solution was precipitated with carbonate of ammonia, and the sulphuric acid from the filtered liquid with chloride of barium. It consisted of—

Oxide of bismuth	84·88	86·59	1	85·52
Sulphuric acid	15·12	13·34	1	14·48

A sulphate salt is obtained in the moist way in acicular crystals by adding sulphuric acid to a solution of nitrate of bismuth in nitric acid. It separates in minute microscopic needles. On ignition it is converted into the above-mentioned salt with loss of water and sulphuric acid; it dissolves in nitric and in muriatic acids, but water decomposes it, extracting sulphuric acid from it, which dissolves a small quantity of the sulphate, and leaves behind a more basic salt. Its composition was found to be—

Oxide of bismuth	68·40	68·36	68·38	1	68·85
Sulphuric acid	23·79	24·16	24·12	2	23·30
Water	7·81	7·48	8·05	3	7·85

The salt is therefore basic, although it crystallizes from an acid solution. To obtain a neutral salt, the author added an equal quantity of sulphuric acid to a concentrated solution of nitrate of bismuth in a little nitric acid. In this case a salt separated, which likewise appeared under the microscope to consist of minute needles. It was freed as much as possible from the liquid and placed on a porous tile, which gradually absorbed the mother-ley. It contained on analysis—

Oxide of bismuth	67·60	68·25	68·14	1	68·85
Sulphuric acid	25·71	24·60	23·72	2	23·30
Water	6·69	7·15	8·14	3	7·85

It is therefore beyond a doubt that no neutral sulphate can be obtained in the moist way.

If the above salt be washed with water, a more basic salt is left, which it is however difficult to obtain of constant composition. It was not possible, even after frequent boiling, to prevent the wash-water from containing sulphuric acid. It gave on analysis—

Oxide of bismuth	80·09	79·77	1	80·30
Sulphuric acid	14·55	14·38	1	13·59
Water	5·36	5·85	2	6·11

Sulphate of Bismuth and Potash.—If to a solution of nitrate of bismuth in nitric acid a solution of neutral or bisulphate of potash be added, a precipitate is obtained, into the composition of which potash enters. Sulphate of soda does not afford a similar precipitate. This salt was found of different composition under various circumstances; the concentration of the liquid and the quantity of the sulphate of potash used appear especially to exert some influence. When a concentrated solution of the salt of bismuth and a large excess of sulphate of potash were employed, a salt of constant composition was obtained. Each of the following analyses was made with a separately-prepared quantity of the salt:—

Oxide of bismuth	36·42	36·30	37·44	35·79	1	38·26
Sulphuric acid	39·09	38·86	39·36	39·35	6	38·86
Potash	20·32		23·81	24·73	3	22·88

This salt contains therefore the neutral salt, which could not be obtained in an isolated state.

Precipitates were procured from dilute solutions of oxide of bismuth by means of sulphate of potash, which did not always exhibit the same composition. Twice only did the author obtain a salt whose compositions were approximatively in chemical proportions, viz.—

Oxide of bismuth	49·54	48·13	1	47·31
Sulphuric acid	31·79	32·05	4	32·04
Potash	17·28	16·96	2	18·85
Water	1·39	2·36	1	1·80

Nitrate of Bismuth.—The neutral salt is sufficiently known. All the methods hitherto employed for its analysis have failed in separating and determining the nitric acid. M. Heintz reduces the nitric acid to nitrogen, and measures it as such; the experiments gave a very satisfactory result. An apparatus for the disengagement of carbonic acid, which was so arranged as to yield a current of carbonic acid for 4 or 5 hours, was connected with a long chloride of calcium tube, and this with the drawn-out extremity of a combustion tube, which contained a narrower tube with the weighed quantity of the nitrate, and further on was filled with copper turnings, which had been heated to redness in the air, to remove organic substances, and in a current of hydrogen to reduce the oxide of copper formed. A weighed chloride of calcium tube was connected with this tube of combustion, and this with a tube curved in the form of an S, which dipped under mercury. The operation was now effected in the following manner:—In the first place carbonic acid was passed through the apparatus for about a couple of hours, the copper then heated to redness, and then a graduated bell-glass, filled partly with mercury, partly with a solution of caustic potash, placed over the mouth of the S-curved tube; the tube, with the substance to be examined, was gradually heated to redness. The following are the results:—

Oxide of bismuth..........	48·90	49·01	1	49·31
Nitric acid		33·76	3	33·83
Water	18·16	17·33	9	16·86

Numerous analyses of the *basic nitrate of bismuth*, executed according to the same method, gave the following results:—

Oxide of bismuth..	80·74	81·92	79·92	80·72	79·40	1	78·96
Nitric acid	15·10	15·34	17·85	17·09	17·78	1	18·05
Water	4·28	2·23	2·17	2·24	2·40	1	2·99

It is evident that these numbers differ so considerably from those of Duflos, as not to admit of his formula for the basic nitrate of bismuth being considered in future as correct. If the salt is washed with water, some nitric acid is removed, but water taken up in its place.

Carbonate of Bismuth.—When a solution of nitrate of bismuth in nitric acid is mixed with a solution of carbonate of soda, a white precipitate is formed, which does not lose its whiteness by boiling. It is very easily edulcorated, dissolves with effervescence in muriatic and nitric acids, and is converted by ignition into yellow oxide of bismuth. It is perfectly free from nitric acid and from soda, if in its preparation the mixture of the two solutions has been boiled for some time. When heated in a small dry flask, some traces of water are deposited on the sides. The salt was analysed by conveying a weighed quantity into a small retort, to which a weighed chloride of calcium tube was fitted, and heated to redness, so that pure oxide of bismuth remained. This was weighed, and also the water absorbed by the chloride of calcium; the loss was calculated as carbonic acid:—

Oxide of bismuth ..	91·34	91·58	91·71	91·62	1	91·50
Carbonic acid	8·00	7·84	7·34	7·37	1	8·50
Water...........	0·66	0·58	0·95	1·00		

The small quantity of water is undoubtedly owing to a slight impurification of the salt with hydrated oxide of bismuth.

Oxalate of Bismuth.—When to a solution of nitrate of bismuth in nitric acid pure oxalic acid is added, a white precipitate is formed, which contains oxalic acid, oxide of bismuth and water. On washing it, after the free nitric acid has been for the greater part removed, the water abstracts considerable quantities of oxalic acid from the precipitate; it is therefore best to boil it previously with water, and then to wash it on a filter with boiling water. In this manner a white crystalline powder is obtained which is insoluble in water, readily soluble in muriatic acid, but very sparingly in nitric acid. Dilute nitric acid of about 1·08 spec. grav., dissolves none of it in the cold. When heated to from 392° to 464° it is decomposed, and when entirely pure yields only carbonic acid; but it is very difficult to obtain it in this state; it must be washed for a very long time, and even then it frequently contains a slight excess of oxalic acid. This is explained from the circumstance, that in the first case a neutral oxalate of bismuth is thrown down from the acid solution, from which on edulcoration a certain quantity of acid is removed. The crystalline granular form of the precipitate prevents the free access of the water to all parts of the salt; consequently each granule contains interiorly a minute portion of the undecomposed neutral salt, which on ignition gives rise to the production of a small quantity of carbonic oxide, as is evident from the following analyses:—

Oxide of bismuth ..	72·87	73·04	72·59	72·46	2	73·47
Oxalic acid	22·90	23·23	22·95	23·34	4	22·35
Water	4·36	4·26	3·94	4·05	3	4·08

This composition appears to be rather complicated, but if the relation between the quantities of oxygen of the components of this salt be taken into consideration it will be found to be a very simple one. The oxygen of the water is to that of the oxide of bismuth and of the oxalic acid as 3 : 6 : 12, or as 1 : 2 : 4.—Pogg. *Annalen*, lxiii. p. 55.

On the Occurrence of a new Nitrogenous Substance in Urine.

By M. PETTENKOFER.

The author precipitated the alcoholic extract, obtained from carefully-evaporated urine, and which had been neutralized with a little carbonate of soda, with a concentrated alcoholic solution of chloride of zinc. He obtained first an amorphous precipitate, insoluble in water, and then minute granular crystals, soluble in a large quantity of water, and very similar to lactate of zinc. They form four-sided prisms with oblique terminal surface, and are insoluble in alcohol and æther. The adherent metallic chloride is removed from them by digestion in boiling alcohol. When they are dissolved in water and warmed with hydrate of barytes, the colouring matter is precipitated along with some oxide of zinc; the barytes and oxide of zinc are then removed as carbonates by passing carbonic acid through the solution; the filtered liquid is evaporated to dryness, re-dissolved in spirit, the barytes still present thrown down by sulphuric acid, the sulphuric and hydrochloric acids removed by boiling with oxide of lead, and any lead contained in the filtered solution got rid of by sulphuretted hydrogen. On evaporating the solution filtered from the sulphuret of lead, a white crystalline neutral substance is obtained, which dissolves easily in water and alcohol, has a slightly bitter pungent taste, and is not precipitated from its alcoholic solution by chloride of platinum, which is however the case with chloride of zinc, when it yields the above-mentioned combination with chloride of zinc, which crystallizes from a large quantity of water. It is nitrogenous, and contains 39·37–39·28 per cent. C, 6·79–7·39 H, 33·63–34·41 N; the formula $C^8 N^3 H^8 O^3$ requires 39·2 C, 6·4 H, 34·7 N, and 19·7 O.—Liebig's *Annalen*, liii. p. 97.

On Pectine, Pectic Acid and Metapectic Acid. *By* M. Chodnew.

Pectine.—On separating by ebullition the albumen in the juices of pears, apples and other succulent fruits, a liquid is obtained which forms a gelatine on the addition of alcohol. The substance which is precipitated in this form by alcohol was called pectine by Braconnot from its being coagulated. Mulder and Fremy subsequently examined its composition; but although their results do not agree, they both assign to pectine the same composition as to pectic acid.

The author first prepared some pectine from pears; these were grated, boiled and the juice filtered, first through linen and then through paper. A perfectly clear transparent liquid was obtained, which on the addition of absolute alcohol yielded a gelatinous precipitate. This was washed several times with alcohol, and finally with æther, being on each occasion pressed between the hands, when it lost its gelatinous appearance, and became opake and fibrous.

The pectine prepared in this way was coloured somewhat red; it was easily reduced to a powder, and dissolved in water to a clear liquid. The solution was neutral towards test-paper, and yielded with chloride of barium and chloride of calcium no precipitate, not even on the addition of ammonia; with neutral and basic acetate of lead it gave a gelatinous slightly-adherent precipitate; towards sulphate of copper it acted as towards acetate of lead; most of the other bases gave no precipitate. An excess of caustic potash or caustic lime precipitated a transparent gelatine.

The pectine dried at 230° yielded once 8·76, and on another occasion 8·5 per cent. ash, in which lime, magnesia, oxide of iron, potash, sulphuric acid, phosphoric acid and chlorine, were detected. The organic substance contained 45·88–46·19 C, 5·44–5·56 H.

The author likewise examined pectine prepared from apples, but this time he did not boil the pulp and the juice together, but previously pressed the grated apples, and employed only the juice for the preparation of the pectine; it was boiled, and the pectine treated in the manner above described. It yielded 6·48 per cent. ash, which on being moistened with muriatic acid effervesced considerably. When the pectine is redissolved in water mixed with a little dilute muriatic acid, precipitated with alcohol, and treated as above, a pectine is obtained which leaves much less ash. A pectine which had been prepared in this manner and dried at 239° was colourless, and yielded 1·59 per cent. ash, which contained a large quantity of phosphate of iron, but not a trace of carbonic acid. The analysis gave 43·7–43·8 C, 5·63–5·41 H. Pectine from pears, treated with muriatic acid, gave 43·79 C, 5·84 H; the formula $C^{28} H^{21} O^{24}$ requires 44·09 C, 5·51 H.

The pectine which had been treated with acids dissolved in water; the solution, however, was opalescent, and had a faintly-acid reaction. Its behaviour towards bases, and indeed towards the various tests, was precisely the same. It was sometimes found that the solution of pectine reduced the oxide of copper when potash and sulphate of copper were added with caution.

Although pectine yielded insoluble combinations with oxide of lead and oxide of copper, it was nevertheless quite impossible to ascertain from them its atomic weight; for in the first place, the pectine sometimes behaves perfectly indifferent towards the two bases above-mentioned; and in the second place, a varying amount of lead was obtained from two preparations made at different times, once 23·0, and another time 30·45 per cent.

Pectic Acid.—Most of the experiments were made with pectic acid prepared from turnips; the principal difference between the author's method of preparing pectic acid and those previously employed consists in using the same manipulation as in the case of pectine. The grated, washed and expressed turnips were boiled from a quarter to half an hour with dilute caustic potash, and filtered through fine linen. The solution thus obtained is however never sufficiently clear, and must be filtered again through paper; it ought not to be coloured if the turnips had been well-washed. The last filtration generally proceeds very slowly; it is therefore more advantageous, especially when a solution of pectic acid is desired, to precipitate the pectic acid immediately after filtration through linen, to wash it in the manner about to be described, then to re-dissolve it in ammonia, and to filter it through paper, since the ammoniacal solution filters very rapidly, and may be employed for the preparation of almost all the salts. The pectic acid is precipitated from the alkaline solution with muriatic or nitric acid, washed several times, first with acidulated, then with pure water, and finally with alcohol, and at every washing expressed with the hands.

The washing with alcohol has a twofold object; in the first place, the pectic acid is very soon obtained dry; and secondly, without alcohol it is quite impossible to obtain the pectic acid in so pure a state, for when the washing with water has been continued until the pectic acid begins to be tolerably free from inorganic acid, it deliquesces on the filter, and allows no water to pass through. The pectic acid, treated as above described, entirely loses its gelatinous appearance and resembles fibre, which form it retains after desiccation. It may then be easily reduced to a powder, is colourless, and only acquires a yellowish tint by long drying at 248°. It burns without tumescence, and leaves after combustion less than 1 per cent. of ash, which consists principally of phosphate of iron. It dissolves but very sparingly, frequently not at all, in boiling water, but readily, even after drying in alkalies, to a clear liquid. All the inorganic salts, with the exception of the perchloride of mercury, produce in the alkaline solutions gelatinous precipitates, which are soluble in an excess of potash or soda. The acid dried at 248° consists of—

Carbon	42·03	42·25	42·39	28	42·42
Hydrogen	5·30	5·29	5·13	20	5·05
Oxygen........	52·67	52·46	52·48	26	52·53

Atomic weight of the acid, 2475 × 2 = 4950.

The author examined several of the *pectates*, and he succeeded not merely in obtaining them in chemical proportions, but likewise in ascertaining the atomic weight of pectic acid.

The correct method of preparing the pectates is short and simple; pectic acid, in the purest state possible, is dissolved in ammonia, or still better, the barytic compound is treated with carbonate of ammonia, the liquid filtered, and the excess of carbonate of ammonia expelled by slow evaporation. An excellent means of obtaining pure pectates consists in decomposing pectate of potash or soda with a metallic salt. The pectic acid is thrown down by a solution of the metal, the salt of which is desired, in a gelatinous state, which is perfectly transparent when the salt is quite pure. When this gelatine is brought on to a filter, washed with water and dried, no two results are found to agree, for this gelatine owes its voluminous consistence to the large quantity of water which it takes up at its formation from the liquid in which the pectic acid was dissolved. This water however contains not only the newly-formed alkaline salt, but likewise a portion of the metallic salt added in excess, which cannot be entirely separated from the pectate even by long-continued washing. This was the main cause of the inconstancy of the combinations formerly prepared, and not any variation in the capacity of saturation of the pectic acid, as asserted by Fremy.

Another source of error may depend on the acid properties of the metallic solution employed for the preparation of the pectate of silver. In this case the free acid which exists in the solution precipitates a portion of the pectic acid, which from the immobility of its particles is not able to combine with the metallic oxide.

The correct method of preparing pectates consists in pressing the salt after precipitation between the hand in the liquid; treating it in the same manner several times with fresh water, by which operation the salt loses its gelatinous appearance and becomes fibrous, dries quickly, and is very easily converted after drying into a fine powder. The salt retains most frequently the colour of the metallic oxide. Perfect transparency of the pectates in the gelatinous state is the best sign of their purity.

The lime salt was obtained from a neutral ammoniacal solution of pectic acid with chloride of calcium. It formed a transparent clear gelatine, which possessed totally different properties from pectic acid, being hard, and yielding less easily to pressure. All the pectates possess this property when they have been thrown down from a *cold* solution. The lime salt so obtained was washed in the above-mentioned manner, and dried at 248°; after perfect desiccation it acquired a yellowish tint, which could not be avoided in all the colourless salts. It consists of—

Carbon........	36·89	36·65		28	37·08
Hydrogen......	4·53	4·77		20	4·41
Oxygen........	46·20	46·16		26	45·94
Lime..........	12·38	12·42	12·46	2	12·57

Atomic weight = 2499.

The salt of *barytes* possesses exactly the same properties as the lime salt; it consists of—

Carbon	30·50	28	30·58
Hydrogen	3·69	20	3·64
Oxygen	38·13	26	37·90
Barytes	27·68	2	27·88

Atomic weight 2498. Dried at 302° the salt gives 31·57 C, 3·29 H, 28·68 BaO, which corresponds to the formula $C^{28} H^{18} O^{24}$.

The *soda* salt was prepared by precipitating the solution of pectic acid in a slight excess of caustic soda with alcohol, and washing the gelatine obtained with alcohol. After drying at 248° it resembled fibre, and could not be reduced to a powder; it dissolved however in water, and was perfectly neutral. On ignition in a platinum spoon or in a crucible it puffs up, which circumstance was only observed on the combustion of pectic acid in combination with the fixed alkalies. It contained 13·73 per cent. soda, which corresponds to the number 2456 for the atomic weight of the salt.

These results speak in favour of the formula $C^{14} H^{10} O^{13}$, which give as atomic weight 2475. But this must be doubled, as the following salts show.

Pectate of lead was prepared according to the author's method; he obtained, on precipitating in the cold, a salt with 36·06 PbO, which was decomposed on agitation readily into flakes, and on drying yielded a gelatine, easily becoming yellow. The formula $C^{28} H^{20} O^{26}$, 2PbO, requires 36·03. But if a hot solution of pectic acid be precipitated with acetate of lead, a basic salt is obtained, which contains 23·06 C, 2·55 H, 46·32 PbO. The formula $C^{28} H^{19} O^{25}$, 3PbO, requires 23·28 C, 2·63 H, 46·37 O.

The *potash salt*, dried at 248°, contains 33·8 C, 4·31 H, 18·89 KaO; $C^{28} H^{20} O^{26}$, 2KaO, requires 34·25 C, 4·07 H. Dried at 302°, it yields 35·44 C, 4·02 H, 20·00 KaO, which corresponds to the formula $C^{28} H^{18} O^{24}$, 2KaO.

The green salt of the *oxide of copper*, dried at 248°, contains 35·09 C, 4·21 H, 16·80 CuO; $C^{28} H^{20} O^{26}$, 2CuO, requires 35·34 C, 4·19 H, and 16·68 CuO.

The *ammonia salt* is precipitated from its solution by alcohol as a delicate colourless gelatine, which on drying becomes brown, dissolves with a slight colour in water and with an acid reaction.

The *silver salt* is obtained of constant composition only when a perfectly neutral solution of silver is employed. The salt, dried at 212°, contains 26·45 C, 3·1 H, 36·70 AgO. The formula $C^{28} H^{20} O^{26}$ requires 26·73 C, 3·18 H, and 36·96 AgO.

According to this, pectic acid would be $C^{28} H^{20} O^{26}$; its neutral salts, at 248°, $C^{28} H^{20} O^{26}$, 2M O; the basic salt of lead, $C^{28} H^{19} O^{25} + 3PbO$. The potash and barytes salts, dried at 302°, appear to show that sometimes 2 atoms of water of the acid are expelled by bases, and salts $= C^{28} H^{18} O^{24}$, 2M O formed; according to which, therefore, the free acid may be regarded as $C^{28} H^{18} O^{24} + 2H O$. The salts however become at this temperature very brown. The pectic acid itself cannot be examined at 302°, as it becomes black at this temperature. That pectic acid should in fact be considered as $C^{28} H^{20} O^{26}$, and not $C^{14} H^{10} O^{13}$, is more evident from the author's examination of pectous and subpectic acid, than from the constitution of the basic salt of lead, which at the same time proves that the formula $C^{28} H^{21} O^{24}$ for pectine is correct.

[To be continued.]

Observations on Euphorbia Esula *and* E. Cyparissias.

M. Stickel draws attention to the fact, that the above widely-distributed plants contain a considerable quantity of a yellow, very beautiful colouring substance, which may be precipitated from the decoction prepared with water containing alum, by basic acetate of lead or protochloride of tin. Æther extracts from these plants a tolerable quantity of caoutchouc; alcohol then yields a tincture from which on long standing, a white, crystalline, highly volatile camphor-like substance, with a burning taste, is deposited. The liquid separated from this yields on evaporation a dark green resin, which has a burning taste, gradually hardens by exposure to the air, and greatly resembles euphorbium; the author also found gallic acid.—*Archiv der Pharm.*, xc. p. 30.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Method of ascertaining the Quality of Soaps.

To determine the quantity of water, thin slices are cut from the edges and from the centre of the bars. A portion is then weighed, about 4 or 5 grms. (60 to 75 grs.), and exposed to a current of air heated to 212° F., or in an oil-bath, until it ceases to lose weight. The dry substance is then weighed; the difference between the first and last weighing will indicate the quantity of water evaporated. If it be a soft soap, it is weighed in a counterpoised shallow capsule. In good soap the amount of water varies from 30 to 45 per cent., in mottled and soft soaps from 36 to 52 per cent.

The purity of soap may be ascertained by treating it with hot alcohol; if the soap be white and without admixture, the portion remaining undissolved is very minute, and a mottled soap of good quality does not leave, when operating on 5 grms., more than 5 centigrms., or about 1 per cent.

If there should be a sensible amount of residue from white soap, or more than 1 per cent. from mottled soap, some accidental or fraudulent admixture may be suspected, silica, alumina, gelatine, &c., the quantity and nature of which may be determined by analysis.

The quantity of alkali contained in the soap is easily determined by means of the alkalimeter.

10 grms. in thin slices are taken, for instance, and dissolved in 150 grms. of boiling water; and this solution is saturated with a

normal liquor containing in a quart of water 100 grms. of sulphuric acid, spec. grav. 1·848, or with 1 atom of water.

The volume of this liquor required for complete saturation will indicate the corresponding weight of sulphuric acid, which is itself nearly equivalent to an equal weight of dry carbonate of soda. The quantity of pure potash or soda may be thus deduced.

There is no difficulty in ascertaining in the same assay the quantity of the fatty substance. For this purpose 10 grms. of pure white wax free from water are added to the liquid after saturation with sulphuric acid, and the whole heated to complete liquefaction; it is then allowed to cool, and when it has become solid, the cake of wax and fatty matter which have united is removed and washed, dried and weighed; the augmentation in weight beyond the 10 grms. employed will give the weight of the fatty matter.

The liquid decanted from the solidified wax may afterwards be tested to ascertain the purity of the base.

The solution of the sulphate may also be evaporated, and by an examination of its crystalline form, or by means of chloride of platinum, it may be ascertained whether the base be soda or potash, or a mixture of the two.

As to the nature of the fatty substance, it is ascertained, with more or less certainty, by saturating the solution of the soap with tartaric acid, collecting the fat acids, and taking their point of fusion. It is possible, at least, by this to prove the identity or the absence of identity with the sample in the soap supplied, for instance whether it is made from oil or tallow, &c. The odour developed by the fatty acids, at the moment of the decomposition of the soap by acids assisted by heat, will often indicate the nature of the fatty substance employed in its fabrication, or that at least of which the odour may prevail.

The soap is proved to contain an excess of fatty matter not saponified, by separating the fatty acids by means of hydrochloric acid, washing with hot distilled water, then combining them with baryta, and thoroughly washing the new compound with boiling water. The non-saponified fatty matter is easily separated from the barytic soap, by treating the mass with boiling alcohol, which dissolves the fatty substance. We can moreover assure ourselves that it has no acid reaction on moistened litmus-paper, that it is fusible, and that it possesses the general characters of a neutral fatty substance.—Dumas, *Chimie appliquée aux Arts*, tome vi.

On the Manufacture of Borax. *By* M. KOEHNKE.

The author gives the following directions for the carrying out of his process:—

In the preparation of borax from crude crystallized carbonate of soda and crude Tuscan boracic acid, a solution of caustic soda is prepared, amounting to about 170 lbs. of 1·090 to 1·095 spec. grav., which requires on an average 50 lbs. of soda and 30 lbs. of good caustic lime, the latter mixed to a paste with 4 times its weight of water. When the mixture has been boiled in an iron pan, and converted into caustic ley, it is carefully covered, and after the lapse of a few hours the clear ley drawn off by means of a siphon, the residue again treated with a further quantity of water, well-agitated, and the clear liquid again drawn off after a few hours' rest. A further quantity of water is poured over the residue, which is subsequently removed to be employed in washing the crystals of borax obtained.

The leys thus obtained are boiled down to 170 lbs. or to 1·090–1·095 spec. grav., and then 40 lbs. of good Tuscan boracic acid introduced, and further boiled until the ley is reduced to 120 to 125 lbs., or indicates 1·175–1·180 spec. grav. Upon this the liquid is poured boiling-hot into a wooden tub, which is well-surrounded with woollen cloths and straw, and carefully covered to retain the heat as long as possible, so that a good and regular crystallization may be effected.

When borax crystallizes from a warm solution at from 95° to 105°, octahedral crystals are obtained, which contain only 5 atoms of water of crystallization, and consequently entail a very considerable loss in product. This is not to be feared in the above process, but great attention should be paid to the specific gravity of the ley; for if the hot ley, placed aside to crystallize, has been reduced by boiling to beyond 1·180 octahedral crystals are likewise obtained. It should moreover be observed, that the boracic acid, which has been introduced according to the above directions for the first time, is by no means sufficient to convert the whole of the soda into biborate, but an excess of soda has a very beneficial influence on the crystallization. It is moreover advantageous not to remove the dissolved lime from the caustic ley, but rather to add a little free caustic lime, as this serves partially to destroy the sulphates contained in the crude boracic acid. After three days the first crystallization is complete. The crystals are collected and broken, washed with the above-mentioned dilute caustic ley, and placed aside; the borax ley, on the contrary, is mixed with the wash liquors and placed aside, in order that it may deposit the sulphate of lime formed and any other impurities. As soon as the ley has become clear, it is carefully drawn off, boiled down, and during this operation 8 lbs. more boracic acid gradually added to it, and it is then treated as above. The ley which is now left still requires from 2 to 5 lbs. boracic acid; what remains after this third crystallization may be saturated with sulphuric acid, and obtained as sulphate of soda.

The re-crystallization of all the crystals obtained must generally be repeated twice, for which purpose they are dissolved in 2½ parts rain water, the ley brought by boiling to the above-mentioned specific gravity, and conveyed boiling-hot into a wooden vessel protected from rapid cooling. The evaporation of the residuous ley is repeated. The crystallization is always terminated within two or three days. There is no need of filtration except on the last recrystallization. The product amounts, when good substances have been employed, and with careful treatment, to from 60 to 62 lbs. of pure crystallized borax.

The preparation of borax from crude soda and boracic acid is more advantageous, but at the same time more difficult; for this purpose a solution of caustic soda is likewise made, amounting to 300 lbs., of 1·090–1·095 spec. grav., which requires about 100 lbs. good crude Alicant or Teneriffe soda and from 45 to 50 lbs. caustic lime; the ley is prepared in the same manner, and from 45 to 48 lbs. of Tuscan boracic acid added to it, upon which the ley is concentrated to about 180 to 185 lbs., or spec. grav. 1·175 to 1·180; in the mean time the froth is now and then removed, and finally the whole placed aside to crystallize. To the first mother-ley from 8 to 10 lbs. of boracic acid are added, and to the second residuous ley 2 or 3 lbs. more, frequently however, according to the substances employed, even as much as 10 lbs., which must be determined by a previous examination of the borax ley. The mode of operation is precisely the same as described in the preceding method; a greater quantity of sulphate of soda is however obtained on saturating the last mother-ley with sulphuric acid; the produce in crystallized borax amounts to from 80 to 90 lbs.

The third method relates to the preparation of the biborate of soda from the half-refined East Indian borax, which contains considerable quantities of smeary or fatty ingredients; it is washed with a caustic soda-ley of 1·370 to 1·380 spec. grav., and then, since it always contains a large excess of soda, it is gradually saturated with Tuscan boracic acid, as described in the previous methods, and purified by 3 to 4 re-crystallizations. The produce may amount to 65, and in a favourable case to 75 per cent. crystallized borax.—*Archiv der Pharm.*, lxxxix. p. 279.

PROCEEDINGS OF SOCIETIES.

Meeting of the Royal Society.

Thursday, Feb. 6, 1845.

"On a new Bleaching Principle produced by the slow Combustion of Æther in Atmospheric Air, and by the rapid Combustion of Bodies in a Jet of Hydrogen Gas." By C. F. Schœnbein, Professor of Chemistry in the University of Basle, &c. Communicated in a letter to Michael Faraday, Esq., F.R.S., &c.

The author, having observed that a peculiar principle, in many respects similar to chlorine, was developed during the slow combustion of phosphorus in the atmosphere, was led to inquire into the product of the slow combustion of the vapour of æther mixed with atmospheric air. He finds, that besides well-known compounds, such as aldehydic, formic and acetic acids, there is evolved a principle hitherto unnoticed, which possesses oxidizing and bleaching properties in an eminent degree. It decomposes indigo, iodide of potassium, and hydroiodic acid, and also, though more slowly, bromide of potassium. When in contact with water, it converts iodine into iodic acid, and sulphurous into sulphuric acid, changes the yellow ferro-cyanide of potassium into the red, and the white cyanide of iron into the blue; it transforms the salts of protoxide of iron into those of the peroxide; and it discharges the colours produced by sulphuret of lead. The author points out the similarity between the action of this substance, in these instances, and that of chlorine and of ozone.

Analogous results were obtained from the combustion of a jet of hydrogen gas in atmospheric air, and even, under particular circumstances, from the flame of a common candle, and also from various other inflammable bodies when burning under certain conditions. The author is hence led to the conclusion that this peculiar oxidizing and bleaching principle is produced in all cases of rapid combustion taking place in atmospheric air, and that its production is therefore independent of the nature of the substance which is burnt.

February 27, 1845.—"An Account of Compact Aluminum," by Professor F. Wöhler of Göttingen, in a Letter to Thomas Graham, Esq. Communicated by Thomas Graham, Esq., F.R.S.

The author has lately found, contrary to the results of his former researches on aluminum made eighteen years ago, that this metal is readily fusible, and that in its reduction from the chloride of aluminum by means of potassium, it presents itself in the form of fused globules, generally so small that their shape is not distinguishable under the microscope, although occasionally they are met with having a sensible diameter. He effects the reduction at once in a clay crucible, the bottom of which he covers with pellets of pure potassium, and places upon these the chloride of ammonium, covering the whole by chloride of potassium in powder. The crucible being then closed up, and heated in a coal fire, the reduction is instantly effected.

Fused aluminum has the colour and lustre of polished tin; it continues perfectly white in the air; it is fully malleable, and the globules may be beaten out into the thinnest plates without cracking at the edges. It is entirely unmagnetic. In other respects the metal in this compact state has the properties which the author formerly ascribed to it.

Chemical Society of London.

Feb. 3rd, 1845. (Robert Porrett, Treasurer, in the Chair.) The following communications were read:—

"On the Metamorphoses of Indigo and Production of Organic Bases which contain Chlorine and Bromine," by Dr. Augustus W. Hofmann, Assistant in the Giessen Laboratory.

After a detailed account of the law of substitution as laid down by Laurent, and the discussions arising from it, the author shows that this law, in which the hydrogen is replaced by chlorine, had no representative among the organic bases, but that the cases experimented on were indifferent bodies or acids, or their compounds with æther.

Dr. Hofmann then reviews the investigations hitherto made on indigo, gives the detail of the preparation of isatine and chlorisatine, and then describes his preliminary experiments on the action of chlorine on aniline and of potash on isatine, which determined him as to the cause of the subsequent investigation. The action of fused hydrate of potash on chlorisatine is then described, by which the base chloraniline is obtained, having an equivalent of chlorine replacing an equivalent of hydrogen without the chemical characters or properties of the aniline being changed. The composition, reactions and combinations of this base are then considered. Its saline compounds with sulphuric, oxalic, nitric, phosphoric and muriatic acids, their formation, characters, composition, and many most interesting properties are detailed. Its double salts with the metallic oxides, their characters and composition, follow next in order. The author then proceeds to the action of oxidizing agents, as chlorine, bromine and nitric acid, on chloraniline, and describes the formation of Erdmann's chloranile through the medium of chlorate of potash and hydrochloric acid. The reproduction of aniline from chloraniline, by passing its vapour over lime at a low red heat, is then described. Dr. Hofmann next passes to the dichloraniline and trichloraniline, and then commences a new series of combinations analogous to the preceding, but formed by the action of fused hydrate of potash upon bromisatine; the base thus obtained consequently containing bromine in the place of hydrogen, instead of chlorine as in the former series. This base, and most of its combinations, are so similar in characters, properties and composition, to the corresponding compounds with the chlorinated base, that it would be mere repetition to give an abstract. The action of fused hydrate of potash on dibromisatine, and the production by these means of dibromaniline, follows, with the composition, characters and properties. A tabular view of the formulæ of the compounds described is then given, and Dr. Hofmann reviews the whole of the paper, and draws his general conclusions on this interesting subject.

Feb. 17*th*, 1845. (The President in the Chair.) "On the Structure of Electro-precipitated Metals," by W. De la Rue, Esq.

Mr. De la Rue first describes the various appearances of electro-metallic deposits, which are distinguished by the terms crystalline, lesser crystalline, malleable, sandy and spongy; these variations being produced by the increase or decrease in the power of the battery, all being essentially crystalline and mere modifications of each other, the malleable or most cohesive being very inferior in strength to the metals wrought by processes in ordinary use. The difficulties attendant upon the successful deposit of metals are then enumerated, arising from the continual change in the strength, and consequently the conducting power, of the fluids and the force of the battery on the one hand, and from the form and surface of the metal on the other. The defects arising from these causes are then fully demonstrated, giving rise to that brittleness and porosity which of necessity must be attendant on a deposition of matter in a crystalline state. A number of drawings from the microscopic investigation of some of the best deposits that could be obtained are given, illustrating most correctly the cavities arising from the exhausted electrotype lodging on the matrix or deposit, and the porosity attendant on the interlacing and shooting of the crystals of metal. The nearest approach to perfect polish in the surface of the mould is shown to produce the best deposits; and all the deviations from this increase the imperfections in the same ratio, but still they are all without exception crystalline, and consequently porous, the crystals merely varying in their size with the power employed for their production. The author, in concluding, strongly advises that the deposits of silver on copper, when it is intended to protect the vessel from the action of certain fluids, should in all possible cases be subsequently partially fused.

"On the true Composition of Chlorindatmit," by Dr. A. W. Hofmann.

In a former memoir on the metamorphoses of indigo, the author describes, under the name of Trichloraniline, a body which may be regarded as aniline, in which 3 equiv. of hydrogen are replaced by 3 equiv. of chlorine:

Aniline .... $C^{12} H^{7} N$.
Trichloraniline .... $C^{12} H^{4} Cl^{3} N$.

This substance is produced by the action of chlorine on both aniline and chloraniline, but in the author's earlier experiments the quantities obtained were too small to admit of satisfactory analyses being made.

Erdmann, in his researches on indigo, describes several different substances produced by the action of chlorine on that compound, when reduced to fine powder and suspended in water. On submitting to distillation the reddish-yellow mass thus produced, a volatile body, called by that chemist Chlorindopten, passes over with the vapour of water, while chlorisatine and dichlorisatine remain in the retort. This chlorindopten, when heated with potash, is further decomposed into an acid (chlorindoptenic), which remains in union with the base, and into a neutral volatile body, chlorindatmit.

From a careful comparison of the properties of chlorindatmit and trichloraniline, M. Hofmann was led to suspect the identity of these two substances, and this view was completely confirmed by subsequent experiments. The nitrogen which chlorindatmit contains was overlooked by M. Erdmann, but satisfactorily demonstrated by the author.

The formation of trichloraniline by the action of chlorine on indigo is not at all surprising, as all the conditions necessary to the production of the various members of the phenyle series are found in those circumstances. The action of chlorine and of potash on indigo is in this respect essentially the same; the only difference is, that in the latter instance pure products of oxidation are obtained, while in the former, compounds often result in which a certain number of equivalents of hydrogen are replaced by a corresponding number of chlorine.

"Abstract of a Letter from Thomas Richardson, Esq., giving the Results of the Analysis of Farm-yard Manure in its fresh and dried State, and of the portions of the Inorganic Matter soluble in Water and in Hydrochloric Acid; as also two Analyses of the Coal-gas supplied to the Town of Newcastle upon Tyne."

THE CHEMICAL GAZETTE.

No. LIX.—April 1, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Pectine, Pectic Acid and Metapectic Acid. By M. Chodnew.

[Continued from p. 130.]

Pectous Acid.—The author observed, on seeking to explain the question respecting the occurrence of pectic acid in plants, and the origin of the gelatine obtained from unripe gooseberries by boiling with acids, that not merely unripe gooseberries and all unripe fruit, but likewise full-grown turnips and all possible kinds of plants containing gelatine, presented the same appearance when boiled with acid. When turnips, reduced to a pulp and well-washed, are boiled with dilute muriatic acid, a liquid is obtained by filtration, which yields on the addition of alcohol an abundant gelatine. This was washed several times with alcohol, and finally with æther, in the manner previously described, and dried. It could not be pulverized, was fibrous, and dissolved even after drying at 248° in water and in alkalies. The aqueous solution had a faintly acid reaction, and gave with an excess of potash or lime-water a gelatinous precipitate; nitrate of silver produced no precipitate, but after a time the entire liquid became thick, and of a faint dark red colour; on adding then a couple of drops of ammonia and warming the liquid, it became of a dark brownish red, but remained clear even after several days. Chloride of potassium produced no precipitate in an aqueous solution; a gelatine was however immediately formed if to the liquid some ammonia had been previously added; this gelatine is soluble in an excess of muriatic acid. Neutral and basic acetate of lead likewise yield a precipitate soluble in acetic acid. The gelatine prepared in the above-mentioned manner from turnips, and dried at 248°, yielded 0·86 ash.

The same substance was likewise prepared from apples; the apples reduced to a pulp were merely pressed, and not washed with water; they contained a little pectine, which caused the amount of carbon to be somewhat too large. This gelatine was of a faint red colour, and left on ignition 0·8 per cent. ash. The analysis gave—

	From turnips.		From apples.		
Carbon	43·02	42·92	43·55	28	43·18
Hydrogen	5·72	5·59	5·48	21	5·39
Oxygen				25	51·22

Pectite of silver is obtained by precipitating the gelatine, to which nitrate of silver has been added, with alcohol; dried at 212° it consists of—

Carbon	33·62		28	34·86
Hydrogen	4·12		20	4·03
Oxygen	39·00		24	38·57
Oxide of silver	23·26	23·17	1	23·40

Pectite of lead was precipitated from an aqueous solution of pectous acid by sugar of lead; in one case the acid from turnips and in the other the acid from apples was employed. The salt was gelatinous in the moist state, but not so thick as the pectates. Dried at 248° it consisted of—

Carbon	33·79	34·25	28	34·17
Hydrogen	4·13	4·32	20	4·07
Oxygen	39·98	39·28	24	39·07
Oxide of lead............	22·10	22·15	1	22·69

Superpectic acid is the name assigned by the author to a new gelatine, which he obtained in endeavouring to ascertain whether the pectic acid exists as such in the plants, or whether it is *formed* by the action of alkalies.

Turnips were boiled with ammonia, but no gelatine was obtained in solution, whence it may be concluded that even if pectic acid is present it must be in combination; this can only be with lime, since the ashes of turnips consist principally of lime. To remove the lime from the turnips, and so to facilitate the solubility of the pectic acid in ammonia, they were boiled in muriatic acid, and the preceding results obtained. It was thence highly probable that the pectic acid was formed from the pectous acid. To be however perfectly certain of this, it was necessary, in the first place, to ascertain whether the pectous acid could in fact be converted by boiling with potash into pectic acid; and secondly, to submit the turnips remaining after the boiling with muriatic acid to further examination.

The pectous acid, washed with acid and pressed, was again dissolved in water, a dilute solution of caustic potash added to it, and the whole gently warmed; the liquid thus obtained yielded a gelatine with muriatic acid which possessed all the properties of pectic acid. It was proved by analysis to be pectic acid, for it contained 42·16 C and 5·36 H.

The turnips, boiled with muriatic acid, washed with water, and again treated in the same manner, were boiled with a dilute solution of caustic potash. In this manner a liquid was obtained on filtration, which on the addition of acids yielded a thick gelatine possessing all the properties of pectic acid. But nothing could be detected in the liquid when the turnips, exhausted with boiling muriatic acid, were digested with ammonia, which militates against the presence of pectic acid in them. The gelatine above-obtained was treated in the manner previously described and analysed. It left, after desiccation at 248°, 0·52 per cent. ash, and consisted of—

Carbon	41·52	41·39	28	41·68
Hydrogen	4·75	4·92	19	4·71
Oxygen	53·73	53·69	27	53·61

This new kind of gelatine dissolved in potash and in soda, but not in ammonia, which distinguishes it essentially from pectic acid. It forms gelatinous precipitates with all the bases; when its alkaline solution is neutralized with acetic acid and precipitated with sugar of lead, a combination is obtained which affords 37 per cent. oxide of lead.

The facts described suffice to disprove the occurrence of pectic acid in turnips; and although the pectic acid, prepared in the usual manner, may be considered as a body which is partially formed from pectous and superpectic acid on boiling with potash, yet the presence of the two latter cannot be detected in it. Pectic acid, for instance, is very sparingly or not at all soluble in water, which militates against the presence of pectous acid; on the other hand, it dissolves readily in ammonia, which does not admit of our supposing the presence of superpectic acid. Although everything necessary to the formation of pectic acid is present in plants, pectic acid itself does not occur in them. Some other plants were examined with the same object in view, and the author obtained exactly the same results; apples, pears, carrots and beetroot always yielded pectous and superpectic acid.

These facts led the author to suspect that probably the gelatine obtained by Fremy, by boiling unripe gooseberries with acids, was nothing else than pectous acid. To decide this, he boiled the unripe well-washed gooseberries with muriatic acid, and so obtained a gelatine which actually possessed precisely the same composition as pectous acid (42·85–43·18 C, 5·53–5·63 H).

It is very difficult to obtain the pectous acid pure from unripe gooseberries. For this purpose the precipitated and washed gelatine must be redissolved in water, boiled for some time, precipitated with alcohol, and the same operation repeated at least three times. The overlooking these precautions was probably the reason that the pectous acid from gooseberries of a former preparation possessed an entirely different composition.

It was stated above that the turnips must be boiled with some mineral acid, in order to obtain the pectous acid from them; but this is not even necessary; it suffices to allow the grated and washed turnips to stand for a day in dilute muriatic acid. In this case the lime is gradually dissolved, and when the turnips are washed with water they likewise afford on being boiled with distilled water pectous acid.

On this occasion a very interesting observation was made. When the grated turnips are allowed to stand with muriatic acid, they lose their opakeness and also in part their fibrous appearance, and become somewhat gelatinous; if they be now washed with water, and then some very dilute lime-water poured over them, the turnips are obtained with their former properties, they again become opake, fibrous, no longer yield a gelatine by boiling with water; in a word, the pectous and superpectic acids have again entered into combination with the lime. On treating them again with acid, the same appearances are observed anew; and this may be repeated at will.

This likewise proves that the origin of the gelatine from unripe fruit, when these are boiled with acids, depends quite simply on the solution of the lime; the acid employed dissolves the lime, setting the pectous acid free, and consequently renders it capable of solution in water. When unripe gooseberries are boiled with potash, pectic acid is likewise obtained, which appears to show that the gelatinous substances occur even in unripe fruit, and are not first produced by the action of an acid.

On comparing the composition of pectous acid with that of pectine, it is seen that the difference between the two is not so great, and is probably merely accidental. However, even if the composition of pectine ought to be regarded as identical with that of pectous acid, the latter name should be retained in science on account of the different properties of these two substances; or pectine must be supposed to be nothing else than impure pectous acid, or rather the pectous acid considered as pure pectine.

Metapectic Acid.—It is certainly correct that when a solution of pectic acid is boiled with a slight excess of potash, it loses after a time its property of being precipitated as a gelatine by acids. However, all acids do not behave similarly towards the solution obtained by boiling with potash; the liquid remains unaltered on the addition of acetic acid, even when a large excess has been employed and when this liquid is allowed to stand for weeks; muriatic and nitric acids however produce after a short time an opakeness, and finally a flocculent precipitate. If chloride of calcium or chloride of barium be added immediately after the addition of one of the two last-mentioned acids, a flocculent transparent precipitate is always obtained in a few minutes. The alkaline solution of metapectic acid, neutralized with acetic or sulphuric acid, likewise affords a gelatine on the addition of alcohol. Sugar of lead produces in the liquid neutralized with acetic acid a gelatinous precipitate, which in its physical properties bears great resemblance to the basic pectate of lead.

The reason of these results differing from Fremy's experiments is considered by the author to be owing to the pectic acid not having been boiled sufficiently long, or that sufficient potash had not been added to it; both were frequently repeated; however, the metapectic acid exhibited the same properties even when it was boiled from three to four days with a large excess of potash.

The author prepared and analysed a lead salt procured from the liquid saturated with acetic acid; after drying at 248°, he obtained the following results:—

Carbon	27·08	28	27·13
Hydrogen	3·16	20	3·23
Oxygen	33·94	26	33·51
Oxide of lead	35·82	2	36·03

It was interesting to ascertain whether the metapectic acid, after the decomposition of the lead salt with sulphuretted hydrogen, remained dissolved in the liquid. For this purpose he passed a current of sulphuretted hydrogen through water in which metapectate of lead was suspended, and obtained a black solution which remained the whole day without change; it could not, even after boiling, be separated by filtration from the sulphuret of lead. The addition of alcohol is of no service whatever; the liquid always passes black through the filter. After a couple of hours the alcoholic liquid solidifies to a gelatine.

The metapectic acid is consequently not a pentabasic acid, does not deliquesce in the air, and forms no soluble salts with lime and barytes. It is not precipitated by acetic acid, and by a mineral acid only after some time, and then not in a gelatinous state. It does not however entirely lose its gelatinous property, as is distinctly evident from the precipitates obtained by alcohol and sugar of lead.

With respect to the action of acids on pectic acid, the experiments of M. Chodnew have led to results differing still more widely.

He always found it impossible to dissolve the entire quantity (even when it was but very small) of the pectic acid prepared in the above manner by boiling with acids in so short a time as Fremy; and even when this was effected after very long boiling, other products of decomposition were constantly obtained than those described by him; an acid resembling the above-described metapectic acid was not to be found among them. When pectic acid prepared from turnips (dried or not dried, it is all the same) is boiled in a flask with dilute sulphuric, muriatic or nitric acid, the liquid very soon becomes faintly red, and then reduces oxide of copper and silver; when sulphuric acid is employed, a small quantity of formic acid is disengaged, which collects in the water which distils over, and carbonic acid, which can be demonstrated with lime-water. These phænomena continue during the entire experiment; the solution becomes gradually redder, and at last smells of caramel; but when the solution is diluted from time to time with water, it remains nearly colourless. It is difficult to attain the point when the whole of the finely-divided pectic acid suspended in the liquid has dissolved; there almost always remains a black substance, which is left on the filter, and which consists in part of pectic acid, when this had not been boiled sufficiently long; but in part of a product of decomposition formed subsequently, when the mineral acid became more concentrated by evaporation. This black substance does not dissolve in water nor in acids, but with the greatest ease in alkalies, from which acids precipitate it in brown flakes. The filtered solution was saturated with carbonate of barytes, filtered, evaporated to the thickness of a syrup in the water-bath, and alcohol added to it. This produced an abundant precipitate, which was readily soluble in water. What remained dissolved in alcohol was again evaporated in the water-bath; the residue consisted of sugar, which was already converted for the greater portion into caramel, as was evident from its odour and taste. With respect to the sugar, its presence was demonstrated by the form of crystal of the combination with chloride of sodium, by the reaction of sulphate of copper and potash, and by fermentation. There was moreover frequently observed a peculiar odour on boiling pectic acid with sulphuric acid, which called to mind hydruret of benzoyle.

The presence of sugar in the liquid explains the origin of the black substance, which has all the properties of humic acid.

With respect to the acid which yielded with barytes the combinations soluble in water, it may partly be formic acid, as the reduction of the oxide of silver even in the cold would lead to believe; and in part consists of another acid, which has very great resemblance to malic acid.

When pectic acid is boiled with concentrated sulphuric, nitric or muriatic acid, the same phænomena occur, with this difference, that the pectic acid is more rapidly decomposed. It is generally stated that on boiling pectic acid with concentrated nitric acid, mucic acid is formed. M. Chodnew however could never obtain the latter in this manner. The incorrectness of this statement is owing to the confounding pectic acid with pectine, which really appears to yield mucic acid when acted upon with nitric acid and the assistance of heat.

Fremy made all his experiments with pectic acid prepared from pectine; in this way however he worked with an acid which exhibits different properties in its behaviour towards potash and acids to the one obtained from turnips. The conversion of pectine into pectic and metapectic acids by means of potash proceeds with such ease that it is scarcely necessary to heat the solution of pectine; with a slight excess of potash it yields, after very short boiling, no longer any gelatinous precipitate with acids, which indeed is even the case when potash is added to a boiling solution of pectine removed from the fire.

The author added a little potash to a solution of pure pectous acid, and then precipitated a gelatine with muriatic acid; this was first washed twice with dilute muriatic acid, and then with alcohol. The gelatine prepared in this manner, and dried at 248°, dissolved readily in cold water, from which it was not precipitated by acids, and yielded with neutral acetate of lead a compound which contained only 23·2 per cent. oxide of lead. These properties, which essentially distinguish pectous from pectic acid, show that the former is not affected by the action of potash in the cold.

Pectic acid prepared from pectine is converted into metapectic acid upon boiling with potash with the same ease as pectine; it is most readily changed by boiling with mineral acids into sugar and an acid, which yields a soluble compound with barytes.

A solution of pectine in water, boiled with a small quantity of muriatic acid, very soon acquires a rose colour; it is then no longer precipitated by alcohol, or merely yields a slight flocculent precipitate after standing if it has not been boiled sufficiently long; the solution contains sugar. Sulphuric acid likewise colours the solution of pectine rose-red on boiling, but the tint is not so beautiful as with muriatic acid. The formation of sugar very soon results, even when the solution, to which a little sulphuric acid has been added, is warmed for a short time in the water-bath. After the removal of the sulphuric acid with carbonate of barytes, a soluble salt of barytes was also obtained. Nitric acid acts quite differently on a solution of pectine; it never becomes coloured, but very soon a white powder is obtained, which easily subsides, and which appears from its physical properties to be mucic acid. Not a trace of sugar is found.

Soon after the discovery of pectine and pectic acid by Braconnot it was suspected that these substances were easily convertible into sugar; but their differing so much in composition from the hydrocarbons and the experiments of Fremy, had rendered the possibility of this conversion very doubtful, but unjustly so.

It was shown, when speaking of pectous acid, that it imparts, in its combination with lime, a certain degree of density to the fruit—their form. Another very important function of the gelatine in fruit, the formation of sugar, is rendered highly probable from the peculiar action of acids on the different kinds of gelatine. In most fruits, roots, berries, &c. no starch occurs, either before or after maturation; from what then can the sugar be formed? The pectine of the juice of apples, pears, &c. decreases and disappears almost entirely when they are preserved for some length of time. Braconnot has shown that the amount of sugar is thereby considerably increased. A conversion of pectine into cellular tissue is out of the question, for pectine itself may in a certain respect be looked upon as a body which has originated from cellular tissue, in which it pre-existed in the form of pectous acid; however, it is not merely the pectine that is destined for the production of sugar; in all probability pectous acid undergoes the same metamorphosis in several roots, as for instance in carrots, which contain a large quantity of sugar, but in the juice of which no pectine is present.

Composition of the Pulp of Fruit.—To ascertain whether the pulp of the fruit employed in the above investigations stood in any relation to the gelatinous substances, some turnips and apples were subjected to examination with this object in view.

The apples were grated, washed with water until they had become tasteless and inodorous, then a couple of times with alcohol, and finally with æther. They left, after drying at 239°, 1·78 ash. Another portion of apples was washed, first with dilute sulphuric acid, and then with water, alcohol and æther; they yielded 0·56 per cent. ash.

A third analysis was made with the pulp of apples, which had been boiled with potash, washed with water, alcohol and æther. Lastly, a fourth, with the pulp from turnips:—

	I.	II.	III.	IV.	Equiv.	Calculated.
Carbon......	45·89	45·92	45·94	45·97	28	45·90
Hydrogen....	6·27	6·28	6·25	6·13	22	6·01
Oxygen					22	48·09

The following tabular arrangement exhibits the relation of the substances examined:—

Pulp of fruit	$C^{28}H^{22}O^{22}$
Pectine	$C^{28}H^{21}O^{24}$
Pectous acid	$C^{28}H^{20}O^{24}+HO$
Pectic acid	$C^{28}H^{20}O^{26}$
Superpectic acid	$C^{28}H^{19}O^{27}$

Ann. der Chem. und Pharm., li. p. 355.

Further Experiments on Bismuthic Acid, Protoxide of Bismuth and Phosphate of Bismuth. By M. HEINTZ.

In a previous memoir* the author has designated the superoxide BiO^2 as the highest combination with oxygen, and has assumed the experiments of Arppe, which pointed to a higher oxide of a red colour, to be owing to some impurity in the substances employed. He has, however, since then repeated the latter experiment under Arppe's direction, with perfectly pure materials, and has found that when oxide of bismuth is suspended in highly-concentrated boiling caustic potash, and chlorine passed into the boiling liquid, a red compound is obtained, above which rests a greenish liquid containing mere traces of bismuth. Even after digestion several times with nitric acid, this combination still contains 1½ per cent. potash; the oxide of bismuth in it approaches very closely to the formula Bi^2O^5, for it contains 84·8 Bi, 15·2 O; the formula requires 15·82 O. By long-continued digestion with nitric acid, for the purpose of extracting still more of the mixed oxide, the amount of oxygen was not increased, but rather diminished. Nor was it possible to obtain more than 15·12 per cent. O in the analysis of the combination not treated with nitric acid, and which still contained 13 per cent. impurities. Nevertheless, these experiments speak decidedly in favour of a bismuthic acid, Bi^2O^5, which it is extremely difficult to free from the inferior oxides. The precipitate appears to be a mixture of Bi^2O^5, KO, HO, with oxide of bismuth in indefinite proportions. Whenever in the preparation the solution of potash is not quite sufficiently concentrated, a black powder is obtained instead of a red one with chlorine gas, which on treatment with nitric acid becomes brown, and leaves behind pure superoxide.

The author has made some further experiments to obtain a protoxide of bismuth, and submitted for this purpose the phosphate of bismuth to reducing influences. He obtained this salt by precipitating nitrate of bismuth dissolved in nitric acid with phosphate of soda, as a white crystalline powder, very sparingly soluble in nitric acid, and which on ignition gave off merely traces of water, and did not fuse. It consisted of—

Oxide of bismuth	76·57	76·51	1	76·84
Phosphoric acid	23·25	23·08	1	23·16

When this salt is heated in hydrogen, phosphuret of bismuth is formed, which again gives off a portion of its phosphorus on the ap-

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* Chem. Gaz., p. 117 of the present volume.

plication of heat. Carbonic oxide has no reducing action on the salt.

When oxide of bismuth is fused together with microcosmic salt, and then heated in a current of hydrogen, metallic bismuth is separated. Carbonic oxide produces no distinct reduction.—Poggendorff's *Annalen*, lxiii. p. 559.

Note on the Coating of Casts for Electrotyping.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,

I am not aware that the following method has been published, but I know it is not known to some who are forming a collection of medals, &c. by the electrotype; by it I have procured copies of large plaster casts, &c. in as little time as I could small seals. After the usual process of black-leading, I first breathe on the mould to make it damp, then apply copper-bronze with a soft brush, then well breathe on it again, and proceed as usual with a Daniell's battery. With black lead alone it takes a long time to coat a large mould having a deep recess with copper, but by using the bronze it is done instantly. I have procured some upwards of three inches square in two days, of a tolerable thickness.

If you think the above worthy of a place in your valuable Journal, it is at your service.

I am, Sir, respectfully yours,

Warwick, March 22, 1845. J. MARSHALL.

On the Respiration of Frogs. By Prof. F. R. MARCHAND.

The experiments of the author, as will be seen from the description of his method, were performed in a manner which removes all objections, and moreover so that in estimating the normal proportions the animals were surrounded by an atmosphere which was constantly changed. From them we learn in general that more oxygen is constantly absorbed than is necessary for the production of the exhaled carbonic acid, and that water is certainly formed. The experiments take account, not only of the matters exhaled from the lungs, but also from the skin. How much however of the phænomena is dependent upon the latter cannot be determined for the present. As regards the loss of nitrogen, which Boussingault ascertained indirectly, in no case is it pure gaseous nitrogen; since, as the author satisfactorily ascertained, ammonia is exhaled from both the skin and lungs; nor is it at all probable that pure nitrogen is evolved. If this happens, the consumed amount of oxygen will appear too high, but at the most the error is very small. Besides ammonia, organic carbo-hydrogens are evolved from the lungs; for when the expired air is perfectly freed from water and carbonic acid, and then burnt with oxide of copper, a little carbonic acid and water are constantly obtained. In Marchand's experiments these matters were condensed in the sulphuric acid; their very minute quantity is certainly contained in the exhaled watery vapour.

Respiratory Apparatus.—A glass cylinder formed the abode of the animals which were used for experiment. It was 10 inches high, 3½ broad, and contained exactly 422 cubic inches at 65° F. The cylinder had a broad rim, to which a brass plate was accurately ground. To make it shut perfectly air-tight, this rim was smeared with grease, and the plate, after having been firmly pressed down, was fastened tight to it by eight screws. It is best to place a moderately thick brass ring under the rim, so that the margin of the glass may not be broken by the pressure of the screws. The plate itself was bored through in three places. The middle aperture received a thermometer, by which the temperature of the interior of the cylinder was accurately determined. When this was not used, a screw closed the aperture air-tight. In the other openings two glass tubes were inserted, cemented air-tight, one of which nearly reached to the bottom of the cylinder, the other opened immediately beneath the plate. Through the latter the fresh air was admitted, through the former the air was withdrawn. As the two apertures were at the opposite extremities of the apparatus, in drawing through the air, at least the greater part of the contents of the cylinder must be rapidly removed, and by the continued withdrawal the air within the cylinder is entirely renewed. Cocks are connected with the tubes by means of caoutchouc, by which the cylinder may be closed. The cock of the tube, which allows the egress of the air, has no peculiar arrangement; the other is bored through laterally as well as longitudinally; a tube passes sideways from its centre, so that by a certain turn of the cock this lateral tube communicates with the cylinder, but not with the *efferent* tube; by the opposite turn of the cock this is reversed. When the cock is placed longitudinally, the cylinder is brought into communication with the following part of the apparatus, and at the same time with the lateral tube; when this position is reversed, the latter communication only is closed. A glass tube, bent at a right angle, communicates with the lateral tube; this is graduated in millimetres; it dips into a cylinder which is half-full of mercury. If the pressure of the air in the cylinder is diminished when the cock of the *efferent* tube is closed, and the cock of the *afferent* tube is placed transversely, this is rendered evident by the ascent of the mercury.

The cylinder used for the experiment communicates by means of the *afferent* cock with a U-shaped tube, 10 inches high and 1 inch broad, and filled with dried caustic potash, to which the bulb-apparatus, filled with sulphuric acid, is joined. Two U-shaped tubes, filled with fused chloride of calcium, terminate in this. This apparatus serves to free the air entering the cylinder completely from water and carbonic acid.

By means of an aspirator, made in the manner recommended by Mohr, a constant exchange of the air in the cylinder is maintained, which being thus uninterrupted is filled with air free from moisture and carbonic acid. The air withdrawn passes into three tubes 5½ inches high, ½ an inch broad, which are filled with freshly-fused chloride of calcium. In these the aqueous vapour carried off by the current of air is condensed. The third chloride of calcium tube did not increase in weight; it was therefore subsequently omitted. A tube filled with cleansed pumice-stone moistened with sulphuric acid was annexed to the chloride of calcium-tubes. The sulphuric acid was previously distilled, and the product evaporated to half its volume; it absorbed all gaseous organic substances. Next to this was placed a bulb-apparatus, filled with solution of potash. If the bulbs are not very large, by the long continuance of the passage of the air, the froth becomes so great as to cause it to overflow. Finally, appended to the bulb-apparatus are three potash-tubes, 4½ inches long. The latter of these did not alter in weight during the whole course of the experiment. The first, as also the first chloride of calcium tube, must often be changed, as both the chloride of calcium and the potash after some time are dissolved, and even when this does not occur there is fear of the apparatus being stopped up by the solidification and crystallization of the masses which have become moist. The moisture which the first potash tube absorbed of course proceeded from the evaporation of the solution of potash. The ley in the bulb-apparatus was also always renewed after each experiment, or at most was used for three short successive experiments.

In the sulphuric acid tubes the small quantity of gaseous organic matter was condensed, which was not absorbed by the chloride of calcium. In these also the traces of ammonia were taken up, which were formed during the confinement of the animals in the cylinder.

As it was especially necessary to avoid any admission of atmospheric air which had not previously passed through the purifying apparatus, the latter were next filled, corked and varnished with melted sealing-wax by a brush, next fastened to the air-pump, the other extremity of the tube closed air-tight by means of a glass rod fastened by a caoutchouc tube, and the air then pumped out. The air-pump barometer ought not to alter for half an hour whilst the apparatus is connected with it. In the same manner the lateral tubes were tested. Finally, the cylinder itself was connected with the air-pump, emptied, and it was observed whether or not the barometer retained its level after exhaustion. No parts of the apparatus were used for the experiments until they had been carefully proved.

First of all the weight of each part of the apparatus was separately taken. The cylinder with the brass plate, the eight screw-pieces, the cemented tubes, the efferent cock and its caoutchouc tubes, and the four silk threads belonging to them were weighed. Their weight amounted to 993·200 grms. To estimate it accurately would have been useless, as a knowledge of the absolute weight of the animals contained within was not necessary, at least further than the gramme weight, and merely the relative alteration of their weight was of importance for the experiment.

The animals, well-dried, were now placed in the cylinder; this was smeared with grease at the margin, and the plate fitted on air-tight. The previously-weighed parts of the apparatus were at the same time annexed, and now the apparatus containing the animals very accurately weighed. The balance with which the weight was estimated, when loaded with 10 lbs., turned with 2 milligrms.

The tubes which contained the caustic potash, as well as those filled with sulphuric acid and chloride of calcium, and the bulb-apparatus, were weighed in an ordinary chemical balance, by which they could be accurately estimated to within $\frac{1}{2}$ a milligrm.

When the separate parts of the apparatus were united, the efferent cocks were closed, and the air withdrawn by means of the aspirator. The solution of potash rose in the bulb-apparatus; some air passed through it, this however soon ceased; the cock of the aspirator being now closed, the height of the solution of potash ought not to alter, not even when the cock of the aspirator is again opened. In this way the air-tight closure of the several parts of the apparatus between the aspirator and the cock was ascertained. When this was opened, an admission of air again took place; the other cock being closed, so that the tube dipping into the mercury communicated with the cylinder, the aspiration was likewise stopped, and the mercury stood at a certain height. When the cock of the aspirator is closed, neither the level of the solution of potash nor the quicksilver ought to alter. That the purifying apparatus was air-tight was proved in the same manner. After having ascertained this perfectly, a slow current of air was conducted through the apparatus by means of the aspirator, so that about 2–3 litres of air passed through the cylinder per hour, and thus it was filled with fresh air about twice in the same space of time. Sometimes the current was allowed to pass through more slowly, at others more quickly; it continued, if the experiment was carried on during the night, without intermission and with the same velocity.

In the chloride of calcium tubes the water was condensed; and in the sulphuric acid tube, what little water remained uncondensed and a small quantity of volatile animal matter, by which the sulphuric acid after continued use became red; in the bulb-apparatus and the potash-tubes the carbonic acid was absorbed.

The animals passed a quantity of fæces and urine*, especially when freshly caught. Its amount could not be accurately ascertained, much less that of the water, which condensed in the cylinder; consequently these substances were weighed together with the frogs and the cylinder. The method of calculation is thus very simple. The amount of the expired water is certainly in this manner lost as a known quantity. Since it cannot, however, be estimated by this method, because the amount separated by perspiration and urine was mixed with it, this cannot enter into the calculation.

Normal Respiration of the Animals.—To render the results, which are merely enumerated further on, more intelligible, we have copiously detailed the first experiment in the table containing the results of all the experiments.

Four large animals, which were caught on the 9th of July and were very lively, were placed in the cylinder on the 11th of June, and left therein for 52 hours. Notwithstanding they had been well-dried, the cylinder was almost immediately moistened with condensed aqueous vapour, and at the end of the experiment a large quantity

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* In one experiment, five frogs, which together weighed 450 grms., had passed about 50 grammes of excrement.

of moisture had collected in the cylinder. The animals did not lose any of their liveliness during the whole experiment. At the commencement of the experiment the apparatus with the animals weighed 993·200+284·887 grms.; after the experiment, with the enclosed excrements and liquids, 993·200+283·382 grms. The apparatus had thus lost 1·505 grms. in weight. This loss must consist of vaporized water and expired carbonic acid, or rather of their elements, given off by the animals. The chloride of calcium and sulphuric acid tubes had gained in weight 1·312 grm. (from evaporated water); the potash apparatus 2·151 grms., consisting of carbonic acid. If the matters thus removed be added to the weight of the animals after the experiments, there must be an excess above the original weight of the animals, which, if we consider the nitrogen in normal respiration as perfectly indifferent, must consist of absorbed oxygen:—

	Grammes.
	283·382
	1·312
	2·151
Total........	286·845
Weight of the animals before the experiment ..	284·887
Absorbed oxygen	1·958

The expired carbonic acid, 2·151 grms., contains ·587 grms. of carbon and 1·564 of oxygen. Thus ·394 grm. more of oxygen is absorbed than was required for producing the exhaled carbonic acid. The oxygen was probably used in the formation of water; this is rendered more probable by Boussingault's experiments on the nutrition of turtle-doves, in which the whole of the hydrogen of the food was not found in the excrements:—

Number of the frogs.	Their weight before the experiment.	Loss during the experiment.	Expired carbonic acid.	Carbon contained therein.	Evaporated water.	Absorbed oxygen.	Oxygen contained in the carbonic acid.	Oxygen contained in the water.	Duration of the experiment in hours.
4	284·887	1·505	2·151	·587	1·312	1·958	1·564	·394	52
5	449·120	1·220	2·112	·576	·965	1·857	1·536	·321	24
4	466·765	·750	1·007	·275	·672	·929	·732	·197	24
7	519·665	·780	1·492	·407	·668	1·380	1·085	·295	25
7	543·742	·888	1·599	·437	·690	1·401	1·163	·238	24
5	325·411	1·021	1·044	·285	·964	·987	·759	·228	42
5	396·225	2·353	3·373	·920	1·876	2·896	2·453	·443	44

From a survey of these experiments it is seen that a much larger quantity of oxygen is absorbed than is necessary to form carbonic acid. The author observed the same in an experiment on a rabbit, which was performed with an exactly similar apparatus, except that the cylinder was exchanged for a larger one. The animal was in good condition and confined in the apparatus for 8 hours. It had passed but a small quantity of urine (9·162 grms.):—

	Grammes.
Weight of the animal before the experiment....	777·103
Weight of the animal after the experiment	776·683
Loss..................................	·420
Expired carbonic acid	8·846
Evaporated water	·831
Absorbed oxygen	8·257
Oxygen in the carbonic acid...............	6·433
Consequently there had served for the oxygenation of the hydrogen	1·824

On the Influence of the Time of the Day on the Respiration.—Prout has shown that the quantity of carbonic acid expired varies at different periods of the day. Marchand confined his experiments to ascertain whether the respiration of these animals was diminished during the night. The animals were put into the apparatus soon after being caught. They weighed 525·352 grms., and were seven in number. The experiment lasted from 9½ o'clock in the morning until the same time in the evening. The carbonic acid expired during this time amounted to ·570 grm. = ·155 grm. of carbon. ·507 grm. of oxygen was absorbed, of which ·415 grm. was in the carbonic acid, and ·092 grm. in the water. The proportion of the absorbed oxygen to the carbon consumed was as 327 : 100.

The animals were left in the apparatus, and the experiment concluded in 12 hours. During the night they had produced only ·435 grm. of carbonic acid = ·119 grm. of carbon; ·407 grm. of oxygen was absorbed, of which ·316 grm. was required for forming carbonic acid and ·091 water. The absorbed oxygen was in the proportion of 342 : 100 to the consumed carbon. It is very remarkable that the amount of oxygen required for the formation of water remained the same both by day and night, whilst that for the production of carbonic acid was so essentially altered.

In another experiment, four frogs of 273·745 grms. weight, from 9½ in the morning to the same time in the evening, expired ·230 grm. of carbonic acid = ·063 carbon. They absorbed altogether ·178 grm. of oxygen; ·167 for the formation of carbonic acid, and ·011 for the production of water. During the next 12 hours of the night ·125 grm. of carbonic acid (=·034 carbon) only was expelled, ·084 grm. of oxygen was absorbed, whilst the carbonic acid produced ought to have required ·091 grm. of oxygen. The animals had become very weak from the continued fasting.

Influence of Temperature on the Respiration.—The influence which the temperature of the surrounding air exercises on the respiration was examined, by supporting the cylinder on blocks of wood in another cylinder which was higher and broader, and which was filled with water of different temperatures, which were thus at the same time communicated to the inner cylinder. The thermometer indicated the constant temperature of the confined atmosphere. To regulate the temperature of the surrounding water, it was arranged so that it might flow over the top, whilst fresh water ran from a reservoir standing above through a long funnel to the bottom of the vessel, whence it forced its way from below upwards. When water colder than the atmosphere was used, the arrangements were reversed. The water flowed out near the bottom, entering from above:—

Weight of the six frogs.	Temperature.	Time and duration of the experiment.	Expired carbonic acid.	Carbon contained therein.	Absorbed oxygen.	Oxygen in the carbonic acid.	Oxygen in the water.
	Fahr.	*o'clock.*					
436·251	35–37°	8–2	·102	·0278	·0800	·0742	·0058
436·051	43–45°	3–9	·325	·0886	·3190	·2364	·0826
430·125	53–57°	6–12	·306	·0835	·2860	·2225	·0635
428·800[*]	64–68°	4–10	·289	·0790	·2630	·2100	·0530
428·705	82–86°	9–3	·201	·0546	·1570	·1464	·0106

It is seen from this table that in these animals the respiration was most active at a tolerably low temperature, 43–57°, and that an alteration of 43–45° had but little effect. When the temperature fell nearly to the freezing-point the respiration was much diminished; it approached nearly to the combustion of pure carbon. The same occurred at a tolerably high temperature, 82–86°, at which the animals became much weakened.

[To be continued.]

Experiments on the Formation of Lactic Acid from Cane-sugar.
By Prof. H. VON BLUCHER.

1. With a view of repeating the experiments of Pelouze and Gelis on the formation of butyric acid[†], the author added to a solution of 1800 grms. of cane-sugar in 9500 grms. of water some well-washed caseine, and finely pulverized chalk, and exposed this mixture in an open glass vessel for $4\frac{1}{2}$ weeks, in a drying chamber, at a temperature from 86° to 94°, agitating it almost every day. In the course of 17 days some aggregated crystalline masses separated, which in the course of a few more days increased to such an extent, that being carried to the surface with the ascending bubbles of gas, they formed a compact crust, several inches in thickness, on the surface of the liquid. In 31 days the whole liquid had become converted into a thick crystalline paste. The water which had evaporated during this time had always been restored. The entire mass was now

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[*] The animals had diminished in weight from the separation of excrements.

[†] Chem. Gaz. vol. i. p. 477.—ED.

filtered through fine linen and well-pressed, again dissolved in boiling water, and exposed in a cold place to crystallize; it yielded 1121 grms. crystallized lactate of lime, which, besides its water of crystallization, contained about 1½ per cent. humidity. This large amount of lactate of lime was perfectly white after the first crystallization, and only acquired a slight brownish tint after long drying. On recrystallization the salt remained white, and was perfectly pure.

2. The author now made several experiments, in which the solutions were exposed to a temperature of 80° to 82°. They all underwent the same change, with apparently the same phænomena. 600 grms. cane-sugar, 2800 water, and 150 grms. moist caseine, yielded with a sufficient quantity of chalk, in the course of 4½ weeks, 469 grms. of well-dried lactate of lime. The expressed liquid gave a residue of 82·1 grms., containing 16·91 grms. lime.

300 grms. sugar, 1400 grms. water, &c., gave under the same circumstances 213 grms. crystallized lactate of lime. The residue, evaporated in the water-bath, weighed only 29 grms., in which were found 6·01 grms. lime.

These experiments prove, at all events, that 92 per cent. of the constituents of the sugar, which have not escaped in a gaseous state, have become converted into lactic acid, and probably, if we suppose the 6·01 grms. lime contained in the evaporated residue to be combined with 17·2 grms. lactic acid, even 99 per cent.

3. 1400 grms. cane-sugar were dissolved in 6000 grms. water and 400 grms. moist (containing 94 grms. dry) caseine, and a sufficient quantity of finely-pulverized chalk mixed with it, and the whole exposed to a temperature of 77° to 86°. For the first 14 days the liquid remained perfectly clear with exception of the sediment, and retained a sweet taste; but soon the separation of crystalline lactate of lime took place with an apparently considerable evolution of gas, and in the course of 4 weeks the whole mass formed a crystalline paste, as in the previous experiments. After one re-crystallization 870 grms. crystallized lactate of lime were obtained; and the mother-ley, somewhat evaporated, yielded 162 grms. crystallized mannite. The latter however was not perfectly pure, and contained 3·6 per cent. lime, probably in combination with lactic acid. In the liquid separated by filtration and pressure from the mannite, there subsided, on evaporation over the water-bath, a further quantity of minute crystals of mannite, which however could not be isolated from the syrupy liquid, and the whole was therefore evaporated in the water-bath. The residue obtained in this manner weighed 732 grms., and contained 12¾ per cent. lime.

350 grms. of this dry residue were dissolved in 1200 grms. water, mixed with caseine and pulverized chalk, and placed in the warm chamber; in 7 days it had become converted into a crystalline paste, from which were obtained on recrystallization, &c. 210 grms. crystallized lactate of lime. The ley concentrated in the water-bath yielded a residue of 26 grms., in which were found 5·53 lime. If the product of 210 grms. be extended to the entire residue of 732 grms., this would have yielded 439 grms. of the salt; consequently

the above 1400 grms. sugar would have produced 1309 grms. crystallized lactate of lime, and estimating the loss approximately at 3 per cent., 1348 grms. Notwithstanding the formation of mannite, therefore, more lactic acid was formed than in the experiments 1 and 2.

That the cane-sugar is not decomposed in the so-called lactic fermentation into mannite and lactic acid, appears to be placed beyond a doubt by the preceding experiments; perhaps however it is first converted into mannite, and this into lactic acid, which is not improbable, judging from the products of decomposition of the residue of 350 grms. To decide, if possible, this question, the author placed a portion of the mannite obtained, mixed with caseine, &c., in the drying-room; but not a trace of any formation of lactate of lime was perceptible after 8 days, nor could the author observe any sign of the formation of mannite in a solution of cane-sugar which had been mixed with caseine, &c., and exposed to a suitable temperature, after the course of 8 days on careful evaporation.—Poggendorff's *Annalen*, vol. lxiii. p. 425.

ANALYTICAL CHEMISTRY.

On a new Method of analysing Blood, and on the Constitution of the Blood-Globules. By L. Figuier.

The author objects to the methods of analysing blood generally in use, that several of the constituents are not determined directly by weighing, but are deduced from the loss. The method which he proposes is founded on an observation of Berzelius, that when sulphate of soda is added to blood freed from fibrine by beating, it can be filtered without the blood-globules passing through. In this manner the fibrine, blood-corpuscles and albumen can each be ascertained by direct weighing; and the method has moreover the advantage that only very small quantities of blood are required, which renders it possible even in diseases when but very little blood can be taken from the patient, to ascertain whether it may contain other substances.

The blood as it comes from the vein is beaten until all the fibrine has deposited itself on the twigs of the rod; it is then filtered, the fibrine washed from the rod with water on to a filter, and edulcorated, deprived of fat by a little æther, dried and weighed. At present about 80 to 90 grms. of the filtered solution are mixed with double its volume of a solution of sulphate of soda of from 16° to 18° Beaum., and filtered through a simple weighed filter which has been previously moistened with the saline solution. But very few of the globules pass through. By dipping the filter several times in boiling water, by which the globules are coagulated and rendered insoluble, the sulphate of soda is removed, and the blood-globules after drying can be weighed. Neither tannin nor corrosive sublimate throws down any perceptible quantity of organic substance from the wash-water. The albumen is then precipitated from the filtered serum by boiling, pressed in a piece of linen, washed, dried at 212°, and weighed. The amount of water of the blood is lastly determined by drying a sample of 20 to 25 grms. The salts and the fat are deduced from the loss. In an analysis made according to this method, the author obtained 80·29 per cent. water, 13·06 blood-globules, 0·39 fibrine, 5·06 albumen, and 1·20 salts.

The blood-globules contain albumen and fibrine besides hematine. The fibrine gradually subsides from an aqueous solution of the blood-globules separated by sulphate of soda in the form of a red coagulated mass, which is especially distinct with the globules from frogs' blood. The blood-globules suspended in water yield a filtered solution, which is coagulated by boiling, acids and alcohol; it contains therefore albumen, since the solution of hematine is not coagulated by these agents. It is best to extract the hematine from the blood-globules with alcohol containing a little ammonia, which leaves behind a brown coagulum. The red solution yields on evaporation a bright red residue, from which a little fat may be extracted by æther.—*Ann. de Chim. et de Phys.*, xi. p. 503.

REVIEW.

Outlines of Chemistry for the Use of Students. By William Gregory, M.D. Part I.—*Inorganic Chemistry.*

The present work, the author informs us in his preface, is designed exclusively for the use of students attending lectures on chemistry. We have not the least doubt, however, that it will be as much patronized by those persons whose time or means have not allowed them to attend courses of lectures, it being in fact one of the best elementary introductions in the English language to the larger treatises on this branch of science that has yet come under our observation.

The arrangement is excellent, the style clear and concise; in a word, it is just such a work as might be expected from so able a chemist as Dr. Gregory, and differs widely from the generality of works of this kind, which frequently are mere crude compilations by persons imperfectly acquainted with the subject.

A remarkable feature in this work is the omission of the chapters on light, heat, electricity and magnetism; and the reasons assigned for so doing are in our opinion so excellent and well-deserving of the attention of lecturers, that we are induced to lay them before our readers:—

"For nearly ten years past," says Dr. Gregory, "I have been in the habit, in my lectures, of treating these subjects very briefly, partly because, in my opinion, they belong almost entirely to the province of physics, but also, and chiefly, because the enormously increased extent and importance of chemistry, especially of organic chemistry, rendered every moment of time in a course of lectures, which at best could be but imperfect, precious in the highest degree.

"Since I had the honour to be appointed to the Chair of Medicine and Chemistry in the University and King's College, Aberdeen, in 1839, I have altogether discontinued the teaching of the above-mentioned subjects, *as regular sections of the course*, and have only taught them incidentally, that is, where they naturally come into very close connexion with chemistry; and by this means I have been enabled to devote about three months, out of five and a half, to organic chemistry, a branch of the subject of the highest importance to medical students, and, as is well known, of daily increasing interest and value, from its applications to physiology and the useful arts. I am inclined to believe, that if, by the omission of the imponderables as a regular part of the course, anything has been lost, the comparatively full, although yet too brief, development of organic chemistry has furnished more than sufficient compensation.

"But, in truth, the imponderables are now very generally, as they undoubtedly ought to be, taught as a part of physics by the lecturers on natural philosophy, so that the teacher of chemistry is not absolutely required to do more than to explain their most important bearings on chemistry."

We ought perhaps to apologize for occupying so much of our space with the above extract; but the views therein expressed are of very great importance, for unfortunately it is too frequently the case in this country that a great part of the session is consumed in treating of the imponderables, the course draws to a close, and the portion relating to that important branch of the science, organic chemistry, in which the medical student is most specially interested, is briefly and hurriedly got through.

We must here however close our notice of this work, strongly recommending it to all students. Some of the subjects are treated of rather too briefly, for instance the compounds of antimony, which being of importance in pharmacy, deserved more particular attention.

The Second Part, containing Organic Chemistry, is promised early in the spring.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

March 3rd, 1845. (Thomas Graham, Vice-President, in the Chair.) The following communications were read:—

"Contributions to Actino-Chemistry," by Robert Hunt.

In this paper Mr. Hunt describes many new properties imparted to bodies by exposure to sunshine and to radiation, disturbing known chemical forces, and sometimes establishing a new order of affinities. Light is used to distinguish those radiations which produce vision and colour; heat, those effecting any thermic phænomena; whilst those radiations on which certain chemical changes are supposed to depend are distinguished by the epithet of actinic. The terms actinism, actinicity, actinized and actinic influence, and other similar terms, are then defined.

The influence of the solar rays on precipitation of solutions of platinum, manganesiate of potash, sulphate of iron, iodide of silver, bichromate of potash, &c. by various reagents are then described, also the colour of the precipitates produced; the effects are shown to vary according as they are exposed to the different-coloured rays of light, the indigo ray producing the maximum of effect, the yellow the minimum; and generally, with regard to the colour of the precipitates, that they are brighter according as they are effected under the stronger influences of the sun's rays.

The actinic influence on chemical combination is next considered, and the effect of protosulphate of iron upon solutions of acetate of silver and acetate of mercury, upon exposure to sunlight and when kept in the dark, is then detailed. The effect of other chemical solutions are also stated, in all of which it appears that sunlight has a powerful agency in producing precipitation, and in brightening the colours of the precipitates. Mr. Hunt then refers to a communication he made in 1840 to the 'Philosophical Magazine,' on actinic influence on electro-chemical action, and from two new experiments he describes draws these conclusions:—

1. That electro-metallic precipitation is prevented by the influence of the sun's rays.

2. That light is not the retarding agent, but that the exercise of electrical force is negatived by the direct influence of actinism.

Mr. Richardson exhibited and described the formation of the beautiful coloured film produced on the surface of melted lead by exposure to the air, and generally known under the name of lead-skimmings.

A letter from Dr. Gregory was read, communicating the discovery of a new and remarkable phosphate of magnesia, of which the formula is $3MgO + 2PO^5$. This substance is dense and granular, and as completely insoluble as the sulphate of barytes. It is formed on heating magnesia, or any phosphate of magnesia, with excess of glacial phosphoric acid; and its production is likely to offer a superior process to those generally followed for the separation and quantitative estimation of that earth.

THE CHEMICAL GAZETTE.

No. LX.—April 15, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Potash upon Sugar, Starch, Gum and Mannite.

By M. Gottlieb.

The following experiments were principally made with cane-sugar; the author, however, has fully convinced himself that starch, gum and mannite yield the same results.

When a concentrated solution of potash, evaporated to such a degree that it solidifies on cooling, is gradually brought into contact with about 1 part sugar to 3 of the hydrate of potash, and heated without interruption, the mass becomes brown, with constant evolution of hydrogen, and the smell of caramel is distinctly perceptible, which however soon disappears to make place for a more aromatic odour. After a few minutes the violent part of the action is over, the mass becomes thick, and froths constantly until the brown colour disappears, when the whole becomes tolerably solid, and the operation may be looked upon as terminated. The saline mass is of a light yellowish colour after cooling. It is dissolved in a little water and an excess of moderately-dilute sulphuric acid added to it, when it evolves considerable heat, which should be avoided as much as possible, and also gives off a large amount of carbonic acid. At the same time an abundant precipitate of binoxalate of potash is formed; the liquid filtered from it is distilled in a retort; the product, which is very acid, contains formic acid, acetic acid, and a new acid which the author calls *metacetonic acid.* To remove the formic acid, the mixture is boiled with an excess of oxide of mercury as long as any evolution of carbonic acid results, when the per- and protosalts of mercury formed are decomposed by sulphuretted hydrogen, and the two acids saturated with carbonate of soda. It was found impossible to separate the acetic from the metacetonic acid in any other way than by the crystallization of their soda salts, and even this method presents several difficulties. Metacetonic acid is extremely similar in its properties to acetic acid; their silver salts have nearly the same solubility; mixtures of acetate and metacetonate of copper, zinc, barytes, &c. do not crystallize, and moreover the two acids have a great tendency to form double salts in combination with the same base.

Since the metacetonate of soda crystallizes with the greatest difficulty, while the very opposite occurs with acetate of soda, it is easy to remove the greatest portion of the latter, but extremely difficult to separate the last traces of it from the metacetonate, as a distinct crystallization scarcely ever takes place in the syrupy mother-ley. In such case it is most advantageous to dilute the solution somewhat, and to remove the last portions of acetate by very slow evaporation. If, after a considerable interval of time, no more crystals of acetate of soda make their appearance, the salt is pure. To ascertain the composition of metacetonic acid, its silver salt was prepared by adding nitrate of silver to a moderately-concentrated solution of the metacetonate of soda as long as a thick white precipitate resulted; the whole was then boiled, when a slight reduction took place, and quickly filtered. On cooling, the metacetonate of silver separates in shining, white, heavy granules, which appear under the microscope in the form of small clusters of short acicular crystals. A small quantity more of the salt may be obtained by evaporating the mother-ley.

Metacetonate of silver is not very sensitive towards light; but when heated to 212° it soon becomes blackish-brown, and is partially decomposed; it must consequently be dried *in vacuo* over sulphuric acid. When a strong mineral acid is poured over it, it disengages the peculiar odour of metacetonic acid, which calls to mind both that of butyric and acrylic acids. It melts quietly when heated in a porcelain crucible, and burns without the least noise, differing therefore essentially from the acetate and acrylate of silver. It consists of—

	Found.		Equiv.		Calculated.
Carbon	19·76	19·72	6 =	455·12	20·05
Hydrogen	2·74	2·82	5	62·39	2·74
Oxygen........	13·54	13·77	3	300·00	13·24
AgO	63·96	63·69	1	1451·60	63·97
				2269·11	

Metacetonic acid consequently belongs to that series of acids whose hydrate contains the carburetted hydrogen CH; its place is between acetic and butyric acids. It is soluble in every proportion in water, possesses a peculiar odour, and when tolerably concentrated has a strong acid taste.

The double salt which metacetonate of silver forms with acetate of silver has already been noticed. It is obtained when the original mixture of acetic and metacetonic acid is boiled with oxide of silver and filtered, or by decomposing the mixture of acetate and metacetonate of soda with nitrate of silver. It crystallizes from the hot solution in beautiful, shining, dendritic crystals, which appear to possess no resemblance to either the metacetonate or the acetate of silver. The filtered salt is light, loose, and may be dried at 212° without decomposition. It consists of—

Carbon	17·70	17·78	5 =	379·27	17·39
Hydrogen	2·38	2·39	4	49·91	2·28
Oxygen	13·47	13·62	3	300·00	13·75
AgO	66·45	66·21	1	1451·60	66·58
				2180·78	

The formula $C^5H^4O^3 + AgO$, multiplied by 2, gives $C^{10}H^8O^6 + 2AgO = (C^4H^3O^3 + AgO) + (C^6H^5O^3 + AgO)$.

The author likewise once obtained the double salt of soda accidentally, for it could not be prepared at will. It forms minute shining needles, very similar to the acetate of soda, is readily soluble in water, and contains water of crystallization. It contains 35·12 per cent. NaO and 31·2 aq.

Metacetonic acid combines easily with æther, and the metacetonate of the oxide of ethyle is obtained without difficulty on boiling the metacetonate of silver with sulphuric acid and absolute alcohol, and then mixing it with water, when the æther separates as a light fluid, possessing an agreeable fruity odour, but which has no resemblance with the butyrate of ethyle.

On taking into consideration the formula for metacetonic acid, it is evident that it may be considered both as a higher degree of oxidation of acetone, as also of Fremy's metacetone. The treatment of cane-sugar with potash likewise presents numerous analogies to the process by which Fremy obtained acetone and metacetone on heating sugar, gum and starch with lime. It was highly probable therefore, that the metacetonic acid owed its origin in the above reaction to a previous formation of acetone or metacetone. To decide this, M. Gottlieb prepared large quantities of acetone and metacetone, employing for the first the method described by Zeise, for the latter the one prescribed by Fremy. In both cases it is far more advantageous to employ, instead of the prescribed proportion of lime and sugar, only about half the former, when the process proceeds more quickly and the produce is far more abundant. The preparation of metacetone is considerably facilitated by taking to 1 part sugar only 3 parts of lime, and gently heating the mixture (from 10 to 15 lbs. at once) in an ordinary still, provided with a good cooling apparatus, which may be done without the least injury resulting to the still.

When metacetone is dropped on fusing hydrate of potash, nearly the whole distils off without being further altered, and in this manner only traces of a volatile acid are obtained. It is likewise difficult to form metacetonic acid by the action of potash-lime upon metacetone, since when heated too high carbonization readily ensues, while with too low a temperature the metacetone passes over unchanged. Metacetonic acid is however obtained most abundantly and quickly by oxidizing metacetone with a mixture of sulphuric acid and bichromate of potash. The reaction is at first very violent, and must be effected in a spacious flask, which is connected with a cooling apparatus; a considerable quantity of carbonic acid is disengaged, the whole becomes very much heated, when some unaltered metacetone passes over, and at last it is requisite to assist the action by heat. As soon as the disengagement of gas has ceased, the receiver is changed, and the acids formed distilled over. These are the acetic and metacetonic acids, which are saturated with carbonate of soda and separated by crystallization. The author prepared a silver salt from the metacetonate of soda obtained in this manner, which agreed perfectly in its properties with the salt obtained by the action of hydrate of potash upon sugar, gum, &c. The analysis yielded 64·00 per cent. AgO, 19·76 C, 2·80 H. The double salt was also prepared, which likewise agreed in all its properties, and possessed the same composition as that produced from sugar. It gave 66·58 AgO, 17·16 C, 2·42 H.

The author could not succeed in preparing metacetonic acid from acetone. Dumas states that only carbonic acid and carburetted hydrogen are formed by the action of heated potash-lime on acetone. The author obtained, in all the experiments in which he passed vapours of acetone over potash-lime after saturation of the same with sulphuric acid and distilling the acid liquid, a considerable quantity of acetic and formic acids. Chromic acid yielded with acetone only acetic acid, as asserted by Dumas.

It is consequently proved that the metacetonic acid is actually produced by the oxidation of metacetone, and we are now able to form a clear idea of the action of fused hydrate of potash on sugar, starch, &c. The sugar is first decomposed into carbonic acid, acetone and metacetone; the metacetone into metacetonic acid, but the acetone into acetic and formic acids, which are both partially oxidized further to oxalic acid.—*Ann. der Chem. und Pharm.*, lii. p. 121.

On the Respiration of Frogs. By Prof. F. R. MARCHAND.

[Continued from p. 151.]

Respiration in pure Oxygen.—The respiratory cylinder was filled with the pure gas, by first filling it with water which had been boiled, inverting it over water of the same kind, and then passing the oxygen into it. Meanwhile the frogs were placed in a second cylinder, which was closed by a glass plate, and was weighed with the animals. The cylinder containing the oxygen was likewise covered with a glass plate, and the second one inverted over it. The plates were removed, and the animals fell into the cylinder containing the oxygen. This was covered as quickly as possible with the brass plate. The cylinder containing the oxygen and animals was then weighed, the aspirator removed, and a gasometer containing pure oxygen, which was conducted to the animals, was attached to the other end.

During 24 hours about half a cubic foot of oxygen was conducted through the apparatus. After the completion of the experiment the animals were weighed in the cylinder filled with oxygen; the oxygen contained in the potash and chloride of calcium apparatus was displaced by atmospheric air before the weighing.

The animals which were used in the experiment had previously served for another, instituted in the usual manner, so that it might be ascertained how far the result had been modified by the use of oxygen:—

		In oxygen.
Weight of the animals before the experiment ..	525·352	501·202
Weight of the animals after the experiment....	524·507	501·025
	·845	·177
Carbonic acid expired	1·005	1·030
Carbon contained therein	·274	·281
Evaporated water	·754	·278
Oxygen absorbed	·914	1·121
Oxygen contained in the carbonic acid	·731	·749
Oxygen contained in the water................	·183	·372

The quantity of expired carbonic acid is thus almost unaltered, whilst the quantity of absorbed oxygen has remarkably increased; consequently a much more considerable oxidation of hydrogen must have resulted from the action of the oxygen; in fact, twice as much hydrogen had been oxidized as when atmospheric air was used. Nitrogen must necessarily have been exhaled in the respiration of oxygen, as was observed by the older chemists, since this gas, which is contained in blood, must have been separated in consequence of the power of diffusion of the inspired oxygen.

Respiration in pure Hydrogen.—The author in his experiments has taken especial care that the hydrogen was not only free from oxygen, but also from other substances injurious to the animals. To wash the gas with alcohol is worse than doing nothing; for, as is well known, frogs are so sensitive of alcohol that they are soon killed by it. The pure hydrogen was collected in a gasometer over water which had been boiled; a weighed cylinder, arranged in exactly the same manner as that first used, was provided with two cocks; in it the animals intended for the experiment were placed. A tube united one of the cocks with a double-barrelled air-pump, which exhausted it remarkably quick. The gasometer was joined to a tube 5 feet long, containing finely-divided copper, and this with a U-formed tube filled with pieces of caustic potash. This took up every trace of carbonic acid mixed with the hydrogen, which could only arise from the water employed in filling the gasometer. The oxygen, or at least the greatest part, arising from the water used in filling the cylinder, was separated by placing a number of lamps supplied with double currents of air beneath the long glass tube, by which the latter could be kept so hot at several points, that there was almost fear of its melting. Moreover a broad glass tube, filled with spongy platinum, was placed between them. If this is to be completely efficacious, it is necessary to warm it slightly. In this manner the tube was heated to redness at several places, and the remaining portion kept hot by moving a lamp to and fro beneath it. There was no doubt therefore of the hydrogen being free from oxygen. The experiment itself was made in the following manner:—

The animals were weighed in the cylinder, and this, with the cocks closed, was united with the rest of the apparatus; hydrogen was introduced into the cylinder from the gasometer until the tubes were full, so that on heating them they should not explode. The cock nearest the gasometer was closed, the other opened, and exhaustion applied as rapidly as possible; the tubes were heated, and the upper part of the gasometer filled with water, the cock of the gasometer being still closed. As soon as the exhaustion was completed, an assistant opened the cock of the gasometer, and at the same time that of the cylinder. The gas was allowed to pass tolerably slowly, so that no oxygen should escape unburnt. When the barometer had again completely fallen, the operation was repeated a second and third time. In this manner there could be no doubt that the animals were surrounded by hydrogen gas free from oxygen, and that their lungs were free from carbonic acid. The cocks were closed, and the animals soon died, with the appearances described by Müller. They were left for 2 hours in the atmosphere of hydrogen; the cylinder was then attached to the ordinary apparatus, the hydrogen displaced by atmospheric air, and the carbonic acid removed. The current of air which was passed through the cylinder was abundantly sufficient to replace that contained within it four times in half an hour. The apparatus was taken to pieces after the lapse of an hour, and the animals were preserved; they did not however again come to life. Four animals, together weighing 257 grms., produced in this experiment ·079 grm. of carbonic acid. Another experiment yielded ·079 carbonic acid from frogs weighing 307 grms.

Effect of a Vacuum on the Animals.—Six animals, caught three days previously, were placed in the cylinder, as in the first series of experiments, except that the bulb-apparatus and the tube filled with sulphuric acid were exchanged for a U-shaped dry potash and a chloride of calcium tube, as the apparatus containing fluids could not be made use of in this experiment.

The cock with the three apertures was turned so that the cylinder was completely closed. The air-pump was fastened air-tight to the last potash tube, and the air very slowly pumped out. The water and carbonic acid thus withdrawn passed through the chloride of calcium and the potash tubes, in which they were absorbed.

The last potash and chloride of calcium tubes hardly increased in weight at all. On gradually pumping out the air, the animals were at first very quiet; but on continuing the exhaustion to 2 inches, they began to be very restless, and soon after showed symptoms of commencing death, with stupor, from which they could be roused by shaking, when they partly stood up and jumped violently in the apparatus. On continuing the exhaustion to 2 lines, the animals swelled up enormously. In some the tongue, much blown up, was considerably protruded; its several plates separated; nevertheless the animals lived in this state more than 50 minutes, even at this time occasionally crawling about, and with an atmospheric pressure of not more than 2 lines. At an interval of several hours the air, which was dry, and contained no carbonic acid, was admitted. The animals now shrunk up exceedingly, appearing as if consisting of skin and bones. The exhaustion was now again repeated; the animals again swelled, but not nearly so much as before; air was again admitted, and this repeated six times. The animals were weighed, and also the parts of the apparatus. If the experiment was perfectly and accurately performed, the increase in weight of the apparatus should exactly equal the loss in weight of the animals. It was however to be supposed that the apparatus would indicate a slight excess in weight, as a vacuum could not be produced immediately after the animals were placed in the apparatus.

The weight of the animals before the experiment amounted to	486·323
The weight of the animals after the experiment amounted to	485·485
Loss	·838
Water carried off in vapour	·605
Carbonic acid absorbed	·242
	·847
Difference	·009

It might be assumed that by this experiment the whole amount of carbonic acid contained in the animal was ascertained. The experiment appeared to answer so well, that it would have been cruelty to repeat it *.

It was now modified as follows:—Four frogs, which were caught 4 days before the experiment, were placed in the apparatus:—

The weight amounted to	325·231
After exhausting three times they yielded carbonic acid =	·073

They were now left in hydrogen until they were dead. The air, which was then passed through, carried off ·070 grm. more carbonic acid, which had been exhaled in the hydrogen.

Finally, the cock, with three outlets, was closed, and exhaustion induced until the animals were strongly swollen. In this case the animals exhaled ·052 grm. more carbonic acid:—

Thus in all	·195
Watery vapour	·574
	·769
The loss of weight which the frogs experienced amounted in all to	·762

To ascertain what was the average amount of the carbonic acid which was contained in the animals' lungs, six frogs, weighing 440·250 grms., were placed in the cylinder, and the air exhausted to within 6 lines. This vacuum was maintained until some of the animals were apparently dead, which occurred at the end of ten minutes. Atmospheric air was now admitted; the operation was repeated five times. The animals produced ·083 grm. of carbonic acid. This

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* This experiment may serve to determine the quantity of blood in the animals, if the quantity of carbonic acid contained in their blood be previously found out with accuracy. Of course, in every instance, the carbonic acid, and consequently the blood, is estimated too highly, as the carbonic acid is not all contained in the blood. Still we may thus ascertain the *greatest* quantity of blood an animal may contain.

carbonic acid is probably exhaled from the lungs only, not from the blood. This yields the carbonic acid with much greater difficulty; it did not commence to do so until the atmospheric pressure amounted to less than 2 lines.

Respiration in a confined Atmosphere.—In these experiments the animals were each time confined for 4–5 consecutive hours. The atmosphere within the cylinder was then displaced by fresh air, and the product estimated:—

Weight of the animals.	Duration of the experiment in hours.	Carbonic acid expired.	Carbon contained therein.	Oxygen absorbed.	Oxygen contained in the carbonic acid.
379·977	8½	·674	·184	·629	·490
379·977	9½	·522	·142	·529	·380
519·665	7	·296	·081	·222	·215

We here see that the animals absorbed considerably more oxygen at the commencement of the experiment than subsequently; and at the end they absorbed only so much oxygen as was required to form carbonic acid, as in the case of the animals after they have become much exhausted, as for instance from a high or low temperature and want of food. If the animals are allowed to die in a confined atmosphere, an extraordinarily large volume of carbonic acid is found therein, and there must necessarily be a considerable quantity of nitrogen absorbed. The following experiment will clearly demonstrate this:—

Five animals, which were caught a short time previously, were placed in the closed apparatus. They weighed 402·162 grms. The night after they were dead, and had exhaled 1·068 grm. of carbonic acid = ·296 grm. of carbon. This carbonic acid would occupy about 570 cubic centimetres; the cylinder contained 920 cubic centim. of air, about 184 of which consisted of oxygen. A quantity of carbonic acid in the blood must therefore have been exchanged for nitrogen; consequently a much greater increase in weight is apparent than could possibly result from the absorption of oxygen alone.

Respiration of the Animals when fasting.—The animals were mostly used for experiment soon after being caught. After one experiment, which lasted for nearly 24 hours, they were placed in spring water, and this was renewed every 2 or 3 days; they had no food. They remained very lively the whole time. At the end of 8–12 weeks some had sores, especially on the joints and haunch-bone. This occurred frequently when they were not able to remain some time on land; the skin and flesh then disappear, and the bones and ligaments are exposed. In this case they soon die. The animals which were used together in one experiment were tolerably equal in size and weight. Notwithstanding they had no food all the time, Marchand found that the animals sometimes weighed more on one day than the previous, and indeed sometimes considerably more; this must have arisen from absorption of water. At the end of several weeks the animals voided no perceptible excrement; mere membranous threads, consisting apparently of epithelium, were found in the cylinder and in the water. It was remarkable how much the animals were altered in colour whilst kept in the respiratory cylinder. Their bright green colour in some was converted into brown and perfectly dark yellow.

Number of the experiment.	Duration of the experiment in hours.	Oxygen contained in the water.	Oxygen contained in the carbonic acid.	Oxygen absorbed.	Carbon contained in the exhaled carbonic acid.	Carbonic acid and watery vapour exhaled.	Weight of the animals after the experiment.	Weight of the animals before the experiment.
1st Series.—5 *Frogs.*								
1	42	0·228	0·759	0·987	0·285	1·044 C.* 1·964 W.†	324·390	325·411
2	62	0·312	0·978	1·290	0·367	1·345 C. 0·753 W.	311·137	311·945
2nd Series.—*In the* 1*st Experiment,* 4 *Animals* ; *in the* 2*nd,* 5.								
3	52	0·394	1·564	1·958	0·587	2·151 C. 1·312 W.	283·382	284·887
4	48	0·410	1·323	1·733	0·496	1·819 C. 0·787 W.	295·574	296·447
3rd Series.—5 *Frogs. After the* 6*th Experiment* 1 *Animal died.*								
5	44	0·443	2·453	2·896	0·920	3·373 C· 1·876 W.	393·872	396·225
6	42	0·235	1·167	1·402	0·438	1·605 C. 1·415 W.	399·205	400·820
7	48	0·257	1·233	1·490	0·463	1·696 C. 1·423 W.	395·486	397·115
8	24	0·172	0·489	0·661	0·184	0·673 C. 0·764 W.	378·895	379·659
9	21	0·106	0·354	0·460	0·133	0·487 C. 0·713 W.	374·237	374·977
10	30	0·372	0·621	0·993	0·233	0·854 C. 0·892 W.	358·567	359·320
11	24	0·123	0·406	0·529	0·152	0·558 C. 0·700 W.	286·766	287·495
12	25	0·004	0·265	0·269	0·099	0·364 C. 0·680 W.	279·440	280·175
13	24	0·004	0·258	0·262	0·097	0·355 C. 0·582 W.	273·070	273·745

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* C signifies carbonic acid.

† W signifies water.

Number of the experiment.	Duration of the experiment in hours.	Oxygen contained in the water.	Oxygen contained in the carbonic acid.	Oxygen absorbed.	Carbon contained in the exhaled carbonic acid.	Carbonic acid and watery vapour exhaled.	Weight of the animals after the experiment.	Weight of the animals before the experiment.
4TH SERIES.—7 *Frogs. After the 2nd Experiment* 1 *Frog died.*								
14	24	0·238	1·163	1·401	0·436	1·599 C. 0·690 W.	542·854	543·742
15	24	0·204	0·759	0·963	0·284	1·043 C. 0·621 W.	511·488	512·189
16	16	0·211	0·367	0·578	0·138	0·505 C. 0·771 W.	439·552	440·250
17	24	0·270	0·625	0·895	0·235	0·860 C. 0·868 W.	428·855	429·688
18	24	0·131	0·554	0·685	0·208	0·762 C. 0·758 W.	417·855	418·690
19	25	0·095	0·596	0·691	0·224	0·802 C. 0·641 W.	388·608	389·378
5TH SERIES.—4 *Frogs.*								
20	24	0·197	0·732	0·929	0·275	1·007 C. 0·672 W.	466·015	466·765
21	24	0·340	0·661	1·001	0·248	0·909 C. 0·802 W.	430·878	431·588
22	24	0·206	0·540	0·746	0·202	0·742 C. 0·860 W.	437·739	438·595
23	24	0·238	0·724	0·962	0·271	0·995 C. 0·777 W.	439·950	440·760
24	24	0·179	0·516	0·695	0·194	0·710 C. 0·560 W.	423·660	424·235
25	24	0·112	0·484	0·596	0·184	0·666 C. 0·417 W.	405·610	406·097
6TH SERIES.—9 *Frogs.*								
26	24	0·272	0·656	0·928	0·246	0·902 C. 0·832 W.	271·3	272·106
27	24	0·010	0·468	0·478	0·176	0·644 C. 0·729 W.	230·772	231·667
28	24	0·047	0·316	0·363	0·118	0·434 C. 0·587 W.	201·342	202·000

Upon looking over the preceding table, it is evident that in general, during continued fasting, the animals always absorbed less oxygen and exhaled less carbonic acid. In the 1st, 2nd and 3rd experiments of the 1st series a difference is observable in this respect, as this result was only first perceptible after the fasting had been continued for some time; it was then well-marked. In the 6th experiment of the 3rd series (No. 10) the animals were confined for a long time; hence the difference. The 7th experiment was made with only 7 animals. The respiration was apparently increased; however, this is not real; as the animal which was found dead, and which of course must have been in a diseased state before this time, must have caused a diminished intensity in the respiration.

It is well worthy of remark, that the proportion of oxygen absorbed to the carbonic acid exhaled constantly increases until it has amounted to about 410–430 : 100. Here the greater part of the hydrogen must be oxidized; the proportion then falls, until it comes to a mere oxidation of carbon, for to 100 parts of carbon 270 parts of oxygen are absorbed, whilst 267 would have been required for the formation of carbonic acid. When this low proportion is attained, it remains tolerably constant.—*Journ. für Prakt. Chem.* for Oct. 1844.

Urine loaded with Hippuric Acid in Chorea.

Pettenkofer examined the urine of a girl, aged 13, suffering from chorea. When exhausted with weak spirit after evaporation, and the spirituous extract treated in the cold with muriatic acid, it yielded copious crystals of hippuric acid, especially the morning urine. 1000 parts of the urine left 40·668 solid residue, 31·251 of which (consisting of hippurates, urea, extractives and alkaline chlorides) were soluble in spirit, and 9·417 (composed principally of uric acid, sulphates, phosphates and mucus) were insoluble. The 40·668 of solids left 10·599 ash. This ash contained 30 per cent. of alkaline carbonates. Reckoning these as hippurates, allowing the earthy carbonates for the uric acid, the urine contained 1·2886 hippuric acid, or the solid residue 25·8 per cent. As the nervous malady disappeared, so did the abnormal quantity of the hippuric acid.—*Ann. der Chem., und Pharm.* for Oct. 1844.

On the Wood and Bark of a Mexican Berberis. *By* M. Wittstein.

The author obtained from M. Zuccarini a piece of wood collected by Karwinski, which belongs to an arborescent species of *Berberis*, growing near Santyaquillo and Matehouela in Mexico, and there called *Agrillo*. The piece was a longitudinal section of the stem; the wood was very dense, of a lemon-yellow colour, and from 1 to 2 lines in thickness; on the surface of the section were several fissures, between which a golden-yellow powder was collected, which possessed a very intense bitter taste, and under the microscope appeared in the form of yellow prismatic transparent crystals, precisely like berberine. It dissolved with difficulty in cold water and alcohol, but very readily on the application of heat, and was insoluble in æther; in fact, agreeing in every respect with the berberine from our native species.

The bark was brownish-yellow, light, somewhat spongy, and furnished with a number of deep corrugations and furrows. On digesting it with warm alcohol, a golden-yellow tincture was obtained, which, after the greater portion of the alcohol had been distilled off, had a strong bitter taste, and on spontaneous evaporation deposited some granules of a yellow bitter principle. In the extract, again diluted with water and filtered, carbonate of soda produced a brownish flocculent precipitate, which was carefully washed and dried. Æther shaken with this dry substance did not become coloured, but acquired a bitter taste, and left on evaporation, by exposure to the air, a whitish pellicle, which turned moist turmeric paper brown, and on evaporation in a watch-glass with hydrochloric acid, yielded some verrucous patches of *hydrochlorate of oxyacanthine*.—Buchn. *Rept.*, xxxvi. p. 297.

On the Production and Nature of Ozone. By M. DE MARIGNAC*.

I have made a great number of experiments with the view of verifying the hypothesis of M. Schönbein as to the elementary nature of ozone and the compound nature of nitrogen†. Hitherto my attempts have only led me to a negative result; they prove that this hypothesis cannot be upheld, but they do not yet render any probable explanation. I will here briefly relate the results, retaining the name of *ozone* (by which it has been long known) for the body manifested in different electrical or chemical phænomena by its smell, and by some peculiar chemical reactions, which have been investigated by M. Schönbein:—

1. The production of ozone, at the decomposition of water charged with sulphuric acid by the battery, is independent of the presence of nitrogen. In fact, whatever means of purification I employed to obtain a liquid perfectly free from every nitrogenous compound, whatever precautions I took to expel the air entirely from this liquid, its decomposition by the pile has always given rise to the production of ozone. The experiment was made in an apparatus entirely exhausted of air, and into which no trace of it could enter; and after having continued in action several days, when about a fourth of the water had been decomposed and disengaged in the state of gas, the smell of ozone was exactly the same as at the first instant, if the voltaic current had the same intensity. Care must however be taken to maintain the flask in which the decomposition takes place at a low temperature; for, as M. de la Rive has long since observed, the odour of ozone disappears when the water becomes hot.

2. By boiling peroxide of lead with some sulphuric acid diluted

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* Extract from a letter to M. Dumas.

† An account of M. Schönbein's experiments on this subject will be found at p. 420 of the second volume of this Journal.—ED.

with water, I observed most of the phænomena described by M. Schönbein, with this difference however, that the odour which he attributes to some ozone appeared to me to be that of nitrous acid; and this seemed confirmed by the action which the gas exercised on litmus-paper, which was reddened but not decolorized. The production of this nitrous acid ceased as soon as the passage of air into the boiling mixture was discontinued.

Operating in the same manner with a mixture of sulphuric acid and of bichromate of potash, I did not perceive any odour.

3. The most convenient method of obtaining ozone consisted in directing a current of air, by means of a gasometer, through a tube 1 metre long and 6 millimetres in diameter, containing a number of pieces of phosphorus. The following experiments, on the circumstances under which ozone is produced, and on the properties of air charged with it, were made by means of this apparatus.

4. Perfectly dry air does not generate ozone; the phosphorus becomes covered with a white crust, probably phosphoric acid; the gas has simply a phosphoric odour, and remains without action on starch mixed with iodide of potassium.

5. The air, completely deoxidized by its passage over incandescent copper, does not produce ozone with phosphorus. As soon as all the copper is oxidized, the odour of ozone becomes manifest; and although the air contains but very little oxygen, so that a lighted body is directly extinguished in it, the formation of ozone appears as abundant as with ordinary air.

6. Pure oxygen does not produce ozone; the gas has merely the smell of the phosphorus; it has no action on starch mixed with iodide.

7. Nitrogen obtained by boiling nitrite of potash with hydrochlorate of ammonia does not produce ozone. An artificial mixture of 1 part of oxygen and of 4 parts of azote gives rise to the production of ozone, as does also atmospheric air.

8. A trace of nitrous acid, hardly perceptible to the smell, diffused in the air, entirely prevents the production of ozone. Blue litmus-paper then becomes red from the presence of nitrous acid, but is not decolorized.

9. Pure carbonic acid, passed over phosphorus, does not produce ozone; but a mixture of 1 per cent. of oxygen with 3 or 4 per cent. of carbonic acid, generates this body, like the mixture of oxygen and nitrogen, apparently however in smaller quantity.

If, after having ascertained the efficacy of the gaseous mixture, the carbonic acid is subtracted from it by potash, ozone ceases to be produced.

10. Hydrogen alone does not produce ozone; but as soon as a small quantity of oxygen is mixed with it, the gas immediately, in passing over the phosphorus, produces a thick smoke; a very strong smell of ozone is manifest, and the starch, mixed with iodide, directly becomes blue. The production of ozone by this mixture of hydrogen and of oxygen appeared much more abundant than with atmospheric air. But the quantity of the fumes and the hot state of the phosphorus making me fear that it might take fire, and determine the

explosion of the gaseous mixture, I went no further with the study of this process.

11. Ozonized air, whether moist or dry, loses entirely its odour and its peculiar properties by its passage through a tube heated to a temperature of 570° or 750°.

12. Ozone does not appear to be absorbed nor altered by water, concentrated sulphuric acid, chloride of calcium, ammonia or barytic water.

13. Ozone is absorbed with the greatest facility by a solution of iodide of potassium; the liquor soon becomes yellow; a portion of the iodine is set at liberty, and carried off by the current of air. When all the iodide is decomposed, the liquor becomes colourless, and the odour of ozone again appears.

A month was necessary to decompose entirely in this manner the solution of 2 grms. of iodide; the apparatus was constantly in action day and night, the gasometer circulating 100 or 120 litres of air in 24 hours. At the end of this time the liquor had again become colourless; it contained no more iodide; I was unable to detect in it anything but a mixture of iodate and of carbonate of potash.

14. Ozone is easily absorbed by the metals. Thus, in passing ozonized air through a small tube of 10 to 12 centimetres long, filled with pure porous silver, as it is obtained by incinerating the acetate, this air completely parts with its smell and its properties, and the silver is converted into a blackish-brown substance. But the presence of humidity is indispensable; if the ozonized air is completely dried by its passage through several tubes filled with pumice-stone moistened with sulphuric acid, it yields nothing to silver nor copper, nor even to zinc; the smell of ozone no longer disappears.

If the ozonized air is passed over the silver without being dried, but only freed from the acids of phosphorus by its passage through tubes filled with pumice-stone, or with asbestos moistened with water, the silver is transformed into a black substance, which by desiccation *in vacuo* acquires an olive-brown colour. This substance, introduced into a tube of glass and heated to redness, reproduces some metallic silver, with disengagement of a colourless inodorous gas, which has all the characters of pure oxygen.

If, before reaching the silver, the ozonized air is but imperfectly dried by its passage through sulphuric acid, the ozone may still be absorbed by the silver. But this is transformed into a brown matter, which seems to be a peroxide of silver; in fact, this substance, placed in contact with water, produces a lively effervescence by the disengagement of some oxygen, after which the residue presents all the characters of the ordinary oxide of silver.

Such are the principal facts which I have observed, several of which had been described by M. Schönbein; but from their importance they deserved to be verified. I will not yet hazard any explanation, but shall only remark, that the continued production of ozone at the time of the decomposition of the water by the pile, and its formation by the contact of phosphorus with a mixture of oxygen and carbonic acid, or of oxygen and hydrogen, sufficiently prove that nitrogen does not interfere in these phænomena. It is evident that they must be attributed to the oxygen alone, or to some peculiar compound of oxygen and hydrogen; but further experiments can alone decide this question.—*Comptes Rendus,* March 17, 1845.

Pleischl's Kryometer.

This is a thermometer for very low temperatures, the thermometric substance of which consists of sulphuret of carbon coloured violet by a little iodine. The instrument is 31 centimetres in length, and the scale is graduated from + 40° to — 120° Reaum. The author found, on comparing it between + 40° and — 19° with a good mercurial thermometer, a very close coincidence in the course of the two instruments, which differs from the published observations of Gay-Lussac and Muncke, according to which the expansion of the sulphuret of carbon agrees more closely with that of alcohol.—Poggendorff's *Annalen,* lxiii. p. 115.

On the Occurrence of Quinic Acid in the Alburnum of Pinus sylvestris. *By* Prof. Wöhler.

Many years ago Berzelius discovered an acid in the alburnum of the fir, which appeared to him to be identical with quinic acid. Wöhler has found that not a trace of quinone can be obtained from the aqueous extract, nor from that prepared with acid or alcohol; the alburnum therefore certainly contains no quinic acid*.—*Ann. der Chem. und Pharm.,* lii. p. 142.

Sesquicarbonate of Barytes.

Boussingault has asserted that sesquicarbonate of potash precipitates from cold solutions of barytes a sesquicarbonate of barytes. M. Bley found the precipitate obtained with pure sesquicarbonate of potash and nitrate of barytes, and dried between 104°–122°, to contain 77·68 per cent. barytes and 22·62 carbonic acid; it was therefore the neutral salt.—*Archiv der Pharm.,* xl. p. 263.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

March 17*th*, 1845. (The President in the Chair.) The following communications were read:—

"On brown Iron Ore," by Lieut.-Colonel Yorke.

Some observations of the author having led to the belief that the composition assigned in systems of mineralogy to the crystallized

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* The same conclusion was arrived at by Dr. Stenhouse in a paper read before the Chemical Society Dec. 2, 1844.—Ed. *Chem. Gaz.*

hydro-oxide of iron really belonged to another substance, the following experiments were undertaken to clear up the point. It will be proper to remark that the conclusions arrived at agree with those of Kobell, as quoted by Dana in the second edition of his 'Mineralogy,' a work which had not been seen by the author before the experiments were completed.

Crystallized brown iron-ore, from Restoomel mine near Lostwithiel. Specific gravity of a crystal = 4·37; of the powder, 4·24. Its form appeared to be derived from a right rhombic prism whose obtuse angle measured 95° 14′. It contains in 100 parts—

Red oxide of iron	89·55
Water	10·07
Oxide of manganese	·16
Silica	·28
	100·06

Neither alumina nor phosphoric acid was present.

These numbers agree very closely with the formula $Fe^2 O^3 + HO$, which gives in 100 parts—

Red oxide of iron	89·89
Water	10·11
	100·00

Analyses made on other specimens of brown ore, amorphous or indistinctly crystalline, appeared to render it highly probable that this constitution is very far from rare among such bodies. Kobell is however inclined to the supposition that a hydrate with 3 equiv. of water is more abundant; this would give about 14·5 per cent. of water. One specimen (from Cornwall) possessed this composition very nearly, but contained in addition some oxide of manganese with traces of alumina and oxide of tin. No phosphoric acid was found in any of the specimens.

"Observations on Animal Charcoal," by Robert Warington, Esq.

After noticing the causes which had led to the experiments detailed, the author describes the power of animal charcoal in removing completely and rapidly the bitter flavour from decoctions of hops, quassia, oak-bark, *Cinchona cordifolia* and aloes, but not in his first experiment from nux vomica; finding however that the principal of these facts had been already noticed by MM. Duflos and Hirsch in their 'Oekonomische Chemie,' his attention was directed to the examination of the experiment when a decoction of the *Cinchona cordifolia* had been employed; as from the whole of the bitter having been removed, it appeared as though the active principle, or kinate of quina, had also been abstracted; and this, on trial, was found to be the case; disulphate of quina was rapidly removed from watery solution; strychnia was also abstracted, as also acetate of morphia and the whole of the bitter of nux vomica, it being found that the former experiment had not been carried sufficiently far. Reasoning by analogy, the author was next led to try the action of this agent on inorganic salts, and found that a considerable quantity was removed from their solutions in water, as sulphate of magnesia, chloride of bromine, and others.

PATENT.

Patent granted to François Stanislas De Sussex, Bethnal-green, *and* Alexander Robertson Arrott, Torrington-square, *for Improvements in the Recovery of Manganese used in making Bleaching Powder.*

These improvements consist in producing peroxide of manganese, more or less pure, from salts and other combinations of that metal which contain it in a lower state of oxidation.

By this invention the residuum that is left after the disengagement of chlorine or oxygen from manganese, and which is a product of little or no value, can be converted into a substance of great value, viz. superoxide of manganese, which is peculiarly fitted, by the large proportion of oxygen it contains, to serve the purpose of affording either chlorine or oxygen gas again, according to the process it is subsequently subjected to. The said residuary matters, after the extrication of the chlorine, in the manufacture of chloride of lime, or bleaching powder, and of chlorate or hyperoxymuriate of potash, consist principally of chloride and sulphate of manganese; but as these residuums may and have been occasionally converted, more or less, into sulphuret of manganese, when they are used to purify coal-gas from its sulphur or sulphuretted hydrogen, the patentees include, not only the above sulphate and chloride, but also the sulphuret of manganese, among the waste or refuse products, which they convert into a valuable peroxide of that metal. This invention is also applicable for converting all oxides, carbonates, and other combinations of manganese, whether native or factitious, which contain the metal in an inferior state of oxidation, into a superoxide of manganese, adapted to produce chlorine by the agency of hydrochloric acid, and oxygen by the agency either of heat alone, or of heat along with sulphuric acid.

The manner of carrying this invention into execution is as follows:—The conversion of manganese, whether combined or uncombined, from a lower state of oxidation into the higher state of superoxide, is effected by two distinct operations. First, it is well known that when peroxide of manganese (called in its purest native state pyrolusite, and also gray manganese ore) is digested with hydrochloric or muriatic acid, the oxygen of the metal combines with the hydrogen of the acid to form water, and leaves the chlorine of the acid free, while the manganese, thus partially stripped of its oxygen, combines with the rest of the hydrochloric acid to form a muriate of manganese: likewise, when more or less dilute sulphuric acid, common salt (chloride of sodium) and peroxide of manganese are so mixed and treated as to be made to react on one another, the hydrochloric acid which is disengaged is converted by the oxygen of the manganese into water and chlorine; while both the soda produced from the common salt and the partially deoxidized manganese combine with the sulphuric acid into sulphate of soda and sulphate of manganese. The chloride, sulphate, sulphuret or carbonate is converted into a sesquioxide or deutoxide of manganese by one or other of the three following processes:—1st, the dried chloride of manganese is subjected to a strong heat, produced either by the united action of burning fuel, and a jet or jets of an oxyhydrogen blowpipe, or of a stream of atmospheric air thrown upon the burning fuel by a fan or other suitable impulsive power, thus forming a kind of blowpipe or blast-furnace, in which the chemical decomposition and reaction are rendered quicker and more complete. The furnace is constructed like an ordinary reverberatory furnace, with the addition of a box or chest of iron, open at top, set in the fireplace, close to the bridge; this box is filled with iron turnings, borings, or other small fragments of iron, upon which, in their strongly ignited state, water is allowed to trickle or drop down slowly from a pipe, so as to be decomposed and to disengage a stream of hydrogen, which is impelled over the bridge of the furnace upon the hearth by means of a fan or other blowing machine acting at the entrance or door of the fireplace. The manner in which the furnace is regulated is as follows:—The fuel, either common coals, coke, anthracite, wood, turf, &c., is first lighted upon the grate, and being subjected to the blast of air, soon creates such a temperature as to raise the box of iron turnings to a red white-heat, in which state the water being allowed to trickle down into the box, is decomposed with the copious disengagement of hydrogen gas. The chloride of manganese may be exposed on the hearth of the reverberatory furnace, either in a more or less concentrated liquid state, or in a dry state, to the action of the intensely-powerful flame, generated as above described, and becomes thereby decomposed by the hydrogen, with the disengagement of its chlorine in the state of hydrochloric acid or muriatic acid gas, while the remaining protoxide of manganese becomes at the same time oxidized into the deutoxide. The hydrochloric acid gas disengaged is condensed by means of vaults or large chimneys, containing wet coke or flint nodules, in the way often practised in soda manufactories. Instead of the above-described hydrogen flame, a simple reverberatory furnace, fed with ordinary fuel, either with or without blast, is sometimes employed.

In the second process, the chloride of manganese, instead of being acted on by the flame of combustible matter on the hearth of a furnace, is subjected, in fire-clay retorts, to an intense heat, by which the chlorine is expelled partly in the state of hydrochloric acid and partly of chlorine; and the manganese left in the retorts may be afterwards peroxidized by a process to be presently described.

In the third process, chloride of manganese and carbonate of lime, or quicklime, are mixed together in the proper equivalent proportions for mutual decomposition, and then subjected to the strong heat of the above-described compound hydrogen flame; by this means a mixture of chloride of calcium (muriate of lime) and oxide of manganese is obtained: the latter is peroxidized by a process about to be described. Magnesia, or magnesian limestone, may be substituted for lime, or its carbonate, in this process. When the carbonate of lime is used with rather too low a heat in the furnace, carbonate of manganese may be formed. In all cases the resulting mixture of chloride of calcium or magnesium and oxide of manganese is to be treated with water, so as to dissolve out the said chlorides and leave the oxide of manganese.

The following is the mode of decomposing sulphate of manganese, however formed, so as to obtain from it an oxide of manganese, to be peroxidized by an after process:—The sulphate of manganese is mixed with sawdust, ground coke or charcoal, or any like combustible matter, only in such proportion as to be capable of decomposing the sulphuric acid present, when the mixture is subjected to a strong calcining heat in retorts of iron or fire-clay, whereby a sulphuret of manganese is obtained mixed with more or less oxide of manganese. This operation is finished by introducing into the said residuary mixture fragments of coke, charcoal or coal, and continuing the application of heat for some time, while the mouth of the retort is left open, whereby the manganese is desulphurated in a greater or less degree, and its sulphuret is converted into an oxide. In case any salt, or other compound of soda, should have been mixed with the sulphate of manganese, the soda compound is to be separated from the manganese, by means of water, after the above-described calcination in the retorts. The sulphuret of manganese sometimes produced in coal-gas works, as a residuum of the purification of the gas, may be desulphurated in retorts, as above described, or by exposing it, mixed with pieces of coke, charcoal, coal or wood, on the hearth of the above-described reverberatory hydrogen furnace. The coke, &c. should be used in distinct pieces, and not in powder, whereby it may be readily separated from the oxide of manganese afterwards either by a sieve or other suitable means.

The second operation, or series of operations, for converting the deutoxide of manganese, produced in the before-described processes, as also all lower oxides and the carbonated oxide of manganese, whether natural or factitious, into a superoxide, fit for affording chlorine by the action of hydrochloric acid, and oxygen by heat, is carried on in one or other of the three following ways:—1st, the said oxides or carbonates are converted from their lower to the much higher state of oxidation of an acid of manganese, by subjecting a mixture of them with alkaline matters, such as potash or soda, either caustic or carbonated, on the hearth of a reverberatory furnace, to the joint agency of heat and atmospherical oxygen, which may or may not be impelled and diffused by mechanical means; about 1 part of the oxide or carbonate of manganese mixed with about 3 parts of alkaline matter forms a suitable proportion for the production of an acid of manganese. The said mixture fuses, with the production of a manganate or permanganate of potash or soda, according as one or other alkali has been used in the mixture. The fused mass is run or ladled out of the furnace, and when cooled is dissolved in hot water. This solution, of what is sometimes called chameleon mineral, on being exposed freely to the air, becomes decomposed, by the absorption of carbonic acid gas, into peroxide of manganese, which precipitates in a black powder, and carbonated alkali, which remains in solution. Where carbonic acid gas can be conveniently procured at a very cheap rate, the above-described decomposition of the chameleon mineral may be promoted by a due application of the said acid gas; or otherwise the alkaline bicarbonates obtained from a preceding decomposition of chameleon mineral, may be employed for decomposing a fresh-made solution of the said chameleon, whereby a precipitate of peroxide of manganese is immediately obtained. The supernatant alkaline liquor is in all cases decanted or run off, and preserved for subsequent use. The patentees also decompose chameleon mineral, with the production of peroxide of manganese, by the action of various organic products, such as starchy or gummy matters; but they greatly prefer to effect the desired production of peroxide of manganese by carbonic acid gas or an alkaline bicarbonate.

The second method of producing peroxide of manganese from its lower oxide or carbonate, consists in subjecting a mixture of about 1 equiv. chemical proportion of either of these and about 1 equiv. of lime to the chlorine expelled by heat from chloride of manganese contained in the retort, as before described; or by treating 1 equiv. proportion of that lower oxide of manganese, called by chemists sesquioxide or deutoxide, with one-half of an equivalent proportion of aqueous or liquid hydrochloric acid, there is obtained simultaneously one-half of an equivalent proportion of protochloride of manganese in solution, and one-half an equivalent of peroxide in the state of a black powder. A like reaction, with the production of a solution of protochloride of manganese and black peroxide, may be effected, by treating the said sesquioxide with aqueous hydrochloric acid in one vessel, and transmitting therefrom the chlorine disengaged into another vessel, containing a like sesquioxide in a moist state.

The third method of converting the lower oxide or carbonate into peroxide of manganese consists in directing over the surface of either of these, in a moist state, the deutoxide of nitrogen, frequently called nitrous gas, which is obtained as a waste product in certain chemical operations, as in the manufacture of oxalic acid, or nitrate of lead, or of copper, &c.; in this case the nitrous gas becomes reduced to a lower state of oxidation, and by imparting oxygen to the lower oxide of manganese converts it into peroxide.—Sealed August 29, 1844.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on the Oil of Garlic. By T. WERTHEIM.

To prepare this oil, to which the garlic principally owes its aromatic properties, the bulbs of *Allium sativum* reduced to a pulp are distilled with water in a large retort. The largest quantity of the oil passes over with the first portions of water. A hundredweight of garlic yields from 3 to 4 oz. of impure product. It forms a dark brownish-yellow oily fluid, which is heavier than water and of a disagreeable garlic odour. Great care must be taken in purifying it by repeated distillation, for if heated to boiling-point, which is near 302°, a rapid evolution of heat suddenly occurs, accompanied with decomposition, which cannot be arrested. Vapours of an insupportable suffocating odour are disengaged without a trace of garlic oil passing over, while a blackish-brown viscid mass is left behind. This decomposition is, as it were, announced by a remarkable change in colour of the liquid;—at about 284° the previously brownish-yellow oil gradually becomes of a dark yellow: it is therefore requisite to carry on the distillation in a water or salt-water bath, when the oil distils over pretty quickly without entering into ebullition. The oil thus purified is lighter than water, and is not decomposed by boiling; it is of a pale yellow, and has a less disagreeable odour than the crude oil. The last portions are of a darker colour, distil over more slowly, and are heavier than water. A dark brown mass, of a very disagreeable odour, and which melts with difficulty, is left in the retort. The quantity of the rectified product amounts to about two-thirds of the crude substance. The rectified garlic oil is scarcely soluble in water, but very soluble in alcohol and æther; dilute acids do not alter it. Fuming nitric acid produces a violent decomposition; when this has terminated the liquid contains sulphuric and oxalic acids. On dilution with water, yellowish-white flakes separate. Concentrated sulphuric acid dissolves the oil with a purple-red colour; on dilution with water, the oil is separated apparently unaltered. Dry muriatic gas is absorbed in large quantity by the anhydrous oil; the deep indigo-blue solution is gradually decolorized by exposure to the air, and almost immediately by dilution with water. Solutions of salts produce no changes except the solutions of some oxides of the precious metals. On heating it with caustic potash, no ammonia is disengaged; it is therefore free from nitrogen. With potassium it forms a large quantity of sulphuret of potassium. A series of analyses gave widely-differing numbers:—

	I.	II.	III.
Carbon	59·06	60·57	55·39
Hydrogen	8·19	8·42	7·70

In each of these analyses, however, the relation between the carbon and hydrogen is the same; so that if in each of them one and the same arbitrarily-selected number be substituted for the found quantity of carbon, and from this the proportional quantity of hydrogen be deduced, nearly the same value is found for this latter for each of them. We have, for instance—

	C.		H.		C.		H.
(1)	59·06	:	8·19	=	63·33	:	8·78
(2)	60·57	:	8·42	=	63·33	:	8·80
(3)	55·39	:	7·70	=	63·33	:	8·80

The numerous determinations of sulphur gave highly-varying results, but in almost every case there was a loss, which must be ascribed to an amount of oxygen. These facts render it probable that the rectified oil of garlic is a varying mixture of several sulphur compounds and of an oxygen compound of one and the same radical.

When pieces of metallic potassium are thrown into garlic oil, which has been purified as much as possible by repeated rectification, and has been freed from water over chloride of calcium, they are soon seen to become covered with a liver-brown coating. At the same time a faint evolution of gas takes place, which burns with a pale blue flame. On distilling after some interval, when the evolution of gas has ceased, the liquid from the sediment which has formed, a product is obtained, which has no further action on potassium. It is colourless, amounts to about two-thirds of the rectified garlic oil, and exhibits the above-described behaviour towards reagents.

It is difficult to effect the oxidation of the sulphur by means of fuming nitric acid, since the action results with explosive violence; this evil, however, can be avoided by bending the neck of the glass vessel containing the oil parallel to its body; the fuming nitric acid heated to boiling, in which the orifice of the glass bulb bent in the above manner is immersed, now gradually effects the complete oxidation of the vapours of the oil which escape. The analyses yielded:—

	I.	II.	III.				
Carbon........	63·01		63·43	6	=	455·07	66·33
Hydrogen......	9·07	8·72	8·78	5	=	62·40	8·68
Sulphur			27·23	1	=	201·16	27·99
						718·63	100·00

On examining the residue in the retort after distillation over potassium, there is found in it a considerable quantity of sulphuret of potassium; moreover, a small quantity of an organic substance, insoluble in water, and very sparingly soluble in æther. Consequently there must be contained in the rectified oil of garlic a still higher sulphuret of $C^6 H^4$, which on distillation over metallic potassium is reduced to $C^6 H^5 S$, while the excess of sulphur forms sulphuret of potassium. The sulphur in $C^6 H^5 S$ may however be replaced by O, as will be subsequently shown. If such a combination did occur in the oil of garlic, the analysis would yield a larger amount of carbon and hydrogen; and this result was in fact obtained on examining oil distilled over potassium, but in which the action of the metallic potassium had not completely terminated. In this case, as will be seen from the following analyses, the excess of sulphur of the highest sulphuret had been already entirely removed by the metallic potassium before the oxide of the body $C^6 H^5$ had been decomposed by it:—

	I.	II.
Carbon	65·17	64·73
Hydrogen	9·22	9·15

In this case the above-mentioned relation between carbon and hydrogen occurs; in the present instance, however, a higher percentage amount of carbon and hydrogen was obtained, while in the previous results they were somewhat too small. The oil examined last contained, together with the protosulphuret, an oxide, while in the rectified garlic oil there was moreover a higher sulphuret; this, as well as the oxygen compound, may have either existed originally in the garlic oil, or may have been formed subsequently, a portion becoming oxidized by the absorption of oxygen from the atmosphere, while the separated sulphur unites with another portion of the protosulphuret.

In the pure garlic oil ($C^6 H^5 S$) the sulphur may be replaced by its equivalent of oxygen or chlorine; moreover, the unaltered body may be combined with metallic sulphurets, and these combinations present the character of sulphosalts, analogous to the corresponding compounds of the sulphuret of ethyle. The group $C^6 H^5$ consequently possesses all the essential characteristics of an organic radical, for which the author proposes the name of *Allyle* = All; pure garlic oil is accordingly the *sulphuret of allyle.*

Platinum Compound.—When a solution of chloride of platinum is added to garlic oil, a yellow precipitate, resembling the ammonio-chloride of platinum, is formed, especially on employing an alcoholic somewhat dilute solution. If too much water be added quickly, or there remain an excess of garlic oil, a yellowish-brown resinous body is deposited; the addition of water should consequently cease as soon as a considerable turbidness is evident. The precipitate is nearly insoluble in water, and very sparingly soluble in alcohol and æther. It is precipitated almost entirely from its alcoholic solution by dilution with water. Fuming nitric acid quickly decomposes the combination; a perfect solution results, in which the platinum exists partly as sulphate, partly as chloride. Hydrochloric acid and sulphuretted hydrogen are without action upon it.

The analysis of the platinum compound gave—

	I.	II.	III.	Equiv.	Calculated.
Carbon	17·87		17·82	24	17·95
Hydrogen ..	2·86	2·87	2·89	20	2·47
Platinum....	48·68	48·40	48·50	4	48·64
Chlorine	13·18	13·43	13·04	3	13·09
Sulphur			18·29	9	17·85

which lead to the formula $(PtCl^2, C^6H^5Cl) + 3(PtS^2, C^6H^5S)$. After frequent agitation with sulphuret of ammonia, the yellow precipitate gradually becomes converted into a light brownish-red one; chloride of ammonium remains dissolved in the liquid. This precipitate is wholly insoluble in water, alcohol and æther. It was found to consist of—

Carbon	19·37	6	19·29
Hydrogen....................	3·11	5	2·65
Platinum	52·09	1	52·38
Sulphur	25·43	3	25·68

This composition corresponds to the formula $PtS^2 + C^6H^5S$. On the application of heat some sulphuret of allyle is expelled, viz. at 212°, 6 equiv. of the sulphuret of platinum and allyle lose 1 equiv., at 320° 2 equiv.

Combination with Perchloride of Mercury.—On mixing concentrated alcoholic solutions of oil of garlic and corrosive sublimate, a white precipitate is formed, which is further increased by standing and dilution with water. It consists of two combinations, one of which may be extracted by strong boiling spirit, and may then be again precipitated by dilution with much water. After drying, it forms a heavy white powder, which becomes black in the sunlight. When heated, it becomes black, with evolution of vapours which smell of garlic and sulphurous acid. Heated in a glass flask, it yields a sublimate of mercury and protochloride of mercury. The methods adopted for its analysis were those recommended by Bunsen in his treatise on the Cacodyle series; the sulphur was determined from the loss:—

Carbon	10·76	10·70	11·26	12	11·33
Hydrogen ..	1·54	1·59	1·70	10	1·55
Mercury ..	63·83	63·88	63·31	4	63·06
Chlorine ..			16·41	3	16·54
Sulphur....			7·32	3	7·52

which lead to the formula $2(HgCl) + AllCl + 2(HgS) + AllS$. On pouring a moderately-concentrated solution of potash over this combination, the white colour of the powder is converted into a yellow one, a proof that the mercury exists in the combination in the state of perchloride. If the oxide be extracted with dilute nitric acid from the precipitate, a perfectly white body remains, which is probably the isolated sulphosalt $2(HgS) + AllS$. ?

Combination with Palladium.—On adding small portions of garlic oil gradually to an excess of an aqueous solution of the protonitrate of palladium, a loose chermesian-brown precipitate is obtained, resembling the sulphuret of platinum and allyle. It is an inodorous and tasteless powder, insoluble in water, alcohol and æther. When heated to 212° it smells of garlic, and at a higher temperature of sulphurous acid. On analysis it yielded—

		Equiv.	Calculated.
Carbon	22·24	12	22·54
Hydrogen	3·17	10	3·10
Palladium	49·58	3	49·46
Sulphur	25·01	5	24·90

These results answer to the formula $2(AllS) + 3(PdS)$.

Combination with Silver.—If to an excess of a concentrated alcoholic solution of nitrate of silver oil of garlic be added, very soon a precipitation of sulphuret of silver results, but subsequently a crystalline body separates. If after 24 hours the liquid be boiled with the precipitate and filtered while hot, flat prisms, having a very strong lustre and arranged in fan-shaped groups, separate on the cooling of the solution. Washed with alcohol, and then with some water, and dried between blotting-paper, they form a white powder, which becomes black by exposure to light and to a temperature of 212°, dissolves sparingly in æther and alcohol, more readily in boiling spirit and in water; on ignition it explodes somewhat, and leaves metallic silver. This body is decomposed by hydrochloric acid and sulphuretted hydrogen; it is dissolved by ammonia, when drops of oil of a peculiar odour collect on the surface of the liquid. No sulphuric acid is formed by treatment with nitric acid, which decomposes it very rapidly:—

	I.	II.	III.	Equiv.	Calculated.
Carbon	15·96	15·94	16·22	6	16·57
Hydrogen ..	2·11	2·16	2·26	5	2·27
Silver	48·67	48·87	49·21	1	49·22
Nitrogen			6·35	1	6·45
Oxygen			25·96	7	25·49

From this results the formula $AgO + AllO + NO^5$. Judging from the reaction with ammonia, the body is the nitrate of the oxide of allyle and oxide of silver. The oil which separates is oxide of allyle, for if it be carefully removed from the liquid and a drop of nitrate of silver added to it, the nitrate of the oxide of allyle and silver is again instantly formed.

This oxide of allyle appears to preexist in the crude oil of garlic, for if a very concentrated solution of nitrate of silver be mixed with oil of garlic, it frequently happens that before a separation of sulphuret of silver has taken place, a considerable amount of nitrate of allyle and silver has already subsided.—*Ann. der Chem. und Pharm.*, li. p. 289.

On some new Combinations of Tungstic Acid with Alkalies.

By M. Marguerite.

It is known that tungstic acid, in combining with the alkalies, forms some salts in which the oxygen of the acid is thrice that of the base; and that the tungstates, considered as neutral, are decomposed by acids in the cold.

The combinations which I am about to describe show that not only tungstic acid is capable of forming combinations in different proportions from those of the known tungstates, but that it also undergoes certain modifications in its reactions and its ordinary properties, which are of some interest.

If wolfram be calcined with an excess of carbonated alkali, a fused mass is obtained, which on treatment with water affords a solution representing a neutral tungstate, mixed with the excess of the carbonated alkali employed.

On gradually decomposing this solution by an acid, for instance hydrochloric acid, a white precipitate is formed of hydrated tungstic acid, which soon disappears on agitation; but on adding an excess of acid the precipitate reappears, and is no more dissolved. This is the ordinary method employed for preparing the hydrated tungstic acid.

But if this acid liquor is filtered, and is placed in contact with a slip of zinc, it acquires a very intense blue colour, indicating the presence of a large amount of tungstic acid in solution.

Now from what is known of the properties of this acid, there should only remain in the liquor a quantity corresponding to the solubility of the hydrate in water, which is finally deposited by ebullition or evaporation. After having evaporated this solution, I obtained, after successive crystallizations of alkaline chloride, a definite combination which was able to exist and crystallize in the midst of an acid liquor. With the small quantity of this compound, thus obtained, it was easy to recognise that it contained tungstic acid and an alkaline base.

In seeking the causes which had presided at the formation of this salt, I thought it right to ascertain if the excess of alkaline carbonate was necessary in the primitive liquor.

A moderately-concentrated solution of the tungstate was treated with some drops of hydrochloric acid; a precipitate resulted, which was permanent while cold, but which, on exposure to a gentle heat, entirely disappeared. It was then evident, from this experiment, that the hydrate of tungstic acid was capable of dissolving in the absence of an excess of carbonate in the non-decomposed neutral tungstate.

In fact, when a solution of the neutral tungstate is boiled with hydrated tungstic acid, it rapidly disappears, and in considerable quantity. The liquor having reached the point of saturation deposits upon cooling a certain quantity of the hydrate which it had dissolved at a higher temperature. The formation of these deposits proceeds during evaporation, but finally a combination crystallizes in forms varying according to its composition. This salt may be dissolved anew, boiled and crystallized, still retaining its properties.

Such is the simplest means of procuring these peculiar tungstates; there is however another mode of preparation, which consists in boiling a caustic alkali or subcarbonate with an excess of hydrated tungstic acid, which however amounts to the same as if we set out with a neutral tungstate.

The combinations which are produced in this manner differ in their properties and their composition from the neutral tungstates, the only ones known except the acid tungstates prepared by fusion, with which M. Wöhler obtained his very remarkable combination with soda.

The ordinary process for determining quantitatively tungstic acid, the exactness of which however was acknowledged to be insufficient by all chemists, could not be applied to the analysis of these salts; for a difference of 1 to 2 per cent. constitutes a tungstate of 4 or of 5 equivalents of acid.

M. Berzelius, however, in his 'Annuaire' for 1841, describes an exact method for determining the quantity of tungstic acid in the neutral salts by the nitrate of mercury; but I feared that the excess of nitric acid set at liberty would react on the precipitate of tungstate of mercury, and would destroy the accuracy of this process.

The following is the process I have employed, and it yielded satisfactory results. I therefore propose it as being very simple and perfectly exact.

The salt to be analysed is placed in a small platinum crucible, and several times its weight of pure concentrated sulphuric acid added. At first a gentle heat is employed, and then the temperature is gradually raised to a red heat. After calcination the residue is composed of an acid sulphate and of free tungstic acid. It is thrown on a filter, washed with water charged with sal-ammoniac, which prevents the tungstic acid from combining with water and from passing through the filter, which frequently happens even when it has been ignited.

When the last washings no longer precipitate chloride of barium, the residue is ignited to drive away the sal-ammoniac, and a few drops of nitric acid added, to obviate any error that might arise from a slight reduction which the tungstic acid may have undergone, and to ensure the perfect combustion of the last traces of charcoal of the filter. In this manner the water may be determined by a simple ignition, the tungstic acid directly.

Having endeavoured to ascertain the amount of alkali by the quantity of sulphuric acid fixed, I found that tungstic acid, like silicic and boracic acids, decomposes the neutral sulphate at the temperature requisite to destroy the bisulphate. The tungstic acid then reenters into combination with the alkali, forming a more or less acid tungstate. It is therefore important not to go as far as this limit.

The bisulphate has the advantage of presenting some sulphuric acid, which acts energetically at this high temperature, to the portions of salt which might not be decomposed. It is readily ascertained whether the salt has been entirely decomposed, that the tungstic acid has not become hydrated again, consequently dissolved, by immersing a slip of zinc in the first washings, to which a little hydrochloric acid has been added. Not the slightest blue colour is produced, and very minute quantities of a tungstate would be detected, under these circumstances, by this property.

According to this process of analysis, I obtained the following results on the salts prepared by the methods above described :—

1. Bitungstate of soda (lamellated crystals), which may be decomposed by acids in the cold, $NaO\ (WO^3)^2\ 4\frac{1}{2}HO$.

2. Tritungstate of ammonia (octahedral crystals) fuses in its water of crystallization and under water, like phosphorus, $NH^4O\ (WO^3)^3\ 5HO$.

3. Quadritungstate of soda (crystallized in tablets from an acid liquor), $NaO\ (WO^3)^4\ 3HO$.

4. Pentatungstate of potash (prismatic crystals) . . . . $KO\ (WO^3)^5\ 8HO$.

5. Hexatungstate of ammonia (well-defined lamellated crystals), $NH^4O\ (WO^3)^6\ 6HO$.

6. Double bitungstate of ammonia and of potash . . . . $KO\ (WO^3)^2\ NH^4O\ (WO^3)^2\ 6HO$.

It will be seen that series of tungstates exist with 1, 2, 3, 4, 5, and even 6 equiv. of tungstic acid, to a single equivalent of base; and though I do not here present the complete series for each base, it will be easy, taking the most acid tungstate, and dissolving in it a definite quantity of alkali, to prepare the intermediate tungstates.

Since a neutral tungstate dissolves a great quantity of hydrate by ebullition, which it again deposits upon cooling, it is possible that by changing the medium a tungstate of a greater degree of acidity than those I obtained might be precipitated or crystallized.

These tungstates possess some interesting properties :—

I. In contact with hydrochloric, nitric and sulphuric acids, they are not decomposed in the cold, nor even as far as boiling-point. It is not till after a time, more or less short, both when cold and at boiling-point, that they deposit tungstic acid under their influence. This singular stability in presence of acids, which always instantly decompose the neutral tungstates in the cold, seems to increase with their degree of acidity. Thus the tungstates of soda of the first and second degree are decomposable in the cold by acids, but that of the fourth degree is perfectly stable.

2. Their solubility is far from diminishing according to the quantity of tungstic acid which they contain, for the quadritungstate of soda is much more soluble than the bitungstate.

3. Treated with an excess of alkali, they again become decomposable when cold by acids, because they are brought back to the condition of neutral tungstates. Under the influence of a caustic alkali, or of a carbonate, a white precipitate is formed, which is insoluble in the excess of cold alkali, and which only disappears on boiling; but in a solution of neutral tungstate it dissolves instantly. This precipitate is hydrated tungstic acid, retaining a certain quantity of alkali, from which it cannot be freed entirely by edulcoration, for it dissolves gradually in the same proportions as the elements of which it is constituted. But what is remarkable is the insolubility in the cold of the tungstic acid precipitated from an acid tungstate

by an excess of alkali, whilst the hydrate, precipitated from a neutral tungstate by an acid, is entirely soluble under the same circumstance.

When sufficiently diluted solutions are acted upon, and too great an excess of alkali is avoided, the addition of an acid causes the precipitated hydrate, which forms in the solution of an acid tungstate, to disappear.

4. They have a very decided acid reaction on litmus-paper, whilst the neutral tungstates appear to have a slightly alkaline reaction.

5. Their taste is peculiarly bitter, and much more decided than that of the neutral tungstates.

6. When ignited, they part with their water of crystallization and of constitution, becoming yellow, and ceasing to be soluble; they without doubt contain some free tungstic acid. Heated to 428°, they part with a certain quantity of their water of crystallization without becoming yellow and insoluble, and it is only at a higher temperature that the combination is destroyed, and becomes insoluble in losing the last quantities of water, which it retains more strongly.

7. They form, by double decomposition, some corresponding insoluble tungstates, which even at the moment they are precipitated are soluble in the acids for some time without being decomposed; but after spontaneous desiccation, either *in vacuo* or even in the medium in which they are formed, they soon lose this property. Their stability in presence of acids seems therefore to be inherent to their state of hydration.

8. They form acid double salts by combining with each other in different proportions, and they possess the same properties; for instance, the double salt of ammonia and potash.

Whatever explanation may be given of these facts, whether the existence of an isomeric modification of tungstic acid soluble in mineral acids be admitted, whether water be made to intervene as acting the part of a true base, it is interesting to find that a salt decomposable by acids becomes stable by taking an equivalent more of tungstic acid; that it preserves, I may even say that it acquires, a greater solubility where it should lose it; for, with regard to soaps, M. Chevreul has made this general observation, that the more a salt composed of an acid naturally insoluble is acid, the more insoluble does it become.

What induces us to admit that water plays the part of base in these combinations is, on the one hand, the tenacity with which a certain quantity is retained beyond 428°, the yellow colour, and the insolubility which these salts acquire when they have been deprived of the water by heat; and, on the other hand, the fractional composition for water, apparently peculiar to some of these salts; for having operated on a salt, perfectly pure and re-crystallized several times, I cannot doubt the exactness of the analysis; and although the fractions of equivalents of water are not usual, I must however admit them in the composition of the bitungstate of soda.

Thus, instead of grouping the entire quantity of tungstic acid around the alkali, water may be made to intervene so as to represent some tungstates of water and of alkali; but then for the tungstate of ammonia and potash, for the same reason, we must admit that it is a triple tungstate of two alkalies and of water. It is however only possible to form hypotheses with respect to the molecular constitution of these combinations.

Molybdenum, which already presents so much analogy with tungstene, will probably give similar molybdates; and the solubility of molybdic acid in acids must be favourable to the formation of such compounds.

Tungstic acid presents analogous properties to organic acids to those which it shows towards mineral acids; for example, its complete stability in the state of hydrate in oxalic and tartaric acids; in the different oxalates and the bitartrate of potash; its precipitation by alkalies under certain circumstances, and the property which these acids possess of decomposing the tungstates, without precipitating tungstic acid.—*Comptes Rendus*, Feb. 3, 1845.

On the Æthereal Oil of Alliaria officinalis (Erysimum alliaria). *By* M. Wertheim.

The author distilled the roots of this plant with water, and obtained from 25 lbs. of the fresh roots 4 grms. of an oil exactly resembling that of mustard. On analysis it gave C 41·65, H 7·2, N 24·0, S 27·15, which agrees with the composition of oil of mustard. The leaves of the plant with water yielded a distillate, which smelled and tasted strongly of garlic. No oil however could be obtained from it.—*Ann. der Chem. und Pharm.*, liii. p. 52.

Further Remarks on the Bile. By E. A. Platner.

I have shown in a former communication* that the principal constituent of the bile may be procured in a crystalline state. The action of acids and certain salts upon an aqueous solution of these crystals has been also detailed. In consequence of my having, on distilling the æther used in the preparation of these crystals, procured as a residue a substance identical with Gmelin's biliary resin, consequently free from nitrogen, I was led to believe that the bile was composed of two different substances, one of which is free from, and the other contains nitrogen. When in combination with soda, I denominated the first choline-soda and the last choloidine-soda. The substance which remains on evaporating the æther does not however exist as such in the bile, but is a product of decomposition; for if the bile, as occurred in my experiments, was partially separated from the soda, that portion only of the bile which remained in combination with soda was undecomposed; that which was completely freed from soda is decomposed when water and a high temperature are employed; biliary resin (choloidic acid) and some taurine are formed. Consequently two different bodies do not preexist in the bile in the manner I formerly thought.

Nevertheless two distinct substances do occur in perfectly fresh

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* Chem. Gaz., vol. ii. p. 515.—Ed.

bile, as a new discovery which I have made undoubtedly proves. I have been able to cause bile, which was evaporated in a water-bath, and freed from mucus and the greater part of its salts by repeated solution in alcohol, to crystallize immediately. For this purpose nothing further is necessary than to add æther repeatedly to as strong an alcoholic solution of the bile as possible, and then to set it aside in a cool place. The principal and most important constituent of the bile then crystallizes in the same manner as in my former experiments; but $\frac{1}{6}$–$\frac{1}{4}$ of the bile used does not crystallize, but remains as a yellowish-brown syrupy liquid. I have not been able to succeed in separating this in any manner from the crystals; consequently I can say nothing more concerning its nature. It is however evidently a different substance from the principal constituent of the bile, perhaps even a product of its decomposition. The decomposition of the bile begins even in the organism, and it is impossible to examine fresh bile which is not partly decomposed. The brown liquid appears to consist principally of biliary colouring matter. I must however remark that the crystals have also a slightly yellow tint. By this new observation my former communications are confirmed. The principal constituent of the bile is a compound of soda with a peculiar organic body, and this compound may be immediately procured from the bile without its undergoing any important alteration. Liebig called this compound *bilate* of soda; I have denominated it choline-soda. It does not appear to me sufficiently proved, that the principal organic constituent of bile is positively an acid. It is possible that, like albumen, it may combine with acids as well as with bases. The most recent examinations of the bile by Berzelius would then be partly true. Further experiments must decide this. These however are peculiarly difficult, because in separating the bile from soda an acid body may undoubtedly be formed. From the above observation it is further evident that the formula advanced by Liebig for bilic acid must be incorrect; for Kemp, Theyer and Schlosser have not analysed the essential biliary ingredient in a perfectly pure state, but have always at the same time included the brown syrupy fluid. Finally, it is evident from these communications, that in precipitating bile by metallic salts, different precipitates must always form, as Gmelin supposes, and that Liebig is in error when he opposes this view. I thus conclude, believing that the disputations concerning the bile may be considered as settled, at least on the main point.—Muller's *Archiv*, 1844, Heft v.

Observation on the Action of Guano.

M. Graf has found that diseased orange plants, whose leaves were yellow and constantly covered with a saccharine exudation, were completely restored by covering the soil with guano, when the exudation ceased, and the leaves again acquired their green colour.—*Archiv der Pharm.*, November 1844.

On Basic Phosphate of Lime. By M. Berzelius.

As many chemists appeared to doubt the existence of a basic phosphate of lime, consisting of $8CaO, 3P^2O^5$, or $2(3CaO, P^2O^5) + 2CaO, P^2O^5$, this induced me to repeat the analyses of this salt, which were made 26 years ago. A solution of phosphate of ammonia was treated with ammonia free from carbonic acid, and a solution of chloride of calcium free from chloride of magnesium was dropped into this until about half the phosphoric acid was precipitated. The fluid was then filtered, and the filtrate again treated with chloride of calcium in excess, until the fluid contained it in great excess. Both precipitates were well-washed, dried, heated to redness, weighed and analysed, by dissolving them in nitric acid, and precipitating the solution with excess of acetate of lead; the phosphate of lead thrown down was well-washed, dried, heated to redness, again dissolved in nitric acid, and the solution thrown down by sulphuric acid. From the weight of the sulphate of lead, the amount of oxide of lead was calculated, and thus that of the phosphoric acid found. The liquid which was treated with the acetate of lead, after being mixed with the evaporated wash-water of the phosphate of lead, was freed from lead by sulphuretted hydrogen, supersaturated with ammonia, and precipitated by oxalic acid. The oxalate of lime was heated to redness, dissolved in muriatic acid, then converted into sulphate of lime, the acids driven off by evaporation, and the sulphate of lime heated to redness over a spirit-lamp until it ceased to lose weight. The quantity of lime was calculated from the weight of the sulphate. The first of these basic salts which was precipitated consisted of—

	Found.	Atoms.	Calculated.
Phosphoric acid	48·5	3	48·737
Lime................	51·5	8	51·263

It consequently had the above composition.

The second precipitated basic salt, which was left for 24 hours in the liquid which contained the lime and ammonia in excess before it was filtered, contained only 46·658 per cent. of phosphoric acid; it was thus passing into Ca^3O^3, P^2O^5, but was not yet completely converted into this.

Next a solution of chloride of calcium, mixed with a considerable excess of ammonia, was precipitated by phosphate of ammonia, without throwing down the whole of the lime it contained. On analysis this salt was found to be $3CaO, P^2O^5$, and it was thus true basic phosphate of lime. This precipitate differs in aspect from the preceding. It is not so gelatinous and semitransparent, but more mucous, and resembling artificially prepared fluoride of calcium. When dried and heated it has an earthy fracture, whilst the last is denser and somewhat shining. These observations leave us in doubt concerning the saturating power of the bone-earth phosphate of lime. Thus the bones contain carbonate of lime; and when a solution of bone-ash in concentrated muriatic acid is thrown down by caustic ammonia, the first precipitate is $= 8CaO, 3P^2O^5$; but towards the end

$3CaO, P^2O^5$ is also formed, so that the precipitate thrown down may consist of both. They thus require a new examination, which would be best performed by dividing the bone-powder into two equal parts, one of which should be dissolved in muriatic acid, and from this the amount of liberated carbonic acid ascertained with the greatest possible accuracy; the other part should be burnt to a white ash, and from this the amount of both phosphoric acid and lime ascertained, whence the proportion of lime to the two acids would show the saturating power.—Liebig's *Annalen*, Feb. 1845.

On Ferrocyanide of Lime and Magnesia.

It is well known that salts of lime and magnesia yield white crystalline precipitates with ferrocyanide of potassium, if the solutions are sufficiently concentrated or alcohol is added. The precipitates produced are soluble in water and dilute acids. According to Marchand, these compounds are triple salts, into the composition of which cyanide of potassium enters. At least he found in the lime precipitate oxide of iron, potash and lime, in the proportions of 1·114, 1·225, 0·734, which would correspond with the formula $FeCy + CaCy + KCy + 3HO$.—*Archiv der Pharm.*

On the Action of Acids and Alkalies on Tartar-Emetic.

By M. SCHWEIZER.

That the whole of the oxide of antimony exists in tartar-emetic in the state of base is certainly evident from the fact, that bases separate all the oxide of antimony, and take its place, while acids yield a basic salt of antimony and bitartrate of potash, as is proved by the following experiments of the author with ammonia and nitric acid.

When *ammonia* is added to a tolerably saturated solution of tartar-emetic, the liquid becomes turbid, and in the course of a few minutes a flocculent precipitate of oxide of antimony is formed, which gradually increases; the precipitate is immediately produced on the application of heat. As soon as no further increase of the precipitate took place, it was separated; the filtered liquid however still indicated the presence of a considerable quantity of oxide of antimony. On evaporation, a crystalline salt gradually separated, which was proved by its properties and by analysis to be bitartrate of potash (100 parts contained 24·44 per cent. potash). The residue was treated with water, which left a quantity of the bitartrate behind. The concentrated solution still contained a considerable amount of antimony. The solution was again evaporated to dryness, and the residue treated with a little water, when a further quantity of bitartrate of potash separated. This operation was frequently repeated, and each time the author observed a formation of the bitartrate of potash, and at the same time he noticed during the evaporation a constant liberation of ammonia. There must consequently exist in the solution an easily-soluble salt, which is partially decomposed at the temperature of the water-bath, disengaging ammonia, and depositing in the same measure bitartrate of potash.

The author now dissolved a small quantity of tartar-emetic in water, added an excess of strong ammonia to the solution, and placed it aside for several days. The liquid filtered from the oxide of antimony was treated with alcohol, when a considerable crystalline precipitate formed, which was collected on a filter, washed with spirit, and subsequently well-dried by great pressure. In this manner a snow-white crystalline salt, very easily soluble in water, was obtained, consisting of tartaric acid, potash and ammonia, with a small amount of oxide of antimony, which was evidently not an essential constituent, but was derived from a small quantity of undecomposed tartar-emetic. On heating the solution of the salt, a separation of bitartrate of potash resulted, together with an evolution of ammonia; heated to a higher temperature in the solid state, the combination could almost completely be converted into bitartrate of potash. This behaviour sufficiently proves that the combination is the known double salt of tartrate of potash with tartrate of ammonia.

The author dissolved 2 grms. tartar-emetic in water, and treated the solution as above described with ammonia. The precipitate of the oxide of antimony was collected on a weighed filter, well-edulcorated, and then dried in the water-bath until it lost no more in weight. It yielded 43·35 per cent. $Sb^2 O^3$. Sulphuretted hydrogen was passed through the filtered liquid, in order to precipitate the antimony still contained in it, which was then determined in the usual way from the sulphuret; it amounted to 1·1 per cent. Both determinations gave 44·45 per cent. $Sb^2 O^3$; according to Dumas, tartar-emetic contains 44·86 per cent.

The reason why, in the above experiments, after the action of the ammonia, there still always remained a considerable quantity of oxide of antimony in the liquid, is owing to the ammonia effecting the decomposition of the tartar-emetic very slowly.

Nitric acid produces in tartar-emetic immediately a considerable precipitate of oxide of antimony, which increases on the application of heat. The more tartar-emetic is taken, the longer does it require for the decomposition to be complete, as in the action of ammonia; after removal of the separated oxide of antimony a liquid is constantly obtained which still contains a considerable amount of antimony, leading to the supposition that a new combination with oxide of antimony is formed. To ascertain this, the author evaporated the solution, when a further quantity of oxide of antimony separated, which was removed by filtration; and finally, after the complete removal of the excess of nitric acid, a white salt, readily soluble in water, was obtained, which consisted of oxide of antimony, potash, tartaric and nitric acids, and being heated deflagrated. It was a mixture, for nearly the whole amount of nitric acid could be removed by alcohol; the residuary combination contained antimony, and no longer burnt off on ignition.

To obtain the latter perfectly pure, the author decomposed a fresh quantity of tartar-emetic with nitric acid, applying heat until no more oxide of antimony separated; after which he added a large quantity of spirit to the solution, which produced a considerable flocculent precipitate, which was collected on a filter, washed with alcohol, and dried by great pressure and a gentle heat. In the analysis of the pulverulent salt, a result approaching so closely to the composition of tartar-emetic was obtained, that the author was convinced that the antimonial compound in question was nothing further than undecomposed tartar-emetic, and the above-mentioned residue a mixture of undecomposed tartar-emetic with the true products of decomposition.

To ascertain the nature of the latter, the author subjected a small quantity of the tartar-emetic (8 grs.) to decomposition, since this with larger quantities extends only to a portion of the salt. He observed that the last portions of the oxide of antimony, which were separated on the application of heat, were gradually redissolved. The residue obtained in the above-mentioned manner was now treated with alcohol of 80 per cent., and the solution evaporated to dryness. The residuary crystalline mass had a strong acid reaction, and scintillated on ignition.

It was treated with water, and a small quantity of bitartrate of potash remained, and the solution again evaporated; in this operation some crystals separated, which were recognised to be nitre, and were removed; the strongly acid mother-ley left, after complete evaporation, a considerable quantity of nearly pure tartaric acid. The reaction of nitric acid on tartar-emetic is consequently as follows:—The oxide of antimony is separated by the nitric acid as basic nitrate of antimony; bitartrate of potash is formed, which however remains dissolved in the excess of nitric acid. On the application of heat a large portion of the bitartrate is decomposed by the nitric acid, tartaric acid being separated and nitre formed. Since the whole of the bitartrate is not decomposed at the same time, there is a constant separation of basic nitrate of antimony on the application of heat, which is redissolved by the free tartaric acid.

The formation of bitartrate of potash in the action of acids on tartar-emetic, with separation of a basic salt of antimony, confirms the decomposition of tartar-emetic by muriatic acid, which immediately produces in a solution of this salt a thick caseous precipitate of basic chloride of antimony, which redissolves in an excess of acid. The liquid contains bitartrate of potash.—*Journ. für Prakt. Chem.*, xxxiii. p. 470.

ANALYTICAL CHEMISTRY.

On the Detection of Mercury in Cases of Poisoning.

By MM. DANGER *and* FLANDIN.

THE only progress of recent date in the toxicological study of mercury, is the discovery and use of Smithson's battery. The elements of this little apparatus consist of a plate of tin lined with a plate of gold in a spiral form. The tin constitutes the electro-negative, and the gold the electro-positive element. When immersed in a solution containing mercury, this pile separates the metallic element, which combines with the gold, and imparts a white colour to it; at the conclusion the metal is volatilized in a small tube, to obtain it in the state of the characteristic fluid globule.

After a comparative examination of the reactions for discovering mercury in its solutions, we are satisfied that the galvanic or galvanoplastic action is the most sensitive. We have been able to detect by means of this test the mercury in a solution containing only $\frac{1}{100,000}$th.

It is not the galvanic apparatus which Smithson invented that we employed in our researches; we only preserved its principle. For toxicological researches, this ingenious instrument would have been subject to inconveniences which we wished to avoid; we substituted for the apparatus of the English chemist one in which the vessel containing the suspected liquid was inverted in a kind of funnel terminating in a tube drawn out to a bore which was almost capillary, so that the liquid might flow out of it at the rate of about 1 drop in 5 seconds; it was caught in a capsule. The flow could be regulated by varying the inclination of the apparatus. The electro-positive pole was placed in the capillary tube, the negative in the wide part of the funnel; they were placed nearly in contact, and both, or at least those parts which touch the liquid, should be made of pure gold. When the pile (Bunsen's), which consists of a single pair of plates, is in action, evolution of gas takes place at both poles, and the mercury contained in the solution is deposited upon the electropositive pole, which it whitens. To be certain that this effect is produced by mercury, the metal need only be volatilized in a reduction-tube.

Being certain of detecting the slightest trace of mercury with this apparatus, we still had to find a suitable process for separating the mercury from the organic matters, and to isolate it from them as far as possible without loss. The Academy approved of the process of carbonization by sulphuric acid proposed by us, and this process is now generally practised in cases of medico-legal inquiry. We tested its application to the detection of mercury, and succeeded in this without having recourse to distillation, as we at first feared we should be obliged to do. After numerous trials we adopted the following process:—At a temperature of about 212° we liquefy the animal matters by one-third or half of their weight of monohydrated sulphuric acid in the ordinary manner. This liquefaction being completed, which requires only an hour and a half, or at the most two hours, the capsule is taken from the fire and left to cool to a certain extent. Then, after having placed the vessel underneath a chimney with a good draught, to protect the operator against the disengagement of vapours, we throw into the black carbonized liquid saturated chloride of lime in separate pieces, stirring the mixture at the same time with a glass rod. By degrees, as the matter thickens, and becomes white, distilled water is added, which favours the action of the chlorine, and this is continued until the liquid to be separated by filtration appears almost colourless. The quantity of chloride of lime must always be very nearly in relation to the amount of sulphuric acid required for the perfect liquefaction of the animal matters. For 3 oz. of liver, on account of the bile and fats which this organ contains, sometimes 1½ oz. of sulphuric acid and 1½ oz. of chloride of lime are necessary; but it is scarcely ever requisite to exceed this proportion. The substance, which is whitened and rendered of a chalky aspect, is well-moistened whilst cold with absolute alcohol, then diluted with distilled water and filtered, and the precipitate washed repeatedly. The liquid, if too abundant, is concentrated by evaporation, after which it is submitted to the action of a galvanic current, in the apparatus described. It was proved by experiment that the voltaic current favoured the precipitation of the mercury on the gold wire, and that in all cases it at least possessed the advantage of accelerating an operation, which without the concurrence of this action would perhaps require much time to accomplish.

The metal being obtained on the electro-positive conductor of the pile, it is necessary to wash the gold wire in boiling æther or alcohol to remove all fatty matter, and to dry it before introducing it into the reducing-tube. This should be perfectly free from moisture, which might stain the globule of mercury, which is sometimes extremely small, and must be made perceptible to the eye.

The efficacy and sensitiveness of this process has been ascertained by numerous experiments. We have required 3 oz. only of the liver of an animal poisoned with corrosive sublimate to obtain an appreciable quantity of mercury from it. In future therefore it will not be more difficult to detect corrosive sublimate than arsenious acid, or any other metallic compound.—*Comptes Rendus,* March 31, p. 951, 1845.

Curious Case of Poisoning with Arsenic.

In the examination of the corpses of two men, supposed to have been successively poisoned by the wife, Wöhler distinctly detected arsenic, even after an interval of seven years and six months. He incinerated all the soft parts of both corpses with nitre. In the man who died last, it was found that during the last moments of his life he had taken phosphuretted oil, and had therein consumed altogether about 16 grms. of phosphorus. On examination of the stock of phosphorus in the apothecary's shop whence it had been obtained, it was found to contain about a half per cent. of arsenic. The phosphorus used in the preparation of phosphuretted oil ought therefore in future to be tested for arsenic.—*Ann. der Chem. und Pharm.*, liii. p. 141.

CHEMICAL PREPARATIONS.

On the Preparation and Composition of the Iodide of Ethyle.

By Prof. R. F. MARCHAND.

THE best method of preparing iodic æther, if not wanted very quickly and in very large quantity, is as follows:—A flask capable of holding a pound of water is closed *air-tight* with a cork into which a platinum wire has been fitted, wound spirally at one of its extremities. A piece of phosphorus is placed in this spiral, so that it is suspended vertically in the flask, which is then filled with from 200 to 300 grs. of absolute alcohol in which 50 grs. of iodine have been dissolved. It is still better to introduce the iodine into the flask and to pour the alcohol upon it, agitate it somewhat, and then fit in the cork with the phosphorus. The dark brown liquid gradually loses its colour, and finally becomes perfectly colourless, and first of all in the vicinity of the piece of phosphorus. If any has remained undissolved, the flask is gently shaken, that a fresh quantity of iodine may be dissolved, which colours the liquid brown; this again becomes colourless, &c.

It is requisite to guard against the phosphorus ever coming into contact with the iodine; otherwise a considerable evolution of heat results, the alcohol begins to boil, and a reddish-brown mass, consisting of phosphorus and a combination of iodine and phosphorus, is formed. As soon as the whole of the iodine has disappeared a fresh quantity is added, taking care to restore the cork as quickly as possible.

The decoloration, which proceeds more slowly at a low than at a high temperature, is hastened by frequent shaking. The oily, very acid liquid dissolves a considerable quantity of phosphorus when this has been left in contact with it for some length of time, so that it fumes strongly on exposure to the air. If now a solution of iodine be added to it, the liquid becomes much heated, iodic æther distils over, and it is decolorized almost instantly. The phosphorus, which, with the stated quantities, remains for the greater part behind unaltered, is partially coated with a red powder. Kopp has shown that this is the red modification of phosphorus. On dissolving the red powder in potash, which was accompanied with evolution of phosphuretted hydrogen, evaporating the alcoholic solution and igniting, no iodine could be detected in the residue. It is remarkable that this red modification is only formed when the solution of iodine is very concentrated; with dilute solutions the phosphorus remains as transparent as when first employed.

On distilling the liquid separated from the excess of phosphorus to within one-fifth of its volume, the iodic æther passes over along with the alcohol. It can be almost entirely separated by the addition of water. The acid residue in the retort consists of æther, phosphoric acid, a little hydriodic acid, and another organic acid containing iodine, which, even in its salts, is very readily decomposed by exposure to the atmosphere.

The separated iodic æther, if the phosphorus be not immediately removed from it, always contains phosphorus, which causes its boiling-point to rise to 163°. The phosphorus is removed by the addition of iodine and distillation. The brown liquid, containing iodine, which passes over, is shaken with mercury, so that protiodide of mercury is formed; on rectifying it again, the æther is entirely freed from iodine. If it has been left sufficiently long in contact with fused chloride of calcium, it is anhydrous on distillation. It boils at 756^{mm} B at 148° F., and possesses at 61° a specific gravity of 1·92.

The specific gravity of the vapour was found equal to 5·417. The analysis yielded—

Carbon......	15·31	4 =	300·0	15·46
Hydrogen ..	3·28	5	62·5	3·22
Iodine		1	1578·3	81·32
			1940·8	

Nitric acid instantly decomposes the æther, and a large quantity of iodine is separated; iodine is likewise immediately separated by the action of chlorine on the æther, and chloride of ethyle escapes; when the action is continued long, chloride of iodine is formed.

The author desired to learn what amount of æther could be obtained from a fixed quantity of iodine; the fluid obtained with 680 grms. of iodine was therefore mixed with water as long as anything separated; the æther collected amounted in weight almost accurately to 400 grms.; these contain 324 grms. iodine, consequently nearly half of the amount employed.

A second experiment was made in the manner first described; 110·09 grms. iodine yielded 64 grms. iodic æther, which was distilled from the fluid in which it was dissolved, and was precipitated from the product by water. The æther contained 52 grms. iodine; it may therefore be admitted that half the iodine passes into the æther.

This experiment enabled the author to ascertain at the same time the amount of phosphorus requisite to produce this reaction. The phosphorus was weighed, and a platinum wire introduced into the flask, containing the entire amount of iodine to be used, so that it did not require to be opened before the reaction had terminated. The 110·09 grms. iodine, 14·443 grms. phosphorus were employed; in nine days the liquid was decolorized (the temperature did not exceed 48° F.). The residue of phosphorus, which was weighed immediately after the decoloration, so that merely a trace could be dissolved mechanically, amounted to 8·897 grms.; consequently 5·546 grms. phosphorus have disappeared with the 110·09 grms. iodine, but 110·09 iodine are equivalent to 27·348 phosphorus, the fifth part of which = 5·469. For 1 equiv. phosphorus therefore 4·93 equiv. iodine have disappeared, consequently 5 equiv.

In a second experiment, in which 38 grms. iodine and 2·420 grms. phosphorus were employed, 1·898 grms. of the latter disappeared, while one-fifth of the equivalent would amount to 1·887.—*Journ. für Prakt. Chem.*, xxxiii. p. 186.

On the Purification of Honey. *By* M. Veling.

The white of 1 egg is beaten up with 5 lbs. of honey till it froths; as much water is then added as is sufficient to form the consistence of a thinnish honey; it is then mixed, and boiled until the albumen can be removed with the froth; it is then poured into an upright vessel, 2 or 3 inches above the bottom of which a cock is inserted; it is well-covered, and set aside in a cellar for 6–8 weeks. The impurities, which otherwise stop up the filter, or the finer portions of which pass through, become coagulated in the vessel, and collect at the bottom and on the sides, and the honey can be drawn off clear by the cock.—*Archiv der Pharm.*, xl. p. 155.

On the Preparation of Chlorine Water.

MM. Riegel and Waltz, in their experiments on the quantity of gas contained in chlorine water at different temperatures, have arrived at results exactly similar to those of Pelouze, except that they found the maximum somewhat greater than he did (3 vols. at 50°). They did not find Buchner's method* preferable to that of the fifth edition of the Prussian Pharmacopœia. They also consider the preparation in the dark, and the preservation in bottles with glass stoppers, as unnecessary. The water appears to be best preserved in small bottles with good corks, and covered with bladder. That which contains about $2\frac{1}{2}$ volumes of chlorine, and preserved at 54° Fahr., appears to keep best. They recommend therefore that the chlorine evolved from 12 parts of well-dried chloride of sodium, 9 parts of peroxide of manganese, 10 parts of concentrated sulphuric acid and 10 water, be conducted into distilled water which is retained at the temperature of 54° Fahr. until it is saturated. The chlorine contained in it is best tested, according to the authors, with a solution of pure indigo in sulphuric acid, which is so diluted as to contain $\frac{1}{184}$th of indigo. 2 parts of chlorine water of the above strength are exactly sufficient to decolorize 1 part of this solution of indigo. To detect muriatic acid, the authors recommend metallic mercury, and for chlorous acid the protochloride of mercury.—*Jahrb. für Prakt. Pharm.*, ix. p. 154.

Testing of Essential Oils by means of Sulphuric Acid.
By M. Voget.

The author considers concentrated sulphuric acid as the best reagent for detecting adulterations of essential oils with oil of turpentine. The peculiar colour which the former assumes with sulphuric acid is much altered by the intense reddish-brown colour which the oil of turpentine yields; and moreover the heat evolved with the oil of turpentine is greater than that with other oils. In testing, the oils are best dropped upon a glass plate, beneath which is placed a

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* This method was described at p. 311, vol. ii. of this Journal.—Ed.

piece of white paper; 5 drops of the oil are then added to 1 drop of fuming sulphuric acid, and the two are mixed with the finger.—*Archiv der Pharm.*, xl. p. 164.

Adulteration of Saffron.

J. Müller recommends concentrated sulphuric acid as the most certain test for saffron, for it immediately turns the colour of pure saffron to indigo blue (it however soon changes to dark red and brown). The leaves of *Crocus vernus*, which form the most frequent adulteration, are coloured of a dark green by sulphuric acid.—*Archiv der Pharm.*

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

An Account of the Manufacture of Glass in Bohemia.

By L. P. DEBETTE.

Of Glass in general.—Every transparent, or at least translucent substance, which is brittle at ordinary temperatures, becomes soft and ductile, and finally melts at a high temperature, the fracture of which, when cold, presents a peculiar, well-defined lustre, known as the vitreous lustre and the vitreous fracture, and is called, in the most general sense of the word, glass. Many acids, such as the phosphoric and boracic, as well as many silicates, phosphates, borates, arseniates, fluorides, and some metallic chlorides, such as those of lead and silver, different mixtures of these bodies with each other, and with other substances, among which the alkalies and the earths hold the first place, produce glasses by their fusion. That which in the arts is more especially meant by the term glass is a compound of silica, potash or soda, or both together, and of lime and oxide of lead alone or mixed. This compound gives, by fusion, an amorphous and transparent mass, which is not soluble in water, nor in any acid except the hydro-fluoric.

Travelling in 1842 through Bohemia, I visited with interest the most renowned manufactures of glass and crystal, and especially the various groups of the Böhmerwaldgebirge. The beauty of the productions of these workshops, and the veil which still covers their processes of manufacture, have induced me to publish here the few observations which it has been in my power to make.

CHAPTER I.—*Composition and Properties of Glass.*

Glasses are silicates which must contain at least 50 per cent. of silica; the more there is of it, the more perfect, unalterable, hard and infusible is the glass. The hardest, most beautiful and most perfect glass is found in nature in the state of pure silica in rock crystal;

but as this is fusible only at the highest temperatures which can be produced in our laboratories, such as those produced by employing Newman's blowpipe, or by the aid of a galvanic or electrical battery, it is impossible to procure it artificially. To render silica fusible, certain fluxes must be added; these fluxes are potash, soda, lime and oxide of lead.

Silica fuses very well with the alkalies, but the resulting glass is rapidly changed by absorbing moisture from the air. To prevent this alteration, it is always necessary, in the manufacture of glass, to introduce a certain quantity of lime or of oxide of lead.

In the following table the analysis of a certain number of varieties of Bohemian glass is given, which will indicate their composition with precision:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Silica........	71·6	71·7	69·4	62·8	75·9	78·85	70·0	57·0
Potash	11·0	12·7	11·8	22·1		5·5	20·0	25·0
Soda		2·5			17·5	12·05		
Lime........	10·0	10·3	9·2	12·5	3·8	5·6	4·0	12·5
Magnesia	2·3							
Alumina	2·2	0·4	9·6	2·6	2·8	3·5	5·0	3·0
Oxide of iron..	3·9	0·3					0·6	1·3
Oxide of manganese	0·2	0·2					0·4	0·4
	101·2	98·1	100·0	100·0	100·0	100·5	100·0	99·2

I. Bohemian glass from Neufeld (M. Gras); its composition is represented nearly by the formula $CaS^5+(Al, F)S^5+(K, Mg, Mn)S^5$*.

II. A fine table glass from Neuwelt (M. Berthier); it is exceedingly beautiful, and is prepared, according to M. Perdonnet, with a mixture of 100 parts of quartz, 50 caustic lime, 75 carbonate of potash, and a very small quantity of nitre, arsenious acid and oxide of manganese. The presence of arsenic cannot be detected by analysis. The composition of this glass is expressed by the formula $CS^6+(K, N)S^6$.

III. Old Bohemian glass (M. Dumas); its formula is $(Al, C, K)S^4$.

IV. Crown glass of German manufacture (M. Dumas); its composition is expressed by the formula $(K, C)S^4$.

V. Glass for mirrors (M. Dumas); it is represented by the formula $(N, Al, C)S^6$.

VI. Another glass for mirrors (M. Dumas); its formula lies between BS^5 and BS^6.

VII. White table glass from Silberberg near Gratzen; its composition is exactly expressed by the formula $2(K, Ca)S^5+(Al, F)S^5$.

VIII. Mirror glass from Neu-Hurkenthal, for the manufacture of cast mirrors. It shows a greenish tint in section, and softens at a

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* The reader will remember that these are mineralogical, and not chemical symbols; hence the letters signify the oxides or acids, and not the elementary bases, as they would in chemistry.

gentle heat. Its composition is nearly represented by the formula $(Al, F)S^3 + 6(K, C, M)S^3$, or more simply $(K, C, Al)S^3$.

I shall give the composition of the mixtures which are introduced into the pots, when I come to describe the manufacture of each kind of glass.

Properties of Glass—Transparence, Freedom from Colour.—Transparence and freedom from colour are the first properties of glass. To obtain them, the materials must be employed extremely pure, and the least possible flux added; an excess of potash imparts to glass a greenish tint; soda and its salts give it a yellow tint, and lime renders it milky. A very small quantity of the sulphate of potash or soda gives it a yellowish or blackish-brown green; iron colours it strongly bottle-green; and an excess of the manganese employed to remove the coloration due to oxide of iron gives it a bluish tint, which becomes a decided violet by the action of the solar light. If the minium employed in the manufacture of crystal contains a little copper, which very often happens, the crystal takes a slight emerald-green tint; this however is not to be feared in Bohemia, where there is but a single establishment which makes lead glass.

Charcoal colours glass of a topaz yellow, more or less dark, and sometimes reaching a purple, so that it is impossible to obtain a perfectly colourless glass in furnaces which smoke, or in those which are heated by turf, lignite, or bituminous coal; and in these cases it is necessary to employ covered crucibles, as is done in the manufactory of crystal at Choisy-le-Roi; it is also necessary, on this account, when in the fabrication of glass the alkaline carbonates are replaced by sulphate of soda, to add in the crucibles a little (about one-thirteenth) less of carbon than would be necessary to reduce the sulphate completely; and even thus only common glass is obtained by this process, since the slight excess of sulphate of soda which must be left gives a blackish-brown tint.

Hardness, Elasticity.—The Bohemian glass is, within certain limits, perfectly elastic and very sonorous; when well-made it is sufficiently hard to strike fire with steel, and is scratched with difficulty. The lead glasses, on the other hand, have but little hardness, and less in proportion as they contain more oxide of lead; besides which they rapidly lose their brilliancy by use.

Fusibility, Cooling, Annealing, Devitrification.—All glass is more or less fusible; when it is softened by the action of heat, it may be worked with the greatest ease, and may be drawn out into threads as fine as those of the cocoon of the silk worm. Glass, when it is submitted to rapid cooling, becomes very fragile, and presents several remarkable phænomena, among which I will cite as an example Prince Rupert's drops. Glass supports variations of temperatures better in proportion as it has been more slowly cooled; thus when it has been but slightly annealed, or not at all, its fragility may be considerably diminished by annealing it in water, or, better, in boiling oil.

All glass exposed during a longer or shorter time to a heat sufficiently elevated loses its transparency, and becomes extremely hard and much less brittle than before. A phænomenon occurs precisely similar to that which we see taking place every day by the slow cooling of the slags of our smelting furnaces, and especially in volcanic lavas. Glass with a soda base is more fusible and less hard than that whose base is potash.

Density.—Below the densities of several glasses not containing lead are given:—

Old Bohemian glass (Dumas)	2·396
Bohemian bottle glass	3·782
Bohemian window glass	2·642
Fine glass called Bohemian crystal	2·892
Mirror glass of Cherbourg (Dumas)	2·506
Mirror glass of St. Gobain (Dumas)	2·488
Mirror glass of Neuhaus, 1812 (Scholz)	2·551
Mirror glass of Neuhaus, 1830 (Scholz)	2·564

Action of Atmospheric and Chemical Agents.—The harder and more infusible a glass is, the less is it alterable by the action of atmospheric and chemical agents, with the exception of hydrofluoric acid. Glass which is too alkaline absorbs gradually the moisture of the air, and loses its lustre and polish. Many glasses are perceptibly attacked by a prolonged boiling with water, and *à fortiori* by acid and alkaline solutions; thus bottle glass is frequently attacked by the tartar which is found in the wine. According to Guyton Morveau, all glass which is attacked by prolonged boiling with concentrated solutions of alum, common salt, sulphuric acid or potash, is of bad quality.

CHAPTER II.—*Of the Choice and Preparation of the Raw Material.*

The silica which is employed in Bohemia in the manufacture of glass is obtained by calcining crystalline quartz, and afterwards pounding it while dry. The quartz is sometimes found in veins in granite and gneiss, as at Neu-Hurkenthal; but it is more frequently met with either under the form of rolled pebbles in the torrents of Böhmerwaldgebirge, or in more or less angular fragments, scattered through the vegetable soil, which is derived from the decomposition of the primitive rocks. It is evident that these fragments are the remains of the quartzose veins, which, presenting a greater resistance, have escaped the disintegration of the granite or gneiss which enclosed them, and which have been more or less rolled in their transportation.

Such of these fragments as appear to the eye exempt from metallic matters are bought and sent to the glass works at the average price of 0·65 franc per 100 kilogrammes (6½*d.* per cwt.). These fragments are roughly assorted at the manufactory; those of smoky quartz, called topazkies by the inhabitants, are laid aside as the purest, and reserved for the manufacture of glass of the finest quality, or crystal.

The quartz is calcined, either in reverberatory furnaces or in furnaces of a peculiar form.

When the quartz has been heated to a cherry-red, it is withdrawn from the fire and thrown immediately into a large and shallow tub, the water of which may be continually renewed by a stop-cock, and its heating thus prevented; the quartz thus calcined and cooled is picked out by hand by women, who gain 0·4 franc (4*d.*) for 12 hours' work. The fragments which are too large and too hard, which have not been sufficiently calcined, are broken into pieces and thrown back into the furnace; the rest is broken up into small fragments, and those parts which are perfectly white are alone employed in the manufacture of glass. All fragments which present the least trace of metallic oxides (ordinarily oxide of iron) are separated with the greatest care, pulverized separately, and employed upon iron wheels in grinding the cut glass.

Upon an average, 0·07 stere of pine-wood is consumed in calcining 100 kilogrammes of quartz ($1\frac{1}{4}$ cubic foot per cwt.). The quartz, after being calcined and picked out, is then pounded while dry; the pestles are armed with cast iron heads, the weight of which varies from 120 to 150 kilogrammes (264 to 330 lbs. av.); their play is from ·5 met. to ·6 met. (1·64 to 1·99 ft.), and each of them falls into a hemispherical mortar, about 10 in. in diameter, cut in a large beam which extends throughout the length of the pounding machine. The use of iron and stone mortars had to be discontinued for fear that the head of the pestles might detach sufficient ferruginous particles to diminish perceptibly the purity of the glass.

The powder obtained from the pounding machine is sifted, and that which remains upon the sieve is pounded over again. Each pestle of the pounding machine pulverizes in 12 hours 90 lbs. of quartz.

Potash.—Almost all the Bohemian glass is potash glass, because soda and its salts give to glass a sensible yellowish tint, and because the difference of the price of potash and soda is far less in Bohemia than in most of the countries in Europe. A small quantity of the potash used in Bohemia is made in that country, but the greater part is obtained from Hungary. There the Carpathians are covered by immense forests, the greater number of which are, in the present condition of things, unavailable, on account of the low price of fuel and the difficulty of communication. They are therefore used by burning them standing, and withdrawing the common potash from their ashes by washing.

To obtain potash of the second quality, the preceding is treated cold with its own weight of water, then decanted; the decanted liquor evaporated to dryness, and the potash thus obtained calcined at a heat high enough to frit it.

Finally, to obtain the finest potash, or that of the first quality, treat the potash of the second quality as before, using only one-half of its weight of cold water.

It is of the greatest importance that the trees which have furnished the potash shall not have grown upon a metalliferous soil, that is a soil perceptibly charged with metallic oxides and salts; for we know that these substances are absorbed by the sap, and that we can even imitate artificially by this process a great number of coloured woods, by causing certain metallic solutions to be successfully absorbed by woods of analogous structure and tissue.

When this is the case, the potash which is obtained by washing the ashes of the trees, although it may appear very pure at first sight, contains almost always a sufficient quantity of metallic oxides to colour the glass perceptibly, which must cause it to be rejected in the manufacture of fine glass. This remark, and the recollection that the value of the Bohemian glass depends peculiarly upon its perfect freedom from colour, have caused the adoption in this country of a process of testing altogether different from the alkalimetric processes employed in France, which give only the amount of alkali, without at all indicating the nature and proportion of the foreign and injurious materials which it may contain. This test, which is still further facilitated by the small size of the glass pots, which in Bohemia do not contain more than from 120 to 200 lbs. of calcined and fritted materials, is performed by replacing in one of the pots in which fine glass is made the potash ordinarily employed by its weight of the potash to be tested, and comparing the articles made with the glass obtained with glasses of known composition, made once for all, by varying the quality and quantity of the alkali.

Thus, by the perfect whiteness, or by the more or less decided shade of colour of the glass obtained, the nature and proportion of the metallic impurities, and even approximately the alkaline contents of the potash tested, are ascertained; and thus its commercial value can be directly obtained.

In the works of the Böhmerwaldgebirge, the prices of the different kinds of potash per cwt. are as follows:—

	£	*s.*	*d.*
Common potash (third quality)	0	19	2½
Fine potash (second quality)	1	3	0
Superfine potash (first quality)	1	8	6½

Soda.—Soda is, as I have before remarked, but little employed in Bohemia, where it is used only in the manufacture of common window glass. Common soda costs 15*s.* 4*d.* per cwt.

Sulphate of Soda.—Sulphate of soda, or glauber salts, is obtained in chemical works as a residue from the manufacture of nitric acid by means of nitrate of soda and sulphuric acid, and it is employed only in certain glass works annexed to these establishments (as at Gross-Luckawitz, near Chrudim), where they make the bottle-glass retorts and matrasses used in the works themselves (one-thirteenth of its weight of carbon must be added).

Lime.—The lime employed in the glass works of the Böhmerwaldgebirge is obtained from a saccharoidal limestone, found both in Moravia and in Bohemia (near Winterberg), in beds enclosed in gneiss, which shows the same stratification; whilst in certain places, and especially near Winterberg, the granite upon which these beds rest may be seen to send forth veins into them. This fact appears to demonstrate in a clear manner that this limestone and gneiss, which are regarded as primitive by many German geologists, and among others by Professor Zippe of Prague, are the effect of a metamorphosis due to the appearance of the granite, which has elevated the chain of the Böhmerwaldgebirge.

This saccharoidal limestone is perfectly white, and presents two extreme varieties; one of which, with broad laminæ and very transparent, imitates to deception the most beautiful ancient statuary marble (such as that of Paros), while the other, with an extremely fine and close grain, has a greater analogy with the Carrara marble.

These limestones are calcined in the same furnaces which serve to burn the quartz, and are then suffered to slack spontaneously in the air, and care is taken to frit again the powder thus obtained before placing it in the crucibles of the glass furnace. In the mixture, from 6 to 20 parts of calcined lime are introduced for 100 parts of silica.

Peroxide of Manganese.—The peroxide of manganese is but little employed in Bohemia, at least in the manufacture of fine glass; it serves to destroy the bottle-green colour due to the protoxide of iron.

Arsenic.—The arsenic is obtained in the state of arsenious acid from the Erzgebirge and from the Riesengebirge, where it is obtained both as a principal product of the roasting of arsenical pyrites and as an accessory product of the roasting of ores of tin and cobalt. It is much employed in Bohemia, especially in the manufacture of fine glass. It serves, first, to destroy the greenish tint due to a small quantity of the protoxide of iron; secondly, to destroy the topaz-yellow colour which the glass assumes if the furnace smokes, or if the wood in crackling should throw small sparks of charcoal into it; and thirdly, it serves to agitate the melted matter and assist the disengagement of bubbles.

Nitrate of Potash.—Saltpetre, or nitrate of potash, is employed in some of the establishments, together with white arsenic, to produce the same effects.

The pieces broken off in grinding, old broken glasses, glass which has been spilled upon the hearth of the furnace by an accidental fracture of the glass pots, &c., are broken up, washed, and classed according to their nature, their colour and purity, and commonly employed in the manufacture of common glass. The pieces from making the fine glass alone are used in the manufacture of white table glass.

Combustibles.—The combustible used in the glass works of Bohemia is resinous wood, of which the prevailing species is the Scotch fir (*Pinus sylvestris*); this species is also the best for working glass, because it crackles least in the fire and gives the most flame. The flanks and summits of all the mountains which form the chain of the Böhmerwald and Riesengebirge are covered with forests of resinous woods. These forests are cut when of full growth, about every 80 or 100 years. The wood is cut during the summer, then in winter it is transported to the water-courses which wind through the valleys by means of slides made in the snow, and when these melt it is floated down to the glass-works. The mean price, when delivered at the establishments, throughout the whole of the Böhmerwaldgebirge, is 1*s.* per cubic yard. The wood, before it is used, is completely dried, and even slightly roasted, in cast iron boxes, heated externally by the flames which escape from the glass furnaces. I have seen but the five glass-works of the Count de Buquoi, where this process has been abandoned for some fifteen years, and I do not know the motive of its disuse.

By the preliminary roasting of the wood, an œconomy of 10 per cent. in the fuel is gained; and besides, the fire becomes much more easily regulated.

Clay for the Crucibles.—The clay employed in the manufacture of the crucibles, in the glass-works to the east of the Böhmerwaldgebirge, comes from Moravia; that employed in the glass-works situated in the western part of that chain is taken partly from the environs of Pilsen in Bohemia, partly from the neighbourhood of Nuremberg in Franconia.

These clays are very white, very aluminous, and but slightly adhesive; by calcination they lose nothing of their original whiteness. A specimen of the clay from Moravia, employed at Silberberg in the manufacture of glass pots, gave by analysis the following results:—

Silica....	45·8	Oxygen....	23·8	Ratio	2
Alumina..	40·4	... .	11·4	... .	1
Water ..	13·8	... .	12·1	... .	1
	100·0				

Which gives for its formula $AS^2 + Aq$, which represents triklasite or fahlunite. Except that this clay contains no combustible matter, it presents in its composition a very great analogy with the refractory clays of Stourbridge and Stannington, the analysis of which has been given by M. Le Play*, in a very remarkable memoir upon the manufacture of steel in Yorkshire.

[To be continued.]

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* Annales des Mines, 4th series, vol. iii. p. 646.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Conversion of the Essential Oil of Mustard into the Essential Oil of Garlic. By CHARLES GERHARDT.

THE artificial production of substances which are generated in the process of vegetation or in the animal œconomy becomes more and more frequent as organic chemistry advances. I shall now draw attention to one which seems to me to merit attention.

The essential oil to which garlic owes its characteristic odour has been recently analysed by M. Wertheim[*], and according to this chemist contains $C^6 H^5 S$. It is therefore a sulphuretted body like the essential oil of black mustard, but free from nitrogen.

From the analyses of M. Lœwig, and from the researches recently made by Dr. Will, we know that the essential oil of black mustard does not contain oxygen, and that its true formula is $C^8 H^5 NS^2$. The result of M. Simon's observations also appears to be, that the essential oil of the Scurvy grass (*Cochlearia*) is identical with that of mustard; moreover, M. Hubatka[†] has proved that the horse-radish yields the same essential oil; and M. Wertheim[‡] has also met with it in the oil obtained by distilling the root of another cruciform plant, *Alliaria officinalis*, with water.

Considering these facts, and comparing the composition of the essential oil of garlic with that of mustard, I have been induced to try to convert one into the other by the means which science affords.

The oil of garlic only differs from that of mustard by the elements of cyanogen and of sulphur; we have, in fact,

$$C^8 H^5 NS^2 = C^6 H^5 S + C^2 N + S.$$

In acting with potassium on the oil of mustard, I had to take away the cyanogen as well as a part of the sulphur, and to set free the oil of garlic.

My suspicions were entirely realized; when some pieces of potassium, previously dried over some chloride of calcium and rectified afresh, are thrown into the oil of mustard, it is attacked immediately. It may be slightly heated in a retort to favour the reaction; care

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[*] Chem. Gaz., p. 177 of the present volume.

[†] Ibid, vol. i. p. 673.

[‡] Ibid, vol. iii. p. 186.

must be taken however not to raise the temperature too much, for the substance might take fire, as has frequently happened to me.

If the operation is performed with care, the substance does not become much coloured, some gas is disengaged, a white salt is deposited in the oil, and oil of garlic distils over. It is an interesting experiment, the difference of smell between the two oils being so striking: the smell of the garlic is immediately so evident, that this alone might suffice to prove that the conversion takes place as I have just described it.

But I desired to have chemical proofs. I therefore collected the oil which had been produced in the reaction; it was colourless, possessing in a high degree the characteristic odour of garlic, and presented the reactions described by M. Wertheim; shaken with a solution of nitrate of silver, it afforded a black precipitate of sulphuret; with the bichloride of mercury (when the aqueous solution was slightly heated to dissolve more oil) it yielded a white, and with the bichloride of platinum a yellow precipitate.

Burnt with oxide of copper, it yielded the same relative quantities of carbon and hydrogen as were obtained by M. Wertheim in the analysis of the oil extracted directly from garlic, and rectified without potassium, viz.—

	My produce.	Rectified oil of garlic. Wertheim.	Oil of Mustard.
Carbon..........	58·8	59·1	48·5
Hydrogen	8·4	8·2	5·1

I have not been able to make more analyses, from want of material.

The salt which separates in this reaction is *sulphocyanide of potassium*; in fact it dissolves easily in water, and gives with the persalts of iron the characteristic dark red colour; it also yields a white precipitate (protosulpho-cyanide of copper), with a mixture of deutosulphate of copper and of protosulphate of iron, &c. I was unable to discover sulphuret or cyanide.

However, in rectifying the artificial oil of garlic a second time over potassium, I found much sulphuret in the residue. This reaction appears secondary. Besides, to understand the reaction well, it will be necessary again to examine the gas which is evolved, which want of material prevented me from doing.

The above results seem to be sufficiently conclusive to prove that the oil of mustard is really converted into the oil of garlic by the action of metallic potassium. I intend however to return soon to this metamorphosis.—*Comptes Rendus*, March 24, 1845.

On the Occurrence of Bromine in the Urine. By Dr. Heller.

The author examined the urine of a patient who had been taking bromide of potassium for a syphilitic affection; it was of a full yellow colour, but presented no remarkable alterations in either its general properties or its constituents; when treated with nitric acid, it assumed a reddish colour, and starch being added the colour became more intense; when chromate of xyloidine and nitric acid were added, it became of a beautiful peach-blossom colour; by repeating the experiment until the right proportion of the reagent was obtained, the colour became intensely rose-red, especially by allowing it to repose. The bromine was also found in the serum of the blood.—Heller's *Archiv*, heft i. p. 39.

On a new Photographic Paper. By JOHN HORSLEY, Esq.

We have been favoured with a communication from Mr. J. Horsley, in which he recommends the following photographic paper as the simplest and most effective, yielding proofs of great depth and beauty, and free from any shade of brown.

Superfine writing paper (without water-mark) should first be primed with a solution of muriate of soda or muriate of ammonia, in the proportion of about 2 drms. to 1 pint of soft water. Pour the solution into a flat dish, in which immerse your paper, turning it over for a few minutes, then dry between blotting-paper, sop up the superfluous moisture with a clean cloth, and dry in the air. A number of these papers should be kept on hand, as they are very soon made fit for use; and it is always better to defer the next process till just before it is required, as the papers are so very liable to change colour.

Next, put into a bottle containing 3 drms. of *Liquor ammoniæ* 1 drm. of crystallized nitrate of silver, and 5 grs. of suberic acid, with which, when the solution is clear, go over your paper (having previously marked one side) with an even coating, dry by the fire, but not too near, and place in your copying-frame as quickly as possible.

Your copies (which will take from 5 to 10 minutes, or more, according to the depth required and the favourableness of the weather) may be fixed by first dipping them for a minutes in water in which has been put a little *Liquor ammoniæ*, then into a solution of hyposulphite of soda (1 part of the salt to 6 parts of water), let them remain for a few minutes, re-immerse in *plain water*, dry between blotting-paper, and finally by the fire, which will bring out the colour.

Ryde, Isle of Wight, April 14, 1845.

On the Composition and Properties of the Biliary Colouring Matter. By Prof. SCHERER.

These experiments were made in the summer of 1844 with the colouring matter of the bile, which abounded in the urine of a patient affected with severe jaundice. This urine, when fresh, was of a yellow tint, inclining to brown, and by repose became deeper in colour, not unfrequently assuming a grass or dark green hue. The urine, which when fresh was almost neutral, or even slightly alkaline, on the occurrence of this alteration in colour became acid, and deposited lithic acid in abundance. The latter was rendered of a brownish or green colour by the biliary colouring matter, which arises from the tendency colouring matter has to combine with substances on their being deposited from liquids. The urine was tested most carefully for bilic acid, but no trace of it could be found; I have never been more successful with other specimens of jaundiced urine, even with the most careful experiments. It is probable therefore that the earlier statements of Simon, who thought that he found biline, &c., as well as the colouring matter, in the urine of jaundice, are incorrect. Moreover, in the blood of this patient, the serum of which was of an intensely yellow colour, besides the colouring matter no other constituent of the bile except cholesterine could be detected. In both the bile and the blood the presence of bilic acid was sought for by treating them with basic acetate of lead, and boiling the dried precipitate with alcohol. No trace of bilate of lead was dissolved. Pettenkofer's test, with which I was also then acquainted, likewise yielded a negative result.

A very dark green fluid, vomited by a patient, and which the physician suspected to contain verdigris, was examined with the greatest care by Dr. Menges under Scherer's superintendence; it contained a large quantity of free muriatic acid, and the dark green colour was produced by an enormous quantity of colouring matter of the bile, which was partly separated in flocks by the muriatic acid. Notwithstanding this abundant effusion of biliary colouring matter, and consequently of bile, into the stomach, no trace of bilic acid could be detected in the liquid; a proof how quickly this is decomposed when in contact with organic matters, in this case, with the acid gastric juice and pepsine.

The biliary colouring matter was separated from the above-mentioned urine in the following manner:—The fresh urine, after filtration to remove the mucus and uric acid which had separated, was treated with chloride of barium. The green precipitate was then washed with water, thrown on a filter, and the colouring matter separated from it by two different methods.

1. The precipitate was boiled in water with carbonate of soda, and the resulting yellow solution filtered and decomposed by muriatic acid. The colouring matter, which is almost insoluble in the acid liquid, thus separated from the soda, was then placed on a filter, and dissolved in a mixture of 2 parts of alcohol and 1 of æther, to separate it from any lithic acid thrown down with it, and the beautiful dark green solution thus obtained was evaporated. The colouring matter adhered to the sides of the porcelain dish, in the form of a dark green mass, which by slow evaporation was completely dried, and was then readily reducible to a fine powder. This powder was washed with distilled water as long as any muriatic acid could be detected by nitrate of silver. As the colouring matter thrown down from the soda solution by muriatic acid was filtered with difficulty, it was subsequently found best to evaporate the solution decomposed by muriatic acid at a gentle heat, and to separate it by the above mixture of alcohol and æther from the chloride of sodium and precipitated uric acid.

2. Another method, and one much simpler, which I subsequently found out from a more accurate knowledge of the properties of the colouring matter, is this:—The barytes precipitate was at once decomposed by digestion with alcohol and muriatic acid at a gentle heat; the alcoholic solution was evaporated, washed on a filter with water, then dissolved in a mixture of alcohol and æther, and again evaporated.

The colouring matter, obtained by either process and washed with distilled water to remove the muriatic acid, forms a very beautiful dark green powder, almost insoluble in water, readily soluble in alcohol and spirit, but with some difficulty in pure æther. If a little caustic or carbonated alkali be added to the water, it is dissolved in large quantity, and the fluid acquires a colour varying from green to brown; it is also more soluble in water containing alkaline salts than in distilled water. When digested for some time with muriatic acid, the green colour is gradually converted into a blackish brown; this also occurs when it is gently heated for some time with alkalies. In both cases it is rendered less soluble in alcohol, becomes somewhat more soluble in water, and at the same time also loses the property of yielding the characteristic alterations of colour with nitric acid.

Neither does the colouring matter which has been rendered green by muriatic acid exhibit these alterations in colour, but it does so beautifully if subsequently dissolved in an alkaline fluid. To be certain that the colouring matter, after being washed with distilled water to remove the muriatic acid, did not contain any of the acid in chemical combination, 0·192 grm. of it was treated with pure potash, evaporated and heated to redness. The resulting saline mass was dissolved in muriatic acid, and decomposed by nitrate of silver; an inappreciable quantity of chloride of silver was left. I convinced myself of the absence of sulphuric and phosphoric acids in the same way.

0·274 grm., on being heated to redness, left an inappreciable quantity of ash. On combustion with chromate of lead, the colouring matter obtained by the first process yielded in 100 parts—

	I.	II.
Carbon	67·409	67·761
Hydrogen	7·692	7·598
Nitrogen	6·704	6·704
Oxygen	18·195	17·937

To ascertain whether the manner of obtaining this substance in purity has any influence on its composition, that procured by the second process was then subjected to elementary analysis, and gave in 100 parts—

Carbon	68·192
Hydrogen	7·473
Nitrogen	7·074
Oxygen	17·261

In consequence of my not having enough of the substance, I was unable to decide whether the slight difference in the quantity of carbon between the former and the latter was constant, or merely an ordinary analytical difference.

However, to ascertain what alteration this colouring matter underwent by the slow action of the air, acids and alkalies, one portion was treated with excess of muriatic acid, and the other with excess of carbonate of soda and a little caustic potash, and kept for fourteen days in shallow open vessels, at a temperature of 86°–95° Fahr., whereupon it underwent the alteration in colour we have mentioned; it was then re-obtained pure by the first process.

1. Of the portion digested with excess of muriatic acid—

0·275 grm. on combustion with chromate of lead yielded 0·615 carbonic acid and 0·160 water.

0·316 grm. with soda and lime gave 0·452 ammonio-chloride of platinum.

2. Of that which was digested with the carbonate of soda and caustic potash—

0·269 grm. burnt with chromate of lead yielded 0·604 carbonic acid and 0·159 water.

0·354 grm. burnt with soda and lime gave 0·396 ammonio-chloride of platinum;

or in 100 parts—

Carbon	61·837	62·086
Hydrogen	6·464	6·567
Nitrogen	9·080	7·101
Oxygen	22·619	24·246

From these analyses it appears certain that the biliary colouring matter loses a considerable amount of carbonic acid and hydrogen by the continued action of the air.

The results of the analysis of the pure colouring matter of the bile, which I have detailed, differ very considerably from those I formerly obtained with the biliary colouring matter of gall-stones*. The amount of carbon in these was 74 per cent., of hydrogen 6·3, and of nitrogen 14·4. As it appeared to me highly probable that this difference might depend upon the large quantity of inorganic ingredients, and especially on the carbonate of lime and phosphate of magnesia found in the ash of these gall-stones, the first of which probably existed as such in the calculi (which were treated with æther, alcohol and water, and not with muriatic acid, so as to avoid subjecting it to any alteration by acids), the phosphate of magnesia however as ammonio-phosphate of magnesia, I treated a small quantity of this biliary calculus, which I had by me, with muriatic acid as well as alcohol, æther and water; a tolerably copious effervescence occurred from the escape of carbonic acid, and on adding potash, and applying a gentle heat to the filtered fluid, the ammonia arising from the ammonio-phosphate of magnesia was perceived. It was therefore evident that the excess of nitrogen and carbon was derived from the inorganic substances which had been set free on ignition.

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* See Chemische u. Mikrosk. Untersuch. zur Path. v. Prof. Scherer. Heidelb 1843.

For the sake of comparison, the substance, likewise washed with muriatic acid, was submitted to elementary analysis, and the following composition was obtained:—

Carbon	62·491
Hydrogen	6·148
Nitrogen	8·169
Oxygen	23·192
	100·000

whence it is evident that the colouring matter in the black, easily-powdered gall-stones, and which contain but little cholesterine, approaches closely in composition to that which is formed by treating the ordinary colouring matter with acids or alkalies, and exposure to air. Moreover, that in addition to this colouring matter, which we have analysed, and which forms the greater part of the smaller biliary calculi, they contain another, probably richer in carbon and hydrogen, and more closely resembling the normal colouring matter, is evident from the fact, that on boiling them with alcohol and æther, and especially on treating them with muriatic acid, these liquids become coloured, and consequently a portion of the colouring matter is dissolved. The quantity I had was too small to allow of my ascertaining this more accurately.—*Ann. der Chem. und Pharm.*, March 1845.

Observations on the preceding Article. By J. W. Griffith, *M.D.*

It is satisfactory to find my experiments[*] relative to the presence of the colouring matter of the bile alone in urine confirmed by so able a chemist as Dr. Scherer. Still I think we ought not to be hasty in denying that the organic matter of bile is ever present, particularly as it is stated to have been found by Simon[†] and Lehmann[‡]. Simon ascertained that it was only occasionally present; and we can readily imagine that, in cases where in addition to the jaundice there is some obstruction to the pulmonary function, it might remain in the blood and even the urine. Simon relied principally upon the bitter taste of the biline (bilic acid) for the detection of its presence in the urine. He also recommended the following process for estimating the biline quantitatively, and some of his analyses actually indicate the quantity. His process was this:—Evaporate the urine, separate the salts insoluble in alcohol and the aqueous extract by spirit (0·85), evaporate the spirituous solution and exhaust the residue with anhydrous alcohol, evaporate the alcoholic solution, dissolve the residue in a small quantity of water, and digest it with muriatic acid until the biliary resin has separated; then dry and weigh it[§].

Perhaps the simplest method of detecting the bilic acid in urine or

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[*] Chem. Gaz., March 1, 1845.

[†] Anthropochemie, theil 2, s. 388.

[‡] Physiologische Chemie, p. 310. Lehmann detected bilifellinic acid in the urine of two patients with jaundice, although he found none in their blood.

[§] *Op. cit.* Chem. Gaz., March 1, 1845.

serum of blood would be to add diacetate of lead, pour off the supernatant liquid, digest the precipitate with dilute sulphuric acid (1 to 6), allow the sulphate of lead, &c. to subside, pour off the fluid portion and apply Pettenkofer's test to it; the small quantity of lead present does not interfere with the action of the test; the precipitate with the diacetate of lead however is so peculiar, that it could hardly be mistaken. I may remark that the blood of the icteric patient whose urine I examined* contained no trace of bilic acid.

Analysis of a Belugen† *Calculus. By* F. Wöhler.

This name was applied by Klaproth to concretions found in one of the cavities existing on each side of the cloaca of the *Acipenser Huso*, inhabiting the Caspian Sea. They frequently occur as large or larger than an egg; their form is sometimes that of an egg, sometimes more flattened; they are of a bone-white colour, and are remarkable for their crystalline, concentrically-radiating fibres. Klaproth found them composed of phosphate of lime, 71·5; water and albumen, 26·0; sulphate of lime, 0·5. Their microscopic structure was perfectly homogeneous. By heat they became opake; on continuing the heat to redness, they were blackened, evolving empyreumatic matters. They were fusible before the blowpipe, whereby their calcareous salt is distinguished from the ordinary bone-earth, which is infusible. They readily dissolved in muriatic acid without effervescence, leaving an organic mass of the form and size of the piece acted upon. When dried, this amounted to 0·74 per cent. If the solution be precipitated with ammonia, phosphate of ammonia remains in solution; another remarkable difference between this substance and bone-earth, showing that it contains phosphoric acid in larger proportion; neither alkali nor magnesia were present, and it contained but a trace of sulphate of lime. On ignition these concretions lost 27·0 per cent.; when heated to 392° Fahr. they lost 20 per cent. of water. As their per-centage of organic matter amounted to only 0·74, it is evident that a portion of the water is retained even up to 392° Fahr. The lime was separated by dissolving the concretion in a mixture of concentrated muriatic acid and alcohol, and precipitation with sulphuric acid. The phosphoric acid was estimated by the loss. In this way these concretions were found to consist of phosphate of lime, containing 2 atoms of lime to 1 of phosphoric acid, $2CaO, P^2O^5$, and 5 atoms of water, four-fifths of which are driven off at 392° Fahr. As 1 atom of the water escapes at a red heat, we might imagine that it is basic, and that the salt contains the tribasic phosphoric acid, and is $= 2CaO, HO, P^2O^5 + 4HO$. As is known, bone-earth is $8CaO, 3P^2O^5$, or rather $2CaO, P^2O^5 + 2CaO, 2P^2O^5$.

This concretion contained in 100 parts—

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[*] *Loc. cit.*

[†] The German name for the sturgeon inhabiting the Caspian, *A. Huso.*—Ed.

	Found.	Calculated according to $2CaO, P^2O^5 + 5HO$.
Phosphoric acid	41·34	41·57
Lime	31·66	32·48
Water....................	26·26	25·95
Organic matter	0·74	

Wöhler suggests that it would be interesting to examine the calcareous salts existing in the bones of this fish, as they probably have an analogous composition.—Müller's *Archiv*, 1844, part v.

On the Action of Sulphurous Acid upon Zinc and Iron.
By Dr. Koene.

Zinc.—When pure sulphurous acid is passed into water containing granules or strips of zinc, the water becomes yellow; but when the solution is kept for some length of time in closed vessels, it gradually becomes entirely decolorized. It is however not possible to deprive it wholly of free sulphurous acid by continued contact with zinc, for when boiled it always disengages sulphurous acid. At the same time a white salt is deposited on the zinc, which may be removed by washing, and dissolves in dilute sulphuric acid, with evolution of sulphurous acid, but without any deposit of sulphur. The zinc from which the salt has been removed contains some sulphuret of zinc, since on treating it with dilute sulphuric acid it always disengages sulphuretted hydrogen.

The same takes place when an aqueous solution of sulphurous acid is allowed to act directly upon zinc. In general a little hydrogen is disengaged, but only very minute traces of it if the zinc was *pure.* The temperature has no influence on the result any more than the degree of concentration of the sulphurous acid.

The author met with several difficulties in the analyses of the products; most of the oxidizing agents give false results, because they expel a portion of the sulphurous acid during the oxidation, and consequently the proportion of the zinc to the sulphurous acid appears too high. This is the case with chlorine and nitro-muriatic acid, which generate muriatic acid in the operation; with nitre and chlorate of potash, which only oxidize perfectly when fused; but before this happens a portion of the sulphurous acid is driven off. Fuming nitric acid answers best; this yielded, with pure hyposulphite of zinc, the proportion $Zn : S = 13{\cdot}35 : 0{\cdot}865$, or in equivalents 0·28 : 0·43, which at least approximates to 1 : 2. It is evident however that there is still a loss. A second difficulty in the examination of the products is occasioned by its not being possible to remove the free sulphurous acid without some decomposition. If the operation be interrupted in the middle, in order to prevent the deposit of white salt, and the liquid be then evaporated to dryness, the Zn is to S as 61·6 is to 38·4, or in equivalents as 4 : 5, if the evaporation had been effected *in vacuo*, or in an atmosphere free from oxygen; but if it be carried on exposed to the atmosphere, the proportion is as 66 : 34 or 27 : 28. If the first numbers be assumed to be correct, they correspond to the formula $ZnO\,S^2O^2 + 3ZnO\,SO^2$;

but if this originates from 4Zn and $5SO^2$, 2O remain, which can only have been obtained from reduced sulphurous acid, and in fact some sulphur occurs in the form of sulphuret of zinc.

In another experiment some zinc foil was shaken in a small flask with sulphurous acid, and after 24 hours the small quantity of the white powder separated; it was dried, the quantity of sulphur in it determined, and the liquid evaporated and oxidized. The following proportion was now obtained:—$Zn : S = 57{\cdot}5 : 42{\cdot}5$, or as 2 to 3. The mixture of salt formed contains therefore, as stated by Berzelius, $ZnO, SO^2 + ZnO, S^2 O^2$.

Berzelius regards the formation of sulphuret of zinc as accidental, and owing to the violence of the reaction; it occurs however under *all* circumstances. The correct view of the reaction appears therefore to be that at first 6Zn and $9SO^2$ give rise to $4ZnO, SO^2$ and 2ZnS, while $3SO^2$ remain free. Upon this the sulphuret of zinc acts upon the free sulphurous acid, and from 2ZnS and $3SO^2$ there is formed $2ZnO, S^2 O^2$, while S is set at liberty, which however in its nascent state combines with 1 of the 4 atoms of sulphite of zinc, forming hyposulphite, so that there finally results equal atoms of sulphite and hyposulphite. It may very readily be shown, that however little sulphur acts in the moist way upon sulphites, still in its nascent state it is capable of transforming them into hyposulphites. In the present instance therefore, owing to the greater affinity of bases for hyposulphurous acid, this latter is formed from the sulphurous acid with the cooperation of the sulphuret of zinc. In fact, hyposulphurous acid is never formed directly by the oxidation of sulphur or of a metallic sulphuret. If oxygen be allowed to act on an alkaline protosulphuret, perfectly free from hydrosulphate or any higher sulphuret, there is formed first a sulphite, then a sulphate; only in the presence of sulphuretted hydrogen, or some higher sulphuret, is a hyposulphite formed from the previously-generated sulphite. Crystallized sulphuret of barium yields, when washed, only sulphate of barytes, but when not washed, hyposulphite. The latter arises from the presence of some hydrosulphuret of barium.

These observations lead the author to the view that hyposulphurous acid is by no means a peculiar oxide of sulphur, but sulphuric acid in which the third equivalent of oxygen is replaced by sulphur $= SO^2 S$, *oxy-sulpho-sulphuric acid.* In his opinion trithionic acid is only a compound acid, consisting of sulphuric and oxysulpho-sulphuric acids, analogous to the combinations of the acids of antimony with one another, and of sulphuric acid with the oxychloro-sulphuric acid, &c. It will be interesting to ascertain whether trithionates might be formed directly from sulphates and hyposulphites; the results obtained by the author were doubtful. The monosulphuret of iron or sulphuret of zinc in contact with aqueous sulphurous acid yield, with separation of sulphur, a crystalline salt, with all the characters of a trithionate. If metallic plates of iron, which are slightly coated with sulphuret of iron, are immersed in sulphurous acid, sulphur is likewise separated, but only hyposulphite of the protoxide of iron is formed.

Iron.—When iron acts on a solution of sulphurous acid, phænomena similar to those which are observed in the action of zinc are manifested. The liquid becomes warm, acquires at first a brown and then a greenish-yellow colour, and finally becomes emerald-green. A large excess of sulphurous acid gives rise, after some weeks, to a precipitate of sulphur; an excess of metal causes a deposit of sulphite. When boiled in a retort, the solution evolves a considerable quantity of sulphurous acid, depositing at the same time sulphite in the form of a crystalline grayish-white powder. During the cooling of the solution, the white powder absorbs oxygen, acquires a more or less dark colour, and is converted first into persulphite, and finally into basic persulphate of iron; if it be digested with a solution of sulphurous acid, both the ochreous deposit, as well as the unaltered sulphite, dissolve, and the yellow colour disappears. In the reciprocal action of the iron and the acid there is always formed on the surface of the former a sulphuret, which entirely disappears as soon as it is formed. The constant formation of this sulphuret, the slight solubility of the protosulphite of iron in water which does not contain a great excess of sulphurous acid, requires the same precautions in determining the positive elements of the reaction as in the case of zinc.

The analysis yielded $Fe : S = 53 : 47$, or in equivalents 2 to 3; the reaction consequently is precisely similar to that with zinc.

Oxysulpho-sulphate (hyposulphite) of Zinc.—To prepare this salt, a flask was filled with a solution of sulphurous acid saturated at 32°, some slips of zinc inserted, and then hermetically closed. After some days the liquid is evaporated over sulphuric acid *in vacuo.* The saline residue is exhausted with alcohol of 0·833 sp. gr., the alcoholic solution poured off, precipitated with aqueous æther, and the oily substance situated at the bottom separated by a funnel. This substance is heated to 104° until it no longer diffuses any odour, and finally dried *in vacuo.*

The salt forms a gummy mass of a pale yellow colour. It is soluble in every proportion in water, very soluble in alcohol, but sparingly so in æther. On exposure to the atmosphere, it first deliquesces, then becomes oxidized, deposits sulphur, and changes into sulphate. Its aqueous solution does not undergo any change, except beyond a temperature of 212°; but when the salt is dry it is decomposed at a lower temperature, forming sulphur and sulphite.

If an alcoholic solution of oxysulpho-sulphate of zinc be left for a time, it deposits sulphuret of zinc; the æthereal solution induces at the same time the formation of sulphur. An aqueous solution of this salt even deposits sulphuret of zinc when placed for some weeks in contact with zinc.

The salt, as precipitated by æther from its alcoholic solution, yielded on analysis—

Zinc	50·30	49·45	1
Sulphur..............	49·70	50·55	2

which leads to the formula $ZnO\,SO^2\,S$.

Sulphite of Zinc is deposited either when the acid solution resulting from the action of zinc upon sulphurous acid is boiled in a retort until a third of the liquid is distilled over; when the metal is left for some days in contact with a saturated aqueous solution of sulphurous acid; when the mixture of salt obtained from the reaction of the zinc is exhausted with alcohol; or, lastly, when a solution of oxide of zinc in sulphurous acid is evaporated spontaneously or concentrated in a retort.

It should be observed, that with the first process the operation must be discontinued before a third of the liquid is distilled over, for at this stage the liquid, owing to its degree of concentration, attains such a temperature that the oxy-sulpho-sulphate of zinc deposits sulphur, and is converted into sulphite of zinc, which is itself decomposed at a somewhat higher temperature.

The sulphite of zinc, which is deposited from an acid boiling solution, forms a pure white heavy crystalline powder, while that which separates from the acid solution on spontaneous evaporation forms transparent plates. It is sparingly soluble in water, but very soluble in an aqueous solution of sulphurous acid; with the assistance of this acid, it likewise dissolves in alcohol. The oxy-sulpho-sulphate of zinc dissolves so much of it, when the products from the reaction of the zinc are evaporated *in vacuo* to the consistence of syrup, that the whole solidifies on the addition of absolute alcohol. The salt does not change perceptibly in dry air, but in moist it passes slowly into sulphate. Heated in a glass tube, it is decomposed somewhat above 392° with tumescence, disengaging sulphurous acid, and leaving behind oxide of zinc. Analysis gave—

Oxide of zinc	45·45	45·00	1
Sulphurous acid	36·20	36·06	1
Water	18·35	18·94	2

The great solubility of the sulphite of zinc in sulphurous acid might induce the belief that a salt existed with more than 1 equiv. of acid. In order to leave no doubt on this point, the author analysed some moist sulphite which had formed in an acid solution by spontaneous evaporation. After pressure between bibulous paper, the author found this salt to have the same composition as the above.

[To be continued.]

CHEMICAL PREPARATIONS.

On the Preparation of pure Phosphoric Acid.

By Dr. Gregory.

Dr. Gregory states that he has not found the alcohol process for separation of the phosphate of magnesia, in the preparation of phosphoric acid (described in his recent work, p. 110), to answer. He recommends the following as preferable:—

Having removed the lime by means of sulphuric acid, and evaporated the filtered liquid (filtering again if any sulphate of lime separates during the evaporation) to the consistence of syrup, a few drops of sulphuric acid are added, to make sure that no lime remains. Of course, if turbidity ensues, the lime has not been completely separated before; and the addition of sulphuric acid, filtration after adding some water, and evaporation, must be repeated till the syrupy liquid continues quite clear when sulphuric acid is added. This liquid now contains only the phosphoric acid, the magnesia, and the excess of sulphuric acid. It is concentrated, and heated in a covered platinum crucible until the whole of the sulphuric acid has been expelled, and the residue has acquired a low red heat. On cooling, it forms a glass, perfectly colourless and transparent, which contains only phosphoric acid and the magnesia of the bones. This glass when boiled with water dissolves rather slowly, but completely. When the solution is again concentrated in a capsule of platinum until most of the water is expelled, and the temperature rises to between 595° and 600° Fahr., it suddenly, while hot, becomes turbid, from the separation of a peculiar phosphate of magnesia. At the same moment the phosphoric acid begins to crystallize like the granular sugar deposited in honey, a form ascribed by Peligot to the bibasic or pyrophosphoric acid. If the same temperature be kept up for 15 minutes, the whole of the magnesia separates in the form of a powder, which is quite insoluble in acids or water; when cold, the mass is digested with water, which dissolves the phosphoric acid, leaving the phosphate of magnesia as a heavy, fine, snow-white powder, of a faint silky lustre. *The filtered liquid is free from every trace of magnesia,* and may be considered as pure phosphoric acid. If the bones contain chloride of sodium, a trace of phosphate of soda will remain. In that case the burnt and powdered bones ought to be boiled with water, to remove any soluble chloride. Dr. Gregory recommends this process as a simple one for obtaining pure phosphoric acid. It is necessary to keep up the heat of about 600° for 12–15 minutes, but not to go beyond that temperature, because a stronger heat would again, no doubt, produce the glass formed in the first fusion, which as we have seen is entirely soluble in water. The acid is easily tested for magnesia by diluting and supersaturating with ammonia; when, if magnesia be present, it very soon appears as ammoniaco-magnesian phosphate. The phosphate of magnesia thus separated is a peculiar and anomalous salt. From six analyses Dr. Gregory induces the formula $2MgO + 3P^2O^5$, that is, an acid sesquiphosphate of magnesia, according to the older notions of phosphoric acid. This composition cannot be reconciled with any of the three generally admitted modifications of phosphoric acid; and it would seem to indicate, either that another modification exists, or that the theory of phosphoric acid and the phosphates at present admitted is erroneous. Dr. Gregory is engaged in the examination of this point. The insolubility of the phosphate is very great, and presents a great obstacle; for boiling nitric acid, aqua regia, are almost entirely without action upon it; and it is, he believes, the only salt of magnesia insoluble in acids.—*Medical Gazette.*

On the Preparation of Strychnic Acid. *By* M. Rousseau.

Strychnic acid is best prepared by forming 3 parts of strychnine with 1 part chlorate of potash and some water into a thick paste, and warming this with the addition of a few drops of sulphuric acid, after which from 8 to 10 times the weight of distilled water is added, and the whole boiled for a few minutes. On cooling, frequently some sulphate of strychnine or pure strychnine is deposited; they are separated by filtration and the filtered solution evaporated to crystallization. The acid may be then purified by washing with alcohol. It is of a pure white colour, readily soluble in water, but with difficulty in alcohol, has a strong acid reaction, and decomposes carbonates; it dissolves the oxides of copper, zinc and iron, and yields crystalline salts; it crystallizes in fine needles of a pure acid taste, is not volatile, but is decomposed by heat. The potash salt is white, soluble in water, insoluble in alcohol, crystallizes in four-sided prisms, and has a cooling taste. The persalt of iron is brick-red, of very acrid taste, and extremely deliquescent. The persalt of copper crystallizes in green rhombic prisms, has a styptic taste, and is soluble in water but insoluble in alcohol.—*Journ. de Chim. Méd.*, 1844, p. 415.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

An Account of the Manufacture of Glass in Bohemia.

By L. P. Debette.

[Continued from p. 204.]

Chapter III.—*Of the Glass Works of Bohemia generally.*

On the Situation and Composition of the Glass Works.—The principal thing to be considered in the location of glass works being the facility of procuring fuel, they seek as much as possible to establish them in the midst of forests, and upon the banks of a water-course which will allow the floating of the wood to them, and upon which may be also established, at no great distance, the stamping machines, and the mills for cutting the glass (*Schleifenmühle*), which are almost always driven by a water-wheel. The power of the stream of water is increased when necessary by putting it into communication, by means of sluice-gates, with the small pools which are met with in such quantity among the mountains. As the forests can be cut only about once in a century, it is often advantageous, after having cut off all the wood in the neighbourhood of an establishment, to transfer it for a certain time to another place, where a supply can be more easily found, until this in its turn also becomes exhausted. This instability in the location of the greater part of the works has, from motives of œconomy, led them to construct the buildings which enclose the furnaces entirely of wood; so that, at first sight, nothing is more miserable than the appearance of these works, which seem lost in the midst of endless forests, and which show themselves from afar off by the clouds of smoke which rise above the trees. It is only those works which are certain of what may be called an indefinite supply, such as those of MM. Meyer, situated on the banks of the Moldau, which are in part constructed of stone.

The glass works of Bohemia are generally composed of two melting-furnaces (*Schmelzöfen*, or *Glasöfen*), one of which is in action while the other is undergoing repair, so that one is always in activity.

When the establishment makes window-glass, it has besides one or two furnaces to flatten the glass (*Streckōfen*, flattening kilns), which are placed under a separate shed attached to the works.

The store-house for the raw materials is also attached to the works. The stamping machine and the furnaces for calcining the quartz and the lime are also attached to the works whenever the stream is of sufficient power to allow it, but generally they are separate and placed at some distance, either above or below. The same arrangement is made of the shops in which the table-glass and Bohemian crystal is cut, to which is also annexed the store-house for the finished glass.

Melting Furnaces.—As the beauty and quality of the glass, other things being equal, depends particularly upon their perfect fusion, which takes place only at a very elevated temperature, not to be obtained except by a particular arrangement of the melting-furnace (*Schmelzöfen*), this becomes the most important part of the establishment. This furnace should be so constructed that,—1st, a suitable and sufficiently elevated temperature may be produced; 2nd, the flame may circulate freely around the glass pots; 3rd, the greatest useful effect may be obtained with the smallest quantity of fuel.

These conditions have led to the adoption of peculiar furnaces of an elliptical form, furnished with shelves, on which the glass pots are placed. These furnaces are all nearly of the same form; but their dimensions are somewhat variable with the number and size of the pots; they hold 7 or 8. The fire-bricks which are used in the construction of these furnaces are formed of 2 parts by volume of fire-clay mixed with 1 part of the fragments of glass pots, picked and powdered. The vault is always made of a single piece of clay.

Annealing Furnaces.—These furnaces are always accompanied by a *Kühlofen*, or furnace for annealing the glass, heated by means of the flame which escapes from the melting-furnace. The annealing furnace is almost always surmounted by an apparatus for drying the wood, which is composed of four cubic boxes of cast iron, 2·89 feet on each side, exposed on five of their sides to the flames which come from the annealing furnace by four apertures, and afterwards escape from the apertures by a single opening in the upper part.

The operation is conducted far too rapidly, for a complete drying, and even an incipient roasting of the wood is obtained in the course of 1½, or at the most 2 hours; and it would be evidently very advantageous to slacken it by furnishing the openings which communicate with the annealing furnace with moveable registers.

The length of the season is, upon an average, 28 weeks, or 6 months.

Glass Pots.—The glass pots (*Hafen*) used in Bavaria are circular, and made with the greatest care; they are of two dimensions, and have no rims.

The smallest receive a charge of from 140 to 165 lbs. of fritted materials, and are used in the manufacture of fine glass and table glass. Their dimensions are as follows:—

Internal diameter	above	1·28	foot.
	below	1·11	...
External diameter	above	1·47	...
	below	1·38	...
Depth		1·44	...
Thickness at bottom		1·57	inch.

The large pots receive a charge of about 220 lbs. avoirdupois, and are used in making window and bottle glass. Their dimensions are as follows:—

Internal diameter	at the mouth	1·41	foot.
	at bottom	1·25	..
External diameter	at the mouth	1·67	...
	at bottom	1·57	...
Depth		1·7	...
Thickness at bottom		1·87	inch.

The paste of which these pots are made is composed of a mixture of very aluminous fire-clay, of which I have given the analysis above, and of very pure quartz pulverized in a dry state; sometimes they employ as a cement the remains of old glass pots, broken up and picked, and then pulverized. After kneading the paste with the feet, in order to make the mixture as thorough as possible, the pots are formed by means of a small wooden beater, and a mould also of wood, which allows the workmen to give them accurately the same exterior dimensions. These crucibles last very differently; at Schwartzthal they last upon an average six weeks; at Silberberg, Winterberg, Leonorenhain, about twelve or sixteen weeks, and sometimes more. These crucibles, after having been sufficiently dried in the air, are baked in the annealing furnaces, or very rarely in a separate furnace. When a change is necessary, they introduce them during the working season by one of the embrasures, which is made of sufficient size for this purpose, and larger than the others. Of course, the new crucibles are brought up to a white heat before being placed upon the furnace-shelf.

The analysis of a selected fragment of the glass pots used at Silberberg gave me—

Silica	61·0	Oxygen, 31·7	Ratio, 3
Alumina	39·0	... 10·8	... 1
Oxide of iron,	a trace.		
	100·0		

Very white particles, which appeared to be small grains of quartz, could be seen with the naked eye in the paste.

Another Bohemian glass pot, whose locality is unknown, gave M. Berthier upon analysis—

Silica..........	68·0	Oxygen, 35·4		Ratio, 4
Alumina	29·0	... 8·1	9	1
Oxide of iron ..	2·2	... 0·6		
Magnesia	0·5	... 0·3		
	99·7			

By use the substance had become excessively hard, of a light gray, and was filled with an infinity of small globular cavities, which indicated a commencement of fusion, and presented besides a multitude of small very white grains, which showed themselves very plainly upon the gray ground of the mass.

Flattening Kilns.—These kilns are either isolated or placed together two by two; I have been informed that there are some placed together in fours. They are always composed of a flattening kiln (*Streckofen*), into which the flame comes from the fireplace by four small chimneys, placed at the end of the bottom of the kiln, and which communicate with an annealing furnace, into which the flame passes from the fireplace by a single opening only.

Of the Persons employed.—The persons employed in glass works consist—

1. Of a director (*Buchhalter*), who superintends the works, keeps the books, receives orders, forwards the goods, pays the workmen, &c.
2. Of the workmen employed in transporting and preparing the raw material.
3. Of women who are employed to pack the finished goods.
4. Of workmen employed in transporting the goods.
5. Of workmen employed in the making and cutting of the glass. Among these are the firemen, the glass-blowers and glass-cutters.

The regulation of the fire requires two firemen for each furnace, who relieve each other in turn, so that there is always one at the furnace. They receive each 4*s.* 3½*d.* per week, or about 8*d.* per day.

Each glass pot is tended by one blower, aided by his apprentice, who brings the moulds, removes the finished pieces, &c. The pay of the blowers, as well as that of the cutters, is 4¾*d.* per shock of glass worked. The number of pieces which form a shock varies according to their nature, and the rate is so arranged that a good workman may easily gain 4*s.* 2*d.* in 12 or 15 hours' work.

Besides this, in the establishments in which the above tariff is established, they are in the habit of giving to each workman, so long as he is engaged in the works, a wooden cottage to live in, and a kitchen garden of sufficient size for his use, and of permitting him to keep a cow, without being subject for these to any extra labour or manorial dues; so that it is extremely difficult to fix in a precise manner the real pay of the workmen, and of course the cost of the glass.

Of the Expense for Fuel.—I shall here give the annual consumption of fuel in each establishment, supposing it to consist, as is usually the case, of two melting-furnaces, the working and repair of which succeed each other, so that there is always one in action.

In the glass works of the Count of Buquoi, where they use dry wood not roasted, they consume annually 1255 cords of wood (160,706 cubic feet) when they are making table-glass or fine glass, as at Silberberg, and 1507 cords (192,847 cubic feet) in making window-glass, as at Schwarzthal; the increase arising from the fact that the glass pots there are rather larger, and the time of working being smaller, a greater number of meltings are made per week.

In the establishments of MM. Meyer at Winterberg and Leonorenhain, where the wood is slightly roasted before employing it to heat the glass furnaces, they consume annually 1130 cords (144,812 cubic feet) in making table-glass and fine glass, which gives an œconomy of one-tenth over the consumption at Silberberg. This great œconomy of fuel is evidently due to the fact, that a certain quantity of heat is necessary to drive out the hygrometric moisture of the wood, and to vaporize it entirely, and that in Silberberg this heat is taken from that developed in the melting-furnace, while in the works of MM. Meyer, as in those which we shall hereafter mention, it is taken from the flames which escape from that furnace. At Goldbrün, Stachau and Vogelfanghütte there is consumed 40·2 cubic feet per day, or 1143 cords (146,578 cubic feet) per year, a result which accords in a remarkable manner with that obtained from the works of Winterberg and Leonorenhain.

[To be continued.]

On a Method of purifying Arseniferous Sulphuric Acid during its Manufacture. By M. ALPH. DUPASQUIER.

Arsenical sulphuric acid is prepared in several large manufactories in France and England by the calcination of pyrites (sulphurets of copper and of iron more or less mixed with sulphuret of arsenic and arseniuret of iron).

From the experiments and observations contained in this memoir it results—

1. That the use of arseniferous sulphuric acid in the arts, and in the production of chemical and pharmaceutical preparations, may lead to serious disadvantages and danger.

2. That arsenic in the sulphuric acids of commerce is in the state of *arsenic acid.*

3. That the proportion of this poison in the acid varies, but that it may be estimated at about 1- or 1½-thousandth.

4. That the employment of hydrochloric acid or sulphuretted hydrogen is insufficient for the purification of arseniferous sulphuric acids.

5. That the use of alkaline sulphurets offers a complete and ready method for the purification of the arseniferous acids.

6. That the sulphuret of barium, both as regards œconomy and the purity of the sulphuric acid, is by far preferable to the other

alkaline sulphurets, and it is moreover cheap and very easy to put in practice during the preparation of sulphuric acids in the manufactories*.—*Comptes Rendus,* March 17, 1845, p. 794.

Detection of the fraudulent Admixture of Spirits with Wine.

An anonymous correspondent of the 'Journal de Chimie Médicale' recommends, as a sure method, heating the wine in an open dish, holding close over the surface of the liquid a small oil lamp with several burning wicks. If spirit has been added to the wine, it inflames even at a moderate heat; but if it contain only its natural spirit, it does not take fire before the wine boils.

PATENT.

Patent granted to William Birkmyre, Millbrook, Cornwall, *for Improvements in the Manufacture of Potash and Soda Alums, Sulphuric Acid and Sulphate of Soda.*

These improvements consist,—1st, in the application of a substance to prolong the disengagement of the oxides of nitrogen from the nitre-pot, in sulphur furnaces or pyrites kilns (employed in the manufacture of sulphuric acid), and which substance will also serve to produce potash or soda-alum; 2nd, in decomposing substances containing potash and alumina, or soda and alumina, by the action of heat and sulphuric acid, or of heat, sulphuric acid and a salt of potash or soda, for the purpose of forming a salt of alumina, in vessels contained within sulphur furnaces or pyrites kilns, and condensing the volatilized sulphuric acid in vitriol chambers; 3rd, in producing sulphate of soda by decomposing a solution of soda-alum by a salt of potash into potash-alum and sulphate of soda.

The patentee proposes to use clay, particularly porcelain or Cornish clay, to prevent the too rapid disengagement of the oxides of nitrogen from the nitrate of potash or soda in the nitre-pot, and to produce at the same time either potash-sulphate of alumina (potash-alum) by the decomposition of nitrate of potash, or soda-sulphate of alumina (soda-alum) by the decomposition of nitrate of soda. The mode of carrying out the invention is as follows:—1600 lbs. of dry Cornish clay in powder are to be mixed with 1 ton of powdered crystals of nitrate of potash; then, for a vitriol chamber, making 1½ ton of sulphuric acid, spec. grav. 1·848, *per diem,* take every 2 hours 18 lbs. of this mixture, and put it into a nitre-pot, and after stirring in 14 lbs. of sulphuric acid, spec. grav. 1·750, place the pot a few inches above the burning sulphur of a pyrites kiln. By the action of the heat and sulphuric acid the oxides of nitrogen begin gradually to escape into the chamber; and the mixture, which becomes converted into a species of burnt alum, should be withdrawn

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* By the employment of this method, not only is the arsenic entirely eliminated, but the nitric acid is also necessarily destroyed, an acid which occurs in most of the sulphuric acids of commerce.

from the kiln at the end of 4 hours. The product in the nitre-pot will generally weigh 22 lbs., and yield, on lixiviating with 10 per cent. of sulphuric acid, as much potash-alum as will be equal to 2½ times the weight of the nitrate of potash employed, or fully half the quantity that can be extracted.

The above process admits of variety in its application; for instance, if 10½ lbs. of nitrate of potash were used with 15 lbs. of Cornish clay and 20¼ lbs. of sulphuric acid, spec. grav. 1·750, the whole of the potash might be converted into potash-alum; but the patentee prefers resorting to the following operation, to convert the whole of the potash into potash-alum:—Put 25 lbs. of powdered Cornish clay into a large nitre-pot, and then stir in 37 lbs. of sulphuric acid, spec. grav. 1·750; place the pot above the burning sulphur of a pyrites kiln, and at the end of 4 hours withdraw it; or instead of 37 lbs. of sulphuric acid, spec. grav. 1·750, 60 lbs. of sulphuric acid, spec. grav. 1·400, may be used. The product resulting from the weaker acid is nearly the same as that from the stronger acid, with the advantage of rendering the use of steam in the chamber unnecessary; the greater part of the acid, in both cases, combines with the alumina and potash or soda of the clay, forming chiefly a sesquisulphate of alumina. Of the substance thus prepared, 168 lbs. are to be mixed with 336 lbs of the product from the nitrate of potash and clay, and the mixture lixiviated with 67 lbs. of sulphuric acid, spec. grav. 1·400, in a leaden vessel, placed over the flue of the reverberatory furnace used for making alkali. In 6 or 8 hours the lixiviation will be complete, and the solution should then be run off, at 36° Twaddle, into a leaden settling cistern, placed in a hot chamber, in order to deposit the silica of the clay and prevent the crystallization of the alum. After settling, the clear liquor may be pumped into the ordinary boilers for concentration.

Soda-alum and sulphate of soda are manufactured by the patentee in the following manner:—1 ton of nitrate of soda is to be mixed with 2000 lbs. of powdered Cornish clay; then, for a vitriol chamber making 1½ ton of sulphuric acid, spec. grav. 1·848, *per diem*, take every 2 hours 17 lbs. of this mixture, and put it into a nitre-pot, stirring therewith 20 lbs. of sulphuric acid, spec. grav. 1·750; then place the pot above the burning sulphur of a pyrites kiln, and at the end of 4 hours withdraw it therefrom. 500 lbs. of this product are to be lixiviated with 67 lbs. of sulphuric acid, spec. grav. 1·400, in a leaden vessel, and at the expiration of 6 or 8 hours the solution is to be conveyed into a settling cistern placed in the open air. The clear liquor from the settling cistern may be concentrated for soda-alum; or it may be decomposed by 250 lbs. of acid sulphate of potash into potash-alum and acid sulphate of soda. The latter should be transferred to a reverberatory furnace, and there converted into sulphate of soda by the addition of 75 lbs. of common salt for every 300 imperial gallons of the solution of acid sulphate of soda at 30° Twaddle.

Instead of Cornish clay, other clays, or albite, or felspar, may be used.—Sealed Sept. 19, 1844.

THE CHEMICAL GAZETTE.

No. LXIII.—May 31, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Sulphurous Acid upon Zinc and Iron.

By Dr. Koene.

[Continued from p. 216.]

Oxy-sulpho-sulphate of the Protoxide of Iron.—On evaporating the solution resulting from the reciprocal action of iron and sulphurous acid *in vacuo*, and treating the saline mass with alcohol of 0·833 spec. grav., the oxy-sulpho-sulphate of the protoxide of iron becomes, on its solution, immediately oxidized by the oxygen of the surrounding atmosphere and that dissolved in the alcohol. If the alcoholic solution be allowed to stand for a couple of days over some iron wire, an ochreous precipitate is formed, and the solution acquires a faint greenish colour. On evaporation *in vacuo* over concentrated sulphuric acid, the salt is obtained in the form of a crystalline mass of a greenish-blue colour. It is very soluble in water and alcohol; neither the aqueous nor the alcoholic solution alters, but if some iron wire be immersed in the latter, sulphuret of iron is deposited in the course of time. When exposed to the influence of sulphurous acid, it deposits in the course of three to four weeks a considerable amount of sulphur, which is not the case with the zinc salt.

On exposure to the air, the oxy-sulpho-sulphate of the protoxide of iron at first absorbs a considerable amount of water; it then becomes oxidized, and finally converted into an amorphous ochreous mass. This salt contains, according to analysis—

Protoxide of iron	18·0	1
Oxy-sulpho-sulphuric acid	25·2	1
Water	23·7	1

Sulphite of the protoxide of iron is deposited when the solution resulting from the action of iron and sulphurous acid is boiled down in a retort, or allowed to stand for some weeks with plates of iron immersed in it, or lastly, when evaporated *in vacuo* to the consistence of a thin syrup. In these three cases the salt separates in the form of a crystalline white powder, with a slight grayish tint. It has so great an affinity for oxygen, that on discontinuing the action of the boiling liquid in which it is dissolved only for two or three seconds, the oxygen entering into the retort colours its moistened sides yellow. The boiling water, with which the salt must be washed to free it from adherent oxy-sulpho-sulphate, cannot prevent oxidation, even when protected from the access of air previous to the edulcoration. It absorbs appreciable quantities of oxygen even while bringing it under the receiver of the air-pump.

The salt is sparingly soluble in water, insoluble in alcohol, but soluble in both in the presence of sulphurous acid. It reddens moist litmus-paper. Heated exposed to the air, it first parts with water, and falls to an extremely fine powder, part of which is carried away by the sulphurous acid gas, which is disengaged at about 482°. After decomposition there remains peroxide of iron mixed with a variable quantity of protoxide. It consists of—

Protoxide of iron	39·73	38·34	2
Sulphurous acid	35·69	35·20	2
Water	25·58	26·46	5

Tersulphite of the Peroxide of Iron.—When hydrated peroxide of iron is suspended in water, and sulphurous acid gas passed into it as long as any is absorbed, a portion of the oxide is dissolved, and imparts to the water a red colour, which disappears the next day to give place to a greenish-yellow one. The residuous peroxide has a lively red colour, and strongly reddens litmus-paper, even after the free acid has been removed by washing with water. Under the influence of sulphuric acid it disengages a faint odour of sulphurous acid, blues the ferrocyanide of potassium, but does not produce any particular colour with the ferridcyanide of potassium, and does not yield with the chloride of barium any precipitate insoluble in muriatic acid.

This substance is not a combination in definite proportions; it constantly parts with acid by washing. The wash-waters always present a darkish brown colour, arising from the presence of a sesquisulphite of iron, which is sparingly soluble in water, but is decomposed by it into a still less soluble tersulphite of iron and sulphurous acid. A certain quantity of the sesquisulphite of the protoxide of iron is dissolved by means of the liberated acid without decomposition. Gradually the liquid becomes colourless, sulphate and sulphite of the protoxide of iron being formed. If the wash-water be heated before decolorization has taken place, vapours are given off which redden litmus-paper; at the same time the brown colour disappears, sulphate and sulphite of the protoxide of iron being formed, together with a small quantity of tersulphite. If sulphurous acid be added to the coloured liquid and the whole then heated, it loses its colour without forming a precipitate; but when it contains a large quantity of salt in solution, and is heated quickly, tersulphite of the peroxide of iron is precipitated, however much sulphurous acid the solution may contain. These properties should be attended to on precipitating the sulphite and the oxy-sulpho-sulphate of the protoxide of iron, to decolorize these salts if they should accidentally be oxidized by the air.

To obtain the tersulphite of the peroxide of iron, recently prepared hydrated oxide is well mixed with water, placed in a cold mixture, and sulphurous acid passed into it as long as any is absorbed. The liquid is filtered into a glass vessel, which contains the same quantity of alcohol of 0·833 to 0·815 spec. grav. as was employed of water. On mixing with the alcohol, the acid liquid deposits the sesquisulphite of the peroxide of iron in form of beautiful yellow flakes. As soon as the liquid begins to pass through slowly, the funnel is placed on another vessel containing alcohol, and of the same density, and the first alcoholic liquid immediately filtered. The precipitate remaining on the filter is then washed with cold water, pressed between blotting-paper, and dried in a current of cold dry air.

In this operation the alcohol precipitates a part of the sesquisulphate of the peroxide of iron with which the water was saturated, owing to the large excess of sulphurous acid. The water extracts from this precipitate a third of its acid, and leaves tersulphate of iron, which is a more stable and less soluble salt.

It frequently happens that no precipitate is obtained, or only traces. This is owing to the temperature, or the duration of the operation, or of the degree of concentration of the acid liquid.

The alcoholic liquid, from which the precipitate has been removed by filtration, does not become turbid on a further addition of alcohol, although it still contains a large quantity of sulphite in solution. On the contrary, the precipitate formed in the alcoholic liquid gradually redissolves as the dissolved sulphite is converted into a protosalt. The precipitate is converted on its re-solution into a protosalt, and after a few days it presents only a faint greenish colour.

As long as the tersulphite of iron is moist, it possesses a faint yellow colour, reddens litmus-paper, has an acid and astringent taste, is very sparingly soluble in water, and disengages sulphurous acid on being gently heated; exposed to the air, it gradually passes into sulphate. Muriatic acid dissolves it with a deep yellow colour; on diluting the solution with water, it is not rendered turbid by chloride of barium, nor does it form any precipitate with ferridcyanide of potassium even after careful saturation with potash, but ferrocyanide of potassium throws down prussian blue. Sulphuric acid dissolves the salt with slight effervescence.

When dry, the tersulphite of the peroxide of iron has a paler colour, is not perceptibly soluble in water, is tasteless, reddens moist litmus-paper only faintly, is not altered by exposure to the air, dissolves only in muriatic acid, and does not part with sulphurous acid except beyond 392°. It consists of—

Peroxide of iron	46·714	1
Sulphurous acid	19·153	1
Water	34·133	6

Sesquisulphite of the Peroxide of Iron.—When the precipitate which alcohol produces in the saturated aqueous solution of sulphurous acid and persulphite of iron, instead of being washed with water, is edulcorated with pure alcohol, a precipitate is obtained which when dry possesses a straw colour. If the washing be neglected, the substance cannot be obtained in a homogeneous state on drying, but frequently becomes coherent, black, and after a certain time friable. The loss in acid which the substance undergoes under these circumstances, and the presence of free acid in the liquid with which the unwashed precipitate is imbued, would render the accurate determination of the composition of the sulphite, as well as of the acid alcoholic liquid, very difficult, if it had not the peculiar property of first gradually deliquescing in the atmosphere, and then drying. This phænomenon is each time apparent when the precipitate is pressed, and then allowed to lie in a place where there is no draught of air.

The analysis of the spontaneously-deliquesced sulphite furnished—

Peroxide of iron	62·31	2
Sulphurous acid	37·69	3

The properties of the moist sesquisulphite of the peroxide of iron resemble those of the tersulphite, but they are more prominent. It differs likewise from the latter salt by being decomposed in water into sulphurous acid and tersulphite of the peroxide of iron; it is not decomposed by alcohol so readily as by water. A current of dry air removes the acid only from the surface, but even this loss can only be ascribed to the vapours of alcohol and water which are formed.

Under the influence of æther and a gentle heat, the moist sesquisulphite becomes brown and aggregates. If it be spread out on a glass plate, it deliquesces to a thick, transparent, beautiful ruby-red liquid, which however soon becomes consistent, and dries very gradually; in this state it forms transparent scales of the same colour. The metamorphosed sesquisulphite of iron but faintly reddens litmus-paper; water seems to have scarcely any action on it; dilute sulphuric acid decomposes it very slowly. It is not decomposed by heat except at a tolerably high temperature.

A solution of this salt in dilute muriatic acid yields with chloride of barium a white precipitate, which is partially soluble in water acidulated with the same acid. If the weight of this insoluble precipitate be subtracted from that which an equal quantity of the salt yields after the complete oxidation of its acid, we arrive at the proportion, sulphurous acid 31·68, sulphuric acid 68·32. Since the ferrocyanide of potassium produces no precipitate in the neutralized muriatic solution, it is evident that the sulphuric acid is formed at the expense of the oxygen of the atmosphere during the metamorphosis. The partial conversion of sulphurous acid by the action of oxygen even admits the supposition that this gas is by no means foreign to the cause which effects the spontaneous decomposition of the sesquisulphite of the peroxide of iron.

Tersulphite of the peroxide of iron and potash is deposited when a very dilute solution of pure potash is added to the alcoholic solution from which the sesquisulphite of iron has been separated by filtration. The solution of potash is added in small portions, and the liquid each time agitated; at first a yellow precipitate is formed, which on agitation disappears, but soon the precipitate becomes permanent, and acquires a dirty yellow colour. The operation is then discontinued, when the liquid diffuses only a faint odour of sulphurous acid. After some hours it is poured off, filtered, the precipitate washed several times with boiling water, and dried in a current of dry air after having been pressed between bibulous paper.

The tersulphite of potash and iron differs from the tersulphite of iron solely by its amount of potash and its colour. As long as it is moist it is of a dirty yellow, but as soon as it is dry it acquires a deep yellow colour. It consists of—

Potash	20·67	1
Peroxide of iron	38·20	1
Sulphurous acid	41·13	3

It is undoubtedly therefore $KaO, 2SO^2 + Fe^2 O^3, SO^2$.—Poggendorff's *Annalen*, lxiii. p. 245 and 431.

On the Products resulting from the Oxidation of Creosote.
By M. Laurent.

When creosote is treated with chlorate of potash and muriatic acid, chloranil is formed in yellow laminæ. If dilute nitric acid be allowed to act on creosote, a brown resin is produced; on treating this with ammonia, then dissolving it in boiling alcohol and allowing the solution to evaporate, some crystalline salts of ammonia are obtained, which are very sparingly soluble in water and alcohol. From the mother-ley the resin is precipitated by nitric acid, submitted again to treatment with nitric acid, ammonia, &c., until the whole is converted into ammoniacal salts. The salts are then recrystallized from water, decomposed by nitric acid, and the separated acids recrystallized from boiling alcohol. In this manner nitrophenissic acid is obtained in six-sided prisms with 8 terminal facets, and two other acids, one of which crystallizes in long yellow laminæ, the other in minute yellow needles. The author calls them for the present creosotic acids.—*Comptes Rendus*, xix. p. 574.

Physiologico-Chemical Experiments. By Dr. C. Enderlin.

After noticing the opinions of former authors on the cause of the alkalinity of the secretions, and the solvent of the albumen in animal fluids, M. Enderlin details some experiments which he made in the Giessen laboratory. He found that tribasic phosphate of soda, both that containing 2 atoms of base ($2NaO + HO, P^2 O^5$) as well as that with three ($3NaO, P^2 O^5$), and especially the latter, possess in a great degree the power of dissolving proteine compounds. He also found that it dissolved phosphate of lime ($3CaO, P^2 O^5$) and phosphate of iron, so that recourse need not be had to the occurrence of free acid to explain the solution of the phosphate of lime. After detailing the constituents of the ash of human blood enumerated by authors, M. Enderlin states, that fresh blood evaporated to dryness, powdered and incinerated, left a yellowish or brownish-red ash free from carbon.

It reacted as follows:—*a.* When treated with acids, no effervescence ensued. *b.* When exhausted with hot water, a strongly alkaline fluid was obtained, which in every case contained alkaline phosphates, sulphates, chloride of sodium, and sometimes potassium, and these salts only.

The aqueous extract exhibited the following reactions:—

a. Neutral solution of nitrate of silver produced a yellowish precipitate, which was partly soluble in nitric acid, with effervescence, leaving chloride of silver undissolved. On carefully neutralizing the filtered solution with ammonia, the characteristic yellow precipitate of tribasic phosphate of silver is deposited ($3AgO, P^2O^5$). After the precipitation of the watery alkaline extract of the ash by nitrate of silver, the fluid is found neutral.

b. On treating a watery solution of the ash with neutral chloride of calcium, a copious gelatinous precipitate of phosphate of lime ($3CaO, P^2O^5$) ensues, which is likewise soluble in nitric acid without the least disengagement of gas. If this nitric solution is treated with nitrate of silver and neutralized with ammonia, tribasic phosphate of silver falls as before. The fluid, after the addition of the chloride of calcium, is neutral.

From these reactions the following conclusions may be drawn:—

1. The alkaline reaction of the ash cannot be caused by an alkaline carbonate, for the ash, as also the precipitates with nitrate of silver and chloride of calcium, are dissolved by acids without effervescence.

2. The alkalinity of the ash cannot be caused by caustic soda or potash; otherwise the fluid would not become neutral after the addition of neutral solution of chloride of calcium.

3. It follows, from the absence of alkaline carbonates in the ash, that the albumen does not exist in the blood as albuminate of soda, otherwise the ash must contain carbonated alkali, or (if sulphate of lime be present) carbonate of lime, as is the case with milk, in which, according to the experiments of Haidlen and Rochleder*, the caseine exists in the form of caseate of soda.

4. It follows, from the absence of alkaline carbonates in the ash, that lactates, acetates and alkaline soaps do not exist in the blood. The author has proved the absence of lactic acid and lactates in the blood in a former paper†.

5. As alkaline carbonates do not exist in the ash, the blood cannot contain any alkaline carbonates. The albumen cannot therefore exist in combination with alkaline carbonates or bicarbonates.

6. As a further proof of the absence of carbonates and compounds of organic acids with alkalies, might be regarded the small quantities of sulphate of lime, which are almost always found, and which would necessarily be decomposed by the alkaline carbonate. Even by boiling powdered sulphate of lime with a solution of carbonate of

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* Chem. Gaz. vol. i. pp. 427, 465.

† Ibid. vol. ii. p. 33.

soda, perfect decomposition ensued. It is more than probable, that wherever in the human body these two salts meet, the decomposition in alkaline sulphate and carbonate of lime ensues. The most complete proof however of the change produced by incineration is illustrated by the following fact:—Soot contains sulphate of lime. If this be incinerated, it then gives no trace of it, because the potash salt being destroyed forms carbonate of potash, by which on heating to redness the sulphate of lime is transformed into carbonate of lime and sulphate of potash (Berzelius). These facts might suffice to convince those but little acquainted with the subject, that analyses of the ash of blood, which contain both sulphate of lime and alkaline carbonate, cannot be accurate, even if instituted systematically and by hundreds.

7. If the alkalinity of the blood-ash does not depend upon either carbonated or caustic alkalies, it can only be produced by phosphate of soda ($3NaO, P^2O^5$).

8. We must further conclude, from the occurrence of the tribasic phosphate of soda in the ash, that the basic phosphate of the older chemists ($3NaO, P^2O^5$) exists in the blood, because this salt alone remains tribasic, and produces the same yellow precipitate as the ordinary phosphate of soda after heating to redness (Graham).

9. If the ordinary phosphate of soda existed in the blood ($2NaO + HO, P^2O^5$), bibasic phosphate (pyrophosphate) would exist in the ash, because at a red heat the third atom of base (HO) escapes. This bibasic phosphate has been lately detected by the author in the ash of blood and the flesh of several animals. The ash in these cases was less alkaline. If the ash of blood is allowed to remain for several hours in a moist air, and then treated with an acid, effervescence ensues; for the tribasic phosphate of soda becomes partly changed into carbonate of soda in moist air; $3NaO, P^2O^5$, is converted into $2NaO + HO, P^2O^5$ and NaO, CO^2 (Liebig), the third atom of the fixed base being replaced by one of a volatile nature (HO). At a red heat the carbonic acid is expelled, and the salt regains its former composition. The phosphoric acid was separated by chloride of calcium, and its weight calculated from that of the phosphate of lime obtained. The alkalies were separated by precipitating with chloride of barium and barytic water, removing the excess of baryta by carbonate of ammonia, evaporating the filtered solution, and heating to redness until the fumes of sal-ammoniac had ceased to escape. The chlorides were then treated as usual with chloride of platinum, &c. The phosphoric acid in the earthy phosphates was estimated by dissolving them in muriatic acid, adding a slight excess of ammonia, and then pure acetate of iron in excess. The phosphate of iron is next dissolved in muriatic acid, precipitated by sulphuret of ammonium, and the sulphuret converted into oxide of iron. The difference between the weight of the oxide and phosphate of iron is equal to the weight of the phosphoric acid. The oxide of iron remaining in the filtrate was precipitated by ammonia, the lime then thrown down by oxalate of ammonia, and the magnesia by phosphate of soda and ammonia. 100 parts of human blood-ash contain—

a. Soluble in water.

Tribasic phosphate of soda	22·100	83·746
Chloride of sodium	54·769	
Chloride of potassium	4·416	
Sulphate of soda	2·461	

b. Insoluble.

Phosphate of lime	3·636	15·175
Phosphate of magnesia	0·769	
Oxide with some phosphate of iron	10·770	
		98·921

There was no sulphate of lime in this ash.

The saliva is composed as follows:—

Tribasic phosphate of soda	28·122	92·367
Chlorides of sodium and potassium	61·930	
Sulphate of soda	2·315	
Phosphate of lime		5·509
Phosphate of magnesia		
Phosphate of iron		
		97·876

The tribasic phosphate of soda, as well as the phosphate of iron of the saliva, are very important in the formation of blood and digestion. From our ash analyses we have arrived at a different view from any of the earlier ones, and have no hesitation in declaring digestion to be a simple chemical solution of the food in phosphate of soda, choleate of soda and chloride of sodium.

100 parts of the ash of fæces yielded—

Chloride of sodium and alkaline sulphate	1·367
Bibasic phosphate of soda	2·633
Phosphates of lime and magnesia	80·372
Phosphate of iron	2·090
Sulphate of lime	4·530
Silica	7·940
	98·932

Liebig's *Annalen.*

On Digitalic Acid and the Digitalates. By M. Pyrame Morin.

To prepare this acid, the leaves of the plant are to be treated with hot water; the infusion is acid, and is to be evaporated on the water-bath to the consistence of a thick syrup; to the residue a large quantity of alcohol is to be added until it produces no further precipitation; it is to be suffered to remain for some days till a deposit is formed, which ought not to be bitter, but which is so if the alcohol be too strong.

The liquid is then to be filtered, and distilled in a water-bath till it becomes a thick extract, which is to be treated with pure sulphuric æther, and kept at a moderate heat for an hour and eventually boiled; this operation is to be repeated several times.

The æthereal tinctures thus obtained are acid, and have a slightly greenish-yellow colour, especially the first portions. By this process the bitter principle, or digitaline, and the digitalic acid are dissolved; to this æthereal solution barytes in fragments is to be gradually added, which forms a yellowish precipitate, and when any remains insoluble, or the solution restores the blue colour of reddened litmus, enough barytes has been added.

The liquor, which contains only digitaline, but not perfectly pure, is then to be filtered. The precipitate is to be collected, which is to be washed with æther to remove all the bitterness, and then with alcohol, till it passes but slightly or not at all coloured.

The precipitate is to be diffused through cold water and mixed with sulphuric acid to precipitate the barytes; and it is better to leave some digitalate of barytes undecomposed than to add too much acid. By filtration, a strongly acid, reddish-coloured solution is obtained; this is to be slowly distilled in a glass retort in order to separate much of the water, and care is to be taken that the heat is not too great. On cooling, a small quantity of a brown substance decomposes, the clear liquor is to be poured off, and sufficient alcohol is to be added to it to precipitate any digitalate of barytes which may have escaped decomposition; by evaporating the liquor *in vacuo,* crystals are abundantly formed.

In all these operations it is requisite to avoid the contact of air as much as possible, for the digitalic acid is converted by it into a brown substance: notwithstanding the evaporation *in vacuo,* the formation of this substance cannot be prevented, and the crystals are consequently formed in a liquid of a deep colour: the more the action of the air is prevented, the purer are the crystals obtained. The crystals are to be separated by and pressed between filtering paper, dissolved in a small quantity of alcohol, and again crystallized *in vacuo,* by which they are obtained white.

The properties of digitalic acid thus obtained are, that it crystallizes in long needle-form crystals; it possesses a slight peculiar odour, which is increased by heat, and it yields a suffocating vapour, a small quantity of which occasions coughing; at a higher temperature it melts, becomes black, and burns with a white flame; it leaves a charcoal which readily burns without residue; no ammonia is produced during the decomposition by heat.

The acid when pure is perfectly white; but the action of light, heat and air upon it is very great, readily converting it into a brown product, which colours the solution, and from which it is difficult to free it, and on this account the greatest care must be taken during its preparation. When the acid is dissolved in a small quantity of water, it may be converted during evaporation by the water-bath into a deep-coloured substance: this is itself acid, insoluble in water, slightly soluble in æther, and readily so in alcohol.

Digitalic acid becomes still more readily brown by the action of alkaline bodies; thus in preparing it excess of barytes must be avoided.

Digitalic acid has a sour but not disagreeable taste; it immediately reddens litmus paper, expels carbonic acid from carbonates, and forms digitalates, and combines directly with basic oxides, and the soluble salts which it forms become readily yellow in the air.

M. Morin states the properties of the following digitalates:—

Digitalate of Soda.—Obtained by exactly saturating the acid with carbonate of soda, and evaporating the solution under the air-pump vacuum. It is white, and crystallizes very well, but by exposure to the air it becomes quickly yellow, and so also does the solution. It is very soluble in water.

Digitalate of Potash.—Obtained by decomposing the carbonate in the same way as the preceding. It crystallizes with difficulty and is very soluble in water.

Digitalate of Magnesia.—Obtained from the acid and carbonate of magnesia; soluble in water.

Digitalate of Barytes.—Obtained by saturating the acid either with barytes or the carbonate. It is soluble in water, but insoluble in alcohol and in æther. Quite colourless, but by exposure to air and heat it becomes brown.

Digitalate of Lime is obtained in the same way as the barytic salt, with which it has great analogy; being insoluble in alcohol and in æther, it may be employed for the preparation of digitalic acid.

Digitalate of Zinc.—Obtained by treating the carbonate with digitalic acid; the filtered solution is to be evaporated by the air-pump vacuum.

This salt is formed notwithstanding an excess of carbonate. It is obtained at first as a transparent salt, having the appearance of a thick solution of gum; but after some days a number of small arborescent crystals are formed. This salt does not so quickly become yellow by exposure to the air as those previously described.

Digitalate of Lead.—A white, heavy, insoluble salt.

Digitalate of Copper.—A greenish, soluble salt.

Digitalate of Silver.—A white salt, insoluble in water, but soluble in nitric acid.

A solution of digitalate of soda gives, with protosulphate of iron, an abundant flocculent precipitate; with the peracetate of iron it produces no effect; these reactions prove, according to the author, that digitalic acid cannot be mistaken for gallic acid.

This acid exists, probably, uncombined with digitaline, for after having treated the watery extract with alcohol, an abundant brown precipitate is obtained, which is devoid of bitterness, but possesses an acid reaction, and digitalic acid may be obtained from it.

M. Morin observes, that the peculiar properties of digitalic acid, as such, appear to him to be sufficiently established; though it may, he states, be objected, that it is formed under the influence of the substances, especially of barytes, employed to obtain it; but to this objection it is replied, that the juice of the digitalis possesses an acid reaction as soon as it is procured; that the dry leaves treated with water, alcohol, or æther also yield acid solutions; if the alcoholic or æthereal solution, obtained during the preparation of the acid, be saturated with oxide of lead, the liquor remains bitter, and a precipitate is formed; if this be washed in the water and alcohol, and then treated with hydrosulphuric acid, the excess of which is to be expelled, a very acid solution is obtained, from which digitalic acid is obtained by crystallization. This process the author thinks may, perhaps, be better than that which he has described, unless it be wished to obtain the bitter principle at the same time; in this case the action of the base employed is not sufficiently energetic to allow of the formation of a secondary product; the same effect may be produced with carbonate of lead.—*Journ. de Pharm. et de Ch.*, March 1845, and *Phil. Mag.* for May 1845.

Urine charged with Urea.

M. Herzog found the urine of a woman, æt. 44, and suffering from vomiting and pain in the region of the liver, of a specific gravity of 1·0357, of a saffron colour, containing however none of the biliary ingredients. It yielded 68·84 solid parts in 1000, 55·15 per cent. of which were urea.—Buch. *Repert. Pharm. Cent. Blatt.*

CHEMICAL PREPARATIONS.

On the Preparation of Schlippe's Salt (Sulpho-antimonate of Sodium), and the Golden Sulphuret of Antimony. By M. Jemsen.

When 2 equivalents of the sulphuret of antimony are mixed with 3 of soda, there ought to be formed the combination $3NaS, Sb^2 S^3$, with separation of Sb^2O^3. But since the oxide of antimony has likewise affinity for alkalies, more sulphuret of antimony remains undecomposed; and this excess forms, with a little sulphuret of sodium, an insoluble residue. This sulphuret of sodium and antimony dissolves almost entirely on boiling; but on cooling, it is deposited, along with a combination of oxide of antimony and soda (of which a portion remains in solution), in the form of *Crocus antimonii.* If the solution be boiled with sulphur, sulphuret of antimony is deposited. When for 2 atoms of sulphuret of antimony, 4 instead of 3 atoms of soda are employed, the whole remains dissolved even on boiling with sulphur. 3 atoms of monosulphuret of sodium and 1 atom of sulphuret of antimony yield a clear solution, which dissolves on boiling 2 more atoms of sulphur without becoming turbid. But if more than 1 atom of sulphuret of antimony has been used, there separates on cooling sulphuret of antimony with sulphuret of sodium, and indeed with a large excess of sulphuret of antimony nearly the whole of the sulphuret of sodium enters into the precipitate.

When therefore 2 atoms of sulphuret of antimony are boiled with 2 atoms of soda and 2 atoms of sulphur, a solution of Schlippe's salt is obtained, half the sulphuret of antimony being converted into oxide, which is thus lost for the purpose intended. This may be avoided by employing sulphuret of sodium instead of soda, that is, dissolving in half the soda-ley as much sulphur as it will take up, and then adding the other half of the soda-ley.

If $3NaS^2$ are taken to $1Sb^2O^3$, Schlippe's salt ought to be formed with elimination of sulphur. But there immediately separates some oxide of antimony. This does *not occur* when the NaS^2 has been prepared, not in the moist way, but by ignition of the bisulphate of soda. This is explained by the following experiments:—Concentrated solutions of the mono- and bisulphuret of sodium (by solution) yield precipitates with sulphate of magnesia. If soda-ley be saturated with sulphuretted hydrogen, and diluted with water, sulphate of magnesia does not produce a precipitate, which however happens if to the soda-ley saturated with sulphuretted hydrogen a small quantity of a solution of soda is added. A similar behaviour is manifested on the employment of the pentasulphuret of sodium. The mass of the precipitate which forms is proportional to the quantity of the soda added. It appears therefore as if caustic soda, added to the bi- or pentasulphuret of sodium, was not wholly used up in the formation of monosulphuret of sodium, but that the solutions always contain free soda, and NaS, HS.

If soda be saturated with sulphuretted hydrogen, and oxide of antimony dissolved in it, HS is set free, but not if an additional equal weight of soda had been previously added. NaS and NaS^2, prepared by fusion, yield no HS on dissolving the sulphuret of antimony; but if the solution be diluted considerably, and it be precipitated by sulphate of magnesia, the magnesia separated by filtration, and sulphuret of antimony dissolved in the filtered solution, HS is immediately liberated. A solution of NaS^2, prepared in the moist way, yields no HS either before or after precipitation with sulphate of magnesia, when sulphuret of antimony is dissolved in it. Since therefore no oxide of antimony is formed on dissolving the NaS containing free NaO, and the NaS^2 prepared by ignition with Sb^2S^3, this arises from its being again immediately converted into sulphuret of antimony by the SH of the NaS, HS present.

It is satisfactorily proved that in a solution of NaS, HS, to which some NaO has been added, both combinations can exist in presence of each other, and NaS is not formed, as well as that NaS cannot be dissolved in water without being decomposed into NaO and NaS, HS.

When a solution of NaS, HS is exposed to the atmosphere, it becomes yellow, does not deposit any sulphur, but constantly disengages HS. It finally becomes white again, and then contains only carbonate and sulphite of soda. But when the solution is previously boiled with sulphur in excess, and the yellow solution of NaS^5 obtained exposed to the air, sulphur is deposited and carbonate and sulphite of soda formed. A current of air freed from carbonic acid does not decompose a solution of NaS in the cold. If NaS, HS be boiled with S, and the air excluded, the S is dissolved with evolution of HS. If air freed from carbonic acid be passed through it, HS is disengaged, and sulphite of soda formed without any separation of sulphur. When therefore NaS, HS comes in contact with S, there is never formed NaS^2, but always NaS^5. Further, it is from the NaS^5 only that the sulphite of soda is formed. When NaS, HS is decomposed by the atmosphere, carbonate of soda is first formed, the separated HS is decomposed by the air, whereby S is eliminated, which gives rise to the formation of NaS^5, and it is *from this* that the sulphite of soda is formed. That NaS^5 is produced is evident from the yellow colouring.

In the formation of Schlippe's salt therefore it depends entirely on the sulphur present exactly sufficing to form NaS^5 without any free soda. A pure solution of NaS^5 takes up oxide of antimony, and yields Schlippe's salt with elimination of sulphur; but the compound of oxide of antimony soda is neither dissolved nor decomposed by NaS^5. Too much sulphur can never do any harm.

To prepare therefore Schlippe's salt without any loss of oxide of antimony, a solution of $3NaO\,S^2O^2$ and $6NaS^5$ should be prepared by boiling 9NaO and 36S, and the oxide of antimony (not quite 2 atoms) carefully added to it, so that some NaS^5 is left (*i.e.* a portion of the solution should still yield a white turbidness on treatment with a concentrated solution of sulphuretted hydrogen). Soda is now again added to dissolve the eliminated sulphur, when NaS^5 is regenerated, but no free NaO if some S be left undissolved; more oxide of antimony is now conveyed into it, &c.

The method of fusion however is far more certain; a mixture of 3 atoms (4 parts) sulphate of soda, 1 atom ($3\frac{1}{3}$ parts) sulphuret of antimony, and 1 part charcoal are conveyed into a red-hot crucible, this well-covered, and the mass as soon as it ceases to froth immediately poured out; it is then dissolved in water, and 2 atoms ($\frac{5}{8}$ part) sulphur added to the solution. Impure sulphuret of antimony yields a ley coloured by sulphuret of iron, which is readily removed by a little soda.

If the formation of the compound of oxide of antimony soda has not been avoided in the preparation of Schlippe's salt, the former crystallizes together with the latter, and cannot be entirely removed. Such a salt becomes after a time brown, while when pure it never becomes coloured in the dry state. Its solution is precipitated by sulphuretted hydrogen; with dilute acid it yields a golden sulphuret, which is of a somewhat darker colour, and always contains Sb^2S^3, besides Sb^2S^5.—*Journ. für Prakt. Chem.*, xxxiii. p. 336.

Pharmaceutical Experiments on Copaiva Balsam.

By M. BERTRAND.

The author mixed copaiva balsam with one-tenth its weight of concentrated sulphuric acid by means of a glass rod. Very soon sulphurous acid and a peculiar balsamic odour were given off, accompanied by considerable tumescence, evolution of heat, and a blackish-violet colouring of the balsam. After cooling, the balsam was thick, even hard and brown on the surface. After 24 hours the mass was removed from the sulphuric acid, beaten, and digested with boiling water to remove all acid. With balsam freed in this manner from odour some pills were made, with the addition of 5 per cent. magnesia, and these shaken with a mixture prepared with 10 parts gum-arabic, 5 of isinglass and 125 parts hot water, then agitated with sugar and dried. The pills coated in this manner had scarcely any colour, no smell nor taste. The question now to be decided is, how far they are active.

Balsam which has been treated with sulphuric acid can be purified from it more quickly by solution in æther; the sulphuric acid subsides at the bottom, and can readily be removed. The modified balsam is readily soluble in æther, fatty and essential oils, and in anhydrous alcohol, but insoluble in alcohol of 0·848 spec. grav.; alkalies and mineral acids have no action on it; it is heavier than water, and burns without leaving any residue.

Nitric acid has little action on copaiva balsam; it converts it partially into a transparent yellow crystalline resin. The balsam does not part with its odour. Sulphuric acid has scarcely any action on this mixture of copaiva balsam and nitric acid; neither do muriatic and phosphoric acids deprive the balsam of its odour.

If copaiva balsam be mixed with flowers of sulphur and heated, the sulphur melts before the balsam boils; but as soon as boiling begins, the mass takes fire spontaneously and burns away, diffusing thick vapours, and leaving a black coal of great lustre.—*Journ. de Chim. Méd.*, 1844, Nov., p. 643.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of Ultramarine. By C. P. Prückner.

The materials required in the preparation of this beautiful pigment are, alumina, sulphate of soda, sulphur, charcoal and a salt of iron, common sulphate of iron, or green vitriol, being the best for the purpose.

The quality of the alumina employed in the manufacture of ultramarine "has undoubtedly," says the author, "the greatest influence on the colour;" and he considers that the numerous failures in its preparation are mainly owing to the clay used having contained too much or too little iron. He selects a white clay, which does not become red by calcination, and can consequently contain but a minute quantity of iron. Such clays are found in the author's neighbourhood (Hof), and in the vicinity of Roschitz, not far from Gera, in the principality of Reuss (Saxony), where it is used in the manufacture of porcelain.

The chief ingredients in these clays are silica and alumina in various proportions, which variation however does not appear to exercise any influence on the formation of the ultramarine, as the silica is not apparently the most important ingredient; for the author found that the colour was produced by the use of these clays with an additional quantity of pure alumina artificially prepared. But, on the other hand, an excess of silica was prejudicial; for he found, on heating a mixture of 30 grs. of finely-powdered quartz strongly to redness with 60 grs. of the finest ultramarine, that the colour was entirely destroyed, the mass becoming gray. The author conjectures that the silica had combined with the soda of the ultramarine, destroying the colour in the manner that acids generally are known to do.

White bole, or *Terra sigillata*, the *Bolus alba* of the druggists, is a clay well-suited for this purpose, and is exclusively used in the celebrated manufactory at Nurnberg*.

In general, says the author, a pure clay should be selected, as free as possible from iron, and in which the proportion of alumina to the silica is as 3 to 4, or thereabouts.

The clay generally contains a little lime, which however does not interfere with the result.

The second important material in the manufacture is the soda, which is employed in the form of sulphate, and which should be carefully purified; for "the sulphate of soda, as it is procured from the retorts of the distillers of muriatic acid, contains much free acid, undecomposed salt and oxide of iron, according to the purity of the salt employed, or the iron or glass vessels in which it may have been decomposed." As the presence of any acid is prejudicial to the production of ultramarine, particular care must be taken to get rid of it. The quantity of oxide of iron must also be had regard to; common salt usually contains about $\frac{1}{8}$ per cent. of oxide of iron present as hydrochlorate; but if it has been decomposed in iron cylinders, the crude sulphate of soda may contain as much as $\frac{1}{2}$ per cent., which would be the ruin of the process, as indeed it has been where the sulphate of soda has been used without previous purification.

Sulphur, and particularly purified roll-sulphur, is too well known to need further description. The author considers the arsenic† which has been found in some factitious ultramarines, to have been introduced by the employment of impure sulphuric acid.

The author recommends wood-charcoal in preference to coal used in the Nurnberg manufactory. He recommends, should coal be employed, the varieties richest in carbon, and such as burn without much flame; anthracite would most probably be the best.

The remainder, the purely chemical part of the process, we will give in the author's own words, omitting the description of the muffles, reverberatory furnaces, and machinery for grinding, &c., as encroaching too much on the space we are enabled to allot to this interesting process, and as being generally too well understood in this country to make a particular account of them necessary:—

As preparatory operations, the preparation of the clay, or its purification and washing, and the preparation of a necessary pro-

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* It is probable that pipe-clay, or the clays resulting from the decomposition of felspar in granite, used in the china-works at Roche in Cornwall, or at Dartmoor in Devon, would be found to answer the purpose.—Ed. *Chem. Gaz.*

† See Chem. Gaz., vol. i. p. 24.

portion of sulphuret of sodium. The first is a simple mechanical operation. The dry clay having been broken into small pieces by wooden pestles, is brought into four-sided troughs, about 5–6 feet long and 3 feet broad, covered with water, and allowed to stand several days, when it swells up and slakes, and is often stirred up and worked with an iron rake; it is then removed with a shovel, and thrown into a tub with sufficient water to form with it a thin cream, and well-worked and mixed. The greater the quantity of water used, the finer will be the particles of the wasted earth; and by employing a large quantity of water in the first operation, it will require fewer repetitions. These washing vessels should be placed in stages one above another, and should be three or four in number, and wider than deep; their size will depend on the extent of the manufacture, but a capacity of from 20 to 25 gallons is the most usual.

The earth, thus finely divided, is passed through sieves of the degree of fineness generally used for pharmaceutical purposes, the first being rather coarser.

The clay, thus freed of its coarser and sandy particles by repeating the treatment of washing and deposition two or three times, should be put away in four-sided cases, under a roof, without drying. When it is required for use, a portion is weighed, and then sharply dried, in order to ascertain the amount of dry earth it contains, and the necessary quantity is then taken.

I have alluded above to a method of improving a clay which is highly coloured or too rich in iron. It consists in mixing the creamy mass during the last washing with 3–4 per cent. of common salt and 3–3½ per cent. of sulphuric acid, and leaving it to act for some time, stirring and working the mass well with a wooden rake. The muriatic acid gas hereby liberated extracts the iron in a great measure, and the clay purified from the sulphate of soda by washing is afterwards much whiter in colour and more fitted for the preparation of ultramarine; nevertheless, it is much more advisable to dispense with this operation by the selection of a good and pure clay.

The sulphuret of sodium, proper for the manufacture of ultramarine, is the so-called persulphuret, or, according to Berzelius, pentasulphuret of sodium. Its method of preparation does not differ from that given in elementary chemical works. To obtain the sulphate of soda for this purpose, from the residue of the muriatic acid manufacturers (salt cake), it must previously be freed from all free muriatic acid. This is performed by calcination of the salt in a reverberatory furnace. Pieces about three times the size of one's fist are dipped quickly into water or moistened, unless the salt has become moist by attracting moisture from the atmosphere; for the acid is much more easily and completely expelled from it when moist than when it is dry.

The furnace is filled nearly to its roof with these pieces of the salt, taking care to leave a passage for the flame and draught, and to continue the process as long as the odour of muriatic acid gas is perceivable at the opening near the chimney. The fire should be gentle at first, and very gradually raised until the salt is brought to a gentle red heat, when the whole of the muriatic acid is sure to be expelled, and at most a little sulphurous acid begins to be disengaged. The proofs of the sulphate of soda being well-prepared by this method are, that when it has been powdered and dissolved in water it gives a troubled solution, resulting from the deposition of oxide of iron, or lime if the common salt contained sulphate of lime, and that the solution no longer reddens litmus-paper.

The calcined salt is powdered in mills or mortars until reduced to about the size of coarse gunpowder; and if more has been prepared than is intended to be used at once, it will be best preserved dry by mixing it immediately with the proper proportions of lime* and charcoal, for if it be left by itself in a damp place it attracts moisture and runs into lumps.

The dry sulphate of soda is mixed with the lime and charcoal in the following proportions:—

Dry sulphate of soda	100 lbs.
Charcoal in powder....................	33 ...
Air-slaked lime	10 ...

These must be mixed most intimately together by sifting, or by agitation in a vessel capable of revolving on its axis.

A furnace sufficiently large to allow of the fusion of 2 cwt. of the mixture (15–18 feet) is more advantageous in a practical point of view than larger ones capable of containing 5–6 cwt. The mass to be melted is placed in the furnace, covered with lime to the depth of 1½ to 2 inches, which is pressed tightly on it with an iron shovel. During the melting the mass must not be stirred; it is well also to keep the dampers closed until the mass is seen to be well-fused; it is then stirred once or twice, a few shovels of charcoal powder added, and then left to itself until it has settled down into a state of quiet fusion, and it is seen that no more gas is given off; the mass is then removed from the furnace by means of scrapers or iron shovels, and brought into a four-sided, rather shallow iron trough, where it is allowed to cool. It deliquesces quickly in the air, and should therefore be at once dissolved in water. For its solution 5 times its weight of water is necessary. This solution now contains, besides sulphuret of sodium, caustic soda, carbonate of soda and sulphate of lime, with sulphate and hyposulphate of soda. It is better to use boiling water for its solution, and to boil it some time until the salt is thoroughly dissolved. During the boiling the sulphate of lime is decomposed by the carbonate of soda, and carbonate of lime is formed. This solution is now brought into cast iron vessels, and allowed to repose until all the insoluble matters have subsided. These consist of carbonate and sulphate of lime, and finely-divided charcoal, which require several days for their complete subsidence; the charcoal must be allowed to subside completely, as the smallest portion is sufficient to destroy the bloom of the ultramarine;

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* By the addition of lime the author is enabled to decompose the sulphate in the reverberatory furnace, without rendering the use of close vessels necessary, as without this addition the charcoal would burn away before the sulphate had arrived at a temperature capable of effecting its decomposition.

during this time the fluid must be protected as much as possible from the atmosphere. While cooling, a little sulphate of soda frequently crystallizes from the solution, which may be collected and used in another operation after previously depriving it of its water of crystallization. This solution of protosulphuret of sodium is transformed into persulphuret by boiling with powdered sulphur. The clarified solution is brought into a clean cast-iron boiler, and powdered sulphur added to it while boiling as long as any is dissolved. 100 parts of the fused protosulphuret will require from 40 to 50 parts sulphur. The persulphuret is allowed to cool in the boiler. The solution becomes concentrated by the boiling; this is continued until 4 parts of the solution contain 1 part of dry sulphuret; the specific gravity will then be about 1·200, or 25° B.

The solution of the sulphuret is set aside, out of contact of the air (best in glass vessels), until it has deposited all excess of sulphur and become clear, in which state it is ready for use.

The ingredients being thus prepared, the manufacture of the ultramarine is proceeded with, which should not be undertaken in too large quantities; from 25 to 50 lbs., according to the size of the vessels, &c., is most advisable; a larger quantity is not so easily managed.

100 lbs. of the above solution of persulphuret of sodium is evaporated to the thickness of a syrup, and stirred and intimately mixed with 25 lbs. of the dry clay, or as much of the moist mass before described as is equivalent to 25 lbs. of the dry earths. During the stirring and mixing, a solution of ½ a lb. well-crystallized sulphate of iron free from copper is added, and the whole mixed in the most careful manner. The solution of sulphate of iron may be introduced first, and then the clay added, and the whole well worked together. The mass becomes of a yellowish-green colour as soon as the iron is added, and it must be stirred until the sulphuret of iron formed is uniformly diffused throughout the mass. It is then brought to perfect dryness, stirring the whole time, and when dry it is reduced to the finest degree of powder possible without loss of time, lest it attract moisture from the atmosphere. It is now brought into the muffle, about 3 inches deep, and exposed to a gentle red heat until the mass becomes uniformly red-hot throughout. It is maintained at a red heat from ¾ of an hour to 1 hour, and often raked and thoroughly exposed to the air the whole time. The author has remarked, that too high a heat, or a heat too long continued, is prejudicial; whereas, on the other hand, if the heat be too low no ultramarine is produced.

During the ignition a complete change is observed in the colour of the mass, which becomes liver-coloured, then reddish, green and blue. In the green portions the so-called Nurnberg green is easily recognised, and in the bluer portions the ultramarine-blue is perceptible, some of which already possess great brilliancy. Great attention must be paid to the management of the heat; it requires some experience to obtain the exact degree necessary; when the process has been improperly conducted less intensity of colour is obtained, which gives rise to the variety of tints noticed in artificial ultramarine.

The ignited mass is removed from the muffle, and when cold it is thoroughly washed until the water no longer extracts any saline matter. The wash-water contains excess of sulphuret of sodium, sulphate and hyposulphate of soda, and a little alumina dissolved in caustic soda. The washed mass is drained, and dried on linen bags in a drying chamber; it has then for the most part a greenish or bluish-black colour. The dry mass is again finely powdered and sifted. The pulverization is easily performed in stone, or clean iron mortars with wooden pestles. It is now exposed to a second ignition in muffles which are kept exclusively for this operation; they are capable of containing about 10 to 15 lbs., and are 18–20 inches broad and about 32 to 36 long; the mouth of the muffle should be closed. The fire is maintained at a moderate heat, as a gentle red heat is sufficient to produce the colour. The blue colour first becomes visible at the edges, and progresses towards the centre of the mass, a proof that the oxygen of the atmosphere has a great deal to do with the production of the blue colour. When this blue colour begins to appear, the mass is stirred with an iron rake, and narrowly watched, until it is observed to have acquired a pure deep blue colour. This ignition lasts from $\frac{1}{2}$ to $\frac{3}{4}$ of an hour. A longer or stronger heat is of no advantage. The ultramarine, removed from the muffle and laid out on granite slabs exposed to the air, was often found to undergo a sudden heightening and improvement of the colour as it cooled; often however this change did not take place, nor has the author succeeded in ascertaining what circumstances are necessary to induce it.

The last part of the process consists in the grinding, which is performed on the large scale in mills of the hardest granite, or in smaller quantities in mortars. The powder is rubbed as fine as possible with water, and allowed to repose in vessels which contain the different washings, and which may be numbered according to the different degrees of fineness, as in the Nurnberg manufactory, Nos. $\frac{0}{0}$, 0, 1, 2, 3, 4; and after drying it is ready for sale.

In many places where the artificial ultramarine has been used, it has been observed to be inferior in durability to that prepared from the *Lapis lazuli*, and is frequently found to have lost its beauty; this may, as the author says, be owing to some fault in the mode of preparing it.

He found, on passing hydrogen over it when heated, that the artificial ultramarine lost much of its blue colour after half an hour, and at last became greenish-gray; whereas the natural ultramarine maintained its colour for a much longer time, and at the end of 2 hours was not completely destroyed.—*Journ. für Prakt. Chem.*, Nov. 1844.

On a new Method of detecting the Adulteration of Essential Oils.

By M. Mero.

The sophistication of the different essential oils with oil of turpentine occurs daily in commerce, and no process capable of discovering the fraud with certainty is known; the odour and the various chemical tests have hitherto been insufficient. The essential oils of marjoram, lavender, spikenard, sage, thyme, rosemary, wormwood and peppermint are the most subject to this adulteration.

In 1838, M. Mero discovered a method of detecting the presence of oil of turpentine founded on the circumstance that this oil dissolves the fixed oils with great facility, while the essential oils above mentioned do not. He considered therefore that it might serve to indicate the presence of oil of turpentine mixed with pure essential oils, whose powerful smell conceals that of the turpentine.

After a great number of experiments, he found that the oil of poppies deserved the preference, because it always possesses the same consistence. It gave the most accurate results in the detection of the presence of oil of turpentine, in small proportions, in the above-mentioned essential oils.

About 3 grms. of oil of poppies are poured into a graduated tube, and an equal quantity of the essential oil to be tested added; the mixture is then shaken, and should become of a milky white if the essential oil is pure, whilst it remains transparent if it contain any oil of turpentine.

The value of this process may readily be ascertained, by first testing a pure essential oil, and then some essential oil of turpentine; if the essential oil is then mixed with the oil of turpentine, even in proportions so small that no advantage could accrue to traders in mixing it, it is found to behave like the essential oil of turpentine itself, that is to say, the mixture is not rendered turbid.

To make this experiment successfully, the mixture of the two essential oils should be very intimate. The method employed in commerce for this purpose is this:—The pure essential oil, and the quantity of oil of turpentine which is to be added to it, are placed in a hot water-bath basin, and this is heated until the mixture, which is at first turbid, becomes transparent.

The mixture which is obtained by adding oil of turpentine in the process of distilling the plants is detected in the same manner.

It is to be regretted that the process of M. Mero cannot be applied in a general manner. It will not detect the essential oil of turpentine in the essential oils of thyme and of rosemary. However, it furnishes the means of recognising the adulteration of several of the essential oils most in use.

The *Société d'Encouragement* has voted a medal to M. Mero. In some experiments before the Committee, he proved that he could determine at once the mixtures which contained 5 per cent. of oil of turpentine, and was moreover able to tell very nearly the proportions of the mixtures.—*Journ. de Pharm.*

An Account of the Manufacture of Glass in Bohemia.

By L. P. DEBETTE.

[Continued from p. 222.]

CHAPTER IV.—*Manufacture of Table Glass and Fine Glass.*

As soon as the glass of the preceding casting has been worked up, each crucible is charged with about 154 lbs. of materials previously fritted, taking care to put the arsenic first, at the bottom of the crucible. This mixture varies, in a very notable degree, in different establishments, as may be seen from the following table:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Pulverized quartz	110	100	80	60	120	100	120	120	100
Superfine calcined potash	..	..	..	..	..	30	60	70	55
Fine calcined potash ..	64	..	28	..	60				
Common calcined potash	..	..	..	60					
Carbonate of potash ..	..	75							
Caustic lime	24	50	18	24	25	18	..	10	
Carbonate of lime	..	..	..	..	..	..	24	..	8
Arsenious acid	..	..	$\frac{1}{4}$	2	$\frac{1}{2}$	..	..	$\frac{1}{2}$	
Peroxide of manganese	..	..	$\frac{1}{4}$	..	2	..	$\frac{1}{16}$	$\frac{1}{5}$	$\frac{1}{4}$
Nitre	..	..	$\frac{1}{4}$	..	2	..	2	1	
Old glass broken and sifted	..	..	..	..	..	..	..	..	50

I. White table glass, first quality, from Schwarzthal, a little white arsenic, and a very little peroxide of manganese are added.

II. White table glass, from Neuwelt (M. Perdonnet), a small quantity of nitre, oxide of manganese and white arsenic are added.

III. Very white table glass (M. Penhok).

IV. Common table glass (M. Hermbstädt).

VI. VII. VIII. IX. Fine glass, called Bohemian crystal, from various establishments. To VI. VII. and IX. a little white arsenic is added.

As soon as the glass pots are charged, the fire is increased by putting a very little more wood frequently upon the grate; gradually the mixture contained in the glass pot melts, and soon very small bubbles of gas begin to be disengaged from the midst of the fluid mass; the temperature of the furnace is continuously raised, and from time to time the melted mass is stirred with a piece of wood, in order to facilitate the disengagement of the bubbles, which gradually augment in size. The workman judges that the fusion is nearly completed when the bubbles are formed but rarely, and of large size. He then ceases to stir the fluid mass, and suffers it to rest for a full hour, the fire being suffered to fall slightly, so that the glass may acquire sufficient consistency to be worked. The melting is then finished, and the working, properly so called, commences. Each melting-pot is then served by a blower (*Blaser*) and an apprentice (*Lehrjunge*), as we have already said. The iron tubes which they use are nearly 5 feet (1·5 metre) long, weigh from 8½ to 11 lbs., and are provided with a handle of wood about 13 inches (33 centimetres) long, to assist in the manipulation.

As the working of glass is a thing very difficult to explain, and one which must actually be seen in order to be well understood, I suppose that I may dispense with details upon this subject, feeling certain that in the remarks which I have to make I shall be understood by those who have studied the art of manufacturing glass.

The forms or moulds employed are generally made of two pieces, except in very particular cases, where extremely simple articles are to be made, such as ordinary drinking-glasses, to which a handle is often afterwards added, as in beer-glasses, while the glass is still sufficiently soft to weld. These forms are of wood, clay, brass or copper; those of cast iron being not yet employed in Bohemia. Those most used are of wood, which the apprentice takes care to moisten very frequently, so as to prevent their destruction from taking fire.

In these arrangements it will be seen that there is no division of labour, and the same workman begins and finishes the pieces, so that the work is executed rather less rapidly than in France.

In fine, the melting of the glass lasts from 18 to 20 hours; the working, properly so called, from 14 to 15; making in all 32 to 35 hours for the whole operation. The loss by volatilization is from 15 to 20 per cent., and consists of water, carbonic acid and alkali; from 88 to 110 lbs. per pot of finished glass are obtained, not including the loss during the manipulation.

The annealing of the glass is performed by placing them, while still hot, in clay crucibles, six-tenths of an inch in thickness, placed in the annealing furnace annexed to the melting furnace. The interior dimensions of these crucibles are as follows:—

Diameter at the mouth	15·68 inches.
Diameter at the bottom	15·68 ...
Depth	19·6 ...

When one of these crucibles is entirely filled, it is withdrawn by one of the doors of the furnaces, constructed for this purpose, and suffered to cool slowly in a corner of the establishment; the cooling being retarded as much as possible by covering it with a sheet-iron lid.

It may be easily seen how imperfect this process is, when compared with the continuous annealing furnaces now employed in France, the use of which has not yet extended to Bohemia.

CHAPTER V.—*Of the Manufacture of Bottle Glass.*

The bottle glass of Bohemia is very slightly coloured, and would sell very badly in that country if it had the deep green or yellowish-green colour which our glasses present. In most of the glass establishments they make it by remelting old glass with that which runs out upon the hearth of the furnace when a pot breaks by age or accident. In some other glass works, such as that of Gross-Luckawitz near Chrudim, the bottle glass is made from a very friable quartzose sandstone, belonging to the *quader-sandstein* formation of Bohemia, and sufficiently white for this purpose, from a very calcareous clay, a kind of tertiary marl, very recent, and very often covered with a formation of turf, and from glauber salts (sulphate of soda), the residue from the preparation of nitric acid in the manufactory of chemicals established at the same spot, and belonging to the same proprietor, the Prince Auersperg. There is added besides these a certain quantity of charcoal dust, to reduce the sulphate of soda. This establishment possesses but one circular glass furnace, containing six pots, the charge of each of which is about 177 lbs. The working season of this furnace is six months, the respite necessary for the repairs two months; and the blowers are not paid by the piece, as is the usual custom, but receive each one 1032 francs (41*l.* 5*s.* 10*d.*) for the working season. They are besides exempt from all rent or manorial dues for the small portion of land which is allotted for their use.

The melting of the glass takes place exactly as I have described it in the preceding chapter. Then the blower takes upon the end of his tube a quantity of glass sufficient to form a bottle, by dipping it two or three times in the glass pot, and blows through the tube, which he turns, guiding it by a bar of iron, while the apprentice presses upon the glass a block of wood, which he dips in water from time to time when he sees it take fire. Near the blower there is placed a tub full of water, from which he takes it from time to time in the hollow of his hand to cool his tube when he finds it heat too much. When the piece becomes too cold, he reheats it, introducing it into the furnace by the opening which is above the glass pot; then resting his tube upon an iron hook which projects from the embrasure, he gives it a continuous motion of rotation, in order to prevent the glass from bending or inclining to either side. As soon as it has acquired nearly the desired form and size, he finishes it by placing it in a wooden mould, formed of two pieces, which is held by the apprentice, turning it and blowing into it continually. Sometimes however a mould of a single piece is used, as is practised almost always in France, but here far more rarely. The bottles have ordinarily their bottoms entirely flat.

As soon as the bottle has taken the desired form, the workman withdraws it from the mould, and his apprentice takes it by the bottom by means of a rod having a drop of melted glass upon it. The workman then detaches it from his tube, and forms the head by applying a cold body, or, in case of necessity, even by letting fall a drop of cold water upon the place which he wishes to cut. It is then slightly reheated by his apprentice, and a glass band wound around the neck to strengthen it. The bottle is then finished, and nothing remains but to transport it to the annealing furnace, which is sometimes joined to the melting furnace, sometimes separated, as at Gross-Luckawitz. In the latter case the furnace is kept at a dull red heat for 4 or 5 hours after it is full; then all the openings are closed, and it is left to cool spontaneously. To clean his tube, the workman dips it while yet hot into cold water; the glass at the end crumbles, and is detached by a single blow of a hammer.

To conclude, in the manufacture of bottle glass the melting lasts from 18 to 20 hours, the working 8 to 10 hours; in all from 26 to 30 hours.

CHAPTER VI.—*Manufacture of Window Glass.*

The mixture employed for making window glass varies, so to speak, in each establishment, as may easily be seen from the following table:—

	I.	II.	III.	IV.
Pulverized quartz	60	60	60	100
Fine calcined potash	..	..	..	50
Common calcined potash	40	..	17	
Common calcined soda	..	36	17	
Caustic lime	..	..	6	
Carbonate of lime	5	..	..	80
Debris from working glass	100	100	120	
Old broken glass	100	100		
Nitre	..	..	..	2
Smaltz	..	..	..	$\frac{1}{12}$

I. II. Common window glass (M. Penhok).

III. White window glass, from Schwarzthal and Paulina, near Gratzen.

IV. Very white window glass (M. Herbstädt).

The melting of the glass offers nothing peculiar to arrest us. As soon as it is ended each blower takes upon the end of his tube a quantity of glass varying with the size and thickness of the sheet which is to be made, and blows it, swinging it in a vertical plane, so as to give it the form of an elevated cylinder terminated at each end by a hemispherical cap; he then gives it the desired dimensions in a wooden mould of one piece. He then separates the further end by the application of a cold iron, then reheats the piece, swinging it again, at the same time that he gives a rotary motion upon its axis to the pipe, and thus gives it the form of a cylinder open at one end; he then separates it from his tube by means of a cold iron, or, if necessary, by a drop of cold water; he then cleans his tube, and recommences the same operation. The cylinders thus blown are slit throughout their whole length as soon as they are cool, by means of a red-hot rod of iron. They are then introduced into the flattening kiln (*streckofen*) by sliding them along two long iron rods, until they rest upon a plate of clay moveable upon a railroad. There they are flattened by the heat as the glass softens, and as soon as they are completely spread upon the plate of clay, these are slid upon the railroad into the annealing furnace, and then as soon as the glass is sufficiently cool to resist bending the plates are gradually raised and rested upon rods of iron supported in grooves in the sides of the furnace. As soon as the annealing furnace is full, all the openings are closed, and it is suffered to cool slowly.

Fluted Window Glass.—Besides the plain window glass, they make in Bohemia a great deal which is fluted either in one direction or in two directions, making an angle of 30° or 45° with each other, presenting in this case the appearance of small consecutive lozenges. These glasses have the advantage of enabling us to dispense with window-blinds and curtains, as they disperse the rays of the sun, so that they cannot produce inconvenience, and prevent any prying eye from looking into the room. The fluting of these glasses is effected during their blowing. For the glasses fluted in one direction only, it is sufficient to employ moulds of a single piece, either of wood, clay or metals, and fluted in the direction of their length.

The only difference in fluting them in two directions consists in the use of a more complicated mould made of two pieces, which are separated in order to withdraw the cylinder.

Elliptic Shades.—The shades of clocks, &c., which have an elliptic form, are made also by moulding, but as they require a large quantity of air in blowing them, a peculiar process is used, invented in France by a workman in the establishment at Baccharach. This process consists in a hollow cylinder closed at one end, in which is fixed a spiral spring attached to a piston which moves in the cylinder. This is attached to the end of the tube, and the piston being suddenly forced down, all the air contained in the cylinder is driven out through the tube; the shade is then detached from the tube, and the open end finished by cutting.

[To be continued.]

On the Detection of the Adulteration of Wax with Stearine.
By M. Lepage.

The author has made several experiments, however with negative results only; neither the conversion of glycerine by nitric acid into oxalic acid, nor the formation of glycerino-sulphuric acid, could be employed with safety on a large scale. The lowering of the melting-point holds good only when more than one-eighth of tallow has been added; with smaller additions it is very indistinct. The only method therefore is treatment with alkalies or lime water, or the production of acroleine by destructive distillation.—*Journ. de Chim. Méd.*, Sept. 1844.

PROCEEDINGS OF SOCIETIES.

Meeting of the Royal Institution.

Friday, May 2, 1845.

Mr. Napier delivered a lecture "On the Practice of Electro-Metallurgy," the object of which was not only to describe some curious points in the practice of electro-plating, but also to announce a new application of electricity in reducing metals from ores which, like that of copper, can be fused by a flux.

1. *Electro-plating.*—Mr. Napier commenced by noticing the known difference between solid and liquid conductors of electricity, *i. e.* that the latter are decomposed by the current which they convey; on this property the principle of all the electro-processes rests. The mode in which the copper is deposited from the liquid sulphate on a surface connected with the zinc terminal of the battery was then illustrated theoretically by a diagram, and practically by a large sheet of cloth covered by these means. The object of this fabric is to furnish a roofing for houses, lining and ornamenting rooms, and

covering railroad carriages, not only water-proof, but also not liable to be set on fire by sparks falling on it. Mr. Napier here noticed the difficulty of maintaining that equable diffusion of the copper salt through the solution which should ensure the uniform deposit of the metal. This can only be effected by keeping either the liquid or the article in constant motion, or else by placing the latter horizontally at the bottom of the former, care being always taken to ensure the solution being constantly saturated by suspending crystals of the salt in it. In plating goods with gold or silver, recourse is had to the cyanides of those metals. The preparation of the cyanide of potassium from the common yellow ferrocyanide was described. This salt separates silver from the nitrate and gold from the chloride, forming the required cyanide. An instantaneous gilding of several articles was effected before the audience. The subsequent processes of brushing and burnishing, by which the soundness of the work is tested, were then exhibited.

2. *Fabrication of solid Silver Articles.*—On a model of metal, or plaster of Paris, or any other suitable material, is poured a compound of 12 parts of glue and 3 of treacle, melted together. This when cooled forms a perfectly flexible mould, from which any sculptured surface, even if there be much under-cutting on it, can be easily detached. Into a mould so prepared is poured a mixture of 3 parts tallow, 1 wax and ½ resin. This dissolves at a low temperature, and when liquid, and previously to being poured into the mould, it receives ½ an ounce of phosphorus dissolved in sulphuret of carbon. This, diffused through the melted mass thus described, gives it the property of reducing silver from its nitrate. The new model then, taken from the mould, is moistened with nitrate of silver, and becomes covered with a thin film of that metal, on which copper is deposited by the battery current. When this second mould is considered sufficiently thick, the fusible compound is melted away, and the copper mould is protected at the back by non-conducting surface, generally a mixture of pitch and tar. Silver is then deposited within this mould, of any required solidity, from the volution of cyanide of silver and the battery-current; and finally, the copper mould is dissolved by perchloride of iron, leaving the silver pure. By the same process delicate organic textures are gilded. In all cases where it is desired to ensure perfect metallic coating, the article (after having been washed with the sulphuret of carbon and phosphorus) is immersed first in a solution of nitrate of silver, and then of chloride of gold, both very dilute.

3. *Reduction of Copper, &c. from their Ores by Electricity.*—Mr. Napier has proposed the following process for applying this discovery to practical purposes. He mixes the roasted ore with soda and lime, and places the whole on a bed of black lead tiles in a reverberatory furnace; these are connected with the zinc terminal of the battery, and the surface of the mass, when fused, is covered with an iron plate, which is put into connexion with the copper terminal. At the expiration of a period depending on the power of the battery, the complete extraction of the copper takes place, which is found

collected at the bottom, amounting to, according to present experience, from 12 to 16 times the weight of the zinc dissolved in the battery cell. Whether these results are dependent throughout on the direct electrolyzation of the fused mass, or if electrolyzation be the primary effect, deranging the constitution of the compounds, and which, in connexion with the intense heat, produces the results referred to, Mr. Napier cannot as yet say.

Chemical Society of London.

April 7th, 1845. (The President in the Chair.) The following communications were read:—

"On Styrol, and some Products of its Decomposition," by Drs. John Blyth and A. W. Hofmann.

After reviewing the unsatisfactory state of our knowledge on the subject of the balsams, and the like investigations of Simon and others on styrol and styracine, which had still left the matter without any defined results, the authors commence their experiments with the preparation, characters, properties and composition of styrol, which they found to be represented by the formula $C^{16}H^{8}$. The products of the decomposition of styrol by nitric, chromic and sulphuric acids, bromine and chlorine are described, and the resulting compounds fully investigated. The curious change which styrol undergoes by the influence of heat passing from the form of a highly limpid fluid to that of a solid, to which the name metastyrol is given, together with the action of acids on the body thus altered, is next detailed; and the authors conclude their interesting communication by showing that draconyle, a compound lately described by MM. Gnard and Boudault, prepared from dragon's blood, and metastyrol are identical; and this renders the continued investigation of these balsamic substances highly important.

"Note on the Identity of Leucol and Quinoline," by Justus Liebig.

Dr. Augustus William Hofmann has continued his investigations upon coal-gas naphtha, and by a careful comparison of the properties of leucol and quinoline all doubts on the identity of these two substances have been removed. Leucol, when completely pure, gives with chromic acid the yellow crystalline precipitate which Gerhardt describes as characteristic of quinoline.

This fact, which will soon be communicated in detail, was ascertained already the last summer in the Giessen laboratory, and during my absence communicated to Professor Wöhler of Gottingen among others.

"On the useful Applications of the Refuse-lime of Gas-works," by Prof. T. Graham.

This paper contained an analysis of the exhausted lime of the dry lime purifiers, showing that after a few hours' exposure, even in a large mass, it contained no sulphuretted hydrogen, but only the acid oxides of sulphur and free sulphur; that it contains 7 or 8 per cent. of sulphurous acid after exposure for several months, and must therefore be highly deoxidizing. It was recommended that the refuse-lime should be strongly dried or roasted before being applied to the soil as manure; and the refuse-lime in question was shown to be a convenient source of hyposulphites.

Professor Bunsen communicated a paper from M. Genth, "On the Discovery of a large quantity of chemically-pure Oxide of Nickel in the Scum which arises in the smelting of Copper in certain Works in Germany." This oxide of nickel, which amounts to upwards of 13 per cent. in the top skimming, is in a peculiar allotropic condition, being insoluble in acids, and possessing a high specific gravity.

"On Toluidine," by Drs. James L. Muspratt and Augustus W. Hofmann.

After a preliminary introduction on the conversion of organic compounds, the authors commence the first of a series of investigations in this department with the subject toluol. By acting on this consecutively with nitric acid, water, alcohol saturated with ammoniacal gas and hydrosulphuric acid, sulphur and the base toluidine are obtained; the latter passing over on distillation, when purified, as a highly refracting fluid, which in a few seconds solidifies to a colourless, transparent, crystalline mass, having the composition $C^{14} H^{9} N$. It is soluble in alcohol, æther, pyroxylic spirit, acetone, sulphuret of carbon, the fixed and essential oils, and slightly in water. It has an aromatic smell and burning taste; its fusing-point is 40° C., and it boils at 198° C. Its acid solution imparts an intense yellow to fir-wood and elder pith in the same way as aniline and other analogous bases; but it does not afford, like that compound, the beautiful reaction with hypochlorite of lime. It combines with most acids, forming crystallized compounds. The sulphate, binoxalate, hydrochlorate and platinochloride are then described and their composition given; the reaction of binary agents on the base are then detailed, but from the small quantity of material employed nothing determinate is given. The authors close their paper by describing the formation of a very interesting compound, the nitraniline, in which one equivalent of hydrogen is replaced by the elements of peroxide of nitrogen; this is formed by acting on binitrobenzide with sulphuret of ammonium. It crystallizes, and affords crystallizable compounds possessing the same constitution as those of aniline; it is not decomposed by distillation. The authors also state that they find that a large quantity of aniline is formed in Mitscherlich's process for making nitrobenzide.

THE CHEMICAL GAZETTE.

No. LXIV.—June 16, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on the Essential Oil of Black Mustard. By Dr. WILL.

THE following researches, some of the general results of which have been already published in Liebig's 'Organic Chemistry,' do not relate to the question of the origin of this oil, which, as is well known, does not pre-exist in the plant, but to the constitution of the oil itself, such as it likewise occurs in the scurvy grass (Simon), horseradish (Hubatka)*, and *Alliaria officinalis* (Wertheim)†. The principal result is, that if we regard the oil of garlic as sulphuret of allyle, $C^6 H^5 S$, then the oil of mustard is the sulphocyanuret of allyle $= C^6 H^5 (C^2 NS^2)$. By means of hydrate of potash, a combination of the sulpho-cyanuret of allyle with sulphuretted hydrogen $(C^6 H^5, NS^2 + S^2 H^2)$ is obtained, which is analogous to the recently described bisulphuretted sulphocyanogen of Zeise. Previous to the discovery of allyle, the author did not consider it improbable that the oil of mustard should be regarded as an hydrate of the oxide of acryle (acroleine) in which the whole of the oxygen is replaced by sulphur, and which is combined with 1 equiv. of prussic acid. The behaviour of oil of mustard towards bases, parting with sulphur and carbon in the proportion of sulphuret of carbon, and forming a series of new bodies with basic properties, presents however the greatest analogy with the known comportment of the sulphocyanogen compounds. Among the products which originate in this manner, by the action of metallic oxides on the oil of mustard, is *Sinapoline*, already observed by Simon, and formed by the action of barytic water or recently-precipitated hydrated oxide of lead, which separate from the oil of mustard sulphuret of carbon, which however is immediately converted into sulphuretted hydrogen and carbonic acid, so that $2C^8 H^5 NS^2$ with $6PbO$ and $2HO$ give $4PbS$, $2PbO$, CO^2, and sinapoline $= C^{14} H^{12} N^2 O^2$, which consequently has taken up HO in the place of CS^2, which has escaped. The decomposition with potash is far more complicated. Oil of mustard combines directly

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* Chem. Gaz., vol. i. p. 673.

† Chem. Gaz., vol. iii. p. 186.

with ammonia; the compound behaves like an alkali, and has therefore been called *Thiosinammine* = $C^8 H^8 N^2 S^2$; the whole of the sulphur can be removed by oxide of lead from the thiosinammine as sulphuretted hydrogen, and in this way a base containing no sulphur obtained, viz. *Sinammine*, $C^8 H^6 N^2$.

Oil of mustard, in the crude, recently-prepared state, is generally of a bright lemon-yellow colour, highly refractive, and possesses the extremely powerful odour well known to every chemist; the smallest quantity of its vapour immediately makes the eyes water. After long standing the oil becomes darker, sometimes brownish-yellow, even in well-stoppered bottles. By standing over fused chloride of calcium, and rectification of the decanted oil in a glass retort, it is obtained colourless and perfectly limpid. If this transparent and anhydrous oil be left for some time (for instance, for two or three years) in a well-stoppered bottle, exposed to daylight, it gradually becomes darker, almost brownish-yellow, and an orange-yellow body is deposited on the sides and bottom of the vessel, which even under the compound microscope presents not the least crystalline appearance. The specific gravity of the pure oil of mustard = 1·009–1·010 at 59°. Dumas and Pelouze found it = 1·015 at 68°.

Robiquet and Bussy assert that, by heating oil of mustard to 212° for several hours, a colourless oil may be distilled over, which has a faint æthereal odour, does not mix with water, but imparts to it a sweetish taste. According to the same chemist, oil of mustard begins to boil at 230°, and the boiling-point then rises to 311°. The author found, on repeating this experiment, the boiling-point to be perfectly stationary (298°), and the distilled oil to be quite colourless; a small quantity of a blackish-brown resinous substance is left in the retort. It is highly probable that these differences are owing to the circumstance that the oil experimented on by Robiquet and Bussy was not perfectly pure, but mixed with another oil containing no sulphur.

Oil of mustard, as already observed by Löwig*, contains no oxygen. It consists of—

Carbon	49·11	48·68	8	=	600·00	48·37
Hydrogen	5·24		5		62·39	5·03
Nitrogen	14·12	14·12	1		175·82	14·17
Sulphur........	32·11	31·81	2		402·33	32·43
					1240·54	

The specific weight of the vapour Dr. Will found to be 3·54; the calculation gives 3·47, viz.—

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* Löwig states that it is not possible to convert the sulphur of the oil of mustard completely into sulphuric acid by means of nitric acid, which is certainly borne out by the incorrect determinations of Dumas and Pelouze. This however may be effected without loss when the oil contained in a glass bulb drawn out to a fine long point is cautiously treated with very strong fuming nitric acid in a flask with a very long and narrow neck, which is kept cold during the oxidation. However, there is far more certainty of effecting complete oxidation by employing the mixture of nitre and carbonate of barytes proposed by Löwig.

8 volumes carbonic vapour	6·7424
10 volumes hydrogen gas	0·6880
2 volumes nitrogen gas	1·9520
2 volumes sulphur gas	4·4361
	13·8185

$$\frac{13·8185}{4} = 3·47$$

Thiosinammine.—When oil of mustard is mixed with from 3 to 4 times its volume of a strong solution of ammonia, the odour of the oil gradually disappears with the formation of the crystalline compound discovered by Dumas and Pelouze. The mixture solidifies after a time to a mass of crystals, which after draining off the liquid enclosed by them are perfectly pure and white. The crystals are obtained still more readily when gaseous ammonia is passed into the mixture to complete saturation.

The mother-ley poured off from the crystals, after evaporation to expel the excess of ammonia, boiling with animal charcoal and filtration, yields an almost transparent liquid, which crystallizes to the very last drop. The crude unrectified oil generally contains a small quantity of a non-volatile resinous matter, which is left behind on distillation, and which does not enter into combination with ammonia; if this substance be not removed by treatment with charcoal from the mother-ley just mentioned, the last crops of crystals are not so pure, while the crystals themselves are far more developed in their form than when they separate from a pure aqueous solution.

This crystalline combination is the only product resulting from the action of ammonia on the oil of mustard. It is far more soluble in hot water than in cold, and also dissolves in alcohol and æther. In its pure state thiosinammine is inodorous; it has however a permanent and pure bitter taste; its solutions have no perceptible alkaline reaction on vegetable colours. The form of the crystals, especially of those obtained from a not perfectly colourless liquid, agrees exactly with that of the formiate of barytes. Thiosinammine melts below the boiling-point of water (at 158° according to Dumas and Pelouze) to a colourless liquid without any loss in weight; it is however not volatile without decomposition. It gives no solid combinations with sulphuric, nitric, acetic and oxalic acids, nor does it undergo any alteration in weight on treatment with sulphuretted hydrogen gas. Its composition is—

Carbon	40·74	8	=	600·00	41·27
Hydrogen	6·91	8		100·00	6·88
Nitrogen	23·88	2		351·64	24·18
Sulphur	26·50	2		402·34	27·67
	98·03			1453·98	100·00

To ascertain the atomic weight, 0·442 grm. of powdered thiosinammine was saturated in a glass tube with dry muriatic gas until even on gentle fusion no further loss in weight resulted. In this manner 0·247 grm. muriatic acid was absorbed. The atomic weight of thiosinammine = 1584, deduced from this determination, is, it is true, somewhat too high; however, the combination is not very stable, for even in contact with (moist) air it gives off muriatic vapours. If a solution of thiosinammine, to which some muriatic acid has been added, is precipitated with chloride of platinum, yellowish-red precipitates are obtained, which however do not always possess the same composition. A beautiful crystalline precipitate of constant composition is obtained only when the thiosinammine is saturated with muriatic gas and the solution precipitated cold with chloride of platinum. The solution of the platinum may contain a little free muriatic, but no nitric acid. The pure combination of the base with platinum fuses readily, becoming black; on the application of a higher temperature sulphuret of platinum remains, which is decomposed, on long-continued ignition with access of air, into sulphurous acid and platinum, which is left behind of a silver-white colour. The composition of the salt is—

Carbon		8	600·00	14·90
Hydrogen		9	112·50	2·79
Nitrogen		2	351·64	8·73
Sulphur		2	402·34	9·99
Chlorine........	33·90	3	1327·95	32·97
Platinum	30·29	1	1233·50	30·62
			4027·93	

The combinations prepared from a hot solution of thiosinammine, or from one to which muriatic acid and chloride of platinum has been merely added, always yielded a considerably greater amount of platinum.

If a muriatic solution of thiosinammine be precipitated with perchloride of mercury, a white caseous precipitate, soluble in acetic acid, is obtained, which should only be washed with a little cold water. It is pressed strongly between bibulous paper, and dried at a gentle heat, or rather *in vacuo*. The combination thus prepared yielded on analysis the following numbers:—

Carbon	7·92		8	600·00	7·33
Hydrogen			8	100·00	1·26
Nitrogen........	4·64		2	351·64	4·23
Sulphur			2	402·34	4·84
Chlorine........	21·22		4	1770·61	21·36
Mercury........	60·40	60·74	4	5063·30	61·08
				8287·89	

An aqueous solution of thiosinammine dissolves a considerable quantity of freshly-precipitated chloride of silver with the assistance of heat; on cooling, the liquid becomes milky from a deposition of a combination of the base with chloride of silver, which however is not suited for analysis on account of its soft turpentine-like condition.

If to a neutral solution of sulphate of copper a moderately concentrated solution of thiosinammine be added, the blue colour of the former disappears without any turbidness resulting. On the addition of alcohol, a light blue flocculent compound is separated.

A solution of perchloride of iron gradually loses its yellow colour and its acid reaction on the addition of sufficient thiosinammine; on boiling, a flocculent precipitate subsides.

When thiosinammine is boiled with barytic water for some time, a precipitate of carbonate of barytes is formed, and the liquid contains a considerable quantity of sulphuret of barium. In this operation very little ammonia is given off, and this only when the barytic water has become more concentrated by the boiling. The whole of the barytes may be removed by passing carbonic acid into the warm liquid, and on evaporation of the filtered solution a syrup is obtained, which has an excessively bitter taste, scarcely any alkaline reaction on vegetable colours, but otherwise possessing all the properties of a weak organic base.

Sinammine.—When, according to the direction of Robiquet and Bussy, dry thiosinammine is triturated together with 5 parts of peroxide of mercury, immediate decomposition ensues, with evolution of heat, and the mass becomes fluid and black. The same occurs with oxide or hydrated oxide of lead. On extracting the black mass with æther, a syrupy fluid is obtained on driving away the æther, which has all the properties of a strong base. The residue is pure sulphuret of mercury, or when oxide of lead has been employed to remove the sulphur, pure sulphuret of lead mixed with the excess of oxide; it contains neither carbonate nor sulphocyanide of lead. When the sulphuret of lead is boiled with water after the treatment with æther, the water removes from it; when the hydrated oxide of lead employed has not been carefully washed, some basic acetate of lead, which Simon probably mistook for a second organic base. No further product is observed when peroxide of mercury or perfectly pure oxide of lead are employed.

This basic substance is most easily prepared in the following manner:—Thiosinammine is triturated with a paste of recently-precipitated and well-washed hydrated oxide of lead, and the mass warmed in a water-bath until a portion, mixed with more water and filtered, no longer becomes black on the addition of potash and oxide of lead. After complete decomposition the mass is extracted with water, and finally with hot alcohol. The last portions of the sinammine are tenaciously held back by the sulphuret of lead, which renders frequent boiling necessary. The solution is now evaporated in a water-bath, when a colourless thick syrup is left, in which, after an interval of several months, well-defined, hard, shining crystals are formed. They are carefully removed, and freed as much as possible from the adhering syrupy and highly viscous mass by gentle pressure between bibulous paper.

The crystals of sinammine, so obtained, form four-sided columns of the monohedral system; they constitute the hydrate. When left for some time *in vacuo* over sulphuric acid, they lose their lustre; on being heated to 212°, they fuse and part with 9·46–9·51 per cent. water; on cooling, the fused mass solidifies to an opake, faintly-crystalline mass. It again absorbs the whole amount of water by exposure to air. The syrupy sinammine is a mixture of the anhydrous base with less water than corresponds to the above hydrate (3·4 per cent.).

The sinammine melted at 212° consists of—

Carbon	57·66	8 =	600·00	58·43
Hydrogen	7·49	6	75·00	7·31
Nitrogen	33·79	2	351·64	34·26
			1026·64	

The hydrate would therefore be—

Sinammine			1 =	1026·64	90·16
Water	9·46	9·21	1	112·50	9·84
				1139·14	

The origin of the sinammine from the thiosinammine is thus very simply explained from the composition of the two bases; the whole of the sulphur of the latter is removed on treatment with oxide of lead or mercury in the form of sulphuretted hydrogen, without an equivalent quantity of water being taken up by the new base.

Perchloride of Mercury and Sinammine.—To prepare this combination a muriatic solution of the base is precipitated with an excess of an aqueous solution of corrosive sublimate. The precipitate however cannot be washed perfectly without decomposition; it should therefore be pressed strongly after the first wash-water has passed through, and dried over sulphuric acid *in vacuo.* On account of its instability the analyses of this compound do not agree perfectly with the calculated formula:—

Carbon	15·18	14·61	8 =	600·00	13·50
Hydrogen			6	75·00	1·69
Nitrogen			2	350·64	7·97
Chlorine	16·21	17·16	2	885·30	19·91
Mercury	55·56	54·90	2	2531·64	56·93
				4447·58	

Chloride of Platinum and Sinammine.—A solution of sinammine rendered slightly acid with hydrochloric acid gives with chloride of platinum a yellowish-white flocculent precipitate. This combination does not subside immediately and entirely from the liquid, especially when the latter contains alcohol; if the precipitate be separated, after several hours, by filtration, a fresh quantity of the salt is again deposited during the night. However, these precipitates do not present any essential difference in the amount of platinum; care however should be taken to dry the combination very carefully previous to ignition, as it retains very tenaciously the adherent water. 39·2 and 39·82 per cent. platinum were obtained; the formula $C^4 H^3 N$, ClH, $PtCl^2$, or $C^8 H^6 N^2$, $2ClH$, $2PtCl^2$, requires 39·85.

According to these determinations, the atomic weight of sinammine is only half as high as when calculated from the quantity of water. If we adopt the atomic weight deduced from the latter, we shall have a base combining with 2 equiv. of platinum. The behaviour of sinammine at a high temperature towards muriatic gas and sulphuretted hydrogen leads us to conclude that this is indeed the case.

If pure sinammine be heated in a retort in an oil-bath to 326°, it is decomposed without becoming black, disengaging ammonia only. This liberation of ammonia continues up to 392°. The residue is then slightly yellowish, resinous, nearly insoluble in water, but soluble in muriatic acid; the latter solution is rendered turbid by ammonia: on the application of heat the precipitate subsides as a resinous mass; this when dried is brittle, readily pulverized, of difficult solution in alcohol, which solution is rendered turbid on the addition of water; it likewise reacts faintly alkaline. Chloride of platinum produces in the muriatic solution a yellow, and corrosive sublimate a white precipitate.

When dry sulphuretted hydrogen is passed over crystallized sinammine ($C^8 H^6 N^2 + aq$), the crystals become coloured after a few minutes, without any external application of heat, of a beautiful sulphur-yellow; but there is no perceptible separation of water. If the bulb of the tube be now gently heated, the crystals melt, the mass becoming transparent and of a liver-brown colour; at the same time the weight of the tube increases. On the continued application of heat, still however below 212°, water is eliminated, and at the same time the weight of the tube is observed to decrease again. This alteration in weight is not merely owing to the elimination of the hydrate-water of the sinammine, but likewise to that of sulphuret of ammonium, which is distinctly evinced when a slip of moist curcuma paper is held before the aperture of the tube; the red colour of the paper disappears again by exposure to the air.

The mass in the tube is likewise, after cooling, light brown, transparent, perfectly inodorous after dry air has been passed over it, and but sparingly soluble in water and in alcohol. Its solution does not yield any precipitate in the cold with salts of lead, but only a bright red colour; but when the solution is heated to boiling, sulphuret of lead is precipitated, proving that the sulphuretted hydrogen had indeed entered into combination with the base.

Muriatic gas is absorbed by sinammine without the combination becoming liquid; if any attempt is made to assist the absorption by a gentle heat, a violent reaction suddenly occurs, dense white vapours being formed, which are in part carried away by the current of gas, and are in part deposited in the tube; the residuous mass is then puffed up, and cannot be saturated by muriatic acid.

The white vapours which form, consist solely of chloride of ammonium; if the contents of the tube be dissolved in water and supersaturated with solution of potash, a large quantity of ammonia is liberated.

If a cold solution of sinammine be mixed with moderately-concentrated muriatic acid, and then with an excess of caustic potash, no disengagement of ammonia and no turbidness result; but if the muriatic solution be previously heated to boiling, ammonia is separated on the addition of potash, and at the same time a sparingly-soluble basic body is formed possessing all the properties as that obtained on heating sinammine alone.

Sinammine is a powerful base; it has no smell, but like thiosinammine it possesses a strong and very permanent bitter taste. The solution is strongly alkaline towards vegetable colours; it precipitates salts of the oxide of copper, of peroxide of iron, nitrate of lead and nitrate of silver; the precipitate with the latter salt is soft and resinous. It decomposes salts of ammonia, expelling the ammonia; its aqueous solution dissolves chloride of silver like thiosinammine, but not in such quantity. It is precipitated by a solution of tannine, but not by sulphocyanide of potassium. With oxalic acid it forms a combination, which crystallizes with difficulty. The author could not obtain any solid salts with other acids.

[To be continued.]

Decomposition of Metallic Salts by Charcoal in the Moist Way.

By M. Chevalier.

The author, from some experiments made both with vegetable as well as with washed and unwashed animal charcoal, has found that they entirely separate the oxide of lead from the acetate and nitrate, whether these salts are dissolved in water, wine, alcohol or acetic acid, even at the ordinary temperature, but much quicker with the assistance of heat. If acetate or nitrate of lead be distilled with water and charcoal, free acetic or nitric acid is obtained. By mere standing for several days with charcoal, no matter of which kind if it only amount to from 10 to 20 times as much as the lead salt in solution, the whole of the lead is removed from orange-flower water. In legal inquiries, where the organic fluids in which the metallic poison is suspected are decolorized by charcoal, this property may readily cause he poison to be wholly overlooked.—*Comptes Rendus*, xix. p. 1279.

Observations on the Bile.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,

Will you oblige me by inserting a few lines in correction of a little obscurity which occurs in the paper on the bile by M. Platner, in your Number dated May 1st, 1845. The sentence to which I allude is the following:—"From the above observations it is further evident that the formula advanced by Liebig for bilic acid must be incorrect; for Kemp, Theyer and Schlosser have not analysed the essential biliary ingredient in a perfectly pure state, but have always at the same time included the brown syrupy fluid." Any reader would of course understand from this that Liebig's formula was deduced from the analyses which I originally made at Giessen in 1842, and which were confirmed, in every essential point, by MM. Theyer and Schlosser in 1843; this however is not the case, as Professor

Liebig's work on animal chemistry (and consequently his formula for the bile) was published months before my analyses, or, in fact, any analyses of the bile, as an aggregate, were completed. That the formula was incorrect needed no great sagacity to discover, as the very reasoning itself involved circumstances wholly at variance with facts at that time well known and universally acknowledged; and, in a letter which I sent to Prof. Müller of Berlin, previously to publishing my researches in the journal of Erdmann and Marchand, I exposed the error in detail. To Boussingault the physiological world is mainly indebted for a mode of conducting chemical research in a manner more calculated to develope the nature of the changes which occur during the progress of organization and disintegration than any which had been previously adopted; and by applying this mode to the bile, at the suggestion of Prof. Liebig, most important general truths have been elicited, certainly strangely at variance with his opinions, but not on that account meriting less attention; and whether subsequent researches prove the body, which in the ox-bile is combined with soda, to be one acid or more, it must practically and physiologically be considered what I have stated it to be, in the Cambridge Philosophical Transactions, "an electro-negative body in combination with one or more inorganic bases." The ox-bile has now been examined some hundreds of times, by different persons, with different objects, in different countries, under totally different circumstances, with reference to age, climate and mode of feeding, but with one uniform result, that it is as nearly as possible (as an aggregate) uniform in its composition; nor can it be considered of much less importance that, on comparing the composition of the food of animals with the composition of the *chyle*, the difference is such as the addition of a body identical in composition with the bile can alone satisfactorily explain; and that this fluid is not, as supposed by Professor Liebig, an element of respiration, as in that case the excess of oxygen which disappears over that necessary for the oxidation of the carbon would be much greater than observation limits. Some decisive practical proofs of the correctness of my deductions on this subject have recently appeared in the Chemical Gazette, by Prof. F. R. Marchand.

There is little doubt that the interesting researches of M. Platner, when completed by an elementary analysis of the crystalline body he has discovered, will still advance our knowledge of this important fluid. It cannot, however, be useless again to offer the suggestion, that, in order to arrive at good general results, the ox-bile is not the only one to be examined. It is a great misfortune that the term bile has been conventionally substituted for ox-bile, as it clearly appears, from my analyses, that the bile of carnivorous at least, if not of omnivorous animals also, differs most essentially from it. Physiological considerations render this difference necessary; chemical analysis proves it to exist.

I remain, Sir,
Your obedient Servant,
Geo. Kemp, M.D., Cantab.

Isle of Man,
May 7th, 1845.

Products of the Action of Ammonia on Benzil. By M. Laurent.

When dry ammoniacal gas is passed into an alcoholic solution of benzil, there are formed,—1st, *imabenzil,* a white crystalline powder $= C^{56} H^{11} NO^{2}$; 2nd, *benzilin,* in spherical groups of silky needles, isomeric with the preceding compound, but with the double equivalent. By treating the preceding with potash, there is obtained, 3rd, *benzoic æther*; 4th, *benzilem,* a substance crystallizing in beautiful rectangular prisms, which is not decomposed by muriatic acid or potash $= C^{224} H^{40} O^{2} N^{4}$. M. Zinin likewise obtained benzoic æther and a crystalline substance by treating benzil with ammonia. If the last portions resulting from the distillation of the oil of bitter almonds is treated with ammonia, another body is formed, *stilbazid,* $C^{56} H^{10} NO^{2}$. Besides the previously-described compounds, the author has discovered seven or eight new ones by the repeated treatment of the oil of bitter almonds with ammoniacal gas.—*Comptes Rendus,* xix. p. 579.

PHARMACOLOGY.

Observations on Myrrh. By C. H. Ruickoldt.

According to Ehrenberg, myrrh is derived from *Balsamodendron Myrrha,* N. ab Esenb. It is secreted in the form of an oily juice from the bark of the tree, resembling cherry-gum, soon hardens by exposure to the air, and gradually becomes reddish or red-brown. In general only one kind is forwarded by way of Cairo, the *Myrrha naturalis,* which is then sorted in the European markets. It is doubtful what the ancients understood by myrrh. Its use as a medicine was known at the remotest periods; it was employed for fumigation in sacrifices, as a spice with food, for perfumery and for embalming the dead. The following are the kinds known in commerce:—

1. *Myrrha electa.*—Irregular, larger or smaller, angular or tear-shaped fragments, of a light yellow to a dark brownish-red colour, semi-transparent, usually coated with dust, but sometimes bright and possessed of lustre. On the surface of fracture it is uneven, has a waxy or fatty lustre, and exhibits numerous white curvilinear veins. The odour is peculiar, the taste bitter, balsamic. The specific gravity, according to Martius, is 1·360. When breathed on, the fragments exhibit a more lively lustre and are somewhat fatty to the touch. When chewed, this myrrh readily breaks into fragments and adheres firmly to the teeth; at the same time the saliva is rendered milky. On being heated, it puffs up, and burns with a very smoky flame.

2. *Myrrha naturalis seu in sortis* consists of the more impure pieces which remain after picking out the previous sort. We likewise meet in it with the impurities of the *Myrrha naturalis,* espe-

cially *bdellium*, further *gum-arabic* and cherry-tree gum moistened with tincture of myrrh, &c. The *bdellium* resembles the myrrh very much in appearance, possesses a similar bitter taste, but a different, fainter odour, and is characterized by its great amount of bassorine.

3. *Myrrha Indica* (*Myrrha nova*).—Irregular fragments, frequently 3 inches thick, brownish-white, greenish, sometimes nearly black, tear-shaped, opake, with a waxy lustre. In odour and taste it resembles myrrh, but is more bitter.

Martius distinguishes a fourth kind, the *Myrrha alba*, which is sometimes found mixed with the other kinds; the fragments resemble *gum-ammoniacum*, are more or less spherical, tear-shaped or angular, have a conchoidal fracture and a dull waxy lustre; the odour resembles that of myrrh; the taste is intensely bitter.

Myrrh was first minutely examined by Brandes in 1819; subsequently by Braconnot, Pelletier and Bonastre. The myrrh employed by the author in his investigation (*Myrrha nova*) consisted of irregular, knotty and roundish, tear-shaped fragments of about the size of a hazel-nut. It was of a wine-yellow colour, with a reddish tint, sometimes darker. The fresh fracture presented the lustre of wax, at some places that of resin, traversed by white opake stripes and some spots of the same colour; its odour was peculiar and aromatic; its taste likewise aromatic and bitter. Spec. grav. 1·12–1·18. On pulverization it formed into little balls, and left on paper a fatty spot. It did not melt on the application of heat, but puffed up, giving off white aromatic vapours, and was soon reduced to a coal. It left 3·65 per cent. of a white ash, which consisted principally of carbonate of lime, with some carbonate of magnesia, a little gypsum and peroxide of iron. Brandes and Braconnot found potash and phosphoric acid, which the author could not detect. With concentrated nitric acid the myrrh became of a blackish-brown colour, the nitric acid acquired a dirty violet-red colour; after long-continued action the resin was decomposed, and an orange-red sediment separated. When heated with concentrated nitric acid, it became blackish-brown, with the separation of some violet-red flakes, which however soon disappeared again, leaving behind an orange-red resinous mass. To determine the amount of water, 0·764 gr. of the powder was heated in a right-angled glass tube in the water-bath to 203° F. until no more moisture was given off. The fluid which escaped was clear, colourless, had a faintly-acid reaction, and amounted to 1·475 per cent. of the myrrh. The residue, which was half-fused, melted still more on the application of a stronger heat over a spirit-lamp, giving off a yellowish, turbid, strongly-acid liquid, on which floated some dark brown drops of an empyreumatic oil; at the same time a large quantity of yellowish-white vapours was given off.

15 grs. myrrh were heated with about 20 times the quantity of water in a retort until about half the liquid had passed over. When the apparatus had cooled, the upper portion of the retort and the recipient were found coated with a whitish resinous body, which

was soft to the touch, but after a time became hard and brittle. The distillate was milky and deposited some yellowish-white flakes, but no traces of oil. The resinous coating was dissolved in alcohol after removal of the liquid, and left on slow evaporation a light brown solid resin, which dissolved entirely in alcohol, for the greatest portion in æther, and almost wholly in caustic potash, formed a blackish-brown mass with nitric acid, and was nearly insoluble in acetic acid. The gum of the myrrh had dissolved almost entirely during the distillation, so that very little was left on the filter. The nearly-clear filtered solution left on evaporation a brownish extract, which on treatment several times with warm spirit yielded a brownish mass. The alcoholic extract left on evaporation a soft resin, which was almost wholly soluble in alcohol, was not precipitated by water, and had an acid reaction. Æther scarcely altered it; nitric acid dissolved to a clear reddish-brown liquid, which after a few hours became yellow; caustic potash afforded a clear brown solution with it, leaving behind a few flakes.

30 grms. of pulverized myrrh were exhausted with alcohol of 0·831 spec. grav. at a temperature of about 60° F. The dry residue formed a yellowish-white mass easily reducible to powder, of a faint odour and taste of myrrh; it amounted to 48·330 per cent. Amylum could not be detected in it by iodine. It dissolved in cold, but more readily in boiling water, and when filtered left a residue, from which alcohol still removed some resin, the quantity of which after complete exhaustion amounted to 3·862 per cent. of the myrrh. If we subtract the weight of these impurities, as well as that of the ash from that of the entire residue, there remains 40·818 per cent. for the gum, which is very closely allied to Arabin. The aqueous filtered solution yielded no coagulum on boiling, and left a gummy brittle body of vitreous lustre. The somewhat concentrated solution gave, when mixed with twice its volume of alcohol, a white turbidness; with protonitrate of mercury a white precipitate, soluble in an excess of the reagent; with pernitrate of mercury a white precipitate, insoluble in an excess of the precipitant; with neutral and basic acetate of lead a white precipitate; with perchloride of iron a transparent gelatine, and the same with borax. On boiling with nitric acid, the gum was converted into mucic and a little oxalic acid. The alcoholic extract was carefully distilled. When about half the alcohol had passed over, the contents of the retort became turbid, and deposited an oily body, which was separated and the distillation continued, when a further separation took place. To free this balsam-like body from water and alcohol, it was placed for several days over chloride of calcium under a bell-glass. There remained a clear brownish-red liquid, of the consistence of thin turpentine, and of a strong odour and taste of myrrh. Alcohol dissolved it again, and yielded on mixing with water an acid liquid. It was wholly dissolved by æther, was coloured chocolate-brown by cold nitric acid, and on the application of heat formed a porous yellowish-brown mass; the acid became violet, and subsequently yellow. Acetic acid yielded a violet-

red solution with it; caustic potash had very little action upon it. This resinous body presented on elementary analysis the following composition:—

Carbon................	77·130	22	=	77·40
Hydrogen..............	8·870	15		8·68
Oxygen................	14·000	3		13·92

To ascertain the nature and amount of the æthereal oil, the alcoholic extract was distilled until the residue began to acquire a thickish consistence. After removal of the alcohol from the recipient, some grammes of water were added to the retort and the heat was increased; a faintly-yellow oil passed over with the aqueous vapour. The addition of water was renewed, and the distillation continued as long as perceptible traces of oil passed over. The residuary resin was on cooling brittle, clear, light brownish-red. Alcohol dissolved it almost wholly with water; it yielded a white turbid liquid, which had an acid reaction. In æther it was readily soluble; by nitric acid it became first violet, then brown; caustic potash had scarcely any action on it. The distilled oil of myrrh (*Myrrhole*) was of a light vinous-yellow colour, thick, and possessed a penetrating odour and taste of myrrh. After standing for some time exposed to the air, it became thicker and its colour darker; its quantity amounted to 2·183 of the myrrh; it was lighter than water, heavier than alcohol. Both æther and alcohol readily dissolve it. The composition of myrrhole is—

	I.	II.	Mittel.			
Carbon....	79·820	80·150	79·985	22	=	80·440
Hydrogen..	9·867	10·430	10·149	16½		9·920
Oxygen....	10·313	9·420	9·866	2		9·640

It is remarkable that the per-centage composition of myrrhole agrees very nearly with that of colophony and of sylvic acid:—

	Colophony. (Blanchet and Sell.)	Sylvic Acid. (Liebig and Trommsdorf.)	
Carbon	80·04	79·74	79·66
Hydrogen ..	10·01	9·82	9·82
Oxygen	9·95	10·44	10·52

The resin of the myrrh was obtained from an alcoholic extract by distilling off the greater portion of alcohol, and then evaporating it. A portion of the oil must still have remained with the resin. The latter was reddish-brown, transparent, brittle, of conchoidal fracture, and amounted to 44·760 per cent. of the myrrh. When heated, it gave off vapours with the odour of myrrh, readily took fire, and burnt to within a small trace of residue. Its melting-point is between 194° and 203°; it dissolves wholly in æther, but only partially in alcohol; water produced a turbidness in the solution, which did not redden litmus-paper. Muriatic acid produced a flocculent turbidness. Boiling caustic potash dissolved it partially; acetic and sulphuric acids yielded with it a clear solution. It is therefore a neutral resin, and may be called *Myrrhine*. Its composition is—

	I.	II.	III.			
Carbon....	71·960	72·840	72·760	72·400	21	= 72·24
Hydrogen..	8·175	8·129		8·152	16	7·92
Oxygen ..	19·865	19·031		19·448	3	19·84

A small quantity of the resin was heated in a glass tube to 334° until it ceased to froth. The liquid which had collected at the other end of the glass tube was perfectly transparent, and of a strong acid odour and taste. A small quantity of a soft resinous body had deposited itself on the sides of the tube. When cold, the mass was dark reddish-brown, very brittle, transparent, possessed great lustre, but scarcely any odour or taste. Æther dissolved the resin almost entirely, and also alcohol; the latter yielded with water a turbid acid liquid. Nitric acid acquired with it a violet opalescence, and on warming became yellow. Sulphuric acid gave a clear reddish-brown solution with it. Since this acid resin is formed by fusion from the myrrhine, it may be called *myrrhic acid.* Elementary analysis gave—

	I.	II.			
Carbon	75·430	75·310	75·370	24	= 75·222
Hydrogen ..	7·946	8·063	8·005	16	8·250
Oxygen....	16·624	16·627	16·625	4	16·528

According to this analysis therefore the myrrh contained in 100 parts—

Essential oil	2·183
Resin..................................	44·760
Gum (arabine)........................	40·818
Water..................................	1·475
Impurities	3·862
Carbonate of lime with carbonate of magnesia	3·650
Some gypsum and peroxide of iron........	
	96·748

Myrrhole undergoes decomposition by exposure to the air, as does also the resin when heated either alone or with water. It is probable therefore that the *Extractum myrrhæ aquosum* contains an altered resin. It is also probable that the semiresin discovered by Brandes, and also that called by Bonastre subresin, were formed in the course of the analysis by the decomposition of the myrrhine. From the formulæ obtained, the transition of the oil into the resin is readily apparent. If we double the number of the equivalents we have—

Myrrh..........................	$C^{44} H^{33} O^{4}$
Myrrhine........................	$C^{48} H^{32} O^{10}$
Myrrhic acid	$C^{48} H^{32} O^{8}$

The quantity of oxygen is, according to this, smaller in the acid resin than in the neutral one; the latter probably contains a portion of its oxygen and hydrogen in the state of water. The balsam is, at all events, a mixture of oil and resin, and forms the transition from the former into the latter.—*Archiv der Pharm.*, vol. xli. p. 1.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

An Account of the Manufacture of Glass in Bohemia.

By L. P. DEBETTE.

[Continued from p. 249.]

CHAPTER VII.—*Of some peculiar Fabrics of Glass.*

Manufacture of Glass Tubes with circular Bores.—To make cylindrical tubes the workman first blows a cylinder, as in the manufacture of window glass, except that he gives it greater thickness and less internal diameter; then, after reheating it, his apprentice attaches another tube to the free end by means of a drop of melted glass, and the cylinder is drawn out by their rapidly receding from each other. Nothing is then left except to divide the long tube, thus obtained, into sections, and to anneal these sections, the diameter and thickness of which depend upon the quantity of glass employed, the ratio of the external and internal diameter of the original cylinder, and the greater or less extension which it has undergone.

Manufacture of Glass Tubes with flattened Bores.—For some years past capillary tubes with flattened bores have been much employed in the construction of mercurial thermometers, on account of their presenting the advantage of tubes the section of which is very small compared with that of the reservoir, while at the same time the mercurial column is very easily seen when observed in a direction at right angles to the larger diameter of the section.

To make these, the workman takes upon his tube a certain mass of glass, without blowing it, and forms a sausage-shaped lump, which he presents to his apprentice, who seizes it at the end with a pair of small pincers held in one hand, whilst with the other he thrusts into it, in the direction of its length, a kind of double-edged knife, taking care to enlarge the opening, the other lip of which he immediately seizes with another pair of pincers, and draws it out by moving backwards in a straight line without turning the glass, as is done in a common tube. One-fourth or one-eighth of the tube thus obtained is fit for commerce, except that it very frequently happens that the bore is not exactly in the middle of the tube; which however is but a slight inconvenience, provided it be not far from it.

Manufacture of Fine Glass (Crystal) by Moulding and Pressure.—There are but few works in Bohemia which manufacture crystal by moulding and pressing, so that I shall have but very little to say upon the subject.

The principal establishment in which they employ this process is that of Winterberg, where they import from England and France the brass moulds employed, and the articles made are far inferior to the products of our establishments. This is owing, as I believe, principally to two causes:—

1. That the Bohemian crystal is much less fusible and less fit for moulding than our lead glass.

2. That in our best glass-works the use of brass moulds is now

almost entirely replaced by those of cast iron, which besides the advantage of lasting longer are susceptible of a far finer polish, and upon the glass moulded in them, the striæ, so remarkable upon articles made in brass moulds, are scarcely to be seen.

Manufacture of Watch Glasses.—Hollow globes of glass are first blown of sizes and thicknesses varying with the convexity and thickness of the glasses required. A model glass is then laid upon the globe, and the red-hot stem of a clay pipe is passed around its edge; the slightest shock is then sufficient to detach it, and it is finished by grinding.

CHAPTER VIII.—*Of Coloured Glass.*

Coloured glasses are divided into those which are uniformly coloured throughout, and those which are only coloured in particular places.

To prepare the first, the colouring materials are introduced into the glass pot.

It is different in the second case, which is used especially for the more expensive colours and those most difficult to procure, as well as in three operations peculiar to coloured glasses, which consist,—1st, in making coloured or colourless glass vessels with a foot of a different colour; 2nd, in making vessels with an interior very thin and very highly-coloured layer, and with an exterior of colourless glass, which may then be ground off in places without spoiling the uniformity of the tint; 3rd, in forming the vessels in the opposite way, that is, an interior colourless layer, and an exterior more or less thick coloured one, which is then ground off in places, so as to obtain a glass which presents all the shades of the colour.

To obtain these results it is enough, in the first case, to solder the bottom of the vessel to a lump of coloured glass fixed to the end of another tube, then to separate the first tube, and finish as usual; in the second case, the tube is dipped successively into pots of the coloured and of the colourless glass; and in the third case, the operation is reversed.

As we have already said, there exist certain coloured glasses which are not prepared in pots, but in rolls of very deep colour, about 1·2 inch in diameter and a foot long. These are more fusible than the colourless glass, and are such that they melt at the temperature necessary for the complete fusion of 64 parts of colourless glass and 1 of peroxide of manganese. When one of these rods is to be used, a piece of the proper size is broken off, fixed at the extremity of a tube, softened in the furnace, and worked as has been explained.

These preliminaries being settled, I pass to the description of the different matters which are used to colour glass.

Ruby.—The manufacture of this colour, which is extremely difficult to prepare, and is employed only in roll, is still involved in some obscurity. All the establishments which I have visited obtain their colour from the manufactory of M. Meyer at Stubenbach near Berg-Reichenstein. According to a manufacturer of the Riesengebirge, the glass which they used for preparing the cakes of ruby colour (which bears the name of *schmelze*) is composed of silica 500, minium 800, nitre 100, calcined potash 100. A solution of gold is then prepared by treating 10 grammes* of fine gold with 180 *aqua regia* by the aid of heat; when all is dissolved, the liquid is poured into a vessel holding about a quart, which is then filled up with *aqua regia*. It is then poured into a second graduated vessel, and 5 times its bulk of water added. When this is done, they mix intimately 512 of *schmelze*, 48 of prismatic borax, 3 oxide of tin, 3 oxide of antimony, reduced to very fine powders, and $\frac{1}{80}$ of the solution prepared as above.

The whole is then heated for 12 or 14 hours in an open crucible, placed in a glass furnace, and then suffered to cool in an annealing oven. When it is cool they break the crucible and take out the colour. It is not necessary to use closed crucibles, as some manufacturers assert.

If more acid is used than is prescribed above, the crucible is attacked, but the colour is more solid.

The purple of Cassius is only mechanically mixed in the glass, and if this be remelted it often becomes dull, and striæ are formed, which are nothing more than extremely fine particles of reduced gold. In certain cases the quantity of oxide of tin used in the above mixture must be from 2 to 4 parts. The first of these mixtures is used especially for large pieces which have to be worked a long time in the fire, the second for small and delicate articles. Nevertheless, as the process does not always succeed, the greater part of the manufacturers prefer, as I have said, to buy the colour ready-made from other manufacturers, who devote themselves exclusively to this. The antimony appears, in this case, merely to give brilliancy to the glass without colouring it at all.

According to the director of one of the glass-works in the neighbourhood of those of Bohemia, a very beautiful ruby-colour may be obtained in the following way:—Dissolve by heat 1 grm. (15·4 grs. troy) of fine gold in an *aqua regia* composed as follows:—12 grms. nitric acid, 12 grms. muriatic acid and 1 grm. sal-ammoniac. Again, dissolve by heat 1 grm. of tin in an *aqua regia* composed of 20 grms. nitric acid and 6 muriatic acid; then pour the two solutions into a large vessel containing already 500 grms. of clear water, and mix them intimately by agitating the vessel after corking it. The red precipitate of purple of Cassius which forms is washed and dried with care. A peculiar glass is then prepared by mixing together 40 parts of very pure quartz pulverized, 16 parts of nitre, 8 parts of borax, 1 part of white arsenic, 1 part of cream of tartar, finely pulverized and sifted through silk, and a greater or less quantity of the purple of Cassius, according as you want a more or less deep colour. This mixture is introduced into a clay crucible made expressly, not glazed, and of about the capacity of 5 quarts, or else in an ordinary glass pot, then heated in a glass furnace, or in a small furnace made expressly for it, taking care to stir the materials continually until they have attained a dull red heat. The crucible is

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* The French gramme is equivalent to 15·438 grains troy.

then covered, and the heat continued for some time. When the mass is perfectly melted, and gives no more bubbles, the crucible is removed, and after suffering it to cool for 4 or 5 hours in a cellar, it is broken, and the glass obtained separated with care from the impurities which it may contain; it is then ground and sifted. If now there be melted together in a small crucible placed in the glass furnace the following mixture—128 parts of pure quartz pulverized, 64 parts of nitre, 3 parts of borax, and 3 parts of white arsenic, and the glass thus obtained poured into cold water, then ground and passed through a sieve, then mixed with the coloured glass prepared as above, and melted in a glass crucible, a glass will be obtained, which, worked up into articles of a thickness not exceeding 0·16 to 0·2 inch, takes a beautiful ruby colour when exposed to the smoke obtained from burning fir or that of alder.

Bohemian Ruby-Red.—They prepare besides, in Bohemia, a peculiar ruby colour, which is also employed in cakes, and has received the name of *Bohemian Ruby.* It is prepared by melting together quartz powdered and fritted 100, minium 150, potash fritted 30, borax fritted 20, sulphuret of antimony 5, peroxide of manganese 5, fulminating gold rubbed in with oil of turpentine 5. If a little more fulminating gold is used, a magnificent ruby colour is obtained.

Fulminating gold is obtained by precipitating the solution of gold in *aqua regia* by ammonia, and stirring the liquid for some time. The precipitate is then collected upon a filter, and washed rapidly with water boiled and rendered slightly ammoniacal, then dried at a very low temperature. There is thus obtained a powder of a deep brownish-yellow, very explosive, and of which the manipulation requires great precaution.

Ancient Red called Kirschroth (*Cherry-red*).—This colour is generally employed in cake. It is procured by the use of suboxide of copper, which is kept in the state of suboxide by the addition of an equal quantity of protoxide of tin. When it is desired to pass the colour to a fiery red, a little oxide of iron is added. The proportion of oxide of tin must then be reduced, and it may entirely disappear, as in a very beautiful antique red glass found at Caprea in the villa of the emperor Tiberius, the analysis of which gave—

Silica	71·0
Protoxide of lead	14·0
Suboxide of copper	7·5
Peroxide of iron	1·0
Alumina	2·5
Lime	1·5
	97·5

Sometimes the glass is merely coloured with the oxide of copper, and then after the articles are finished they are smoked, which gives them a deep red colour.

Blue.—The azure-blue colour is obtained by the oxide of copper alone, cobalt blue by the oxide of cobalt, or smalts.

Amethystine Violet.—This colour is obtained by the oxide of manganese, mixed with a little nitre.

Yellow.—There are five distinct yellows, which are prepared as follows:—

1. *Topaz Yellow.*—Prepared with charcoal dust.
2. *Antimony Yellow.*—Prepared with a mixture of glass of antimony and minium.
3. *Orange Yellow.*—Prepared with glass of antimony, minium and a little oxide of iron.
4. *A peculiar Yellow.*—Very expensive, which is prepared with chloride of silver, and is only applied in a very thin layer as a sort of enamel; the glass must then be smoked in order to make the colour appear.
5. *Greenish Yellow.*—Which produces a fine effect in daylight, but which appears of a dirty yellowish-white by the light of a lamp or candle. This yellow is prepared with the yellow oxide of uranium of commerce; but since this last contains traces of iron, the yellow glass obtained presents almost always a light green tint upon its edges.

Green.—There are four distinct greens:—

1. *Grass Green.*—Which is obtained by the oxide of chrome, or a mixture of glass of antimony and oxide of cobalt.
2. *Bottle Green.*—Prepared with protoxide of iron.
3. *Ancient Emerald Green.*—Prepared with oxide of copper mixed with a small quantity of finery cinders.
4. *Modern Emerald Green.*—This colour, which is far more beautiful than the preceding, is prepared with a mixture of oxides of nickel and uranium.

Black.—Is prepared with peroxide of manganese, oxide of copper, oxide of cobalt, in equal parts; or else with a mixture of finery cinders, peroxide of iron, oxide of copper, or cobalt.

Hyacinth.—The hyacinthine colour is obtained with a large quantity of red oxide of iron and the oxide of nickel.

[To be continued.]

On the Theory of the Formation of Sulphuric Acid. By M. PELIGOT.

The generally prevalent view respecting the process which takes place in the leaden chambers, is that the nitric oxide in contact with moist air is converted into vapours of hydrated nitrous acid; the sulphurous acid is oxidized, at the expense of the latter, to hydrated sulphuric acid, whereby nitric oxide is regenerated, &c. The author however has some time ago shown that nitric oxide is not oxidized by the air to nitrous acid, but to hyponitric acid, NO^4, which latter however acts upon sulphurous acid only under high pressure; moreover, recent investigations do not admit the existence of hydrated nitrous acid.

The author now attempts to show that the process is rather as follows:—The sulphurous acid is oxidized directly at the expense of the nitric acid, which thus becomes hyponitric acid; water however decomposes the latter into nitric and nitrous acids; the latter is again decomposed, by contact with a large quantity of water, into nitric acid and nitric oxide, which now yields, in the presence of atmospheric air, hyponitric acid, and this is decomposed into nitric and nitrous acid, &c., so that in this manner the process is likewise continuous, but dependent on the uninterrupted regeneration of *nitric acid.* The experiments on which this theory is founded are the following:—

The author passed sulphurous acid gas through two Liebig's bulb-apparatus, the first of which contained distilled water to wash the gas, the second concentrated nitric acid of 1·51 spec. grav. Dry sulphurous gas yields, with nitric acid of this strength, a crystallized compound, described by Provostaye, which however has unjustly been called crystals of the leaden chambers; since, according to the experience of all manufacturers of sulphuric acid, they never form in the regular course of the process, and very rarely occur by accident. In fact, the nitric acid contained in the leaden chambers is never so concentrated.

If, on the contrary, sulphurous acid be passed through nitric acid of 24°–28°, which contains 27–34 per cent. anhydrous acid, the latter is decomposed with formation of red vapours and considerable heat, and the sulphurous acid is absorbed entirely until the whole of the nitric acid is decomposed.

The acid is observed to become green in one bulb after the other, then orange-yellow, and at last again colourless. If the acid is very dilute, the indigo-blue colour likewise makes its appearance. As soon as the whole of the acid has become decolorized, and no more sulphurous acid is absorbed, not a trace of a nitrogen compound can any longer be detected in the liquid, even by the most delicate tests; it contains only sulphuric acid. If the gas which is disengaged in this operation is collected, it will be found on examination to be pure nitric oxide, absorbable without residue by protosalts of iron.

Nitric acid of 13° and less is not decomposed in the cold by sulphurous acid, which however results on the application of heat with the same appearances.

The method of manufacturing sulphuric acid, generally in use at present, of passing the mixture of sulphurous gas and air into the first leaden chamber, which contains vessels filled with commercial nitric acid, is, according to the above, wholly explained; it would moreover result, that sulphuric acid, prepared with a constant excess of sulphurous acid, can contain no nitric acid, and that when such a case occurs it must be owing to a deficiency of sulphurous acid. It ought however to be possible to purify sulphuric from nitric acid by sulphurous acid. The author has convinced himself that this indeed is the case when the sulphuric acid to be purified is diluted; concentrated sulphuric acid contains too little water. Commercial sulphuric acid of 47°–50° may entirely be freed from nitric acid by sulphurous acid gas, a method in fact which is already in practical use in several manufactories.—*Ann. de Chim. et de Phys.*, lxi. p. 263.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Pyine, and its Importance in the Human Organism.

By DR. H. EICHHOLTZ.

THE author endeavours to explain the fact of chemists not having been able constantly to obtain pyine from pus by its frequently occurring only in very small quantity. He, as also Von Bibra, have constantly found it present, and they adopted the method recommended by Güterbock, of precipitating the proteine compounds by alcohol and exhausting the residue with water. Pyine differs from the proteine compounds in its being precipitated from an alkaline solution by aqueous solution of iodine and distilled water; a considerable excess of water redissolves a portion of it; dilute mineral acids (sulphuric, nitric and muriatic), when added in small quantities, precipitate it, but when in slight excess they immediately redissolve it; and moreover, ferrocyanide of potassium causes no precipitate in the clear acid solutions, but a precipitate is produced by an aqueous solution of iodine and distilled water; acetic, tartaric and oxalic acids precipitate it, but do not redissolve it when added in excess; and finally, solution of alum, added by drops, causes a precipitate insoluble in excess; but when alum is at once added in excess no turbidness is produced. The author also found pyine in various other matters. He placed a blister upon his fore-arm, immersed the part for some time in distilled water, and examined the fluid which was secreted, after removing it with a camel's hair pencil. He evaporated it to dryness, after previously precipitating the proteine compounds by alcohol, and dissolved out that part of the residue which was soluble in water. The pyine existed in the extract in considerable quantity. When water was dropped on the wound, which had previously been carefully cleansed, small white flakes were formed; the pyine was thrown down from the alkaline fluid by water; subsequently however a portion became redissolved by the excess of water, and this portion was contained in the extract. A similarity of keratine* and mucus to pyine has already been ima-

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* The word Keratine has been proposed by Simon to designate horny matter, which he considered characterized by its insolubility in water, alcohol and æther; and its solution in acids not being precipitated by ferrocyanide of potassium The term being good, we substitute it here for our author's term, horny matter.—ED. *Chem. Gaz.*

gined to exist, without our being in a condition for giving complete proof of it. The quantity of pyine usually obtained was too small to admit of its being accurately examined; on the other hand, keratine, as it occurs in the epidermis, is insoluble in water, and the solution of it in caustic potash might possibly have exerted some action upon it; therefore, as the author removed the secretion from the surface of the wound, which had only been treated with distilled water, he had, as he *thought himself entitled to suppose,* a solution of keratine, and this, when acted upon by the tests which have been enumerated, was analogous to pyine. The supposition that the sore produced by a blister is a suppurating surface, and that pyine must necessarily be contained in the secretion, as in pus generally, is disproved by the fact that the secretion obtained as above is not composed of the ordinary constituents of pus, but of a fluid plasma and adherent epithelial cells. In the liquid of a fungus, which under the microscope exhibited the fungous corpuscles described by Müller, he likewise found pyine; consequently the presence of pyine is not necessarily associated with that of pus corpuscles. In the filtered aqueous extract of cartilage, Eichholtz found pyine as well as a trace of albuminate of soda. Chondrine behaves like pyine with the above reagents; alum, and the property of chondrine to gelatinize from its solution on cooling, form a distinction, although this is only partial. If we remember that chondrine is obtained from cartilages by boiling, and thus may possibly be changed, the former slightly-different reaction is not a sufficient ground for regarding these two substances as completely distinct. The cause of this difference must necessarily be sought for in the further metamorphosis of a substance forming the common basis of the epidermis and cartilage. To prove the existence of pyine in blood, he half-filled a beaker glass with serum of blood, and very carefully added distilled water to it, to avoid an admixture of the two. The former, being specifically lighter, formed the upper layer. When he had filled the glass, at the point where the serum and water came into contact, a thin film could be distinctly perceived. The water was then very carefully skimmed off, the proteine compound taken up by it precipitated by alcohol, evaporated and washed with distilled water. Pyine was contained in the filtrate in small quantity only, as merely the surface of the serum had come into contact with the water, and as a part only of the pyine thus thrown down was dissolved by the excess of water.

Schwann analysed the cytoblastema of an imperfectly-developed cellular tissue, Simon the fluid from granulations. Both found them identical with pyine, except that excess of muriatic acid did not dissolve the precipitate caused by a less quantity; this may however depend upon a small portion of the albumen not having been completely removed. This considered with the above, *i. e.* that pyine is constantly found in such places where active cell formation exists, justifies the conclusion that pyine may be the formative element of cells, and that the cell walls may be formed from pyine somewhat modified by the continuous metamorphosis.

It is admitted that acids are capable of dissolving cellular mem-the powerful and insupportable smell of the mustard oil. Even before the mixture has become cold, or when the alcoholic solution of potash has not been saturated, and the heat is prevented or partially avoided by external refrigeration, there separates from the brownish-red liquid, after a few hours' repose, a considerable quantity of a white crystalline salt. On washing the salt with absolute alcohol it is obtained perfectly white; its aqueous solution has a strong alkaline reaction; it gives a reddish-brown precipitate with a solution of corrosive sublimate, and effervesces with acids. It proved on analysis to be pure carbonate of potash with 2 equiv. water.

If the strongly-alkaline liquid be now mixed with a large quantity of water, it becomes milky from the separation of an oily body, which after a few minutes collects at the bottom of the vessel in large opake drops. It is the more free from colour the less the alcoholic solution of potash, on its being mixed with the oil of mustard, was allowed to become heated. The simplest way of separating the oil from the aqueous faintly-yellow liquid is to pour it on to a moistened filter, on which the oil collects, and is then removed with a pipette.

The oily body is now repeatedly washed with water until this has no longer an alkaline reaction; if not perfectly colourless, it should be freed from the colouring matters by distillation with a saturated solution of common salt. The oil, when it contains some water in solution or mechanically mixed, is turbid; but if left for several days over fused chloride of calcium, which it does not dissolve, it becomes perfectly transparent and almost limpid. In this state its specific gravity at 57° F. = 1·036; its boiling-point is between 419° and 426°; however, it is impossible to distil it without partial decomposition even in a current of gas. On boiling the oil its vapour is observed to have an alkaline reaction on moist curcuma paper, which arises from the liberation of some ammonia; this alkaline reaction of the vapour even occurs, although in a far less degree, in the distillation of the oil with water. If the oil be distilled alone, a brown resinous body is always left in the retort, which on being further heated gives off much ammonia; this residue contains a non-volatile basic body, which may be extracted from it by digestion with boiling water, but which the author has not yet examined more closely.

The oil, distilled with a solution of common salt or with water, possesses a constant composition, except that its nitrogen varies within certain limits according to the greater or less violence of the action of the alcoholic solution of potash:—

Carbon	50·35	49·92	50·20	28	=	2100·0	50·70
Hydrogen	7·88	7·70	7·84	25		312·5	7·53
Nitrogen	12·30			3		527·4	12·96
Sulphur	20·50			4		804·6	19·41
Oxygen	8·97			4		400·0	9·40
						3944·5	

The oil which was employed for the third analysis had been rectified again, but this oil then gave only 10·40 per cent. nitrogen, and after a fresh rectification only 9·73.

If we add 1 equiv. ammonia to this formula, and then halve it, we obtain the formula $C^{14} H^{14} N^2 S^2 O^2$.

From the analysis of the third product of the action of hydrate of potash upon oil of mustard, it is evident that a body composed according to the latter formula must have been originally formed, and that an equivalent of ammonia had been separated by a secondary action of the alkali or of the higher temperature. This ammonia may be demonstrated in the liquid; it is evolved even on gently heating it.

The oily body just described is closely connected with oil of mustard by its behaviour towards metallic salts; perchloride of mercury and perchloride of platinum are precipitated by it, the latter however only from the moderately concentrated alcoholic solution; salts of silver and lead are decomposed only on boiling with formation of a metallic sulphuret; on boiling with barytic water, sulphuret of barium is formed, and the solution then contains a non-volatile organic substance, which, as is evident from its behaviour towards the chlorides of platinum and mercury, possesses the properties of an organic base.

The odour of the oil is mild, resembling that of leak; its taste is sweetish, cooling, not at all pungent or like that of the oil of mustard; it dissolves in small quantity in water, and mixes in every proportion with alcohol and æther.

The liquid from which the oil has separated on the addition of water contains, besides a small quantity of this latter, a potassium compound of a peculiar, highly remarkable *acid*. This compound may be obtained crystallized when the original alcoholic liquid is evaporated under the air-pump, or the aqueous one in the water-bath, after removing the oily body. In the first case the residue solidifies in a few days to a radiately-crystalline mass, which is frequently imbued with the oil like sponge. This oil may be removed by æther; on treatment with absolute alcohol, the potassium compound dissolves along with the excess of hydrate of potash, while carbonate of potash remains. In the second case, some brilliant crystals gradually form in the syrupy residue after evaporating the aqueous solution; if the evaporation be carried too far, a thick brown oil separates on the alkaline liquid, which no longer dissolves without decomposition on the addition of water, but becomes turbid, with separation of a sulphur-yellow powder, which cakes together like a resin.

If the solution of the potassium compound, not too much diluted with water, be neutralized with acetic acid, it immediately becomes turbid and yellow, as if from separated sulphur. Sugar of lead then produces a precipitate, which at first is of a beautiful lemon-yellow, but rapidly passes into orange-red, and finally becomes black. Salts of copper at first produce in it a greenish-yellow precipitate, which however changes its colour still more rapidly, first into brown, then into black. Nitrate of silver behaves precisely similar, with this difference only,—that the decomposition proceeds more rapidly from the newly-formed silver compound. At the same time, the previously inodorous liquid, even when heated, or possessing merely the smell of the oily body, immediately acquires the unsupportable odour of the mustard oil, which is the more intense the further the decomposition of the precipitate has advanced. If such a precipitate be quickly separated by filtration, and be carefully washed with cold water, the same decomposition nevertheless continues, and constant numbers are never obtained in the analysis of such a salt. The salts of copper and silver cannot be procured in any way in a stable form; the combination with lead however may be obtained in a state fit for analysis by diluting the alkaline liquid from which the oily body has been separated at least with 150 to 200 times its volume of water previous to neutralizing it with acetic acid, and precipitating it with solution of acetate of lead. The liquid must be so diluted that no turbidness, consequently no decomposition of the potassium compound, results on the addition of the acid. The combination with lead then separates at first as a finely-divided precipitate, which on violent agitation of the liquid becomes caseous and the liquid becomes clear. The beautiful lemon-yellow precipitate is now brought quickly on a filter, the greatest portion of the liquid having been previously removed with a siphon, and washed with cold water until what passes through is perfectly colourless and has no longer an acid reaction. The precipitate is then immediately freed, by gentle pressure between several folds of bibulous paper, from the greater portion of water, and dried as quickly as possible *in vacuo* over sulphuric acid. It is impossible to obtain the salt dry with the originally beautiful lemon-colour. If the carefully-dried salt be heated in a tube with a bulb to 212°, complete decomposition immediately occurs, oil of mustard being deposited in colourless drops in the tube. In this decomposition no formation of water or of carbonic acid is perceptible. If, during the decomposition, a slow current of hydrogen gas be passed over the salt, and then into barytic water, not the least turbidness results in the latter. The composition of the lead salt was found to be—

Carbon	19·72		8	=	600·0	20·33
Hydrogen	2·66		6		75·0	2·54
Nitrogen	5·01	4·02	1		175·8	5·96
Sulphur	26·73	26·07	4		804·6	27·28
Lead	45·20	45·00	1		1294·5	43·89
					2949·9	

According to this the salt is a combination of 1 equiv. oil of mustard, 1 equiv. sulphuretted hydrogen, and 1 equiv. sulphuret of lead. If we suppose 1 equiv. of hydrogen less in the compound, we obtain the formula $C^8 H^5 NS^3 + PbS$; it is difficult to decide respecting this equivalent of hydrogen by direct experiment, since, on the one hand, in the combustion of substances containing sulphur, the hydrogen always comes out higher than the usual limits of error;

and, on the other hand, the lead salt in question is not sufficiently permanent to allow of the point being precisely attained in the drying when it has neither parted with oil of mustard nor retained hygroscopic water.

The products resulting from the decomposition of oil of mustard by an alcoholic solution of hydrate of potash are,—1st, carbonic acid; 2nd, ammonia; 3rd, an oily body containing sulphur and oxygen $= C^{28} H^{25} N^{3} S^{4} O^{4}$; 4th, the potassium compound of a peculiar acid $= C^{8} H^{5} NS^{2} + SH + SK$.

The relation of these products of decomposition to the decomposition of the oil of mustard is exhibited in the following manner:—6 equiv. oil of mustard, 10 equiv. water and 2 equiv. potash are decomposed into 1 equiv. ammonia, 4 equiv. carbonic acid, 1 equiv. of the oily body containing oxygen, and 2 equiv. of the potassium compound free from oxygen. It is however evident that the mode of decomposition of the oil of mustard by hydrate of potash must originally be still more simple; and that the formation of ammonia results merely from a secondary or further action of the hydrate of potash on the oily body. The metamorphosis of the oil of mustard is then simply this:—3 equiv. oil of mustard are decomposed with 1 equiv. potash into 2 equiv. carbonic acid, 1 equiv. of the potassium compound containing no oxygen and 1 equiv. of the body $C^{14} H^{14} N^{2} S^{2} O^{2}$. The oxygeniferous oil, on the further action of the alkali, parts with the fourth portion of its nitrogen as ammonia, and we have then the oil $C^{28} H^{25} N^{3} S^{4} O^{4}$.

The dry combination of the new acid with lead or potassium disengages a considerable quantity of sulphuretted hydrogen when sulphuric acid is added to it, without the least odour of oil of mustard being perceptible; but if heated alone, they are decomposed, diffusing an insupportable odour of oil of mustard, and a metallic sulphuret is left, which with the lead compound is sulphuret of lead mixed with sulphur, and with that of potassium a brown hepar, which disengages sulphuretted hydrogen with acids, and colours metallic salts black.

Dumas and Pelouze state that a metallic sulphocyanide is formed in the action of caustic alkalies upon oil of mustard; the author has frequently endeavoured to detect it, but without success. Persalts of iron sometimes produce a slight reddening in the faintly-acidulated liquid, arising from the decomposition of the oil of mustard by hydrate of potash; but it disappears on the addition of more acid, and has not the smallest resemblance in its shade of colour with that produced by a trace of sulphocyanide of potassium added to the same liquid.

Besides the products described none other are formed in the action of hydrate of potash on oil of mustard. If the liquid from which the acid $C^{8} H^{6} NS^{4}$ has been removed by acetate of lead is freed from the excess of lead by sulphuretted hydrogen, and the clear liquid carefully evaporated nearly to dryness, a residue of acetate of potash is obtained from which æther extracts a mere trace of the oily body which had remained dissolved in the aqueous liquid, and from being volatilized with difficulty had not been wholly driven branes as long as the cell is in an early stage of development; but the author has observed that a very dilute acid is capable of causing the cell-membrane to reappear more distinctly. He found the outline of the pus corpuscles in purulent urine very distinct, and observed the same when he mixed pus corpuscles, whose outline was not distinctly perceptible, with slightly acid urine, and set it aside for some hours. As Schultz was able by means of iodine to render blood corpuscles apparent which had been made to disappear by the action of water, it cannot be supposed that the water had dissolved the cell membranes. When the water was allowed to act on them for some time, they could not subsequently be made perceptible by iodine. By endosmosis water is absorbed by the blood corpuscles; they swell, become thinner and paler, burst, and break up into small pieces, which subsequently disappear. The same occurs with acetic acid in the pus globules. Pyine is not soluble in excess of acetic acid; but if the cellular membranes of the corpuscles also consist of pyine, they should not disappear, but the same appears to occur in this case as with the blood corpuscles and water; for after the pus corpuscles have thus disappeared, if a drop of iodine be added to the liquid, they are immediately rendered evident. If a small lamina of cartilage be placed under the microscope, and the acuteness of the outline of a group of cells be accurately noticed, and then a drop of very dilute acetic acid be added, it can sometimes be perceived that the cell-membrane becomes at first more distinct; if more acetic acid be then added, the cell-membrane becomes more transparent and more distended, but without being ruptured. In this condition, iodine immediately restores the sharp outline. If ferrocyanide of potassium is added instead of iodine, a turbidness occurs within the cells, from a precipitation of the albumen contained within them; the cell-membrane however is not rendered more distinct, nor so well-defined as with iodine. This however would occur equally if the cell-membrane consisted of a proteine compound; but solution of iodine precipitates pyine.

The facts, that the fewer the pus corpuscles in pus the greater is the amount of pyine; and moreover, according to the observations of Günther and the author, in a fracture of a bone, the growth of the nail of the corresponding finger or toe is arrested, and does not recommence until the fracture is united, seem further to indicate that pyine is the formative material of the cells; for here the formative material of the nails and epidermis seems to be applied to the formation of callus.—Rust's *Mag. für die gesammte Heilkunde*, vol. lxiv. p. 140.

On the Composition of the Oxalate and Nitrate of Urea.
By R. F. Marchand.

To ascertain if the statement of Regnault, that the oxalate of urea consists of $C^2N^2H^4O^2 + C^2O^3$, was correct, pure urea was precipitated by oxalic acid in excess and crystallized. The compound, dried for a very long time at 230°, was dissolved in water and decomposed by chloride of calcium, the oxalate of lime converted into sulphate, and then weighed. The quantity of lime which was obtained corresponded to 35·1 per cent. of oxalic acid, whilst Regnault obtained 34·3 per cent., and Berzelius 37·4 per cent. The author then endeavoured to ascertain whether the other atom of water would escape at a higher temperature than 230° without the compound being decomposed. He heated the salt, dried in the air, to 248°, whereupon it became opake and lost 14·6 per cent. At a still higher temperature it was decomposed before it began to fuse. The salt, dried at 248°, contained 34·5 per cent. of oxalic acid. The crystallized salt therefore contains 3 equivalents of water, 2 of which (14·6 per cent.) escape at 248°, but the 3rd equivalent is retained until decomposition ensues.

Prout examined the nitrate of urea, and found that when anhydrous it contained 47·37 per cent. of nitric acid. According to Regnault, however, it contains only 43·9 per cent. nitric acid. To test these statements, Marchand used nitrate of urea, which was precipitated from its solution by the addition of nitric acid. It was then separated from the liquid, strongly pressed between blotting-paper, and finally dried at 230°–248°. The aqueous solution was then digested with carbonate of baryta, and the nitrate of baryta decomposed by sulphuric acid. In this manner the calculated nitric acid amounted to 60·66 per cent.; consequently the compound consists of 2 equiv. of nitric acid, 1 equiv. of urea and 1 equiv. of water.

Regnault, the details of whose methods of examination the author has not been able to procure, cannot have analysed this compound, as he obtained far more carbon and hydrogen, and much less nitrogen, than its composition requires. It is also hardly possible that the additional equivalent of nitric acid, which this salt contained more than Regnault's, could be merely adherent. However, the recrystallized compound was examined in the same manner; it again yielded in two experiments 61·2 and 60·92 per cent. nitric acid.

A portion of the same substance was heated to 284°; when treated as above, it yielded a quantity of sulphate of baryta corresponding to 65·72 per cent. nitric acid. It had thus probably become anhydrous, for it would then contain 64·3 per cent. Finally, the crystals of nitrate of urea, which had separated in the cold from an acid solution, and which were recrystallized, were examined and yielded 61·79 per cent. nitric acid. As the neutral nitrate of urea was not obtained in this manner, the author dissolved the acid compound in water and added urea. The crystallized compound was dried at 230°, and lost by this 0·5 per cent. The dried substance contained 55 per cent. nitric acid, consequently 3 equiv. of nitric acid with 2 equiv. urea and 1 water. When the liquid from which the abovementioned salt was crystallized had urea added to it, and the solution was made to crystallize, the author obtained a compound which lost no weight at 230°; after being retained for some time at this temperature, it contained 44·1 per cent. nitric acid.

It is very probable that Prout examined a mixture of these salts.

It must be remarked that the compound separated in analysis does not contain 48·7 per cent. of urea, but only 33·89 per cent.—*Journ. für Prakt. Chem.*, Feb. 28, 1845.

On a double Salt of Perchloride of Mercury and Acetate of Copper.

By Prof. Wöhler.

This salt is formed when a solution of neutral acetate of copper is mixed with a solution of perchloride of mercury, both saturated at the ordinary temperature, and allowed to stand. Very soon concentrically-radiating spheres of a deep blue colour are deposited; they are almost insoluble in cold water, and are decomposed on boiling into a light green powder, while perchloride of mercury is dissolved. The combination is $Cu^2O^2\bar{A} + 2HgCl$, or perhaps more correctly $(CuO + HgCl) + (CuO\bar{A} + HgCl)$.—*Ann. der Chem. und Pharm.*, liii. p. 142.

Researches on the Essential Oil of Black Mustard. By Dr. Will.

[Continued from p. 260.]

Behaviour of Oil of Mustard towards Metallic Oxides in the presence of Water: *Sinapoline.*—If a few drops of oil of mustard be heated in a test-tube with a large excess of saturated barytic water, the oil disappears entirely when the liquid is near boiling, and at the same time the previously clear liquid becomes very turbid from the abundant separation of a white precipitate, which is nothing more than *carbonate of barytes.* The supernatant liquid immediately yields with salts of lead a black precipitate of sulphuret of lead. The liquid contains, besides sulphuret of barium and the excess of barytes, an organic body containing no sulphur, and which was described by Simon under the name of *sinapoline.* It is readily obtained by evaporating the liquid to dryness, and extracting the residue with boiling alcohol. In this decomposition no disengagement of ammonia nor of any permanent gas is observed, any more than the formation of a metallic sulphocyanuret, as asserted by several chemists.

On treating oil of mustard with recently-precipitated hydrated oxide of lead, exactly the same decomposition takes place whether alkaline metallic oxides are present or not; the residuous sulphuret of lead, after being well-edulcorated with water, effervesces strongly with acetic acid; it contains therefore carbonate of lead mixed with the excess of oxide.

On treating oil of mustard with an aqueous solution of caustic potash or soda, a similar transposition of the elements of the oil takes place; but if the mixture becomes much heated, there is almost always observed a liberation of ammonia, evidently resulting from a further action.

Sinapoline is most easily prepared according to the method described by Simon. The oil is digested in the water-bath with freshly-precipitated and well-washed hydrated oxide of lead as long as a fresh addition becomes black, that is, removes sulphur. The residuous mass is then treated with boiling water, when sulphuret of lead, carbonate of lead and the excess of hydrate remain behind, while the sinapoline immediately separates in perfectly pure crystals from the hot filtered solution.

The sinapoline crystallized from the aqueous solution forms laminæ, which are fatty to the touch, have great lustre, and fuse at the boiling-point of water. Melted on a watch-glass or in a little boiling water, it immediately solidifies on cooling to a beautiful crystalline mass. Sinapoline is not soluble in cold solution of caustic potash; on boiling with it, it melts without any evolution of ammonia forming oily drops, which dissolve on the addition of water, but even before complete cooling again separate and solidify to a crystalline mass.

The boiling saturated aqueous solution of sinapoline has a distinct alkaline reaction on vegetable colours; it dissolves readily and without colour in concentrated sulphuric acid, and also in other acids; on neutralization with ammonia it is again separated. It fuses in dry muriatic gas without any external application of heat, without any separation of water, but with considerable evolution of heat. The base saturated with muriatic acid does not alter its weight on passing over it a current of dry air; the mass is syrupy, and gives off in moist air muriatic vapours; on being mixed with water, it deposits a portion of the sinapoline.

On being heated to 212°, the crystallized sinapoline does not lose in weight; at a higher temperature it is partially volatilized, while the remainder is decomposed. Sinapoline consists of—

Carbon......	59·20	59·96	59·99	14 =	1050·00	59·94
Hydrogen....	8·87	8·70	8·78	12	150·00	8·57
Nitrogen	19·82	20·07	20·08	2	351·64	20·08
Oxygen	12·11	11·27	11·15	2	200·00	11·41
					1751·64	

The combination with muriatic acid is composed of—

Sinapoline		1	1751·64	79·40
Muriatic acid	20·35	1	455·13	20·60
			2206·77	

The aqueous solution of sinapoline is precipitated like the other bases by the chlorides of platinum and mercury. The formation of sinapoline has already been explained.

Behaviour of Oil of Mustard towards an alcoholic Solution of Hydrate of Potash.—If oil of mustard be poured by degrees into a concentrated clear solution of hydrate of potash in absolute alcohol, a violent reaction takes place if one or more grammes of oil be used for the experiment, the mixture beginning to boil violently in a few seconds, and sometimes immediately. However, no permanent gas is given off in this reaction; there is scarcely any perceptible liberation of ammonia, but a mild leak-like odour has taken the place of colour or precipitate, according to the degree of concentration. The silver salt, precipitated by double decomposition from neutral solutions, forms four-sided needles, which possess a very strong lustre. Carefully dried at 212°, the salt yielded 43·88–43·9 oxide of silver. The acid in the salt consists of—

Carbon	56·47	56·20	14	=	1050·0	56·38
Hydrogen	6·10	6·16	9	=	112·5	6·04
Oxygen			7	=	700·0	37·58
					1862·5	

The neutral salt of lead is obtained by saturating the acid with oxide of lead; it separates from a somewhat acid solution in cauliflower-like groups of crystals, is white and very soluble. Its formula is $C^{14} H^{9} O^{7}$, PbO; it dissolves more oxide of lead to form a basic salt.

This terebilic acid has therefore precisely the composition of Bromeis's acid, but distinct properties, which probably arises from the author having examined the oil of turpentine from *Pinus maritima* (from turpentine from Bordeaux), and Bromeis probably the oil from Strasburg turpentine (derived from *Abies taxifolia*).

Pyroterebilic Acid.—Terebilic acid is decomposed at 392° into carbonic acid gas and an oily distillate. The latter is purified by redistillation, and is thus obtained as a colourless, highly refractive oily acid, which resembles butyric acid by its odour, has a pungent taste, burns the skin, and produces a white spot on the tongue; it is still fluid at 4°, boils below 392°, and is somewhat heavier than water. The acid is not altered by exposure to the air, dissolves in 25 parts water, and readily in alcohol and æther. It consists of—

Carbon..........	62·90	63·18	12	=	900	63·06
Hydrogen	8·77	8·80	10	=	125	8·76
Oxygen			4	=	400	28·15
					1425	

The salts are represented by the formula $C^{12} H^{9} O^{3}$, MO; they crystallize with difficulty. The alkaline salts produce white precipitates in *concentrated* solutions of lead and silver. The silver salt very quickly becomes coloured by exposure to light, and crystallizes with great difficulty. The lead salt is readily decomposed by treatment with water, with formation of a basic salt.—*Journ. de Pharm. et de Chim.*, Sept. 1844, p. 185.

Further Additions to the Chemical Dynamics of Platinum.

By Prof. J. W. Doebereiner.

I found, in the course of last autumn, that spongy platinum obtained by the pyrochemical decomposition of the ammonio-chloride of platinum exerts, at the ordinary temperature and in contact with the air, as energetic an action on formylic acid combined with

1, 2, 3, and more equivalents of water, as on hydrogen gas under the same circumstances; in fact, when slightly moistened with the above acid, it becomes almost immediately heated to incipient redness, determining by a dynamic action this acid or its radical formyle $= C^2 H$ to combine with a maximum of oxygen, in order to form carbonic acid and water ($C^2 HO^3 + 2O = 2CO^2 + HO$).

This experiment is just as curious as the action of spongy platinum on the explosive gas; it is the more so, since other acids which contain a radical similar to formyle, but perhaps more condensed, viz. $C^4 H^2$, and among which we find—

$$\begin{array}{ll}
\text{Succinic acid} \ldots\ldots\ldots\ldots\ldots\ldots & = C^4 H^2 + 3O \\
\left.\begin{array}{l}\text{Malic acid} \ldots\ldots\ldots\ldots\ldots\ldots \\ \text{Citric acid} \ldots\ldots\ldots\ldots\ldots\ldots\end{array}\right\} & = C^4 H^2 + 4O \\
\left.\begin{array}{l}\text{Tartaric acid} \ldots\ldots\ldots\ldots\ldots \\ \text{Racemic acid} \ldots\ldots\ldots\ldots\ldots\end{array}\right\} & = C^4 H^2 + 5O
\end{array}$$

and several other acids, are not subject to the mysterious power of the platinum, under the circumstances in which I am in the habit of experimenting with this metal, that is to say, with the exclusion of all artificial heat.

I moreover found, a short time previously, that spongy platinum does not act at the ordinary temperature of the air, either on alcohol or on pyroligneous æther, but that it instantly acquires great energy of action if placed at the same time in contact with a concentrated solution of caustic potash or soda. It suffices to moisten it with the mixture of these alkalies and the alcohol or pyroligneous æther. Its temperature then frequently rises to red heat, and it converts the alcohol partly into oxide of ætherine or of acetyle, and into polyosmone, and partly into oxide of retinyle (resin of aldehyde) and into acetylic acid; and pyroligneous æther into formylic acid, which it instantly changes into carbonic acid and water. This act of development of heat and of transformation lasts until the alkali is saturated by the acid formed.

The spongy platinum thus acquires by the presence of the alkali the property of the oxyphorous platinum (which is known under the name of platinum-black), *i. e.* that of absorbing oxygen gas, and of condensing it to such an extent as to render it capable of entering into chemical combination with several organic substances which are easily oxidized; but this activity of the spongy platinum, vivified by the alkali, never equals in power well-prepared platinum-black. The energy of oxidation and of absorption of oxygen increases to such a degree in this latter by being alkalized, that it soon converts all the kinds of fermentable sugar and other organic substances, CHO, into carbonic acid and water.

I have not yet succeeded in vivifying sufficiently the two allotropic modifications of platinum which I have indicated, to cause them to convert ammonia into water and nitric acid, or the chlorides of the alkaline metals into chlorides. They likewise want, at least at the ordinary temperature, the force requisite to raise the oxidizability of the hydrogen gas to such a degree that it would be capable of partially deoxidizing the gaseous carbonic acid and of converting it into the hydrate of oxalic acid, or into carbonic oxide and water.—*Ann. der Chem. und Pharm.*, liii. p. 145.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

An Account of the Manufacture of Glass in Bohemia.

By L. P. Debette.

[Continued from p. 271.]

Chapter IX.—*Of Opalescent Glass.*

The milky-white glass imitating alabaster or opal is prepared like the fine colourless glass, only with the addition of a greater or less quantity of calcined bone-powder according as a more or less opaline glass is desired. A great quantity of opaline glass coloured green is also manufactured in Bohemia; formerly it was prepared by adding to colourless glass a certain quantity of calcined bone-powder, yellow oxide of uranium and oxide of iron (finery cinder).

This colour is altered after long exposure to solar light. For some years past it has been replaced at Winterberg and at Silberberg by a more beautiful colour, due to calcined bone-powder, yellow oxide of uranium and oxide of nickel. The oxide of tin is employed solely in the manufacture of enamels, because it is far more expensive than the calcined bone-powder (phosphate of lime, bone-earth), and because it requires a larger quantity to produce the same effect.

Chapter X.—*Of Hyalite.*

The name hyalite is given to a completely opake glass, generally black, which is distinguished by a hardness and lustre truly remarkable, and forming a beautiful contrast with gold. It may, without any inconvenience, be employed for the manufacture of vessels intended to hold boiling liquids, such as tea-pots, coffee-cups, &c., without any danger of its breaking. It was first made in 1820 at the establishment of Georgenthal near Gratzen, and M. le Compte de Buquoi, who invented this beautiful product, has secured the invention to himself by a patent right. To prepare this black glass, there must be added to the materials for white glass a certain quantity of poor forge-cinders pulverized, charcoal-dust in excess and calcined bone-powder.

It often happens, either that the melting of the glass is not complete, or that the mixture or the proportions of the ingredients was not right. The glass obtained must then be calcined and quenched, powdered again, and remelted after having added to it what may have been missing. The forge-cinder may be replaced by basalt or lava. If sufficient carbon has not been added, the glass takes a more or less deep green colour, and presents upon cutting very regular mottling. The same is true of the more or less deep yellowish-brown hyalite, which is obtained by replacing the forge-cinder by the cinder from the argentiferous lead-furnace of Gutwasser near Budweis.

A red hyalite may also be obtained with calcined bone-powder, oxide of copper, carbon, &c., and all these varieties present a marbled structure upon cutting.

The black colour of hyalite may perhaps be explained in the following manner:—In the presence of an excess of silica the oxide of iron is not reduced, but only brought by the carbon to the state of protoxide, and tends to colour the glass deep green. The excess of carbon, probably by transforming the small quantity of alkaline sulphates present in the glass into sulphurets, tends on its part to colour it of a more or less deep topaz-yellow, passing even in certain cases to a purple-red.

Now we know that we can obtain black by a mixture of green and red; the only difficulty then consists in employing the proper proportions of oxide of iron and carbon.

If the quantity of carbon is insufficient, the hyalite will take a greenish colour, and will be composed of concentric zones having different shades, which may be made apparent by cutting. Should we attribute the formation of these zones to a devitrification analogous to that which is presented by many furnace-slags, to an oxidation, or to a reduction which is propagated from without inwards, during the working and annealing of the glass? This is what cannot be decided without some experiments not yet made. All that we have here said relative to the black and to the marbled green hyalite applies equally to other hyalites; and, in short, we may say that hyalite is fit to take the place of porcelain in a great many cases, possesses far more lustre, and is capable of receiving a more perfect polish.

CHAPTER XI.—*Of the Manufacture of enamelled cast Iron Vessels.*

Iron pots, and especially those of enamelled cast iron, are very extensively used in domestic œconomy. To enamel these vessels, they are cleaned as perfectly as possible with weak sulphuric acid, then washed with cold water, and dipped into a thin paste made with quartz first melted with borax, felspar, and clay free from iron, then reduced to an impalpable powder, and sufficient water added to form a rather thin paste. These vessels are then powdered in the inside with a linen bag, containing a very finely-pulverized mixture of felspar, carbonate of soda, borax and a little oxide of tin. Nothing then remains but to dry the pieces, and heat them in an enamelling furnace. The coating obtained is very white, resists the action of fire without cracking, and completely resists acid or alkaline solutions.

CHAPTER XII.—*Of the Cutting of Glass.*

All the fine glasses called Bohemian crystal are cut. Vertical wheels of iron, wood or stone are used for this purpose, moved by off. The products of the decomposition of oil of mustard by powdered hydrate of potash are evidently the same as by an alcoholic solution of potash; but they are more difficult to trace out, since on employing the former the increase of temperature cannot be so readily avoided, and the oil of mustard is far less soluble in an aqueous than in an alcoholic solution of potash.

Boutron and Fremy state that they observed an evolution of hydrogen on treating oil of mustard with hydrate of potash. When powdered hydrate of potash is warmed with oil of mustard, a very violent reaction soon occurs, the oil beginning to boil as on the employment of an alcoholic solution of potash; ammonia is given off, but no hydrogen gas, and a portion of the alkali is then combined with the above-described acid.

The behaviour of the oil of mustard towards the chlorides, the heavy metals, potassium, the halogens and certain metallic oxides, in the total absence of water, promises further explanation respecting the nature of the oil of mustard; its combination with perchloride of mercury, precipitated from the alcoholic solution, contains chlorine and mercury no longer in the same proportion as in corrosive sublimate; it forms a crystalline combination with chloride of platinum under circumstances which have not yet been accurately ascertained, and which is gradually decomposed in the presence of water with disengagement of carbonic acid and formation of a dark powder; potassium does not decompose oil of mustard, as stated by some chemists, with explosion, but slowly and precisely like oil of garlic.

It was stated at the commencement of this treatise, that the anhydrous oil exposed for a long time (about three years) to daylight in a closed vessel became reddish-brown, of a far darker colour therefore than the crude oil. With this change of the oil in colour is connected the separation of a dirty orange-yellow body, which lines the sides and the bottom of the vessel like a thin membrane.

After pouring off the oil, the yellow body was washed with æther on to a filter, and dried *in vacuo*. It then resembled exactly in appearance the so-called sulphocyanogen, as obtained by decomposing sulphocyanide of potassium by chlorine; it exhibited not the least trace of crystallization under the miscroscope. It dissolved wholly in a solution of caustic potash on the application of a gentle heat with a yellow colour; upon the addition of acetic acid, some sulphur-yellow flakes separated, but nevertheless the clear solution (supersaturated with acetic acid) gave a pale yellow precipitate with acetate of lead; perchloride of iron did not produce the intense red colour, as it does with a soluble metallic sulphocyanide. On heating the body alone, it puffed up, acquiring a darker colour, and diffusing a strong odour of oil of mustard; it finally left a dull charcoal, which on ignition gradually disappeared.

The analysis gave 28·6 C, 5·87 H, 20·72 S; the formula corresponding most to these numbers is $C^{38} H^{44} N^{25} S^{10}$, which requires 29·1 C, 5·6 H, 44·7 N, and 20·5 sulphur. These proportions can however in no way be brought into connection with the composition of the oil of mustard.

The following is a tabular view of the formulæ of the combinations referred to in the present treatise:—

Oil of mustard (sulphocyanide of allyle)	$C^8 H^5 NS^2$ or $C^6 H^5 C^2 NS^2$.
Thiosinammine (oil of mustard and ammonia)	$C^8 H^8 N^2 S^2 = C^6 H^5, C^2 NS^2, NH^3$ or $C^8 H^6 N^2, H^2 S^2$.
Thiosinammine and perchloride of platinum	$C^8 H^8 N^2 S^2, ClH + PtCl^2$.
Thiosinammine and perchloride of mercury	$C^8 H^8 N^2 S^2 + 4HgCl$.
Sinammine	$C^8 H^6 N^2$.
Hydrate of sinammine	$C^8 H^6 N^2 + HO$.
Sinammine and perchloride of platinum	$C^8 H^6 N^2, 2ClH + 2PtCl^2$.
Sinammine and perchloride of mercury	$C^8 H^6 N^2 + 2HgCl$.
Sinapoline	$C^{14} H^{12} N^2 O^2$.
Muriate of sinapoline	$C^{14} H^{12} N^2 O^2 + ClH$.
Oily body I. (still hypothet.)	$C^{14} H^{14} N^2 O^2 S^2$.
Oily body II.	$C^{28} H^{25} N^3 O^4 S^4$.
Acid in the lead compound	$C^8 H^6 N S^4$.

The whole amount of sulphur is readily removed from the oil by the oxides of the heavy metals, and likewise by barytes; the eliminated sulphur, however, is not exchanged for the oxygen of the oxide; but it is at the same time accompanied by a certain quantity of carbon, which is to the sulphur precisely in the same proportion as in sulphuret of carbon. The rest of the oil of mustard takes up, in place of this sulphuret of carbon, an equivalent quantity of water, and we obtain sinapoline.

The sulphur of the oil of mustard can scarcely be removed entirely by dry metallic oxides, or by salts of the heavy metals, dissolved in absolute alcohol, except with the greatest difficulty and some decomposing influence, evidently because without a decomposition of water no carbon can accompany it. If, for instance, a solution of nitrate of silver in absolute alcohol be heated with oil of mustard, a black precipitate is obtained, which has not yet been closely examined; but this mixture may be kept boiling for several days with an excess of silver salt, and still the liquid will contain sulphur. But, if only a few drops of water be added, an evolution of gas immediately takes place, and the whole of the sulphur is precipitated as sulphuret of silver. The gas which is disengaged is carbonic acid; the liquid contains sinapoline. The same decomposition takes place with an alcoholic solution of acetate of lead.

If we treat oil of mustard with a powerful alkaline base, as hydrate of potash or soda, a similar, it might be said precisely the same mode of decomposition results; the eliminated sulphur is likewise accompanied by the same quantity of carbon, but the greater tendency of the alkaline metal to form a sulpho-base causes, as it were, the half of the sulphur in action (of the sulphuretted hydrogen formed) to combine with the still undecomposed oil of mustard to form a peculiar acid; the other half of the sulphur remains (as sulphuretted hydrogen) combined with the sinapoline, or rather prevents its formation.

The behaviour of the hydrate of potash to oil of mustard, compared with that of the oxide of lead, &c., is readily explained, and the mode of origin of products apparently so different becomes extremely simple if we imagine, at the formation of the sinapoline, only water to be acting instead of oxide of lead; we then obtain (which is here of the same importance), instead of sulphuret of lead, sulphuretted hydrogen.

On the formation of the oily body $C^{14} H^{14} N^2 S^2 O^2$, and of the acid $C^8 H^7 NS^4$, by the action of hydrate of potash, we have precisely the same reaction; the same quantity of carbonic acid and sulphuretted hydrogen is formed from the same quantity of oil of mustard; this sulphuretted hydrogen, however, does not in the latter case combine wholly with the oxide of potassium, but half goes to the sinapoline and half to the undecomposed oil of mustard. The half of the sulphuretted hydrogen which has united with the oil of mustard yields its hydrogen to the oxygen of the potash, and the potassium compound of the new acid is formed.

The oily body may, according to this, be regarded as a combination of sinapoline with sulphuretted hydrogen, and the acid as the combination of the oil of mustard with sulphuretted hydrogen.

Sinapoline, which belongs from the number of its atoms of carbon to the benzoyle series, is according to its formula, oil of bitter almonds + 2 equiv. ammonia. The oily body is then the corresponding combination of the oil of bitter almonds with sulphuret of ammonium.

The arrangement of the elements in the radical of the oil of mustard would appear to undergo some change from the reception of ammonia at the formation of the thiosinammine. Mustard oil combined with ammonia only parts with sulphuretted hydrogen on treatment with the oxides of the heavy metals, while all the carbon remains in the newly-formed base. Precisely the same relations are manifested between thiosinammine and the syrupy sinammine, with respect to their constitution, as between sinapoline and the oily body containing sulphur. The whole behaviour of sinammine shows that it is a compound base with ammonia, in which the one-half of the ammonia is less intimately combined than the other, which must be considered as combined with 8 atoms carbon. The thiosinammine would then be the combination of the sinammine with sulphuretted hydrogen.—*Ann. der Chem. und Pharm.*, liii. p. 1.

On the Action of Nitric Acid upon Oil of Turpentine.
By M. Rabourdin.

Bromeis obtained, by acting with nitric acid on oil of turpentine, a non-volatile acid, crystallizing in four-sided prisms, and represented by the formula $C^{14} H^9 O^7, HO$. There is moreover formed in the reaction a nitrogenous resin, which is partly soluble in ammonia. The author's results differ somewhat from the above.

If 500 grs. nitric acid and as much water be poured upon from 25 to 30 grs. oil of turpentine, a lively reaction takes place on warming it, with evolution of nitrous vapours; if it be kept boiling, and small quantities of turpentine continually added, until the resin which separated at first is again dissolved, and the whole then diluted with water, a saffron-coloured precipitate is obtained. The filtered solution yields crystals of oxalic acid on evaporation, if its colour had been light yellow; but if it had been brown, lamina crystals are obtained. By washing with cold water and frequent recrystallization, colourless, oblique, rhombic prisms are obtained, which are very sparingly soluble in cold water, but readily soluble in hot, have an acid taste and reaction, produce effervescence in carbonated alkalies, evolve ammonia when treated with caustic potash, and precipitate salts of lime; in short, exhibit all the properties of acid oxalate of ammonia. The crystals contain 20·44 per cent. C, 4·69 H, and 5·99 N. At 212° they part with 15·4 per cent. water, and then still contain 24·18 C, 3·61 H, 7·32 N. The formula $4(C^2O^3) + NH^3 + 4HO + 4Aq$ requires for the crystallized salt 20·56 C, 4·63 H, 6·06 N; the loss of water should be 15·4, and the dry salt yield 24·34 C, 3·55 H, 7·18 N; the salt is therefore quadroxalate of ammonia. If the brown mother-ley be again treated with nitric acid, it yields the same products as in the immediate treatment of the oil of turpentine with concentrated nitric acid.

If a small quantity of oil of turpentine be heated with concentrated nitric acid, an extremely violent reaction almost immediately ensues; if the addition of oil be continued for some time, always preserving an excess of acid, and it be finally boiled until the resin formed is wholly redissolved, a saffron-coloured resin is likewise deposited on dilution with water. The filtered solution yields, on evaporation to a syrupy consistence, an abundant crop of oxalic acid. The separated mother-ley deposits more resin on dilution with water, and then yields on evaporation granular crystals of a new acid. If these do not appear immediately, an equal volume of nitric acid is added to the mother-ley, which is then evaporated to its former volume.

This new acid, which the author calls *terebilic acid*, may be purified by repeated crystallization, especially from alcohol; it then forms small colourless four-sided prismatic crystals, which dissolve sparingly in cold, more readily in hot water, but best in alcohol and æther, have a pure acid taste, are not further attacked by concentrated nitric acid even on boiling, are not blackened by sulphuric acid, fuse without loss in weight at 392°, and are then decomposed without any residue into carbonic acid and *pyroterebilic acid*, which passes over as an oily fluid. Terebilic acid, dried at 212°, consists of—

Carbon........	53·18	53·00	52·90	14	=	1050	53·17
Hydrogen......	6·25	6·46	6·58	10	=	125	6·32
Oxygen........				8	=	800	40·51
						1976	

The salts of terebilic acid are nearly all soluble; the alkaline and earthy salts crystallize with great difficulty; a solution of the acid, or of its salts, produces in solutions of persalts of iron a blood-red the foot, or oftener by a water-wheel by means of pulleys and endless bands. The iron-mills are used to rough-grind the pieces, water is fed to them continually by means of a shoe placed above, and below is a box containing sand, which the workman throws by hand upon the mill. The pieces are then passed to wheels made of sandstone, and then upon wooden wheels, first with the mud from the sand previously employed, then with emery finer and finer, and finally finished with jewellers' putty, which is often put upon a dry wheel covered with cloth coated with this substance. For some years past many articles have been made partly polished and partly dull. The dull parts are obtained by rough-grinding the glass in spots without polishing it. Hydrofluoric acid liquid or gaseous prepared with 2 parts by weight of fluor spar and 4 parts by weight of concentrated sulphuric acid, is also often used for this purpose or for engraving upon the glass; care is then taken to cover all the glass with a varnish formed with 4 parts of wax and 1 part of essence of turpentine, which is then removed by a graver from the parts to be attacked.

Chapter XIII.—*On the Art of gilding, silvering, platinizing and incrusting Glass.*

Gilding.—To gild glass nearly pure gold is employed, which is dissolved in *aqua regia,* and then precipitated from its solution by caustic potash, or better still by protosulphate of iron, in which case the purity of the gold is altogether indifferent. The precipitate formed is washed upon a filter with boiling water, completely dried, then mixed with a little calcined and finely-powdered borax, and the whole reduced to a thick paste with a little essence of turpentine. This paste is applied upon the glass by a pencil; it is then placed in a muffle-furnace at a temperature sufficiently high to volatilize the turpentine and vitrify the borax. The gold is then found firmly fixed upon the glass, and all that remains is to burnish it, which is done first with a polisher of blood-stone, then with a burnisher of agate. The red and black glasses, the hyalite, and sometimes blue and green glass, are those principally gilded.

Silvering.—The silvering is performed precisely in the same way as the gilding. The powder of silver required is procured by precipitating nitrate of silver by a bar of copper. The silver harmonizes particularly well with the white, green and blue opaline glass.

Platinizing.—Platinizing is much less used than gilding and silvering, and is performed in the same way, the powder of gold or of silver being replaced by the double chloride of platinum and ammonia well-washed. The colour of the platinum approaches more nearly to that of steel than to that of silver.

Incrusting.—The art of incrusting in glass appears to have been invented in Bohemia about six centuries ago; it was afterwards entirely lost, and has but recently been recovered. At present they incrust in a great deal of glass, while making it, small objects in white clay, which have, when the glass is finished, a deceptive lustre and appearance of dull silver.

[To be continued.]

PATENT.

Patent granted to William Henry Ritchie, Lincoln's Inn, *for Improvements in obtaining Copper from Ores.*

This invention relates to the employment of galvanic currents for precipitating copper from solutions of sulphate of copper, obtained by dissolving copper ores. In previous attempts to effect this object, the exciting liquid and the solution of copper have been kept separate; but in the present instance the exciting liquid is in contact with the solution of copper. Another improvement consists in the application of cast iron for receiving the precipitated copper; though when using other parts of the invention other metallic surfaces may be employed, and these surfaces the inventor calls the "generating surfaces." Another part of this invention consists in combining sulphate of iron or zinc with copper ores, when they are being calcined or roasted.

The ores are mixed with as much sulphate of iron or zinc, in the state of crystals, as will be equal to one-fifth of the quantity of sulphate of copper contained in them; they are then calcined in the ordinary manner, and are afterwards dissolved; the solution is then put into any suitable vessel, and on the top of it is placed a solution of sulphate of iron, for the exciting solution. A cast iron plate or "generating surface," and a "conducting surface" or plate of lead, or other suitable metal, are now introduced; and being suspended from a rod of copper, or other suitable material, the copper in the solution becomes deposited on the leaden plate. As many pairs of cast iron and leaden plates may be used as the vessel will contain.

Owing to the difference in their specific gravity, the solution of sulphate of copper will be at the lower part of the vessel, and the solution of sulphate of iron at the upper part, and they will remain in contact without mixing. In the course of working, the solution of sulphate of copper will become lighter at the upper part than lower down, and should be drawn off when it has lost about half its copper; the solution of sulphate of iron, which is made by mixing 2 parts of water with 1 part of a saturated solution, becomes heavier at the lower part than at the upper, and should be drawn off when it is as dense as the weak solution of sulphate of copper that is being drawn off. To keep up a constant equilibrium in the liquids, an outlet is applied to the vessel, so that the solution of sulphate of copper may flow off at the upper part, whilst an equal quantity is entering at the inlet; and there is an outlet for carrying off the solution of sulphate of iron at the lower part of that liquid, whilst a corresponding quantity is admitted into the vessel at the inlet; the sulphate of iron thus drawn off may be crystallized, and used in the process of calcining the ores.—Sealed Oct. 10, 1844.

THE CHEMICAL GAZETTE.

No. LXVI.—July 15, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Double Salts of Tartaric and Racemic Acids.

By Dr. R. Fresenius.

In a former paper on the constitution and behaviour of the racemates, the author stated that he had not succeeded in obtaining a double salt of racemic acid with potash and soda. It was especially from this that he maintained the view that the racemic acid should be considered as a monobasic, tartaric on the contrary as a bibasic acid. Recently, however, Professor Mitscherlich has prepared the racemate of potash and soda, and agrees with Löwig in arranging racemic acid likewise among the bibasic acids.

1. *Racemate of Potash and Soda*, according to Mitscherlich, can only be obtained from a solution containing an excess of potash salt; according to the author, who obtained it by the following methods, this condition is not requisite.

a. Of two equal portions of an aqueous solution of racemic acid, one was saturated with carbonate of soda, the other with carbonate of potash; the two mixed and evaporated by the heat of the sun. *b*. Biracemate of potash was heated with water to boiling, neutralized with carbonate of soda, the solution evaporated and allowed to cool slowly. *c*. A solution prepared as in *b* was left to spontaneous evaporation. *d*. To a solution prepared as in *a* was added an excess of neutral salt of potash and then left to spontaneous evaporation. *e*. A solution prepared as in *a*, with the addition of an excess of neutral soda salt, and evaporated by exposure to the air. *f*. The same, with addition of carbonate of soda. This was evaporated and crystallized by cooling.

In all cases perfectly distinct and regular crystals of the double salt were formed. They constitute tolerably large, hard, colourless, transparent, rhombic tablets or columns of the triklinometric system. They do not effloresce by exposure to the air at a mean temperature, but slightly at the surface at a summer heat. They dissolve readily in water, 1 part of the anhydrous salt requires at + 42°, 2·11 parts or 1 part of the crystallized, 1·32 part (8·7535 solution left 2·8105 grms. of the salt dried at 356°). It dissolves in every proportion in hot water, and can be repeatedly recrystallized without decomposition. Between 194° and 212° the crystals melt to a clear tenacious fluid, which between 248° and 302° gradually becomes more turbid with violent ebullition, and then congeals to a white solid mass, which is not changed on further heating until at 392° it becomes brown, and at a gentle red heat is converted, under evolution of the well-known odour of burning sugar and with considerable tumescence, into a carbonate of potash and soda containing some charcoal. The salt, dried between 356° and 374°, attracts moisture from the air, but on solution exhibits all the properties of a racemate. However long the racemate of potash and soda be kept at 212°, it is impossible to expel the 25·49 per cent. (8 equiv.) water. In one experiment only 22·41 per cent. had disappeared after heating in a water-bath for seven hours; however, that this is solely owing to the fused state of the mass, and not to a more intimate mode of combination of the last atom of water, is immediately evident when the powder of the salt is mixed with an excess of pure fine sand and heated in the water-bath, when the whole of the water is given off within two hours. On recrystallizing a portion of the racemate of potash and soda at a temperature below 47°, the author obtained a salt with 6 equiv. water. The crystals so obtained likewise belonged to the triklinometric system, and could not be distinguished from the preceding in appearance and behaviour.

2. *Tartrate of Potash and Soda.*—The crystals of the tartrate of potash and soda belong to the prismatic system. Since it contains 8 equiv. water, resembling in this respect the first-described racemate of potash and soda, it results, as De la Provostaye has shown to be the case with respect to many others, that the combinations of racemic and tartaric acids with the same amount of water are not isomorphous. The anhydrous tartrate of potash and soda dissolves at 42° F. in 2·62 parts water (12·6804 solution left 3·4994 residue dried at 410°–420°); it is therefore somewhat less soluble than the corresponding racemate. Crystallized tartrate of potash and soda requires 1·70 parts. The crystals melt when heated to between 158°–176° to a clear limpid fluid, which boils at 248°. At 338°–356° the mass becomes tenacious, with large bubbles, and after a short time flows clear and quiet. At 374°–383° it begins to boil afresh, and only leaves off at 410°–420°. It then forms a tenacious clear mass, which remains transparent on cooling and attracts moisture from the atmosphere. At 428° it becomes brown, and passes at a gentle red heat into carbonate of potash and soda, with the same appearances as the corresponding racemate. The two salts, independently of other characteristics, may readily be distinguished by the circumstance, that the double tartrate forms a clear transparent mass after being deprived of its water, while the racemate has a white and turbid appearance.

With respect to the composition of the crystallized tartrate of potash and soda, it was formerly generally admitted to contain 10 equiv. = 29·7 per cent. water. Recently it has been ascertained, both by Mitscherlich and Schaffgotsch, to amount to 8 equiv. or 25·49 per cent.; and subsequently Dumas and Piria have determined it to be 7 equiv. or 23·03 per cent. The author entirely confirmed the statements of Mitscherlich and Schaffgotsch. It is evidently from the circumstance that Dumas and Piria employed a temperature not exceeding 356° that they found on drying only 23 per cent. water; and, in fact, the double salt, heated only so far, loses 7 equiv. water = 23·03 per cent. It is evident therefore that the last equivalent of water is retained with greater affinity than the remainder; and this is placed beyond all doubt when the double salt, mixed intimately with sand, is heated for some length of time in the water-bath, when only 7 equiv. water are expelled, while the last remains in combination.

We have now to consider whether racemic acid should be more correctly considered as a monobasic or as a bibasic acid. This question however depends on the solution of another, which is, what are the true characteristics of a mono- or polybasic acid?

Liebig, who first proposed the classification in question of the organic acids, gives, as characteristic of a monobasic acid, that "The acid salts of monobasic acids when placed in the presence of soluble bases are decomposed into two or more neutral salts, which may be separated by crystallization in case they are unequally soluble or are not isomorphous." As a practical characteristic of a bibasic acid, Liebig mentions, that "The acid salts of bibasic acids contain only 1 atom of acid, whence it happens that no separation results on neutralizing them with other soluble bases."

He views those as tribasic acids in which 3 equiv. of hydrate water must be admitted, each of which can be replaced by 1 equiv. of any base. To these definitions is moreover added, as serving to complete them, the decomposition at a higher temperature; but it is evident from the words that these characters are less general. From Liebig's original memoir, and the researches of others carried out in the same direction, it further results, that double salts of an acid with a base from the magnesian series and an alkali, may equally occur in a monobasic as in a polybasic acid, being formed by the replacement of the alhydrate water; and lastly, that acid salts of bases from the barytic or magnesian series, as also double salts of bases of the barytic series with alkalies, speak in favour of the bibasic or polybasic nature of the acid. Besides these characteristics, Hagen, who has directed attention to the circumstance that 1 atom of a salt can never be combined with ½ an atom of water, has advanced it as a characteristic of a bibasic acid. Fehling regards the hyposulphosuccinic acid as tetrabasic and succinic acid as tribasic; the former because the production of the hyposulphosuccinic acid is best explained on this supposition, the latter because succinic acid forms a basic salt of lead whose formula does not agree well with the assumption of the acid being monobasic; and because, moreover, bisuccinamide differs from the constitution of the other amides, and because on treating succinic æther with oxide of lead water is separated. Cahours comes to the same view as regards succinic acid, because in succinic æther 1 equiv. hydrogen cannot be replaced by chlorine. These characteristics are partly entirely opposed to each other, and partly lead to consequences which have neither been proposed, nor ever can be admitted. Potash and oxide of ammonium are admitted to be isomorphous, potash and soda not; consequently soda and oxide of ammonium are not isomorphous. Now why do we consider the existence of a double salt with soda and potash as affording proof, while no such power is ascribed to a double salt with soda and oxide of ammonium? Why do we not admit the equivalent of sulphuric acid to be double, since its acid salt of soda neutralized with ammonia does not yield two distinct salts, but one well-crystallized double salt? If racemic acid, since it forms such a beautifully-crystallized double salt with soda and potash, is a bibasic acid like tartaric acid, how does it happen that it splits into two when the acid salt of potash is neutralized with barytes, lime or strontia? how is it that it forms no acid salts with these bases and those of the magnesian series? If the first were true the second should obtain. If half an atom of water in a salt is opposed to the monobasic nature of an acid, how is it that we do not double the atomic weight of acetic acid, since its combination with strontia, when crystallized at a temperature above 59°, is represented by the formula $SrO, \bar{A} + 2\frac{1}{2}\,aq$? being, moreover, like racemic acid incapable of acting the part of a bibasic acid in other combinations,—how is it with sulphuric acid whose first hydrate is $SO^3 + \frac{1}{2}HO$? If the reasons advanced by Fehling and Cahours in favour of the tribasic nature of succinic acid are valid; if, accordingly, this acid is really a tribasic acid, how is it that it forms neither acid salts with barytes or magnesia, nor double salts with the alkalies, or with these and the bases of the barytic series? how does it happen that among all the salts examined by Döpping and Fehling there is not a single one in which 1 equiv. acid is combined with the oxides of three different radicals, a case which the prototype of a tribasic acid, the ordinary phosphoric acid frequently exhibits, for instance in the microcosmic salt (PO^5, NaO, NH^4O, HO)?

It is evident that it would not be difficult to increase the number of such questions; but those already enumerated are more than sufficient to prove that order and agreement in the classification under consideration can only then obtain when its principles and the practical characteristics of each class have been fixed in a more precise and definite manner than has hitherto been the case. Nothing will then be easier than to decide whether racemic acid is a monobasic or a bibasic acid.—*Ann. der Chem. und Pharm.*, 1845, liii. p. 241.

On Xanthine (*Xanthic Oxide*). *By* Dr. Unger.

We have already noticed* that Dr. Unger had found the xanthic oxide of Marcet in guano, and that he was engaged in experiments on this remarkable substance in Magnus's laboratory.

He advises retaining the name xanthine for this substance, as it forms definite compounds, not only with acids, but also with basic oxides. The xanthine obtained by treating the guano with muriatic acid and precipitation with an alkali, is always mixed with a brown substance, from which it is very difficult to separate it. It may how-

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* Chem. Gaz., vol. ii. p. 363.

ever be obtained free from it by digesting the guano with thin milk of lime until the liquid ceases on boiling to become of a brown colour, but appears of a pale greenish tint; it is then filtered and neutralized with muriatic acid, which throws down xanthine and uric acid. Boiling muriatic acid dissolves out the former, and on cooling deposits a crystalline compound of muriatic acid and xanthine; the crystals are recrystallized several times, and the xanthine separated by ammonia.

The xanthine used for analysis was obtained in four different ways. The first consisted in decomposing the muriate of xanthine by ammonia; the second, the sulphate of xanthine by ammonia; in the third, the potash salt was decomposed by carbonic acid; and in the fourth, the hydrate of xanthine was heated to expel its water.

The mean of all the analyses yielded—

		Calculated according to the formula $C^5 H^5 N^5 O$.
Carbon	39·58	39·56
Hydrogen	3·42	3·29
Nitrogen	46·49	46·62
Oxygen	10·51	10·53

In the experiments which Liebig and Wöhler formerly made on xanthine obtained from a calculus, they arrived at the following numbers:—

Carbon	39·57
Hydrogen	2·60
Nitrogen	36·95
Oxygen	20·88

As the main difference consists in the amount of nitrogen, it is possible that it arose from error in estimating this by their less accurate method. The following compounds were examined:—

Neutral Hydrochlorate of Xanthine (X, ClH) is obtained by allowing xanthine to absorb hydrochloric acid until it is saturated. It loses half its acid by exposure to a temperature below 212°, and in a current of air even at the ordinary temperature.

Basic Hydrochlorate of Xanthine (X^2, ClH) is obtained by heating the following compound to 212°, or by exposure to the air; at a higher temperature it parts with the whole of the muriatic acid gas.

Basic hydrated Hydrochlorate of Xanthine ($3(X^2, ClH) + 7Aq$) crystallizes from a solution of xanthine in hydrochloric acid. It parts with its water at a temperature below 212°, and at 392° with its hydrochloric acid.

Basic hydrated Sulphate of Xanthine ($X^2 SO^3 HO + 2Aq$) is obtained by dissolving xanthine in concentrated sulphuric acid and dilution with hot water, from which it separates in needles on cooling. These are decomposed by water, consequently they must be washed with alcohol. When heated to 248°, they part with 2 atoms of water; the third is not expelled even by a temperature of 392°.

Hydrate of Xanthine ($X^3 2HO$) is formed by diluting the sulphate copiously with water; it possesses the properties and aspect of xanthine, from which it differs merely in the quantity of water it contains. It may be dried at 212°, and retains its water at a slightly higher temperature, but if this be much elevated the whole escapes.

Basic Nitrate of Xanthine ($X^3\,2NO^5\,6HO$) is obtained by dissolving xanthine in boiling nitric acid, from which it crystallizes on cooling. It deliquesces on exposure to the atmosphere, and loses its acid at a high temperature.

Basic Tartrate of Xanthine ($3X,\ 2\bar{T}\,4HO$) crystallizes from a dilute very acid solution; it loses no water at 248°.

Basic Phosphate of Xanthine ($3X,\ 2P^2O^5,\ 2HO$) crystallizes with difficulty. It exists in the form of small grains. It may be dried at 212°, but parts with its water at 248°.

Basic Oxalate of Xanthine ($3X,\ 2C^2O^3 + 2HO$) is obtained on decomposing the muriate by oxalate of ammonia. It crystallizes with difficulty, but bears a temperature of 248° without loss.

Hydrated Xanthate of Soda ($NaO,\ X + 6HO$).—If xanthine be added to a concentrated warm solution of hydrate of soda as long as it is dissolved, and the solution be then copiously diluted with alcohol, an intricate net-work of crystalline laminæ of hydrated xanthate of soda is obtained; this deliquesces and readily absorbs carbonic acid when exposed to the air. When treated with water, some xanthine separates, whilst part remains in solution.

Hydrochlorate of Xanthine and Chloride of Platinum ($XClH + PtCl^2$) is deposited in groups of needles, when hydrochlorate of xanthine is treated with chloride of platinum. It is insoluble in acids, but readily dissolves in caustic and carbonated alkalies; in the latter case carbonic acid is evolved. Acids precipitate it from the sodaic solution unchanged.

Sulphate of Xanthine and Silver.—Nitrate of silver causes a very voluminous semitransparent precipitate in the most dilute solution of sulphate of xanthine; it cannot be washed, nor consequently analysed. When heated, it is thrown out of the crucible, and changed into a brown powder.

Nitrate of Xanthine and Mercury is difficultly soluble; it is crystalline. When heated it deflagrates without any peculiar noise.—*Bericht über die Verhandl. der Konigl. Preuss. Akad. zu Berlin*, April 1845.

On the supposed Occurrence of Phosphoric Acid in Rocks of Igneous Origin. By Prof. C. Kersten.

In the 'Philosophical Magazine,' vol. xxiv. p. 467, is an abstract of a paper by Mr. Fownes, on the occurrence of phosphoric acid in rocks of igneous origin. Mr. Fownes asserts that he found small quantities of phosphoric acid in combination with alumina, &c. in all these rocks, and supposes that it is probably to this presence of phosphoric acid that many soils which have originated by the decomposition of those rocks owe their fertility. He found phosphoric acid in a porcelain clay from Dartmoor, in the gray vesicular lava from the Rhine, and in the white trachyte from the Drachenfels on the Rhine, in tolerable quantity in the two latter rocks; further, in several basalts, in porphyritic lava inclosing crystals of hornblende from Vesuvius, and in volcanic tufa from the same locality in considerable quantity. As these observations of Mr. Fownes appeared of some importance in a geognostical and agricultural point of view, and, as far as I am aware, no phosphoric acid had hitherto been detected in the above-mentioned rocks, I was induced to repeat Mr. Fownes's experiments.

The following rocks were examined for phosphoric acid:—1st, porcelain earth from Aue in Saxony; 2nd, porcelain earth from Bayonne; 3rd, gray vesicular lava from Niedermennig on the Rhine; 4th, white trachyte from the Drachenfels; 5th, basalt from the Meissner in Hessia; 6th, Trass from Vesuvius.

The following was the mode of examination:—The finely-pulverized rocks were fused with 4 times the quantity of chemically-pure soda, the fused masses digested in water, and the liquids filtered from the insoluble residues neutralized with nitric acid. These neutralized liquids were now evaporated to dryness, and after treatment with water and separation of the silicic acid, tested with nitrate of silver and the other known reagents for phosphoric acid.

In all the above rocks, however, *not the least trace of phosphoric acid* could be detected; consequently the above-mentioned observations of Mr. Fownes are founded on some error. In the gray vesicular lava from Niedermennig there was found a quantity of *chlorine*; and on boiling it in the pulverized state with water and evaporating the liquid, small quantities of *chloride of sodium* were obtained; at the same time with this a brown organic substance was extracted, which coloured the water brownish on evaporation and was carbonified on ignition.—*Journ. für Prakt. Chem.*, March 31, 1845.

On a new Organic Acid found in an Oriental Bezoar. Extract of a Letter from Prof. Wöhler *to* M. Dumas.

I have been occupied in investigating a very remarkable organic body, which constitutes the oriental bezoars, and differs entirely from lithofellinic acid; it is a crystalline acid, insoluble in water, whose composition is represented by $HO\,C^{14}\,H^{2}\,O^{7}$; the solution of the potash salt in hydrate of potash, which has a very deep yellow colour, instantly absorbs oxygen from the atmosphere, and then deposits crystals of a bluish-black colour, which are $KO + C^{12}\,H^{2}\,O^{7}$.

It is especially in a physiological point of view that this bezoaric acid appears to me of interest; for it is either a product of the bile of the animals whence are derived the bezoars, or it is an immediate product of the nutriment of these animals.—*Comptes Rendus,* June 2, 1845.

On the Leaves of Coffea arabica *as a Substitute for Tea.*

Professor Blume of Leyden laid before the meeting of naturalists in Bremen samples of tea prepared from coffee-leaves, which in appearance, odour and taste of the decoction agreed entirely with that from genuine Chinese tea. It has long been employed as such by the lower classes of people in Java and Sumatra. The coffee-leaves are readily distinguished from those of tea by being larger, broader, with the margin entire and wholly smooth, while tea-leaves are narrower and constantly serrated at the margin.—Buchner's *Repertor. für Pharm.*, xxxvii. p. 34.

On the Chemical Composition of Fungi. By Dr. F. SCHLOSSBERGER *and* Dr. O. DOEPPING.

In most dietetic writings, the Fungi occupy a pretty high rank among the nutritive articles of food; and on this account they obtain a prominent part in our materia medica, whether classified under the head of mere articles of diet, or under that of the aphrodisiaca. It is generally supposed that these effects of the edible fungi are owing to the quantity of nitrogen they contain, and for this reason they are also considered as nearly allied to the animal kingdom. This supposition however could not be considered as based upon a scientific foundation until it was confirmed by actual experiment, although many of the phænomena regarding fungi—particularly their great aptitude to pass into decomposition and putrefaction—rendered it extremely probable. Now that Boussingault has given us, in the determination of the quantity of nitrogen they contain, a much more easily applicable, and a much more certain test, for ascertaining the *nutritive power of our aliments,* than was afforded us by the previous experiments, and also given to us a standard of comparison, *by fixing the amount of nitrogen,* in numerous substances, by direct experiment; it appeared that an attempt to determine the quantity of nitrogen contained in various species of fungi, perennial, as well as some of their representatives whose existence is limited to a few weeks, or even days, would not be destitute of interest. For this purpose, the fungi were first carefully dried at a temperature of 212° F.; and after the quantity of inorganic matter had been ascertained, the amount of nitrogen was determined by the method of Varrentrapp and Will, slightly modified.

The following fungi were examined by us:—

	In 100 parts of the fresh fungus are				In 100 parts of the dried (at 212° F.) substance.	
	Water.	Sol. sub.	Ashes.	Nitrogen.	Ashes.	Nitrogen.
1. Agaricus deliciosus (L.)	80·9	13·1	0·90	0·61	6·9	4·6
2. Agaricus arvensis (Schaeff.)	90·6	9·4	1·08	0·77	11·6	8·3
3. Agaricus glutinosus	93·7	6·3	0·30	0·29	4·8	4·6
4. Agaricus russula (Scoff.)	91·2	8·8	0·83	0·37	9·5	4·2
5. Agaricus cantharellus (L.)	90·6	9·4	1·05	0·30	11·2	3·2
6. Agaricus muscarius (L.)	90·5	9·4	0·84	0·59	9·0	6·3
7. Boletus aureus (Sch.)	94·2	5·6	0·38	0·26	6·8	4·7
8. Lycoperdon echinatum (L.)					5·2	6·1
9. Polypones fomentarius					3·0	4·4
10. Dædalea quercina					3·1	3·2

The incineration was, in the most of these fungi, of very difficult accomplishment, and did not succeed perfectly without the addition of a few drops of concentrated nitric acid. The ashes were rich in phosphates, and contained a considerable quantity of manganese (a metal frequent in the soil near Giessen).

The watery extract of most of the fungi, when exposed to the atmosphere, soon became decomposed, the fluid becoming at the same time turbid and very offensive. Among the gases which were generated, sulphuretted hydrogen could be distinctly perceived.

In considering the result of the above investigations, we find that the fungi contain perhaps a larger quantity of water than any other alimentary vegetable, scarcely excepting some juicy fruits, which however seldom come under consideration as pure articles of diet. This excessive quantity of water gives an easy explanation of many striking phænomena observable in these curious vegetable bodies, especially of their proverbially rapid growth, as they spring up after rain in a few hours or days from the smallest rudiment to growths the size of the fist. It also naturally explains the great tendency the fungi have, beyond every other vegetable, to pass into decomposition and putrefaction, as along with a large quantity of water, coupled with a very simple structure, they contain among their solid ingredients a considerable quantity of proteine. The fungi therefore are indeed remarkable for the large quantity of nitrogen they contain, and greatly surpass in this respect, setting aside their large proportion of water, most of our vegetable alimentary substances. Those of the above-named fungi which are poorest in nitrogen approach in the quantity of that aliment the richest in that respect of our common vegetable aliments, for instance peas and beans, which contain in the dried state, according to Boussingault, from 3 to 5 per cent. Most of the fungi, dried at 212° F., contain twice or three times as much nitrogen as wheat.

Unfortunately, our materials were insufficient to make detailed analyses of the ashes of some of the fast-growing fungi, although we determined their total quantity. In all the fungi which we examined we remarked a decided preponderance of phosphates, which appear therefore to stand in direct relation with the quantity of the *proteine* substance. We may now therefore place upon a scientific basis the view which hitherto has rested upon mere probability, viz. that the *fungi possess a considerable alimentary power* in the strictest sense of the term, and that they may powerfully promote the direct formation of blood.

In our experiments we included some poisonous fungi, partly because it may be possible, with little difficulty, to render them available as aliments, either by the mode of cooking or by a slight addition; and partly because the quantity of nitrogen they contain must give them, when obtained in sufficient quantity, a considerable value as organic manure, even compared with guano, which when dried at 212° F. contains, according to Boussingault, only about 6 per cent. of nitrogen. However, agricultural experiments must decide this point.

With reference to the proper substratum of the fungi, namely, their fibres, when properly cleaned, Payen and Fromberg agree that they coincide entirely with *cellulose*; and hence the *fungine* of Braemos and other chemists has been struck out of the list of vegetable proximate substances. We had abundant opportunity, in the course of our experiments, to corroborate these results, as in the fibres of *Polyporus, Dædalea,* &c. It appears remarkable, that scarcely any trace of the phosphates could be discovered in the decayed wood on which the *Dædalea* grew, while in that fungus itself they were present in considerable quantity. Fresenius and Will observed the same fact in the mistletoe, growing on an apple-tree.

With regard to the question, whether the fungi contain *amylum,* we were unable, in any one instance, to produce a blue tint by simply touching the fungus with tincture of iodine; although with the aid of the microscope we detected in the expressed juice of some, as for instance of the *Cantharellus cibarius,* a few grains which were by this means rendered blue. At the same time however we saw many grains, similar in size and shape to those of starch, which were coloured intensely yellow by the iodine. In a few cases iodine produced a greenish hue, which was owing perhaps to the mixture of the blue and yellow grains.

In almost all the mushrooms which we examined we could also detect *mannite, fermentable sugar*; and we made the interesting observation, that many of the succulent fungi (for instance *A. russula, cantharellus, emeticus*), when preserved for some days in a bottle with a narrow neck, but not closed, passed *spontaneously into spirituous fermentation.* They emitted at the same time a very agreeable odour of musk, and on distillation yielded alcohol. Genuine yeast cells were produced, and there was a strong development of carbonic acid. It would therefore appear that the proteine substance of the fungi passes very readily into that state of decomposition, by means of which the sugar which they contain (or the substance which forms sugar, inuline, &c.) is brought into fermentation.—Liebig's *Annalen* for Oct. 1844, as inserted in *Lond. and Edinb. Monthly Journal of Med. Science* for June 1845.

On the Urine in Morbus Brightii. *By* Dr. J. Schlossberger.

It is well known that albumen occurs in the urine in several diseases, so that its presence cannot be considered as a positive indication of that malady. The same holds good with the pouch-like, contorted bodies, which Henle considers as croupy formations from the finest tubuli of the cortical substance.

As regards the composition of the urine, Scherer found a great diminution of the solids, once 12·4, and at another time only 11·7 in 1000 parts, which amounts are exceeded by the contents of healthy twice at least, and generally 3 or 5 times. Simon did not find this variation constant; he even sometimes found it increased. However, in nearly all the analyses a considerable diminution in the amount of urea was found; with a single exception this amounted to $\frac{1}{6}$–$\frac{1}{3}$ of the normal quantity. The urea does not appear to be formed in diminished quantity, but to be partly retained in the blood, in which it has been detected by Babington, Christison and Simon. Schlossberger likewise detected the urea in the serum effused into the cerebral ventricles.—*Jahr. für Prakt. Heilk. von Oesterlen.*, n. i. s. 38–41.

ANALYTICAL CHEMISTRY.

On the Behaviour of Zinc towards Biphosphate of Soda and fused Phosphoric Acid. By M. TROMMER.

IF a small quantity of zinc be added to a bead of the phosphatic salt, and then heated before the blowpipe, a very distinct evolution of bubbles of gas is observed at a high red heat, which, when they appear on the surface of the bead, burst, and burn with a beautiful vivid flame. The appearance is still more beautiful if the bead, after it has been heated to redness, is allowed to cool slowly, as during the cooling the disengagement of gas continues, and the bubbles which burst through the surface burn even at a low temperature with the very characteristic light. This may be repeated several times with the same bead, and always with the same result. On a superficial inquiry into this fact, the zinc, as a volatile metal which burns at a temperature of 752°, and, with access of oxygen, likewise with a lively flame, would be considered as the cause of it. However, it is soon seen that the phænomenon is totally different from that produced by incandescent zinc; further, that not a trace of oxide of zinc is perceptible on the charcoal, which should be the case if the zinc were the cause of the flame; and thirdly, that the light still continues to appear after the bead has begun to cool, consequently that the body producing this phænomenon is more volatile and combustible than zinc. From the colour of the light and the white rings which ascend after the combustion, it is evident that the cause of this phænomenon must be sought for in the formation of phosphorus; and, in fact, when a mixture of fragments of zinc and biphosphate of soda is heated to redness in a small bulb apparatus, phosphorus is distinctly seen to distil over and to collect at one extremity of the apparatus. This experiment succeeds best when the atmospheric air has been expelled from the apparatus by carbonic acid, and a continuous current of carbonic acid is passed over it during the application of heat, since otherwise a portion of the phosphorus burns in the presence of atmospheric air, yielding a mixture of phosphorus and oxide of phosphorus. If the residue be extracted with water, phosphate of zinc may be detected in the filtered liquid, it being extremely difficult to expel the whole of the free phosphoric acid in this manner.

What is most remarkable in this phænomenon is the direct decomposition of the hydrated phosphoric acid; with vitreous phosphoric acid, when fused with a piece of zinc upon charcoal, the decomposition is so violent that fragments of burning phosphorus are thrown about. Anhydrous phosphoric acid yields the same result. With a little practice this behaviour of zinc towards biphosphate of soda may be employed as a blowpipe test for the metal in the more easily-fusible alloys.—*Journ. für Prakt. Chem.*, xxxiv. p. 242.

Test for Sugar in Urine.

Löwig recommends the following method:—Evaporate the urine to the consistence of a syrup; then exhaust the residue with alcohol. The alcoholic urinary solution is then mixed with an alcoholic solution of potash, when, if sugar be present, a white precipitate, a compound of sugar and potash, is formed, which, when washed with alcohol and then dissolved in water, yields a saccharine solution, which is fit for any further examination, and from which the amount of sugar may be ascertained quantitatively if necessary.—Buch. *Rep.*, vol. xxxviii. part. 2.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

An Account of the Manufacture of Glass in Bohemia.

By L. P. DEBETTE.

[Concluded from p. 291.]

CHAPTER XIV.—*Manufacture of Looking Glasses.*

ALMOST all the looking glasses made in Bohemia are small and blown; there is but one establishment, that of Deffernich, belonging to MM. Abele, where they cast their mirrors, and these proprietors being of French origin, use the processes of our own country. I shall therefore have but little to say upon this manufacture.

The Bohemian looking glasses are of potash base, as we have seen, and have for their formula $(\mathrm{K\,Ca\,Al})\,\mathrm{S}^3$; while the French glasses have soda for their base, and their composition, according to Dumas, is expressed by $(\mathrm{N\,Al\,Ca})\,\mathrm{S}^6$. This difference arises from the fact that potash being a less energetic flux than soda, it is necessary to use a much more considerable quantity in order to produce a glass of the same fusibility, and even then the glass produced is less hard than that of soda base, which joined to the greater cheapness of the latter has caused a preference for it, as is the case in France.

Manufacture of Blown Looking Glasses.—The blown looking glasses are made in rectangular furnaces, containing upon each shelf three circular pots, which last from three to four months, and hold about 396 lbs. Each melting furnace has six flattening kilns annexed to as many annealing ovens, and arranged exactly as those of which we have spoken in the article upon the manufacture of window glass, with these differences:—1st, that they are larger; and 2nd, that they place the fuel upon a lateral brick grate, separated by a small bridge from the flattening kiln, from which the flame passes into the annealing oven.

In all these two firemen and five melters are employed at the melting furnace, and three workmen at the flattening kilns. The manipulation is the same as in the manufacture of window glass, and consists in blowing large cylinders, which are then opened in the direction of their axes, only the operation is more difficult in consequence of the size of the pieces worked. After 24 hours' melting, the five melters begin to work the glass of one of the pots; they then rest for two hours, pass to the second pot, and so on. The working of each pot lasts about 2 hours, so that a complete melting lasts about 48 hours; and there is used in this time, in the melting and flattening furnaces (1925·694772 cubic feet), about 15 cords of wood dried in the air.

Manufacture of Cast Mirrors.—The cast mirrors are manufactured exactly as at St. Gobain. The furnace is square, and holds four pots having the forms of a reversed pyramid with a square base, which contain each 246·5 lbs. of glass. When the melting is finished, the thin brick wall opposite to each pot is destroyed, and the pots are then moved to the casting table by means of a carriage composed of curved tongs mounted upon wheels, the degree of separation of which tongs may be regulated by means of a ring sliding upon their handles. The casting table is of copper, and upon the edges are placed two rules of iron parallel to each other, and of a variable height according to the thickness to be given to the mirror; between these the glass is run. The surface of the cast mass is then flattened, whilst it is still soft, by means of a hollow cast-iron roller welded to a wrought-iron axle about 20·5 inches in diameter, which moves upon the iron rules, and weighs from about 650 to 1000 lbs., according to the size and thickness of the mirrors cast. The mirror and the slab which supports it are then slid into an annealing oven previously heated to dull redness, where it is left to cool very slowly.

The Polishing of Mirrors.—The mirrors, whether blown or cast, must be polished before being silvered. This polishing requires a previous rough grinding, which is performed by rubbing one glass over the other with river sand, a granulated and pulverized quartz, or even simply pounded granite interposed; for this purpose the glasses are fixed with gypsum upon slabs of lithographic limestone, which is obtained from Nuremberg.

A water-wheel gives a backward and forward motion to the upper slabs, which are allowed to turn upon themselves, and which slide over the lower slabs which are fixed; the only labour of the workman consists in giving, from time to time, a motion of rotation to the upper slabs, and stirring up the mixture of sand and water upon the lower slabs with a wooden trowel. Of course, sand more and more fine must be used as the operation advances. A single workman can attend to two large glasses or to four small ones. After this the polishing of the glasses is executed by rubbing them with a row of small slabs of Nuremberg limestone, either four or eight, according to the size of the glasses to be polished, and provided upon their rubbing surfaces with felt, coated with colcothar (jeweller's rouge, red oxide of iron).

Silvering the Mirrors.—In silvering the glasses a large slab of Nuremberg lithographic limestone is used, upon which is first spread a sheet of tinfoil by means of a wooden roller, which is then smoothed with a hare's foot, and an excess of mercury poured upon it, which is spread with the same hare's foot until the foil is entirely amalgamated. During this operation a part of the mercury flows off, and is collected upon a table with raised edges, upon which the slab rests. The mirror to be silvered is then slid upon the edge of the lithographic stone, and finally laid flat upon the amalgam of tin, which attaches itself to it. The glass is then covered with slabs of the limestone (wrapped in muslin, so as to avoid scratching it), in order to free it by pressure from the greatest part of the excess of mercury. Twenty-four hours afterwards the whole is lifted up, and the glass is moved to the upper story of the shop, where it is placed upon trestles, first horizontal, then gradually inclined until the mirror has a vertical position. It rests in this way for several days, and may then be exposed for sale. The entire duration of an operation of silvering lasts from two to four weeks, according to the size of the mirrors.

Chapter XV.—*A general Statistical View of the Glass Works of Bohemia.*

The glass works of Bohemia may be divided into three distinct groups. The first two, situated, the one in the north in the Riesengebirge, the other in the south in the Böhmerwaldgebirge, are employed in the manufacture of glass in general; whilst the third, situated in the west in the part of the Böhmerwaldgebirge belonging to Bavaria, includes only manufactories of blown mirrors. In fine, there are in Bohemia one manufactory of cast mirrors (Deffernich); thirty-one manufactories of blown mirrors, of which seven make beside table glass; and sixty-seven glass works properly so called, of which thirteen manufacture window glass, fifteen fine table glass or Bohemian crystal, one hyalite (Georgenthal), one composition glass (Josephthal), one flint glass (Neufelt), and five in which they mould under pressure.

There exists besides in the north of Bohemia, principally near Hayden, a very great number of small establishments, which are employed either in the cutting and finishing of glass which they buy in a rough state at the manufactories, or more frequently in the manufacture of false pearls, which are made of small hollow bulbs of glass into which a solution of the scales of the bleak (*leuciscus*) in æther has been introduced. These different glass works afford subsistence to more than 30,000 persons.—*Annales des Mines*, iv. p. 553; as inserted in the *Journal of the Franklin Institute* for April 1845.

Adulteration of Iodide of Potassium.

M. Destouches found in some iodide of potassium derived from Paris 22 per cent. carbonate of potash. The preparation was milk-white, turned red litmus-paper strongly blue, and effervesced with weak acids.—*Journ. de Pharm.*, 1845, p. 133.

Mode of ascertaining the Purity of Myrrh. By M. Righini.

The myrrh is finely pulverized and triturated for a quarter of an hour with an equal weight of sal-ammoniac powder, then 15 times the weight of water gradually added. If the whole dissolve quickly and entirely, the myrrh is pure.—*Journ. de Chem. Med.*, 1844, p. 33.

PROCEEDINGS OF SOCIETIES.

Royal Society.

May 22, 1845. "Memoir on the Rotation of Crops, and on the Quantity of Inorganic Matters abstracted from the Soil by various plants under different circumstances." By Professor Daubeny, M.D., F.R.S.

The author was first led to undertake the researches of which an account is given in the present memoir, by the expectation of verifying the theory of DeCandolle, in which the deterioration experienced by most crops on their repetition was attributed to the deleterious influence of their root-excretions. For this purpose he set apart, ten years ago, a number of plots of ground in the Botanic Garden at Oxford, uniform as to quality and richness, one-half of which was planted each year, up to the present time, with the same species of crop, and the other half with the same kinds, succeeding each other in such a manner that no one plot should receive the same crop twice during the time of the continuance of the experiments, or at least not within a short period of one another. The difference in the produce obtained in the two crops, under these circumstances, would, the author conceived, represent the degree of influence ascribable to the root-excretions.

The results obtained during the first few years from these experiments, as well as from the researches which had, in the mean time, been communicated to the world by M. Braconnot and others on the same subject, led him in a great measure to abandon this theory, and to seek for some other mode of explaining the falling-off of crops on repetition. In order to clear up the matter, he determined to ascertain, for a series of years, not only the amount of crop which would be obtained from each of the plants tried under these two systems, but also the quantity of inorganic matters extracted in each case from the soil, and the chemical constitution of the latter, which had furnished these ingredients. The chemical examination of the crops, however, on account of the labour it involved, was confined to six out of the number of the plants cultivated; and of these, three samples were analysed, the first being the permanent one, viz. that cultivated for nine or ten successive years in the same plot of ground; the second, the shifting one, obtained from a plot which had borne different crops in the preceding years; the third, the standard, derived from a sample of average quality, grown under natural circumstances, either in the Botanic Garden itself, or in the neighbourhood of Oxford. These analyses were performed by Mr. Way.

The examination of the soils was carried on in two ways; the first, with the view of estimating the entire amount of their available ingredients; and the second, with that of ascertaining the quantity in a state to be taken up at once by plants, the available ingredients being those which are soluble in muriatic acid; the active ones, those which are taken up by water impregnated with carbonic acid gas. This portion of the investigation was conducted in part by the author, and in part by Mr. Way, and has reference to three subjects; first, to the amount of produce obtained from the deficient crops; secondly, to their chemical constitution; and thirdly, to the nature of the soil in which the crops were severally grown.

The plants experimented upon were spurge, potatoes, barley, turnips, hemp, flax, beans, tobacco, poppies, buckwheat, clover, oats, beet, mint, endive, and parsley. The only crop which seemed to show the influence of root-excretions was *Euphorbia Lathyris*, which would not grow in the same ground three years successively, although the soil was found afterwards fitted for rearing several other species of plants. In the remaining cases, there was in general a marked difference between the permanent and the shifting crop, to the disadvantage of the former; and where exceptions occurred to this rule, they seemed capable of being accounted for by accidental causes. The amount of each year's crop is given in a tabular form, and their differences illustrated by diagrams showing the relation between the two crops of each vegetable.

The second part of the memoir commences with an account of the method of analysis pursued by the author for determining the nature and proportions of the ingredients present in the ashes of the crops submitted to examination. This method was, in general, similar to that recommended by Will and Fresenius in their paper published in the 'Philosophical Magazine,' No. 169; but in determining the amount of phosphoric acid, the following mode was adopted in preference to the one therein given.

As the phosphoric acid would seize upon the iron in preference to any other base, the amount of peroxide of iron present in the ash was first determined by precipitating it from a muriatic solution by means of acetate of ammonia. The weight of the precipitate gives that of phosphate of iron, from which that of the peroxide of iron may be readily calculated. This being ascertained, he proceeds to determine the phosphoric acid by operating on a fresh portion of the solution of the ash, into which a certain known weight of iron dissolved in muriatic acid is introduced, in quantity more than sufficient to unite with the whole of the phosphoric acid present. This done, acetate of ammonia is added and the mixture boiled, when all the peroxide of iron, whether combined with phosphoric acid or not, is thrown down. From the weight of the precipitate, that of the phosphoric acid present may be calculated, as both the amount of peroxide of iron present in the ash, and that which was added subsequently, are known.

A report is then given of the analysis of the ashes of barley, of the tubers of potatoes, of the bulbs of turnips, of hemp, of flax, and of beans, all cultivated in the Botanic Garden; and from the data thus obtained, the quantity of inorganic matters abstracted from the soil in ten years by the above crops is deduced; and a table is given showing the relation between the permanent and shifting crops, with respect to their produce, the amount of inorganic matters, that of alkali, and that of phosphates, contained in them.

In the third part of his paper, the author considers the chemical composition of the soil in which the above-mentioned crops were grown. He states, in the first place, the method he adopted for determining the amount of phosphoric acid present in the soil.

An analysis is then given of the soil taken from a portion of the garden contiguous to that in which the experiments were carried on, and from one of the plots of the garden itself; and from these data a calculation is made, that the ground at present contains enough phosphoric acid for nineteen crops of barley of the same amount as the average of those of the permanent crops, and of the same quality as that obtained in 1844. It was also found, that there was a supply of potass sufficient for fifteen crops of barley; of soda, for forty-five; and of magnesia, for thirty-four. When, however, we examine how much of these ingredients is taken up by water containing carbonic acid, the proportion of each is found to be much smaller; and a striking difference exists, in this respect, between the soil which had been recently manured and that which had been drawn upon by a succession of crops. In the first case, the quantity of alkaline sulphate obtained in the pound was 3·4 grs.; in the latter it varied from 0·7 to 0·07; and of phosphate, the quantity in the former was about 0·3, whilst in the latter it varied from 0·18 to 0·05.

From these facts the author concludes, first, that the falling-off of a crop after repetition depends, in some degree, on the less ready supply of certain of the inorganic ingredients which it requires for its constitution; but that two crops equally well supplied by the soil with these ingredients may take up different quantities of them, according as their own development is more or less favoured by the presence of organic matter in the soil in a state of decomposition.

Secondly, that it is very possible that a field may be unproductive, although possessing abundance of all the ingredients required by the crop, owing to their not being in a sufficiently soluble form, and therefore not directly available for the purposes of vegetation: so that, in such a case, the agriculturist has his choice of three methods; the first, that of imparting to the soil, by the aid of manure, a sufficient quantity of these ingredients in a state to be immediately taken up; the second, that of waiting until the action of decomposing agents disengages a fresh portion of those ingredients from the soil (as by letting the land remain fallow); and the third, that of accelerating this decomposition by mechanical and chemical means.

Thirdly, that it is probable that in most districts a sufficient supply of phosphoric acid and of alkali for the purposes of agriculture lies locked up within the bowels of the earth, which might be set at liberty and rendered available by the application of the artificial means above alluded to.

Fourthly, that the aim of nature seems to be to bring into this soluble, and therefore available condition, these inorganic substances by animal and vegetable decomposition, and therefore that we are counteracting her beneficial efforts when we waste the products of this decomposition by a want of due care in the preservation of the various excrementitious matters at our disposal.

Fifthly, that although we cannot deny that plants possess the power of substituting certain mineral ingredients for others, yet that the limits of this faculty are still imperfectly known, and the degree in which their healthy condition is affected by the change is still a matter for further investigation.

Lastly, that the composition of various plants, as given in this paper, differs so widely from that reported by Sprengel and others, that we are supplied with an additional argument in favour of the importance of having the subject of ash-analysis taken up by a public body, such as the Royal Agricultural Society of England, possessed of competent means and facilities for deciding between the conflicting authorities, and supplying us with a more secure basis for future calculations.

PATENT.

Patent granted to Wilton George Turner, Gateshead, Durham, *for an improved Mode of directing the Passage of, and otherwise dealing with, the noxious Vapours and other Matters arising from Chemical Works in certain cases.*

This invention consists chiefly in the application of a draft, produced by mechanical means, to the manufacture of sulphuric acid, muriatic acid and sulphate of soda, and to various metallurgical operations (such as roasting and smelting ores), in aid of, or as a substitute for, the ordinary draft produced by a chimney; by which means, together with certain improved processes, the condensation of that portion of the acid gases and metallic fumes which are allowed to escape into the open air in the usual modes of manufacture is effected.

The apparatus for condensing the fumes arising from various metallurgical operations consists of a vessel, similar in form to the ordinary waggon-shaped boiler, connected at one end with the furnace from whence the fumes proceed, and furnished with a vertical funnel or chimney at the other end; a horizontal shaft passes through the vessel lengthwise, having a large screw upon it, which extends from the furnace-end of the vessel to the chimney-end; and in the spaces between the turns of the screw long arms are fixed upon the shaft, corresponding in length with the radius of the thread of the screw. Water is allowed to flow into the vessel until the edge of the screw is immersed from three to four inches; then a rapid rotation is given to the screw-shaft, and the fumes entering from the furnace are violently beaten about with the water until thoroughly wetted, when becoming too heavy to pass on with the draft they fall to the bottom of the vessel: the water is drawn off from time to time into receivers, in which the metal becomes deposited. When no corrosive gases accompany the fumes, the vessel is made of iron; but if corrosive gases are evolved, the vessel is built of brick or stone, cemented with fire-clay, and the screw is made of or covered with lead.

The means by which the patentee produces a draft and a perfect condensation of the acid gases in the manufacture of sulphuric acid are as follow:—The new part of the apparatus consists of a series of three air-tight wooden vessels or condensers lined with lead; into the lower part of the first condenser, the draft-pipe from the ordinary sulphuric acid chamber is introduced, and its end is covered with acid to the depth of two or three feet; from the top of this condenser a pipe is conducted in like manner into the lower part of the second, and its end is covered with acid; and from the top of the second a pipe is likewise carried to the third. The last condenser (which is only half the size of either the first or second) is connected with two air-pumps, of sufficient capacity to draw through 162,000 feet of air for every 100 lbs. of sulphur burnt, and cause a partial vacuum in the upper parts of the condensers; in consequence of which the gases from the acid-chamber will force their way in a continuous stream through the acid in the condensers, being diffused therein by two inclined leaden plates fixed in the lower part of the first and second condensers.

The patentee states that, in the present mode of manufacturing sulphuric acid, there are three causes which produce the loss of nitre, viz.,—1st, the complete decomposition of nitric acid which accompanies the formation of the crystalline compound of sulphuric and hyponitrous acids; 2nd, the absorption of a portion of nitric acid by the sulphuric acid of the chamber; and 3rd, the escape of nitrous acid from the chamber through the draft-pipe. This loss he prevents, or greatly diminishes,—1st, by avoiding the formation of the crystalline compound of sulphuric and hyponitrous acids, by not throwing in steam; using nitric acid in the acid chamber, instead of nitre in the furnace, thus limiting the action which produces the sulphuric acid to the absorption of the sulphurous acid by the chamber acid, so as to render the great height of the ordinary acid-chamber unnecessary, the top of the chamber, in this case, being not more than two feet above the chamber acid, which is about one foot deep; and 2nd, by the application of the condensers and air-pumps.

In manufacturing the sulphuric acid, the following is the mode of operating:—The acid-chamber is charged with acid of from 1·5 to 1·6 spec. grav., and an addition is made thereto of 3 or 4 per cent. of nitric acid; the first and second condensers are charged with the same, which is kept at a heat of 140° F. by steam-pipes passing through them; and the third condenser is charged with sulphuric acid of 1·7 spec. grav. The air-pumps are now worked, and the sulphur is burnt in the furnace without the addition of nitre. The fumes entering the acid-chamber are absorbed by the chamber acid, and converted into sulphuric acid; but some portion of the sulphurous acid escaping condensation passes through the draft-pipe into the first condenser, where coming in contact with the nitric acid it is converted into sulphuric acid. This is accompanied with the evolution of deutoxide of nitrogen, which mixing with the air in the condenser passes in the form of nitrous acid vapour into the second condenser, and is there condensed; in this way the acid in the first condenser soon loses all its nitric acid, which must be replaced by allowing a small quantity (say 2 or 3 per cent.) to flow in at intervals through a stop-cock at the top. When the sulphuric acid in the first condenser approaches 1·7 spec. grav. the action becomes imperfect, and a portion of the sulphurous acid passes into the second condenser, where it is converted into sulphuric acid, and the nitrous fumes produced pass into the third condenser; at the same time the supply of nitric acid to the first condenser must be stopped, in order to obtain the sulphuric acid perfectly free from nitric acid. As soon as all the nitric acid has passed from the first condenser, the acid in the third, which has now become nitrous, is allowed to flow into the acid-chamber, and a new charge is drawn from the first condenser; the remaining acid in the latter is now drawn off for use, and it is recharged from the acid-chamber. To keep the acid in the second condenser in working condition, its strength (which has the same tendency to increase as that of the acid in the first condenser) is kept down by the addition of water.

To condense muriatic acid in the manufacture of sulphate of soda, a similar set of air-tight vessels and air-pumps may be connected with the furnace in which the salt is decomposed, and the condensation effected by means of water; but as the volatility of the solution of muriatic acid, particularly under the diminished atmospheric pressure caused by the air-pumps, renders their use somewhat objectionable, the patentee prefers to employ the screw-draft apparatus, passing the gases through two vessels furnished with screw-shafts. In this case the vessel should be built of close-grained sandstone cemented with fire-clay, and the screw made of or lined with fire-brick material; the screw may be about three feet in diameter, and fixed upon a wooden shaft.—Sealed August 22, 1844.

THE CHEMICAL GAZETTE.

No. LXVII.—August 1, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Hippuric Acid and its Salts. *By* H. Schwartz.

The hippuric acid used in these experiments was obtained by Liebig's process, viz. evaporating the urine of horses to one-sixth or one-eighth of its volume, treating it with muriatic acid, and purifying the acid thus obtained in the crystalline state. It was rare to find a urine which yielded the acid on the mere addition of muriatic acid without evaporation. To purify it, it was heated to ebullition with milk of lime, by which the greater part of the colouring matter remained in combination with the excess of lime; the filtrate was then precipitated with excess of carbonate of soda or potash, boiled, filtered, and then again treated with an excess of salt of lime, as the chloride of calcium; finally, the acid was precipitated by muriatic acid. The carbonate of lime formed in each process was so intimately combined with the colouring matter, that often after at the most two recrystallizations, the acid was obtained of a brilliant white. It sometimes happened that the hippuric acid was mixed with benzoic acid, which was probably produced by the application of too great a heat during the evaporation. This was easily removed, and without the loss of any of the hippuric acid by the action of æther, which readily dissolved the latter, and but slightly the former. Whether the acid existing in the liquid was benzoic or hippuric was decided principally by the former separating in a milky form from concentrated and cold solutions on the addition of the muriatic acid, and subsequently becoming crystalline; whilst the hippuric acid, in every instance, subsided in distinct, long, and often stellate needles. The microscope enables us, however, to decide more positively; under it the hippuric acid generally appears as small four-sided prisms, with four-sided pointed extremities, whilst benzoic acid occurs in the form of broad leaves or dendritic crystals. The evolution of ammonia, on the addition of the milk of lime, would enable us to say whether benzoic acid had been formed from the decomposition of the hippuric acid or not (inasmuch as an ammoniacal salt is formed at the same time); in fresh urine the milk of lime causes the evolution of a barely perceptible amount of ammonia. The above reactions, the formation of hydrocyanic acid, of the well-known red oil and of the odour of Tonquin bean on the application of heat, prove the substance to be hippuric acid.

The author also endeavoured to employ the urine of oxen to obtain the acid, but it yielded a small and unprofitable quantity*. In the urine of an elephant and of a camel, which he examined, a considerable quantity of hippuric acid was found.

Neutral Hippurate of Potash.—The author obtained this salt by dissolving hippuric acid in carbonate of potash, and neutralizing the excess of alkaline carbonate by the cautious addition of a solution of hippuric acid in hot water; that excess of acid had been added was evident from the crystallization of the acid potash salt described below. After the latter had subsided, the neutral salt was recrystallized from alcohol several times, and washed with æther. When a portion of it was now dried with the filter at about 104° F., the whole mass melted, being slightly soluble in warm æther, forming a viscid mass, which could not be removed from the paper; consequently the washed salt was again dissolved in water and evaporated to dryness. Small yellowish crusts, twisted into intestine-like forms, separated; under the microscope the crystals appeared to be acute rhombic prisms. The formation of the yellow colour could not be prevented, as even perfectly white hippuric acid, with its trace of adherent colouring matter, dissolved in potash, forming a deeply coloured liquid. The colouring matter appears to be coloured brown by alkalies and red by acids. However, this coloration does not interfere with the analysis.

The substance was first dried over sulphuric acid, then burnt, and the potash contained in it estimated as sulphate of potash; it was then dried at 212°, again burnt, and thus its atomic weight was ascertained. The analyses, which agree well, gave the following results:—

	I.	II.	III.			
Carbon	45·784	..	..	18 =	1350·00	45·888
Hydrogen	4·300	..	..	10	125·00	4·255
Potash	..	19·912	..	1	589·91	20·075
Water........	..	..	7·583	2	225·00	7·659

whence we obtain the formula KO + $\overline{\text{Hi}}$ + 2aq.

Anhydrous Salt.

	I.	II.			
Carbon	49·580	..	18 =	1350·000	49·687
Hydrogen	3·873	..	8	100·000	3·681
Potash	..	21·736	1	589·916	21·716

whence we obtain the formula KO + $\overline{\text{Hi}}$.

In incinerating to estimate the atomic weight, an agreeable odour was always evolved, quite different from that which pure hippuric acid gives, and which may perhaps be best compared to that of *Satureja hortensis*. The salt was but little soluble in absolute alcohol and cold æther, more readily so by heat, and it separated in the crystalline form from warm, very concentrated solutions; it

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* It is rather remarkable that in Dr. Fownes's experiments (Mem. Chem. Soc. part 1.), hippuric acid was obtained in abundance from the urine of cows, and in small quantity only from that of horses.—*Ed. Chem. Gaz.*

could not, however, be precipitated by the addition of alcohol or æther to its aqueous solutions.

Bi-hippurate of Potash.—This beautiful salt crystallizes from the above solution of neutral hippurate of potash, even when but little concentrated, in broad satiny leaves, probably from a slight excess of hippuric acid. Under the microscope it appeared to be composed of four-sided prisms, the summits of which had straight surfaces and truncated angles. They were dried over sulphuric acid and burnt with chromate of lead, then dried at 212°, and the potash estimated as sulphate, but calculated for the salt merely dried in the air. They yielded per cent.—

	I.	II.	III.				
Carbon......	52·005	..	..	36	=	2700·000	52·100
Hydrogen....	4·724	..	..	19		237·500	4·583
KO	..	..	11·279	1		589·916	11·383
HO	..	4·767	..	2		225·000	4·342

thus the formula is $KO + HO + 2\overline{Hi} + 2aq$.

Hippurate of Soda.—It was obtained as the potash salt by the careful neutralization of hippuric acid with carbonate of soda, evaporation to dryness, solution in alcohol, in which it entirely dissolves, and repeated crystallization. A pale yellowish saline mass was thus obtained, having a distinctly crystalline structure. The dried salt was finely powdered, and washed with æther, and then with absolute alcohol, which had but little action on it in the cold. To estimate the water of crystallization, the salt was dissolved in water, evaporated to crystallization in the water-bath, and dried over sulphuric acid. It yielded no water of crystallization. The salt, before purification, yielded on analysis exactly the same result as that purified by means of alcohol and æther (III.–VI.).

	I.	II.	III.	IV.	V.	VI.				
C..	51·889	52·399	52·456	52·543	..	..	36	=	2700·0	52·444
H	4·197	4·338	4·289	4·331	..	..	17		212·5	4·103
NaO	..	..	..	..	15·419	15·417	2		781·7	15·325

These analyses yield the following formula:—$2NaO + 2\overline{Hi} + HO$.

Bi-hippurate of Ammonia.—Although excess of ammonia was used in preparing this salt from hippuric acid and solution of ammonia, a neutral salt could not be obtained, for during evaporation ammonia continued to escape until the acid salt had formed. It was readily soluble in water and alcohol, and but little in æther. On heating it to 356°–392° F., a large quantity of ammonia was evolved, and the hippuric acid remained of a beautiful rose-red colour, as described by Liebig. Under the microscope the crystals of the ammonia salt appeared to be four-sided right prisms terminated by four-sided summits. The author observed in them the evolution of numerous minute air-bubbles, a phænomenon similar to that which occurs especially with the butyrate of baryta. When put into water, the salt rotated about on its surface, until after a short interval it entirely dissolved. It yielded on analysis—

	I.	II.	III.	IV.				
C	54·479	54·545	54·815	..	36	=	2700·0	54·894
H	5·956	6·070	6·139	..	23		287·5	5·845
HO ..	..	..	..	4·115	2		225·0	4·105

when we obtain the formula $AmO + HO + 2\overline{Hi} + 2aq$.

Hippurate of Baryta.—This salt was obtained by dissolving hippuric acid in excess of hydrate of baryta, and precipitating the excess of baryta by a current of carbonic acid. The author also procured it by dissolving carbonate of baryta in hippuric acid, leaving however some of the carbonate undissolved. On evaporation a scum speedily forms; and on cooling, the salt crystallizes in crusts, which appear under the microscope as square prisms. After washing with a little water, the salt was dried over sulphuric acid and burned; the water of crystallization was then estimated, the dried salt again burnt and the baryta estimated, sometimes as carbonate, sometimes as sulphate. The hydrated salt yielded—

	I.	II.	III.	IV.	V.				
C....	41·686	41·903	..	..	..	18	=	1350·0	42·235
H ..	3·807	3·658	..	..	..	9		112·5	3·520
BaO	..	..	..	..	..	1		956·8	29·936
HO..	..	..	3·645	3·816	3·766	1		112·5	3·520

Formula:—$BaO + \overline{Hi} + aq$.

The anhydrous salt—

	I.	II.	III.	IV.	V.				
C....	13·957	44·022	..	..	..	18	=	1350·0	43·775
H ..	3·395	3·522	..	..	..	8		100·0	3·243
BaO	..	..	30·913	30·942	30·691	1		956·8	31·028

Formula:—$BaO + \overline{Hi}$.

It is stated that a second, basic, and very difficultly soluble baryta salt exists. This is improbable; otherwise, in preparing the salt with excess of baryta, it would have been formed.

Hippurate of Strontia was prepared by dissolving recently-precipitated carbonate of strontia in hippuric acid. As too much acid may be added, the salt should be recrystallized from cold alcohol. This salt is but little soluble in cold water, alcohol and æther, but readily so in hot water and alcohol. It separates from a hot solution in tufts of broad leaves, which occupy the whole liquid, and form a beautiful net-work.

Under the microscope the crystals appear to be four-sided prisms with straight summits. The salt was first dried over sulphuric acid, and the amount of strontia estimated; it was then dried at 212°, burnt with chromate of lead, and the strontian again estimated as sulphate. On analysis it yielded—

	I.	II.	III.				
SrO	19·306	19·497	..	1	=	647·285	19·000
HO	..	..	16·235	5		562·500	16·512
$\overline{Hi}$..........	..	..	..	1		2127·036	64·488

When dried at 212°—

	I.	II.			
C	48·826	..	18 =	1350·000	48·661
H	3·389	..	8	100·000	3·604
SrO	..	23·421	1	647·285	23·333

Hippurate of Lime.—This salt is procured, like the barytic salt, by dissolving hippuric acid in excess of milk of lime, filtering, transmitting a current of carbonic acid through the solution and crystallization. This took place in exactly the same manner as with the barytic salt. The crystals are acute rhombic prisms. The salt was dried over sulphuric acid; the water of crystallization was estimated by exposure to 212°; it was then burnt, and the atomic weight estimated from the sulphate of lime.

The hydrated salt yielded—

HO	11·999	3 =	337·500	11·966
CaO + $\overline{\text{Hi}}$	88·001	1	2483·055	88·034

The anhydrous salt yielded—

	I.	II.			
C	54·401	..	18 =	1350·000	54·368
H	4·007	..	8	100·000	4·027
CaO	..	14·310	1	356·019	14·337

Hippurate of Magnesia.—This was prepared from hippuric acid and carbonate of magnesia. It crystallized from a tolerably concentrated solution in warty groups of crystals, which, after being washed with the smallest possible quantity of water, were dried over sulphuric acid and analysed.

The salt, dried over sulphuric acid, yielded—

HO	15·347	4 =	450·0	15·271
Mg + $\overline{\text{Hi}}$ + HO	84·653	1	2497·9	84·729

The salt dried at 212° gave—

	I.	II.			
C	53·737	..	18 =	1350·0	54·054
H	5·049	..	9	112·5	4·505
MgO	..	10·232	1	258·3	10·302

This is the only salt, with the exception of the soda salt, which retains an atom of water at a temperature of 212°.

Per-hippurate of Iron.—If a solution of chloride of iron, as neutral as possible, be treated with a solution of hippurate of potash, a voluminous bright cream-coloured precipitate subsided in the cold; it was completely insoluble both in hot and cold water. In the latter it possessed the peculiarity of melting into a brown, resinous, greasy mass. This likewise occurred when it was attempted to dry the precipitate, which had been obtained in the cold, at a temperature of about 86°; it gave off a considerable quantity of water, and shrunk up to the former mass. Although the precipitate was insoluble in water, it was however readily dissolved by hot alcohol. On cooling, the salt again separated, partly in the amorphous, partly in the crystalline form; the crystals were produced by slow evaporation in the air, and formed red tufts of acute rhombic prisms.

Hippurate of Cobalt was obtained by dissolving carbonate of cobalt in hippuric acid; it formed a beautiful rose-red solution. As it was necessary to use an excess of hippuric acid to dissolve the carbonate, the precipitate contained the acid in admixture; it was therefore treated with alcohol, to retain the acid in solution. This at the same time precipitated the hippurate of cobalt, which, when washed with alcohol and dissolved in water, soon crystallized in rose-coloured warty masses, which under the microscope exhibited concentrically-grouped, broad, four-sided prisms. The salt was first dried over sulphuric acid, then at 212°, whereupon its rose-red colour was changed for violet; it was then burnt with oxide of copper, and the amount of protoxide of cobalt estimated by heating to redness and reduction with a current of hydrogen gas.

The hydrated salt contained—

HO	17·535	5 =	562·5	17·806
$CoO + \overline{Hi}$	82·465	1	2596·027	82·194

The anhydrous salt yielded—

	I.	II.	III.			
C	52·054	51·901	..	18 =	1350·0	52·003
H	3·915	4·199	..	8	100·0	3·882
CoO	..	..	17·898	1	469·8	18·107

Proto-hippurate of Nickel.—Obtained by dissolving carbonate of nickel in hippuric acid; as excess of the carbonate remained undissolved, the salt was simply evaporated, and crystallized over sulphuric acid. It formed very indistinctly crystalline apple-green crusts, which subsided from the liquid, like the pellicles of carbonate of lime in spring water. It is rather insoluble in cold water, more soluble in warm water and alcohol, and insoluble in æther. No distinct crystals could be detected with the microscope. The salt was first dried over sulphuric acid, then burnt; it was then dried at 212°, and finally at 284°, by which it lost no more in weight; this was likewise burnt, and its atomic weight estimated by heating the salt to redness, moistening it with nitric acid, and then again subjecting it to a red heat. The formula for the hydrated salt is $NiO + \overline{Hi} + 5aq$.

The anhydrous salt yielded on analysis—

	I.	II.	III.			
C	51·621	..	..	18 =	1350·000	51·965
H	4·129	..	..	8	100·000	3·851
NiO	..	18·056	17·987	1	469·675	18·086

Hippurate of Copper.—This beautiful salt was obtained by mixing sulphate of copper with hippurate of potash. The microscope exhibited the acute rhombic prisms in which it separated, very distinctly. Its aqueous solution was immediately rendered dark-blue on the addition of pure ammonia. Alcohol and æther caused no precipitation; on evaporation very indistinctly crystalline greenish crusts were obtained, which require further examination. The salt was first dried over sulphuric acid, by which it did not lose its blue colour, then at 212°, whereby it lost most of its water of crystallization, and became green; it was then burnt, and the amount of oxide of copper estimated by heating to redness.

The salt containing water of crystallization yielded—

	I.	II.	III.			
C	..	45·524	..	18 =	1350·0	45·620
H	4·618	5·204	..	11	137·5	4·653
HO	..	..	12·333	3	337·5	11·890

The anhydrous salt—

	I.	II.	III.			
C	51·386	..	..	18 =	1350·000	51·473
H	4·036	..	..	8	100·000	4·860
CuO	..	18·896	18·646	1	495·695	18·900

Hippurate of Lead is readily obtained by adding neutral acetate of lead to a cold solution of hippurate of potash, in the form of a white, caseous precipitate, which is but little soluble even in boiling water; it must be strained through a warm filter, otherwise the salt crystallizing stops up the funnel. It crystallized from its hot and tolerably dilute solutions without exception, in delicate, silky, tufted needles, which were too imperfectly formed to enable us to distinguish distinct facets, even with a power of 200 linear. However, these crystals are transformed, and often very suddenly, particularly in concentrated solutions, into tolerably broad shining leaves, which were clearly perceived to be four-sided tables. Particular conditions, as neutral, slightly acid or alkaline fluids, &c., could not be positively determined. The analogies between the fumarates of lead and this salt are well worthy of notice here. Thus, there is a salt $= PbO + \overline{Fu} + 2aq$, and a salt which is precipitated from very dilute, weak basic solutions $= PbO + \overline{Fu} + 3aq$, the former crystallizes in needles. Both the hippuric salts were prepared from the same portion of the dried salt by re-solution, more or less dilution, and longer or shorter repose. After they had been dried over sulphuric acid they were analysed with sufficient accuracy by merely estimating the lead in the form of sulphate.

The anhydrous salt yielded—

	I.	II.			
C	38·498	..	18 =	1350·0	38·338
H	3·023	..	8	100·0	2·840
PbO	..	39·346	1	1394·5	39·600

The salt crystallized in tufts yielded—

PbO	36·922	1 =	1394·5	372·21
$\overline{Hi} + 2aq$	63·178	1	2352·0	627·79

The salt crystallized in leaves—

	I.	II.			
PbO	36·021	36·131	1 =	1394·5	36·136
$\overline{Hi} + 3aq$	63·979	63·869	1	2464·5	63·864

Hippurate of Silver.—This salt is prepared in great beauty by precipitating hippurate of potash with nitrate of silver; a caseous precipitate insoluble in cold water falls, which however dissolves in a large quantity of water, and if filtered whilst hot, separates on cooling in very beautiful silky needles. If allowed to crystallize under the microscope it forms a very splendid object, appearing in the form of needles combined into panicles; the form of the crystals could not however be accurately distinguished, but probably it is similar to that of the copper and first lead salt. The salt was first dried over sulphuric acid, burnt, and its atomic weight estimated; it was then dried at 212°, whereby it lost some water (as was proved by directly heating it in a glass tube); finally, the dried salt was burnt and its atomic weight estimated.

The hydrated salt yielded—

	I.	II.	III.			
C........	36·437	..	..	18 =	1350·000	36·574
H........	3·102	..	..	9	112·500	3·048
AgO......	..	39·008	..	1	1451·607	39·327
HO	..	..	3·417	1	112·500	3·048

The anhydrous salt gave—

	I.	II.			
C........	37·574	..	18 =	1350·000	37·811
H........	3·102	..	8	100·000	2·795
AgO......	..	40·494	1	1451·637	40·563

The atom of water does not exist in the fumarate of silver. The composition of the hippuric acid is, according to the silver salt, as also according to the other salts, $= C^{18} H^{8} N^{2} O^{5} + aq$; its atomic weight ($C = 75$, $H = 12·5$), in the anhydrous state, is = 2127·036; combined with water of crystallization = 2239·536.—*Ann. der Chem. und Pharm., April,* 1845.

Examination of the Organic Acids in unripe Plums (Prunus domestica) *and Gooseberries. By* A. CHODNEW.

The unripe plums were freed from the stones, bruised, stirred with hot water, and the solution filtered. The fluid thus obtained was boiled, again filtered, and precipitated by diacetate of lead, the quantity added being small in proportion to the liquid. The white flocculent precipitate thus obtained became converted during the night into concentrically-grouped needles, which pretty distinctly indicated the presence of malic acid; the crystals were collected on a filter and washed. The portion of the liquid which first ran through yielded a rather copious yellowish precipitate with excess of diacetate of lead, which did not become crystalline by repose, and was not further examined. The above-mentioned crystalline compound was decomposed by sulphuretted hydrogen, boiled until the odour of the gas was no longer perceptible; it was then filtered and divided into two portions. One was saturated with carbonate of ammonia, and then mixed with the other. After evaporating the mixture, the characteristic beautiful crystals of bimalate of ammonia appeared.

To place the presence of malic acid beyond all doubt, its silver salt was prepared, and two analyses of it made:—

	I.	II.		
Carbon..........	13·59	13·86	8	13·78
Hydrogen	1·18	1·31	4	1·14
Oxygen	18·78	18·38	8	18·39
Oxide of silver....	66·45	66·45	2	66·69

The unripe gooseberries, treated in the same manner as the plums, yielded a lead compound (an excess of diacetate of lead was however directly used), which was again decomposed by sulphuretted hydrogen. The acid liquid, saturated with milk of lime, when boiled yielded a precipitate, and a solution containing a lime compound. It was filtered and precipitated with diacetate of lead; the white flocculent precipitate gradually changed by repose into the characteristic needles of malate of lead. The sparingly-soluble lime compound consisted mostly of basic citrate of lime and a small quantity of neutral malate of lime, which was separated from the former by washing with water, being more soluble. The basic citrate of lime was then also dissolved in a considerable quantity of water and treated with nitrate of silver. The author thus obtained a white precipitate, which he at first took for a pure silver salt; however, the analyses and estimation of its atomic weight proved that it was a double salt of lime and silver. The following results were obtained by estimating the amount of oxide of silver and lime, and from two analyses of the prepared salt at different times:—

	I.	II.		
Carbon	15·50	15·49	12	15·85
Hydrogen	1·24	1·29	5	1·10
Oxygen	19·51	19·47	11	19·38
Oxide of silver ..	50·60	50·60	2	51·13
Lime	13·15	13·15	2	12·54

This remarkable double salt, which was obtained twice, requires that the analysis of the acid occurring in unripe gooseberries should be repeated.—Liebig's *Annal.*, vol. liii. p. 283.

Poisoning of Plants by Arsenic.

M. Witting observed that plants of *Chelidonium majus* and *Sempervivum tectorum*, died very soon after being placed in contact with arsenious acid. Arsenic was easily detected by Marsh's apparatus in the upper parts of the plants, which had not stood in immediate contact with the arsenic.—*Archiv der Pharm.*, vol. xci. p. 48.

Researches on Salicine. By M. PIRIA.

In the present state of chemistry, organic substances may be divided into two very distinct classes. Those in the one are very stable and frequently volatile, have a simple composition, and resemble the binary compounds of inorganic chemistry; the other contains such as are fixed and of a more complex composition, and are changed with great facility by the action of reagents; they correspond to the salts, or rather to the double salts. A very essential difference existing between these two classes of bodies, and to which I desire to draw the attention of chemists, is that resulting from their behaviour under the influence of chemical agents.

The bodies of the first category always yield on decomposition single products, which are connected by very intimate relations with the very substance from which they derive their origin. The alcohols, the acetic, benzoic and butyric acids, benzine, and almost all the carburetted hydrogens, glycerine, &c., afford striking examples of this kind.

When, on the contrary, it is question of a complex substance, which contains bodies of a more simple composition in combination, it yields on decomposition products which result from the action of the same reagents upon its constituent principles. On submitting a fatty substance to the decomposing action of bases, acids, oxidizing agents, or to distillation, two series of products are constantly obtained, one of which is derived from the fat acid, the other from the glycerine. Formobenzoilic acid constantly yields, in a number of decompositions, the derivatives of formic acid and of oil of bitter almonds. In a word, the substances of a simple composition always produce one single series of derivatives in their metamorphoses; on the contrary, the complex substances give rise to as many different products as they contain simple organic substances in combination.

The investigation of the metamorphoses of organic bodies may consequently throw much light on their intimate constitution, for they are for researches in organic chemistry what the reactions are for those of mineral chemistry.

It is from considerations of this kind that I was led long since to regard salicine as a combination of two different bodies, which being modified under the influence of reagents gave rise to the numerous substances which result from its decomposition. It is known, in fact, that salicine treated with concentrated nitric acid is converted into carbazotic and oxalic acids, with dilute acids into saliretine and sugar, with potash in a state of fusion into salicylic and oxalic acids, with chromic acid into salicyle, carbonic and formic acids. Now the body which, under the influence of weak acids, is converted into saliretine, could not at the same time yield grape-sugar. That which is metamorphosed by the action of fusing potash into oxalic acid is not the same which yields the salicylic acid, &c. All this leads us to admit that salicine contains two principles of a different nature; one of which gives rise to the oxalic acid, the sugar, the carbonic and formic acids; the other to the carbazotic acid, saliretine and hydruret of salicyle.

These motives have induced me to take up once more the study of salicine, in the hope of establishing its true constitution, and of explaining the origin and mode of formation of the numerous products derived from it. The facts I am about to relate will I hope suffice to solve these questions in a satisfactory manner.

On re-examining the metamorphoses of salicine under the influence of acids in all their phases, I soon perceived that the saliretine is not produced directly from the decomposition of the salicine; on the contrary, it is a product of alteration, resulting from the prolonged action of the free acid on a new substance, which is first set at liberty. If, in fact, instead of boiling an aqueous solution, acidulated with sulphuric or hydrochloric acid, it is merely heated until it begins to become turbid, and then allowed to cool as soon as this phænomenon is manifested, a liquid is obtained, which, on saturation with carbonate of lime and filtration, colours the persalts of iron of a very intense blue. The body, newly formed, which is the cause of this reaction, is soluble in æther, and may be removed by this agent from its aqueous solution. The æther deposits it on evaporation. I have given to this body the name of *saligenine*, which will call to mind its origin.

The facts composing the history of salicine, although very numerous, are nevertheless so intimately related that they may be resumed in a very few words.

Salicine is a natural combination of grape-sugar and of saligenine; the saligenine again is a substance which is very readily altered by chemical reagents. Weak acids convert it into saliretine, concentrated sulphuric acid into rutiline, nitric acid into carbazotic acid, oxidizing agents into hydruret of salicyle, potash in a state of fusion into salicylic acid.

When salicine is submitted to the action of any agent whatever, two cases may occur:—1. If the agent is sufficiently energetic to decompose at the same time the saligenine and the sugar, altered products of these two substances are obtained, as if the experiment were made on a mixture of saligenine and grape-sugar. 2. If, on the contrary, a weak agent is employed, the saligenine only is decomposed and the sugar remains unaltered, but it combines with the modified saligenine. Thus chlorine first converts it into chlorosalicine; then into bichlorosalicine; lastly, into perchlorosalicine: these are combinations of sugar with the saligenine, in which chlorine has replaced 1, 2, 3 equivalents of hydrogen.

Dilute nitric acid changes salicine into helicine. This results from the combination of the sugar of the salicine with the hydruret of salicyle derived from the oxidation of the saligenine. When helicine is submitted to the action of chlorine or bromine, the hydruret of salicyle which it contains is converted into chloride and bromide of salicyle; these products combining with the sugar give rise to chlorohelicine and bromohelicine.

Lastly, all these combinations of saligenine, or its derivatives with sugar, are rapidly decomposed by contact with acids and by synaptase.

In a subsequent memoir I shall describe the nitrogenous acids which are produced by the action of nitric acid on salicine.—*Comptes Rendus*, June 2, 1845.

Occurrence of Starch in Fruits.

Döbereiner found starch abundantly in green and half-ripe apples and pears. Mayer also found a considerable quantity of starch in the juice of apples. According to Schubert, however, starch does not occur until a later period of their development. He found in September that the surfaces of winter pears, exposed by transverse section, yielded as deep a violet colour with iodine as is observed in potatoes similarly treated, whilst no reaction occurred in the immature fruit. The period during which fruits contain starch does not appear to be of long duration.—*Journ. für Prakt. Chem.*, xxxiv. p. 380.

On Sulphurous Æther. By MM. EBELMEN *and* BOUQUET.

In the action of alcohol on the chloride of sulphur, a new æther, sulphurous æther, is produced under the following circumstances:—When absolute alcohol is poured over protochloride of sulphur, disengagement of heat results, with formation of hydrochloric acid gas and a deposit of sulphur. On continuing to add alcohol until all reaction has ceased, and then distilling the mixture, there first passes over at about 176° an abundant product, which is nothing further than alcohol acidified by hydrochloric acid. On continuing the application of heat, the temperature of the liquid rises rapidly, and is rendered clear by the fusion of the sulphur which it held in suspension, becomes of a brownish-red colour, and parts between 302° and 338° with a product, which is collected separately. There remains in the retort a considerable deposit of fused sulphur.

The liquid, distilled between 302° and 338°, having been rectified until its boiling-point remains constant, a limpid colourless fluid is obtained, of a peculiar æthereal odour somewhat analogous to that of mint; its taste is at first cooling, then burning, and it has a sulphureous after-taste. It boils at 322°; its density is 1·085; it dissolves in every proportion in alcohol and in æther at 61°. Water causes a precipitate in these solutions, and redissolves the deposit only very slowly, acquiring a very strong odour of sulphurous acid.

The æther, which had been prepared for some time and preserved in badly-corked bottles, likewise underwent an analogous decomposition from the action of the moist air.

The analysis of this product has led to the formula $SO^2, C^4 H^5 O$, which represents 2 volumes of vapour. The calculated density would be 4·76; the experiment yielded an almost identical number, 4·77.

To complete the history of this body, we have yet to study the action of chlorine on it; this gas is absorbed in large quantity under the solar influence, but the state of the weather has not as yet permitted us to obtain the definitive product of the reaction.—*Comptes Rendus*, May 26, 1845.

CHEMICAL PREPARATIONS.

Experiments on the Preparation, Properties and Composition of Valerianic Acid and some of its Salts. By Dr. C. G. WITTSTEIN.

VALERIANIC acid, the salts of which have of late been so much recommended, is, as is well known, not solely a natural constituent of valerian, but is likewise formed artificially in various chemical reactions upon organic bodies; for instance, in the action of caustic potash upon potato fusel oil. Admitting however that the artificial acid is perfectly identical in a therapeutical point of view with the natural, yet the most advantageous method of obtaining it appears for the present still to be from the plant.

Preparation.—The author brings for this purpose 20 lbs. (18$\frac{2}{3}$ oz.) of dry and finely-cut valerian root with 100 lbs. of water into a copper still, and draws off 30 lbs. The recipient employed is a Florence flask, in order not to lose the æthereal oil, which constantly amounts to 3–3$\frac{1}{4}$ oz. for every 20 lbs. of root. 30 lbs. more water are added to the residue in the still, as much drawn off, and this addition and distillation repeated once more. The root is then so exhausted that what passes over no longer reddens litmus; the contents of the still, however, turn litmus red; but this does not arise from valerianic acid, but from another non-volatile organic acid. No addition of acid, as recommended by Rabourdin to liberate the valerianic acid, is consequently requisite. The three aqueous distillates are saturated after removal of the essential oil with carbonate of soda, evaporated in a copper vessel to within a few pounds, then filtered and evaporated to dryness on a sand-bath in a counterpoised porcelain dish. Having ascertained by weighing the amount of valerianate of soda, it is dissolved in an equal weight of water, poured into a retort of 6 to 8 times the capacity, and a mixture consisting of 1 part concentrated sulphuric acid and 2 of water added, so that there be 4 parts of concentrated acid for every 5 parts of dry valerianate of soda. The soda instantly combines with the acid, forming sulphate of soda, and the liberated valerianic acid floats as a brown oil on the saline solution. By distillation in the sand-bath it passes over along with the greater portion of the water. The contents of the recipient are emptied into a tall cylinder, left some time in quiet, and the oily acid separated from the subjacent aqueous layer; the aqueous solution is likewise preserved, being a concentrated solution of the acid. To concentrate further the acid thus obtained, which is still combined with 3 equiv. water, it is submitted alone to fresh distillation; and as soon as the liquid which passes over appears in clear drops and not turbid, the receiver is to be changed; what now distils over is the monohydrated acid.

Pure valerianic acid is a colourless or pale yellow liquid, resembling an essential oil, of a penetrating odour, somewhat different from the æthereal oil of valerian, and of very acrid, acid, disagreeable taste, calling to mind that of valerian. It floats on water, which dissolves 1 part in 26. The solution has a strong acid reaction, and possesses a somewhat mild and sweetish taste. Its combinations with bases, for instance with soda, have a sweet but at the same time valerian-like taste. It dissolves readily in strong alcohol and in æther. It is perfectly volatile, and when heated in a platinum spoon burns with a luminous flame. Its composition in the anhydrous state corresponds, according to Ettling and Trommsdorff, to the formula $C^{10}H^{9}O^{3}$. The first hydrate contains 1 equiv. water. To determine the composition of the second hydrate, a solution of 30 grs. of carbonate of soda was added to 60 grs. of the oily acid, carefully evaporated and dried a little below 212°. The dried salt weighed 65·5 grs.; on treatment with alcohol of 0·833 spec. grav., 3·4 grs. carbonate of soda remained undissolved, so that the quantity of valerianate of soda formed amounted to 62·1 grs.; consequently the 60 grs. of the oily acid contained 46·63 grs. acid and 13·37 grs. water, or 77·718 per cent. acid and 22·282 water, consequently 1 equiv. acid to 3 equiv. water.

Valerianate of Quinine.—1 part of oily valerianic acid is dissolved in 60 parts water, and 3 parts of pure (recently precipitated is best) quinine added, heated nearly to boiling, filtered while hot, and then placed in a cold situation. The crystals which have separated in the course of a few days are removed, and the liquid concentrated at a temperature below 122°. About 5 parts of the salt are obtained. The aqueous solution of the acid dissolves the quinine with great readiness to the amount of 2 equiv. If, during the concentration, the temperature exceed 122°, oily patches are formed, which solidify on cooling to amorphous resinous masses, contain less water than the crystallized salt, and are scarcely soluble in water. The salt crystallizes in colourless rhomboidal tablets, with a slight mother-of-pearl lustre, or in white opake radiately-grouped needles, has a faint odour of valerianic acid and a very bitter taste. It is not altered by exposure to the air, becomes tenacious when heated, melts to a colourless liquid, and is then converted into the above-described hydrate. When heated more strongly, it gives off white vapours, takes fire and burns without leaving any residue. It dissolves in 110 parts cold, 40 parts boiling water; in 6 parts cold, and in equal parts of boiling alcohol of 0·863 spec. grav.; likewise in æther. All its solutions have a neutral reaction. The amorphous hydrate scarcely dissolves in 1000 parts water; it however imparts to it a bitter taste. In alcohol and æther it dissolves just as easily as the crystallized salt. 20 grs. of the crystals dissolved in water gave, on treatment with a solution of caustic soda, 10·84 hydrate of quinine = 10·271 quinine. The alkaline solution was saturated with carbonic acid, and evaporated to dryness. From this residue alcohol of 0·833 spec. grav. dissolved out 4·0 grs. valerianate of soda. The composition of the salt is therefore—

	Found.	Equiv.	Calculated.
Quinine............	51·355	2	51·411
Valerianic acid......	14·980	1	14·719
Water	33·665	24	33·870

The resinous body separated by boiling the aqueous solution was reduced to a fine powder and dried at a gentle heat. Treated in the above manner, the salt gave—

Quinine	71·855	2	71·629
Valerianic acid	20·225	1	20·505
Water	7·920	4	6·860

According to the Prince of Canino, the quinine salt consists of equal equivalents; he has, however, taken Regnault's atomic weight of quinine, which is just as high again. The quantities, however, found by him are, according to the author, far too low.

Valerianate of the Peroxide of Iron.—60 parts of water are added to 5 parts oily valerianic acid and saturated with carbonate of soda, the solution boiled to expel all the carbonic acid, and left to cool. 3 parts perchloride of iron ($Fe^2 Cl^3 + 6HO$) are then dissolved in 100 parts water, and the cold solution of valerianate of soda added to it until no further turbidness results. The precipitate is washed with a little water, and dried at a temperature not exceeding 68°; at a higher temperature it loses a part of its acid, and on boiling the whole of it goes off. The salt forms a dark tile-red, loose, amorphous powder, which has a faint odour and taste of valerianic acid. Heated slowly, it parts without melting with the whole of its acid; heated rapidly, it fuses, and the acid is volatilized in thick inflammable vapours; but in this operation it undergoes decomposition, for the vapours smell of butyric acid; the residue consists of pure peroxide of iron. It is not moistened by cold water; boiling water gradually extracts all the acid, and leaves behind pure hydrate of peroxide of iron. The salt dissolves readily in hydrochloric acid; the dilute solution is not rendered blue by ferridcyanide of potassium; the peroxide of iron is consequently not reduced to protoxide by the valerianic acid. 20 grs. of the salt boiled with a solution of 10 grs. anhydrous carbonate of soda gave 5·40 grs. peroxide of iron and 18·95 valerianate of soda; therefore in 100 parts—

Peroxide of iron	27·00	3	26·315
Valerianic acid	71·00	7	71·720
Water	2·00	2	1·965

From this we may construct the formula $3Fe^2 O^3 + 7\overline{Va} + 2HO$, or $7\ (Fe^2 O^3 + 3\overline{Va}) + 2(Fe^2 O^3 + 3HO)$. The atomic weight is 11400 or 34200. The precipitate is consequently a basic salt; the 2 equiv. acid wanted to produce a neutral salt are replaced by 2 equiv. water.

Valerianate of Zinc.—1 part oily valerianic acid is dissolved in 180 parts water, and to the solution ½ part of recently-precipitated carbonate of zinc added; the whole is then digested for some hours at a very gentle heat, filtered after cooling, and concentrated at a very gentle heat. The salt separates on the surface in white snow-like aggregations. If the ley be boiled, a portion of the salt adheres firmly to the bottom of the vessel. It crystallizes in snow-white, extremely light laminæ, with a mother-of-pearl lustre, similar to boracic acid, is not altered by exposure to the air, has a faint odour of the acid, and an astringent metallic taste, at the same time resembling that of valerianic acid. When heated on platinum foil, it melts, disengages thick white vapours, then takes fire, burning with a bluish flame, and finally leaves pure oxide of zinc, of which however a portion is volatilized during the combustion, owing to a partial reduction. It dissolves at the ordinary temperature in 160 parts water and in 60 parts alcohol of 0·833 spec. grav. The solutions have an acid reaction, become turbid on the application of heat, but become again clear on cooling. Cold æther takes up only $\frac{1}{500}$th, boiling, on the contrary, $\frac{1}{20}$th of the salt.

The analysis was executed precisely in the same manner as that of the valerianate of iron. 20 grs. yielded 5·9 grs. oxide of zinc and 14 grs. valerianic acid; consequently in 100 parts—

Oxide of zinc	29·50	1	30·08
Valerianic acid........	70·00	1	69·92

The atomic weight is 1672. The salt contains no water.—Buch. *Rep.*, vol. lxxxvii. p. 289.

Preparation of White Protocarbonate of Iron.

A solution of protosulphate of iron is treated with a proper quantity of carbonate of soda, and the precipitate (carbonate of protoxide of iron and hydrated peroxide of iron) is washed in an atmosphere of carbonic acid. If the precipitate be now subjected to a pressure of several atmospheres in the same gas, it acquires its white colour in proportion as it is saturated with the gas. After decanting the supernatant solution of carbonic acid, it is immediately incorporated with a proper vehicle, so as to be formed into pills, pastilles, &c.—Oesterlen's *Jahrb. für Prakt. Heilk.*, 1845.

On a new Method of preparing Chlorate of Soda and Chlorate of Barytes. By Dr. C. G. WITTSTEIN.

When carbonate of soda is treated with chlorine, the chlorate of soda formed cannot be separated by crystallization from the chloride of sodium in the same manner as with the corresponding potash compound, both salts being soluble in nearly equal proportion in water. Nor can their separation be well effected by spirit, since 1 part of the chlorate of soda requires for solution 34 of alcohol, while 1 part chloride of sodium requires 260. When 1 equiv. chloride of sodium is mixed with 6 equiv. lime, and chlorine passed through, not a trace of chlorate of soda is obtained, but the chloric acid generated remains in combination with the lime. The usual method of preparing the chlorate of soda is to mix chlorate of potash with bitartrate of soda, separating the bitartrate of potash by filtration and crystallizing the solution. The chlorate of soda, however, so obtained contains tartrates, as may be seen by its becoming black when heated. As these methods of preparation are by no means advantageous, the author advises the following plan:—3 parts of crystallized sulphate of ammonia and 3 parts of chlorate of potash are dissolved in a porcelain dish in 15 parts hot water, and evaporated over the water-bath to the consistence of a thin paste, being constantly agitated. This paste is then conveyed into a glass flask, 4 times its weight of alcohol of 0·833 spec. grav. poured over it, digested for a day at a gentle heat, filtered, and the residuous saline mass washed with spirit. A fourth part by weight in water is now added to the mixed fluids, the spirit distilled off, the residue diluted with an equal weight of water, 5 parts pulverized, crystallized carbonate of soda added, and when no more ammonia is disengaged, evaporated on the water-bath to dryness. The salt obtained is dissolved in twice its weight of water and crystallized.

On mixing sulphate of ammonia and potash, sulphate of potash and chlorate of ammonia are formed, the former of which is not dissolved by the spirit. Since on careful evaporation of the aqueous mixture a small portion of the chlorate of ammonia is unavoidably decomposed, somewhat less carbonate of ammonia has been given in the above directions than required by theory. By the action of the carbonate of soda on the chlorate of ammonia, carbonate of soda is formed, and the residue is chlorate of soda.

In the same manner chlorate of barytes may be prepared with advantage, only in this case caustic barytes must be employed. A hot solution of barytes, prepared from crude materials (sulphuret of barium and oxide of copper, nitrate of barytes and iron-filings) answers very well; an excess of barytes does no harm, because it is converted into carbonate on evaporation; should, however, the residue still be alkaline, a current of carbonic acid may be passed through the solution.—Buch. *Rept. der Pharm.*, vol. xxxviii. p. 33.

On the Preparation of Medicinal Tinctures. By H. Burton, M.D.

The author recommends the interposition of a bag, in which the matters to be exposed to the action of the solvent are to be suspended, and macerated in the spirit without agitation. By this process almost all the medicated tinctures may be prepared of equal strength to the corresponding tinctures made by the old plan, with less risk of incurring a loss of strength by inattention to the degree and repetition of the agitation which is requisite on the old plan, with less labour, and also a less expenditure of spirit. The bag, which is made of linen or a piece of calico, and fastened with a string, should be of the same shape as the vessel in which it is suspended. The substances, reduced to the state of disintegration directed in the London Pharmacopœia, should be allowed to fall into the bag by their own gravity, without the application of pressure, except in the cases of hop, hyoscyamus and conium, in packing which, especially hop, a moderate degree of pressure will be required to contract their bulks within the requisite limits.

The containing vessel should always rather exceed twice the height of the packed bag, so as to allow of its being raised under cover, and drained above the surface of the tincture. During the process the bag should be raised, and drained under cover, and again lowered as soon as the tincture has entirely ceased to drain. The process is perfected in 2–4 days, when small quantities are operated upon, but is protracted 2 or 3 days when large quantities are prepared.—*Med. Gaz.*, July 4 and 11, 1845.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Glue. By M. SCHATTENMANN*.

DURING my residence in Paris I had the honour of conferring with you relative to the manufacture of glue, and of submitting to you the results of my experience in this branch of manufacture.

In each of the notices which accompanied the samples of the products sent from the establishment of Bouxwiller to the public expositions of 1834, 1839 and 1844, I drew attention to the manner of ascertaining the true value of glue. I found that green glue, which is obtained by dissolving glutinous matters, dried much less easily than the jelly of glue which had been already dried and remelted; and that dried glue, soaked in cold water, imbibes, according to the different sorts and qualities, a greater or less amount of water; and that its body and cohesive force, as tested by this process, is in proportion to its real value.

From these facts I concluded that the green glue derived from the fusion of the glutinous matters contains water of composition more intimately combined with the glue than the water arising from the remelting of dry glue, which is only in a state of admixture, and is disengaged and evaporates much more easily than the water of composition; that indeed the dry glue contains a certain quantity of water of composition, which diminishes by the frequent remeltings and desiccations to which the glue is submitted. I have from this drawn the conclusion that the manufacture of glue in thin leaves, susceptible of a more complete desiccation, is preferable to that in thick leaves, like the glues of Givet and Boulogne.

I have recently made a series of new experiments, to ascertain the value of the dry glue from the quantity of water it imbibes in the cold, and the changes it undergoes by remelting or by more complete desiccation. The result of these experiments seems to me to be of great practical importance; for, if it be true that a dry glue of the same appearance may vary considerably as to strength or body, we must necessarily admit that the determination of the amount of dry glue should be abandoned, and in its place should be substituted that of the jelly obtained by the immersion of the dry glue in cold water at a temperature of 60° to 62° for twenty-four hours, because this jelly is the true expression of the quantity of the glue, and that the jelly thus obtained indicates by its greater or less consistence the quality of the glue.

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* In a letter to M. Dumas.

The bone-glue or gelatine is evidently the best of all the strong glues, as much by its strength as by the consistence of its jelly.

Our manufacture of this glue is so regulated as only to obtain thin leaves perfectly dried of two kinds of glue,—1st, the fine white bone-glue; 2nd, the fine blond bone-glue.

Our fine white bone-glue, by its immersion in cold water during twenty-four hours, imbibes as a mean 12 times its weight of water, that is to say, that a leaf of 3 grms. gives 39 grms. of a firm and elastic jelly of very remarkable consistence.

The fine blonde bone-glue, treated in the same manner, absorbs as a mean 9 times its weight of water, and gives a jelly evidently less firm than the white bone-glue.

The common strong glue of Alsatia or of Germany, made with the offals from domestic animals, treated in the above manner, only imbibes as a mean 5 times its weight of water, and gives a very soft brown jelly, without elasticity and without consistence, and which falls to pieces by handling. This jelly, which is evidently of very inferior value and quality, is not to be compared with the jelly of our fine blonde bone-glue, and still less with that of our white bone-glue.

The Boulogne glue made, like that of Givet, with the parings of skins of wild animals, and subjected to the same treatment after twenty-four hours of immersion, imbibes but 3½ times its weight of water; but after six times twenty-four hours it imbibes 7¼ times its weight of water. Its jelly is tolerably firm, and appears to be of good quality.

The bone-glue, remelted and dried afresh, soaked for twenty-four hours, absorbs as a mean a third more water than the quantity imbibed by the dry glue obtained from bones.

Our remelted bone-glues imbibe therefore as a mean—

The fine white bone-glue, 16 times its weight of water.

The fine blonde bone-glue, 12 times its weight of water.

The jelly obtained from these glues possesses less firmness and consistence than that of the same glues obtained direct from bones.

The loss or diminution resulting from the remelting of our dry bone-glues is about 10 per cent., and thus it is not in exact relation with the superior capacity which the remelted glue possesses of imbibing a greater quantity of water.

I attribute the diminution which the dry glue undergoes by remelting, partly to the losses inseparable to this operation, and partly to a more thorough expulsion of the water of composition; and I find the proof of it in the superior capacity of the remelted glue for imbibing a greater quantity of water, and in this, that the well-dried glues, and especially those which have been remelted, are less hygrometrical than the badly manufactured glues, or those which are made from matters of bad quality which possess this property in a high degree.

I think that the water of composition of the glue injures its quality, and that it paralyses its cohesive force, and that thus its strength increases in proportion to its desiccation.

From what precedes, I conclude that the surest practical means, and the most suitable for ascertaining the strength and quality of the glue, consists in soaking it for 24 hours in cold water in order to convert it into jelly; that its quality must be appreciated from the consistence and firmness of this jelly, and its amount of cohesive matter from the quantity of water it imbibes.

If the facts and principles which I have just exposed be true, as I am led to believe, it must be admitted that in practice the determining the value from the dry glue should be abandoned, because it is irrational and not precise; and that we should substitute for it that of the jelly obtained by the immersion of the dry glue in cold water for a certain time, of at least 24 hours.

The result moreover is, that the glues of inferior quality, at a low price, instead of being œconomical, are, on the contrary, the cause of increased expense and often injurious; for it is not seldom that the common strong glues, and especially the green glues obtained from the cuttings of skins, employed latterly in stiffening woollen goods, become putrid, and infect very valuable goods, especially when these are exposed to humid air or to an elevated temperature.

We sell the fine white bone-glue at 300 francs, and the fine blonde glue at 190 francs the 100 kilogrms. delivered at Paris, as we have mentioned in the notice sent with the sample of our products to the public exposition.

Our fine blonde bone-glue, soaked during 24 hours in cold water, imbibes 9 parts of water, and this gives 10 parts of firm jelly of excellent quality.

The Alsatian or German glue, worth 130 francs the 100 kilogrms., treated in the same manner, only absorbs 5 times its weight of water, and thus it only gives 6 parts of soft jelly, which is brown and of bad quality. The result is that 100 kilogrms. of fine blonde bone-glue, giving 1000 kilogrms. of jelly, and the same quantity of strong Alsatian glue, only giving 600 kilogrms. of jelly by their immersion in cold water for 24 hours at a temperature of from 60° to 62°; the jelly of the first glue costs but 19 francs, whilst that of the second amounts to $21\frac{1}{2}$ francs the 100 kilogrms. Bone-glue is an œconomy of 14 per cent. over the common strong glue, independent of the great superiority of the former in quality. Such is the result which the preference given to low-priced articles frequently leads to.—*Ann. de Chim. et de Phys.*, Feb. 1845.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Thursday, May 29, 1845.

"On the Ashes of Wheat." By William Sharp, Esq., F.R.S.

The experiments recorded in this paper were undertaken principally with the ultimate view of ascertaining with exactness what quantity of inorganic matter is removed from the soil by the seeds of a crop of wheat. The author first inquires what is the average amount of the inorganic or incombustible portion of a given quantity of wheat; a question to which no satisfactory answer has yet been given. The result of the author's experiments is, that wheat yields, by slow combustion, a residue of from 1½ to 1¾ per cent. He then proceeds to determine by experiment the degree in which this result is influenced by previous drying at different temperatures, varying from 230° to 260° Fahr., and finds that a heat of 245° is not sufficient to expel all the moisture contained in wheat; for while the loss of weight is then about 8 per cent. by a heat of 260°, the amount of this loss is 10 per cent. When the heat is so great as to occasion decomposition, the saline matter contained in the wheat fuses, and a portion of the carbon becomes so entangled or firmly adherent to it, as to be incapable of separation by burning. Hence he recommends, in order to obtain greater uniformity in the results, that the wheat subjected to these experiments should be dried at a low temperature, such as that of a room in summer, and be allowed to remain a few days under its influence. The author tried the effect of the addition of nitric acid, with a view to save time by accelerating the combustion; but found that the results could not be relied upon when this plan was adopted, and he was therefore obliged to relinquish it. He next directed his inquiries to the ascertaining whether the quantity of inorganic matter was in proportion to the specific gravity of the grain, that is, to its weight per bushel; and this he found in general to be the case. The conclusion he deduces from this investigation is, that the mean amount of inorganic matter removed from the soil by the grain of a crop of wheat is exactly one pound per acre.

"On Benzoline, a new organic Salt-base obtained from Oil of Bitter Almonds." By George Fownes, Esq., F.R.S.

Pure oil of bitter almonds is converted, by the action of a strong solution of ammonia, into a solid white substance having a crystalline form, and which was termed by M. Laurent *hydrobenzamide*. The author found that this substance, by the further action of alkalies, became harder and less fusible than before, and not differing in chemical composition from the original substance, but exhibiting the properties of an organic salt-base. To this substance the author gives the name of *benzoline*. He finds that the salts which it forms by combination with acids are, in general, remarkable for their sparing solubility; and that many of them, as the hydrochlorate, the nitrate and the sulphate, are crystallizable. Of the properties of these salts the author gives a detailed account.

British Association for the Advancement of Science.—Meeting held at Cambridge, June 19th, 1845.

The following are abstracts of the principal communications brought before the Chemical Section, as reported in the *Athenæum* :—

On a new Property of Gases. By Prof. GRAHAM.

After explaining the law which regulated the diffusion of gases through porous bodies, and stating the fact that the lighter gases diffused themselves much more speedily than the more dense ones, he proceeded to relate his experiments on the passage of gases into a vacuum. To this passage the term Effusion has been applied. The velocity of air being 1·0, the velocity of oxygen was found to be 0·9500 by experiment, and by calculation 0·9487. Carbonic acid, being much heavier than air, gave the number 0·812. Carburetted hydrogen gave 0·1322 as the velocity of its effusion. Hydrogen gave as the velocity of effusion 3·613 by experiment, which was very nearly the amount given by theory. The interference of friction, even of minute orifices, was then described, and shown to admit of easy correction. Some useful applications were mentioned, as in the manufacture of coal-gas, where it is desirable to ascertain the quality as well as the quantity of gas manufactured. As the gas will pass the orifice on its way to a vacuum the quicker the lighter it is, and the more slowly as it increases in density, and as the superior carburetted hydrogen is heaviest, it would be easy to construct an instrument to register this velocity, and thus mark at once the required quality and quantity of gas. It was also proposed that an instrument might be used in mines to detect the presence of light carburetted hydrogen (fire-damp). The passage of gases under pressure through porous bodies was termed by Prof. Graham, transpiration. The mode adopted in experiment was, to take a glass receiver, open at the top, which was closed with a plate of stucco. This was placed on an air-pump, the air exhausted by the pump, and the velocity with which the air passed through the stucco marked by the mercurial gauge of the pump. The transpiration of atmospheric air was found to be greater than that of oxygen. Carbonic acid is found to be more transpirable than oxygen, or even, under low pressure, than atmospheric air. The transpiration of hydrogen is one-third more rapid than that of oxygen. The applicability of this process of experimenting to the explanation of exosmose and endosmose action in the passage of fluids through porous bodies was pointed out.

On the Gases from Furnaces. By Prof. BUNSEN *and* Dr. LYON PLAYFAIR.

The authors described, in the first instance, their method of collecting the gases from the furnaces, which they had succeeded in doing from every part of the iron furnaces, and this in England, Norway and Sweden. The imperfect state of eudiometry was dwelt on, and the mode adopted by the authors described; but as the details necessarily involve a number of purely chemical questions, we shall only refer to the more interesting facts. By the improved method the condition of the atmosphere was first ascertained, and the average of many experiments gave as its composition—

Nitrogen	70·09
Oxygen	20·91

which is nearly the result obtained by other eminent chemists. The analyses of the various carburetted hydrogens, collected from coal and coke, were next detailed, and many improvements named, particularly that the perchloride of antimony completely absorbed all the carburetted hydrogens, whether the fire-damp or the olefiant gas, allowing the carbonic oxide and carbonic acid to pass freely, which were afterwards collected and ascertained in the usual manner. The gases proceeding from iron furnaces were found to be—

1. Nitrogen.
2. Ammonia.
3. Light carburetted hydrogen.
4. Olefiant gas.
5. Carbonic oxide.
6. Carbonic acid.
7. Carburetted hydrogen of unknown composition.
8. Aqueous vapour.
9. Hydrogen.
10. Sulphuretted hydrogen.

The gasification of coal in the furnaces takes place at two different periods; in the first instance, during the distillation of the coal and the formation of coke; and secondly, when the coke undergoes the process of combustion. This result was uniformly observed, and the authors verified it by subsequent experiments on artificial arrangements. The analysis of coal by dry distillation gave—

Coke	68·72
Tar	12·23
Water	7·61
Light carburetted hydrogen	7·04
Carbonic oxide	1·13
Carbonic acid	1·07
Olefiant gas	0·75
Sulphuretted hydrogen	0·75
Hydrogen	0·50
Ammonia	0·17
Nitrogen	0·03
	100·00

This report went very extensively into the various methods adopted by the authors to ensure an accurate determination of all the gaseous products of the hot-blast iron furnaces. It was found that coking was effected in the furnace to the depth of 24 feet, that the distillation of coal reached its maximum at the depth of 14 feet, and that the formation of tar took place at between 17 and 14 feet; hence the coal had to travel 24 feet from the mouth of the body of the furnace to the boshes to be entirely coked. A great diminution of oxygen is found to occur at those points where the gases become developed, and hence they pass away without undergoing combustion; and it has been estimated that 91 per cent. of the heating material in the form of gaseous products are lost in the hot-blast furnaces. The combustible gases driven off from the furnaces were expelled with a force superior to that used in driving coal-gas through the mains for the purpose of lighting towns. These matters having been thoroughly examined, and all the gaseous products submitted to analysis (many of the results being of a very curious character), the authors suggest the propriety of building a canal just above the point at which the gases are given off, for the purpose of conveying these products to other parts where their very high heating and illuminating powers may be employed advantageously. These gases in combustion, with a due supply of oxygen, would give a temperature higher than is necessary for smelting iron; and although the authors do not propose that it should be used for that purpose, they suggest the advantage of employing that waste material for heating steam apparatus, and many manufacturing processes.

Analyses of Three Species of Fucus. *By* E. G. SCHWEITZER.

These analyses were undertaken with a view to ascertain the causes which render one kind of fuci beneficial as a manure, whilst other kinds do not succeed. It was found that in the *Laminaria saccharina* the alkaline carbonates predominated, whilst in the *Fucus vesiculosus* and *Fucus serratus* there was an excess of the sulphates; and in the *Laminaria* potash is found in larger quantities than soda, whilst the contrary is the case with the *Fuci*. The quantity of iodine in *Laminaria* was also greater than in the other two. Some experiments were tried, to ascertain if the *Laminaria* exhaled iodine under the influence of sunshine, but no such exhalation could be detected.

On the Voltaic Reduction of Alloys. By C. V. WALKER.

The process adopted is to prepare a strong solution of cyanide of potassium, and commence electrolysing it by means of a copper anode; as soon as copper begins to be dissolved, the copper anode is removed, and its place supplied with one of zinc; after the action has continued for some little time, brass will be liberated on the cathode. The solution is now ready for use, and is operated upon by two or three Daniell's cells, and with a brass anode. By similar means alloys of gold and copper, or gold and silver, may be deposited. The author reasons, that true brass is a definite chemical compound, and states, it appears possible that the anode, which is a brass of commerce, is a true alloy plus an excess of zinc; and that the solution it produces is a mixed solution, which consists of the potassiocyanide of brass and the potassiocyanide of zinc. This solution is very readily decomposable; it is therefore necessary to prepare it a short time previously to its use. Many specimens of copper and other metals coated with brass were exhibited. The author makes some remarks on the theory of the action; and concludes by stating that it will be quite possible to determine, within certain limits, the character of the alloy that shall present itself, and that we may be enabled to throw down gold and silver according to standard.

Experiments on the Spheroidal State of Bodies, and its Application to Steam-boilers, and on the Freezing of Water in red-hot Vessels. By M. Boutigny.

M. Boutigny, who made his communication in the French language, first proceeded to show that a drop of water projected upon a red-hot plate does not touch it; but that a repulsive action is exerted between the plate and the fluid, which keeps the latter in a state of rapid vibration. At a white heat this repulsion acts with the greatest energy, whilst it ceases and the ordinary process of evaporation takes place at a brown-red heat. The temperature of the water whilst in the spheroidal state is found to be only 96°, and this temperature is maintained so long as the heat of the plate is kept up. To bring this water to the boiling-point (to 212°), it is therefore necessary to cool the plate. These phænomena are explained by M. Boutigny on the supposition that the sphere of water has a perfect reflecting surface, and consequently that the heat of the incandescent plate is reflected back upon it; and some experiments have been made which show that this is the case, the plate becoming visibly redder over those parts on which the vibrating globule played. Several experiments were made in proof of this necessary cooling to produce ebullition. The red-hot plate, with its spheroidal drop, was removed from the spirit-lamp, and after a minute or two the water began to boil, and was rapidly dissipated in steam. Ammonia and æther were shown, although so exceedingly volatile, to act in the same manner; the æther, however, being decomposed whilst in the vibratory condition, in the same manner as it is by the action of platina-wire, forming a peculiar acid. Iodine put upon the heated plate became fluid, and revolved in the same manner as other fluids, no vapours escaping whilst the high temperature of the metal was maintained; but when allowed to cool to the point of dull redness, it was immediately dissipated in violet vapours. The nitrate of ammonia fused on the glowing hot plate, and vibrated with great energy; but on cooling the capsule the salt entered into vivid combustion. The repulsive action was shown by plunging a lump of silver at a glowing red heat into a glass of water. As long as its bright redness was maintained there was no ebullition, but as it slowly cooled boiling took place. In this experiment it appeared as if the glowing metal formed around itself an atmosphere, and the contiguous surfaces of the water appeared like a silvered plate. The application of the principles involved in these phænomena to the tempering of metals was then explained. If a metal to be tempered is in a highly incandescent state, the necessary hardening will not take place on plunging it into water; it is therefore necessary that a certain temperature should be observed. Experiments were made to show that the repulsive power of the spheroidal fluid existed, not merely between it and the hot plate, but between it and other fluids. Æther and water thus repelled each other, and water rested on and rolled over turpentine. The bursting of steam-boilers came next under consideration, and it was shown that many serious explosions may be referred to the phænomena under consideration. In a great many cases the explosions have occurred during the cooling of the boilers after the withdrawal of the fire. An experiment was shown in proof of the view entertained by M. Boutigny. A sphere of copper, fitted with a safety valve, was heated, and a little water being put into it, it was securely corked up and withdrawn from the lamp. As long as the metal remained red everything was quiet, but upon cooling the cork was blown out with explosive violence. The concluding experiment excited great interest. The production of ice in a vessel at a glowing red heat was a result so anomalous, that every one was desirous of witnessing the phænomenon for himself. It was beautifully performed by M. Boutigny, in the following manner:—A deep platina capsule was brought to a glowing red heat, and at the same moment liquid sulphurous acid, which had been preserved in the liquid state by a freezing mixture, and some water, were poured into the vessel. The rapid evaporation of the volatile sulphurous acid, which enters into ebullition below freezing point, produced such an intense degree of cold that a large lump of ice was immediately formed, and being thrown out of the red-hot vessel, handed round to the company in the Section.

On Fizeau's *Process of etching Daguerreotype Plates, and its Application to Objects of Natural History. By* Mr. Goadby.

In a Daguerreotype portrait, the black parts of the plate consist of silver, the white of mercury, and the intermediate tint of a mixture of the two, the degree of darkness or light depending upon the excess either of the silver or of the mercury. In converting a Daguerreotype into an engraved plate, it is necessary to etch away the dark parts and to leave the white untouched. This is done by immersing the plate in a fluid, consisting of dilute nitric acid, nitrous acid, chloride of sodium and nitrate of potash. The nitric acid is so far diluted that no decomposition can take place until the mixture is heated, when the chloride of sodium and nitrate of potash are decomposed, and chlorine and nitrous acid are evolved. These attack and remove the silver, or the *dark* portions of the plate, but have no effect on the mercury; so that the *lights* of the picture, being the mercurialized portions of the plate, constitute the *etching* ground, and effectually defend such portions of the Daguerreotype from the influence of the corroding fluid. After a time, those portions of the plate that have been acted upon by the chlorine, &c. become covered with a protecting coat of the chloride of silver; this must be removed by dilute liquid ammonia, when the biting may be continued by a fresh supply of the mixed acid. Grease and foreign matter must be removed by repeated washings in dilute acid and alkali, and by boiling in caustic potash. These cleansing operations must be repeated after every biting, after washing out the chloride of silver by the ammonia. The plate being thus bitten, but in a slight degree, is to be inked after the ordinary manner of engravers, and allowed to dry; the surface of the plate is then to be thoroughly polished, the ink still remaining in the corroded portions of the plate. It is now to be gilded by the electrotype, those parts alone receiving the gold that have been previously polished. The ink is then to be dissolved out of the hollows by potash; the parts that are gilded now constitute the etching ground, instead of the mercury, and the biting may be henceforth continued by nitric acid, in the customary usage of engravers. The plate thus etched generally requires to be finished by the hand of the engraver, who has the advantage of a *perfect*, although *faint* picture to work upon. The amount of labour which he must bestow will depend upon the goodness of the Daguerreotype and the success of the etching. M. Claudet has fully established the successful application of this process to the purposes of illustrating natural history, by copying from nature and engraving several delicate and difficult dissections of the lower animals, particularly the nervous system of *Aplysia* and *Tritonia* (the latter much magnified), and the nutrimental organs *in situ* of a caterpillar. These preparations, together with the engravings of them, were handed round.

On the Ashes of Narcotic Plants. *By* F. C. WRIGHTSON.

The great problem of chemistry of the present day in its application to agriculture is, to determine the conditions necessary for a soil to produce the largest amount of any given crop of animal food, of food for man or beast. The solution to this question will in some measure be found when we have ascertained the proportions of mineral constituents required by plants of culture for attaining full perfection. The analysis of these plants alone, however, is not sufficient; we must have analyses of the weeds growing upon soils, of plants unfit for the sustenance of animals; for it is shown that they rob the farmer, not only of a large amount of mineral manure, but also of considerable quantities of that valuable ingredient, ammonia; and we shall not have obtained the data necessary for an improved and rational system of culture until we include in our ash analyses a considerable number of weeds and useless plants, especially those of the most destructive kind. Some of them are well-known to the farmer to be of serious injury to his crops mechanically; with respect to their abstracting important constituents of the soil, their injurious effects cannot be questioned. These plants contain more than 8 per cent. chlorine, and from 30 to 50 per cent. alkalies in their ashes. The *dried leaves* contained between 6 and 8 per cent. of nitrogen.—

Observations on the Ashes of Plants. *By* Prof. JOHNSTON.

Prof. Johnston drew attention to the differences in quantity of ash left, not only by different parts of the plant, but by the same part of different plants and by different portions of the same part.

Thus, he stated that the ash of wheat-straw varied from less than 3 to upwards of 18 per cent., that of oats from 3 to 10 per cent. in different samples. But a more interesting result was, that the quantity of ash left by different parts of the straw varied very much. In wheat-straw it generally increases upwards. These facts are of importance, both in a physiological and in a practical point of view, in regard both to what may be considered as essential to the several parts of the plant, and to the functions of the inorganic constituents which are found in them.

On the Manufacture of a Coloured Glass. By M. SPLITTGERBER.

Specimens of glass were exhibited, into the composition of which gold entered as a chloride. These speciments were white, but upon gently heating them in the flame of a spirit-lamp they became a deep red, transmitting the red rays of light only. If again the same reddened glass is exposed to the heat of an oxygen blowpipe, it loses nearly all its colour, a slight pinkiness only remaining. M. Splittgerber considers these results to arise from the oxidation of the chloride of gold in the siliceous compound.

PATENT.

Patent granted to David Metcalf, Leeds, *for a Mode of manufacturing or preparing a new vegetable Preparation, applicable to dyeing Blue and other Colours.*

THIS invention consists in the manufacture of a new vegetable preparation for dyeing, by subjecting the leaves of a certain plant, sometimes called succory, but more commonly known as chicory, to the same process of manufacture or preparation as has been heretofore applied to the leaves of the woad plant, in order to fit them for the dyer's use.

The leaves of the chicory plant are first ground or crushed in a mill, such as is ordinarily employed in the preparation of woad; then the granulated mass is formed into balls, which when sufficiently dry are broken into small pieces, and subjected to the fermenting process termed couching; after which the article is ready for the dyer.

In some cases the leaves of the chicory plant are sufficiently dry, after the first grinding, to be subjected at once to the couching process, without the delay occasioned by the preparatory drying.—Sealed Nov. 21, 1844.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Protosalts of Mercury and some of the resulting Ammoniacal Compounds. By M. J. LEFORT.

THIS memoir comprises the investigation of several protosalts of mercury. I have devoted especial attention to the compounds which have a pharmaceutical application; but as the comparative investigation of different salts of a metallic series frequently explains the constitution of each of them, I have included some salts which have hitherto received no application.

As far as possible I have determined quantitatively most of the elements contained in the different salts; for the estimation of the mercury I had recourse to the analytical method described by M. Millon, with some slight modifications according to the nature of the salt. The formulæ have been calculated with the new equivalent for mercury, 1250·9, as recently determined by Erdmann and Marchand*. The determination of the nitrogen was above all indispensable, in order to fix the formulæ expressing the composition of the nitrates. I have also taken great care to ascertain accurately the quantity of the water, this being the sole means of removing certain doubts which I entertained respecting the formulæ of the nitrates of mercury. I found it impossible to separate the water from the mercury, but I succeeded perfectly in condensing simultaneously the mercury and water; as the precise quantity of the former was known, I obtained the weight of the water by subtracting that of the mercury. A current of pure dried carbonic acid gas was passed through the apparatus employed for condensing the water and mercury, and to the extremity of the apparatus a weighed chloride of calcium tube adapted; the mercury and the water derived from the decomposition of the nitrate, passed either into the bulb, for the condensation of the mercury, or into the chloride of calcium tube. In several cases I had to decide whether the compounds of the protoxide of mercury were true combinations or simple mixtures. The question is one of extreme delicacy, and I dare not affirm that I have entirely solved it. I ascertained however that by rubbing for a few instants the products obtained with the protoxide of mercury on a gold plate, this became white with some, and remained

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* See Chem. Gaz., vol. ii. p. 399.

unaltered with others. When the gold plate became white, I soon detected the presence of metallic mercury and of the salts of the binoxide. This reagent appeared to me to have less decomposing influence than any other on the constitution of the mercurial compounds.

Carbonate of the Protoxide of Mercury.—The processes hitherto described for the preparation of this salt are very inaccurate; they all yield a product of variable appearance and composition, which strongly whitens the gold plate.

A pure homogeneous product, constant in its composition, is obtained by adding in drops a dilute solution of the protonitrate of mercury to freshly-prepared cold solution of bicarbonate of potash. A yellowish-white precipitate is formed, which should be washed with water charged with carbonic acid*. After sufficient edulcoration, the product, which should be guarded from the light during these operations, is dried over sulphuric acid. It forms, when perfectly dry, a bright yellow amorphous powder, which does not turn the gold plate white, but which soon becomes black by exposure to light, and then acts on gold leaf.

This salt is anhydrous; it retains merely a fraction of interstitial water, which it loses at about 212°, being decomposed; at 266° it disengages carbonic acid, leaving binoxide and metallic mercury. Cold water alters it very slowly, but boiling water decomposes it immediately; all the acids liberate carbonic acid. On analysis it yielded 86·51–86·59 per cent. mercury; the formula CO^2, Hg^2O requires 86·95. The salt was submitted to another analytical test, which consisted in measuring the gases given off on complete decomposition, and weighing the metallic residue. The gaseous volume expressed by a mixture of oxygen and carbonic acid agrees with the loss in weight represented by the following numbers:—

0·896 grm. lost 0·113 grm. oxygen and carbonic acid, or in 100 parts, 12·61; according to calculation it should be 13·04.

Protonitrite of Mercury.—This salt, which Dr. Kane regards as basic protonitrate of mercury, is formed under certain circumstances when mercury is acted on by concentrated nitric acid.

Three principal modes of preparation may be distinguished:—

1. Like equivalents of nitric acid with 4 equiv. of water and of metallic mercury are brought into a flask, and the mixture then submitted to the action of heat. On evaporation of the solution, a yellow crystalline salt is obtained, which consists of pure nitrite; it is washed with water, which does not affect it.

2. A nearly syrupy solution of uncrystallizable binitrate of mercury, diluted with 3 or 4 volumes of water, and placed in contact with metallic mercury, deposits an abundant crop of crystals of the nitrite, sometimes mixed with protonitrate.

3. The protonitrates of mercury, heated moderately in an alloy-bath, become yellow at the same time that they disengage water and

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* It is indispensable to add the nitrate to the bicarbonate, as otherwise not a trace of carbonate would be obtained, but in its place a nitrate of a peculiar composition, which will be described subsequently.

red vapours. If the residue be extracted with water slightly acidulated with nitric acid, so as to dissolve the subsalt of binoxide which is likewise formed, protonitrite is again obtained.

This salt is very sparingly soluble in water and in dilute nitric acid; an excess of concentrated nitric acid immediately converts it into nitrate. Exposed to the action of heat, it resists up to 536°, but at 554° it begins to give off red vapours. On analysis it yielded 81·51–81·66 per cent. mercury and 5·83–5·93 nitrogen; the formula NO^3, $Hg^2 O$ requires 81·24 mercury and 5·75 nitrogen.

To estimate the mercury of the nitrite and nitrates, it is indispensable to place some copper turnings in the tube of decomposition, in order entirely to destroy the oxides of nitrogen. The presence of nitrous acid is readily ascertained by decomposing the salt with an excess of weak hydrochloric acid, and then filtering the solution; an abundant deposit of protochloride of mercury results, and the filtered liquid is saturated with nitrous acid, which is readily detected by a solution of sulphuretted hydrogen. With the least traces of nitrite, sulphuretted hydrogen yields a very manifest deposit of sulphur, while a nitrate subjected to the same treatment does not in the least alter sulphuretted hydrogen. It is possible that this reaction may have led Dr. Kane into error, he having determined the mercury of the nitrite in the state of sulphuret; his calculation consequently referred to a mixture of sulphur and sulphuret of mercury.

Oxalate of the Protoxide of Mercury is obtained by mixing solutions of oxalic acid or of binoxalate of potash and of protonitrate of mercury. The white precipitate which forms is wholly insoluble in water, which does not decompose it. The oxalate is not hydrated, as asserted by M. Burckhardt, but merely retains, like most of the anhydrous protosalts of mercury, a small quantity of water, which it does not part with over sulphuric acid, but which is expelled by a temperature of 212°. Exposed gradually to the action of heat in an alloy-bath between 230° and 248°, the protoxalate is decomposed without detonation; but when heated suddenly it produces a somewhat powerful explosion; it should be preserved from the luminous rays, which very readily decompose it. In analysing it, it should be mixed with 8 or 10 times its weight of caustic lime; without this precaution it would explode on the application of heat. It yielded 81·29–81·90 per cent. mercury; the formula $C^2 O^3$, $Hg^2 O$ requires 81·66.

Protiodate of Mercury is obtained very pure by adding a solution of the protonitrate of mercury to one of iodic acid or of iodate of soda; it forms a white powder insoluble in water, is anhydrous, but retains traces of water amounting to 2 or 3 millionths, which it loses at 212°. It is decomposed at about 482° into biniodide and binoxide of mercury and oxygen; boiling water does not affect it; cold nitric acid is without action on it, but if the temperature be raised, red vapours make their appearance, and there is then formed biniodate of mercury. Hydrochloric acid decomposes it into chloride of iodine and bichloride of mercury with disengagement of chlorine. To determine the mercury, a mixture of potash and lime in powder should be placed before the salt in the tube for decomposition, in order to retain the iodine, which would be volatilized with the mercury if lime were alone present. The salt yielded 53·35–53·75 per cent. mercury and 12·46–13·02 oxygen; the formula IO^5, Hg^2O requires 53·42 Hg and 12·82 O.

Acetate of the Protoxide of Mercury.—Of all the salts of the protoxide of mercury the acetate is one of those whose history is best known, and I have little new to add concerning it. When prepared with acetic acid and protonitrate of mercury, the salt is obtained in beautiful white pearly scales; but as a white precipitate when procured by double decomposition of the acetate of potash and protonitrate of mercury. It has been advised to prepare it from the acetate of the binoxide and metallic mercury; but this process has no advantage, for it is requisite to boil for a considerable time, in order to reduce the binacetate to the state of protacetate. In analysing this salt, the first half of the tube for the decomposition should be filled with metallic copper, and the second with caustic lime in order to destroy completely the acetone, or other products that might be formed in the operation. It yielded 77·72–77·29 per cent. mercury; the formula $C^4H^3O^3, Hg^2O$ requires 77·22.

Nitrates of the Protoxide of Mercury.—I shall restrict myself to giving the most precise indications respecting the principal protonitrates of mercury; for it would be far too long, and nearly useless, to discuss each of the circumstances which have induced me to proceed in a different way than according to the directions hitherto given. The protonitrates of mercury, which I have succeeded in isolating, are represented by the following formulæ:—

Acid biatomic nitrate	$2NO^5, 2Hg^2O, 5\frac{1}{2}HO.$
The same salt dehydrated	$2NO^5, 2Hg^2O, HO.$
Intermediate nitrate	$2NO^5, 3Hg^2O, 2\frac{1}{2}HO.$
Neutral biatomic nitrate	$NO^5, 2Hg^2O, 2HO.$

All these nitrates may be connected in a polyatomic and at the same time hydric system $(Hg^2O)^2, HO$. This system would at the same time be subject to the laws of the polyatomic and hydric bases on the union of its components with nitric acid. The above formulæ should consequently be arranged as follows:—

1. Acid biatomic nitrate.... $NO^5, (Hg^2O)^2, HO, + NO^5, 4\frac{1}{2}HO.$
2. The same salt anhydrous.. $NO^5, (Hg^2O)^2, + NO^5 HO.$
3. Intermediate nitrate .... $NO^5, (Hg^2O)^2 + NO^5, HO$
   $+ 2(NO^5 HO (Hg^2O)^2 HO).$
4. Neutral biatomic nitrate.. $NO^5, HO, (Hg^2O)^2, HO.$

The intermediate nitrate represents 1 equiv. of nitrate No. 2 and 2 equiv. of nitrate No. 4.

When the nitric acid is very concentrated, a mixture of binoxide and protosalt, nitrate and nitrite, is always obtained, although there is an excess of mercury. The binitrate, it is true, may be entirely reduced to the state of protosalt by diluting the liquid and boiling it for a long time over mercury, but this conversion requires long ebullition. By taking cold nitric acid containing 4½ equiv. water, diluted with ½ a volume of water, or hot acid diluted with 3 volumes of water, the protosalt of mercury is always obtained if the metal be in excess; in fact, nothing but protosalt is formed from the very commencement of the operation. The investigation of the different protonitrates will show under what circumstances the one or other is obtained.

Acid Biatomic Nitrate of the Protoxide of Mercury.—This salt is procured by dissolving any of the following nitrates in dilute pure nitric acid. It is also obtained by treating in the cold excess of mercury with nitric acid with 4½ equiv. water diluted with 1 or 2 volumes of water; or again, by boiling down to half, over an excess of mercury, nitric acid with 4½ equiv. water diluted with 10 volumes water. The saline solution formed in the latter case should again be evaporated to about half. The salt which subsides on the cooling of the liquid crystallizes in colourless obtuse rhombohedrons, soluble in water with a slight residue. Exposed to the air, this salt loses its water with great facility; to preserve it, it should be pressed quickly between blotting paper, and placed in a bottle which may be hermetically closed. Submitted to the action of heat, it fuses at 158°. On analysis it yielded 69·98–69·06 mercury and 4·90–4·83 per cent. nitrogen; the formula $NO^5, (Hg^2 O) HO, + NO^5, 4\frac{1}{2}HO$ requires 69·69 Hg and 4·94 N.

When the salt is placed over sulphuric acid until it loses no more in weight, it is found to have parted with 4½ equiv. water, or 7·13 per cent.

The anhydrous salt yielded 74·86–74·39 per cent. mercury and 4·98 nitrogen. The formula $NO^5, (Hg^2 O)^2 + NO^5, HO$ requires 74·98 Hg and 5·31 N.

Intermediate Nitrate of the Protoxide of Mercury.—When 1 part of nitric acid with 4½ equiv. water, diluted with 5 parts of water, is boiled for 5 or 6 hours over an excess of mercury, taking care to renew the water as it evaporates, the salt obtained on the cooling of the liquid forms rhomboidal prismatic crystals, which are transparent, and not in the least altered by contact with the atmosphere. If the mixture has not been boiled sufficiently long, some crystals of the acid biatomic nitrate are deposited at the same time with the intermediate nitrate; it contained 79·83–79·42 mercury, 4·14–3·96 nitrogen, and 2·55–2·88 per cent. water. The formula $NO^5, (Hg^2 O)^2, NO^5, HO + 2(NO^5, HO\ (Hg^2 O)^2, HO)$ requires 79·25 mercury, 3·73 nitrogen and 3·24 water.

Neutral Biatomic Nitrate of the Protoxide of Mercury.—This salt is formed when dilute nitric acid and excess of mercury are exposed for some time on a sand-bath heated between 104° and 176°. But it is likewise formed under two very remarkable circumstances:—1. If a solution of bicarbonate of potash be poured into one of nitrate of mercury until the formation of a precipitate, the filtered liquid deposits some very voluminous crystals, which consist solely of biatomic nitrate. 2. When the product resulting from the action of concentrated nitric acid on an excess of mercury is evaporated to dryness, and the residue treated with boiling water, this deposits on cooling crystals of the neutral biatomic nitrate.

This salt forms oblique prismatic crystals, frequently very large, and which are but little altered by exposure to the air. It yielded on analysis 81·67–82·02–82·03 per cent. mercury, 3·51–3·10 nitrogen, and 3·63–3·44 water. The formula $NO^5, HO\,(Hg^2\,O)^2, HO$ requires 81·93 mercury, 2·90 nitrogen and 3·68 water.

The intermediate and neutral biatomic nitrates are decomposed by cold as well as by hot water; the acid biatomic nitrate is likewise decomposed by water, but in smaller proportion. These phænomena of decomposition have puzzled many chemists, who have described as distinct the different grades of this decomposition; but as soon as the water has acted on the two first basic salts, the residue whitens the strip of gold very considerably. H. Rose has moreover very satisfactorily demonstrated that the protosalts of mercury yield, under the influence of boiling water, binoxide and metallic mercury.

Action of Alkalies and of Caustic Ammonia on the Protosalts of Mercury.—M. Guibourt was the first to announce that the protonitrate and the protochloride of mercury, when treated with caustic potash or soda, yielded a mixture of metallic mercury and of the binoxide instead of protoxide, as was generally admitted.

This reaction of the alkalies has been frequently investigated, and with various results. I experimented under the most favourable conditions for furnishing the protoxide of mercury, and have acted on a large number of salts, such as the carbonate, oxalate, iodate, acetate, &c. The product obtained always whitened the strip of gold, and behaved like a mixture of the binoxide and metallic mercury.

Hitherto ammonia has appeared to exert a very different action from that of the fixed alkalies, and in some recent investigations peculiar formulæ have been assigned to the compounds resulting from the action of caustic ammonia on the protosulphate, protochloride and protonitrate of mercury. The experiments and analyses which I have made lead me to believe that ammonia only differs from potash and soda by the peculiar action it has on the bisalts of mercury. Whenever either dilute or concentrated caustic ammonia acts on a protosalt of mercury, the black or grayish product formed possesses the property of whitening a strip of gold; we moreover find in it all the characters belonging to the ammoniacal bisalts of mercury, which are formed in virtue of the peculiar reaction of ammonia on the bisalts of mercury.

Only the protochloride of mercury yields with caustic ammonia a mixture of constant composition; but this is very easily explained by the perfect insolubility of the white precipitate, which equals, so to say, that of metallic mercury. With all the other salts the quantity of mercury increases proportionately to the solubility of the ammoniacal bisalt, either in water or in the caustic ammonia. Thus, on acting with an excess of highly concentrated ammonia on the precipitate formed in the protosulphate of mercury, metallic mercury is obtained as residue.

With the protonitrate of mercury ammonia yields a mixture whose proportions vary most readily. As the products resulting from this reaction are frequently employed in medicine under the name of Hahnemann's soluble mercury, I have established by analysis the changes which the composition of this product may present, for fear any one may advise modifying its preparation. It suffices, as may be seen, to operate at 32° or at 77°, and to wash more or less to obtain in the mixture very different proportions of mercury, although excepting these slight variations of washing or temperature, the conditions prescribed by the formulæ are accurately followed.

Analysis of Hahnemann's Soluble Mercury:—

	Prepared at 32° and washed 8 times.	Prepared at 32° and washed 16 times.	Prepared at 77° and washed 8 times.	Prepared at 77° and washed 16 times.
Mercury . .	83·42	89·47	84·94	91·11

Journ. de Pharm., July 1845.

Analysis of the Urine of the Herbivora. *By* M. Boussingault.

The author finds this urine to contain bicarbonate of potash, and not the subcarbonate, as was formerly supposed. Excluding the urea and hippuric acid, it closely resembles an alkaline mineral water in composition, and may be advantageously employed for the solution of uric acid calculi.—*Comptes Rendus*, July 7, 1845.

Observations on some new Compounds of Phosphorus.

By Paul Thénard.

The analogy which exists between phosphorus and arsenic led me to think it might probably be possible to obtain with phosphorus a similar compound to that furnished by arsenic, and which is known by the name of cacodyle. This idea induced me to pass hydrochlorate of methylene through a large excess of phosphuret of lime at temperatures varying between 356° and 572°. By continuing the experiment for a very long time, I observed that at least five products, three liquid and two solid, were formed.

Among the three liquids there is one which I have examined with much greater care than the others, and which presents some very remarkable properties. This liquid, which I believe to consist of phosphuretted hydrogen and of carbon, in proportions which I have not yet fixed, is a true alkali, which quickly restores the blue colour to reddened litmus-paper, and combines with acids, forming neutral salts. The new alkali is colourless; it has a warm, bitter taste; its odour is somewhat similar to that of ammonia; its tension at the ordinary temperature and pressure is between 430 and 440 millimetres, and its boiling-point between 104° and 106°. I found 2·61 for the density of its vapour; but this number is too high, owing probably to an absorption of oxygen, which all the precautions I employed were not able to prevent.

Exposed to the influence of heat, the alkali distils without being decomposed; submitted to the action of a small current of atmospheric air, it absorbs the oxygen with evolution of light, forming a peculiar acid. This acid immediately combines with a portion of the unaltered alkali, forming a salt, which crystallizes readily in beautiful transparent needles, and in which there is finally an excess of acid. By introducing small quantities of the liquid into a balloon which is kept cool, it is obtained still more easily. Care should be taken not to pour the liquid into pure oxygen, as it would take fire suddenly, and the explosion would be terrible.

Agitated with water, it does not dissolve in it in perceptible quantity, and collects on the surface like a kind of very light oil. Its reaction on the oxide of mercury presents a phænomenon worthy of attention; it takes place in the cold; the oxide of mercury is reduced; the temperature rises considerably, and at the same time some beautiful white needles are sublimed, which appear to be the pure acid into which the alkali is converted by oxidation.

I have combined the alkali with hydrochloric, sulphuric, nitric, phosphoric, tartaric, oxalic and acetic acids; and with all it forms neutral salts, and with some even acid salts. The hydrochlorate precipitates chloride of platinum in the form of a yellow crystalline powder. With solutions of copper it gradually forms an abundant crop of beautiful white needles, reducing the peroxide of copper to the lowest state of oxidation. It reduces the salts of gold. Its capacity of saturation has been determined with sufficient accuracy; it is the same as that of ammonia, for 1 volume of the alkaline vapour requires, in order to be neutralized, 1 volume of hydrochloric gas.

At the ordinary temperature all the salts of the new alkali are decomposed by soda, potash and lime, and the alkali set at liberty. I endeavoured to analyse it by burning it with oxide of copper in the usual way. I found in the first experiment 46·1 per cent. carbon and 11·6 hydrogen, and in the second 46·08 carbon and 11·7 hydrogen, without the appearance of any other gas. The combustion was complete; the numbers appear to come sufficiently near the truth. But in the determination of the phosphorus I have met with difficulties which I have not yet entirely been able to overcome. One of the processes which promises to be most successful consists in passing the vapour of the substance through a long column of an intimate mixture of oxide of mercury, carbonate of soda and fragments of porcelain at a red heat; the whole of the phosphorus burns, forming with the soda a phosphate, which is analysed by the ordinary processes.

Although this last experiment leaves much to be desired, I have strong reasons for supposing that the new alkali does not contain any oxygen, and that it is formed in equivalents of $C^6 H^9 P$, divided into $C^6 H^6$ and PH^3.

The two other liquids whose existence I think I have recognised likewise possess very distinct properties. Both contained phosphorus, carbon and hydrogen; one of them is slightly yellowish and viscous, void of smell, very dense, difficultly volatile, without action on the air at the ordinary temperature, and insoluble in water and most of the acids, with the exception of concentrated hydrochloric acid, which readily effects its solution.

Lastly, the third liquid, colourless like the first, possesses a high refractive power, resembles to a certain extent the odour of cacodyle, and burns with great liveliness by contact with the atmosphere; it must therefore be handled with great precaution. I am inclined to believe that it is analogous in its composition with cacodyle properly so called; at least it is certain that under the influence of weak sulphuric acid it is changed into the sulphate of the alkali whose properties I have above described, and into the second of the liquids of which we have just spoken.

Now if the composition of the alkali is represented by $PH^3 C^6 H^6$, the two other liquids might be, the one $C^4 H^4 P^2$, the other $C^2 H^2 P^2 H$, that is to say, the three compounds of phosphorus and of hydrogen, $P^2 H$, PH^2, PH^3, would combine, the first with $C^2 H^2$, the second with $C^4 H^4$, the third with $C^6 H^6$,—very simple formulæ, which were suggested to me by the formula $C^4 H^4 NH^2$, which M. Dumas advanced for the arsenical cacodyle.

However, for these ideas to be admitted, they must be confirmed by positive analyses, which as yet I have been unable to do. As to the two solids which are formed in the action of the hydrochlorate of methylene on the phosphuret of lime, one of them is well known to me; it is the hydrochlorate of the new alkali, which in fact is obtained pure by treating its solution in water with lime.

I know nothing positive with respect to the second solid, excepting that it is very easily formed under the influence of an excess of lime in the phosphuret of lime, and that it crystallizes in beautiful long white needles.—*Comptes Rendus*, July 14, 1845.

Identity of Bezoardic and Ellagic Acid. *By* M. WÖHLER. (*In a Letter to* M. DUMAS.)

The bezoardic acid, which I mentioned in my former letter*, is nothing more than the ellagic acid of M. Braconnot. It is a very remarkable fact, as it proves that the substance of the bezoars is owing to the nutriment of the animals containing, without doubt, either ellagic acid already formed or tannic acid. The analysis of ellagic acid made long since by M. Pelouze gave the formula $C^7 H^2 O^4$, which, as you will see, differs from mine, $HO + C^{14} H^2 O^7$, by 1 equiv. more hydrogen. There is, however no doubt that the latter is more correct.—*Comptes Rendus,* July 21, 1845.

Experimental Researches on the Chemical Phænomena of Digestion. *By* MM. BERNARD *and* BARRESWILL.

The authors state that the gastric juice contains two active principles,—1st, free lactic acid; 2nd, an organic matter, which is precipitated and destroyed by a temperature of 185°–194°. The digestive power of the gastric juice depends upon the presence of this principle; it loses it completely when this is destroyed by a high

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* Chem. Gaz., p. 299.

temperature. A remarkable property of this organic matter is, that its powers of digestion vary according to the nature of the medium in which it is contained, whether it is acid or alkaline. Thus, in the gastric juice, which is acid, as we well know, it dissolves nitrogenous matters, as fibrine, gluten, albumen, &c., whilst it has no action upon baked starch. If we render the gastric juice alkaline by the addition of a little carbonate of soda, it rapidly dissolves the amidon, whilst it has lost the power of dissolving azotized substances. As these physiological properties are exactly those of the saliva and the pancreatic fluid, it became an interesting point to ascertain if the change in the reaction of these fluids would cause an alteration in their properties, as with the gastric juice. Experience has proved this to be the case; for if we acidulate the pancreatic fluid and the saliva, which are naturally alkaline, we invert their ordinary mode of action, rendering them capable of dissolving meat and azotized matters, whilst they have lost their power of dissolving starch*.

The numerous and varied experiments related in this memoir seem to prove that an organic principle, which is the agent of digestion, exists in the gastric juice, the pancreatic fluid and the saliva, and that it is the nature of the chemical reaction alone which causes its physiological action to vary.—*Comptes Rendus*, July 7, 1845.

PHARMACOLOGY.

Examination of several Varieties of Manna of Commerce.

By A. LEUCHTWEISS.

MANNA, which, as is well known, is the concrete juice of *Fraxinus Ornus*, has already been examined by Fourcroy and Vauquelin, Thénard and Buchholz. The latter found, in 100 parts of the best kind of manna, 60 per cent. mannite, 5·5 mucous sugar with colouring matter, 0·8 of a gummy extractive substance, 1·5 gum, 0·2 of a glutinous substance, 30·0 water and loss. According to Thénard, the manna consists of mannite, a fermentable sugar (10 per cent.), and a nauseous uncrystallizable substance. As it was probable that the earlier or later season of collecting the manna, the care and cleanliness used in this process, as well as the subsequent sorting of the product, must have considerable influence on the quality, on which the value and name of the manna principally depend, the author made some comparative experiments on the most common kinds of manna. The qualitative examination showed that the odorous principle, with its nauseous and irritating taste, might be removed by treating the mannas with æther. The odour of the liquids from which the æther has been removed by gentle heating no longer resembles manna in the least, but calls to mind that of a decoction of

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* The action of the saliva on meat and starch is less energetic than that of the pancreatic fluid.

Marsh-Mallow. The æthereal solution leaves, after removal of the æther, an acid liquid, while the sides of the glass vessel become coated with a yellow film of a resinous substance, of an extremely disagreeable odour and irritating taste.

The presence of the sugar may be ascertained by the reduction of the sulphate of copper on the addition of potash even below 212°, but the test recommended by Pettenkofer is far more characteristic*.

The aqueous solutions of the mannas treated with æther are more or less yellowish-brown and turbid; they are very difficult to filter. When they are evaporated to dryness, and digested with alcohol of 0·833 spec. grav., a portion of the mannite is obtained on the cooling of the alcoholic solution in small white silky acicular crystals, but a portion remains in the yellowish-brown mother-ley. If the spirit be removed by distillation, and the residue be evaporated to dryness, it solidifies after some time into a crystalline mass; on digesting this repeatedly with absolute alcohol, the greater part of the mannite is removed, and there remains a dirty gray residue, which becomes more and more solid from the removal of water by the alcohol, and which possesses a sweet gummy taste. This residue exhibits to the naked eye no crystalline structure; but under the microscope intermixed acicular crystals of mannite are readily detected, which cannot be wholly removed even by long-continued treatment with absolute alcohol. The gummy body may be partially removed from the aqueous solution by acetate or basic acetate of lead; the filtered solution, however, is still of a yellow colour. No other body, essentially distinct from gum, could be separated from it.

Mannite.—In order to obtain pure mannite from manna, the sugar must be first destroyed by fermentation. On evaporating the filtered solutions to crystallization, and then adding as much boiling alcohol of 0·833 spec. grav. as is requisite for perfect solution, the greater portion of the mannite separates on cooling in crystals, which may be obtained beautifully white and pure by washing with cold spirit. The author obtained from 32·2–42·6 per cent. mannite.

The yellowish-brown mother-liquors yielded, on evaporation to dryness in the water-bath, 40·8–42·1 per cent. of a dark brown-coloured residue, dried at 212°; this still contained mannite, which, as above mentioned, was extremely difficult to remove entirely by means of alcohol. In preparing mannite, it would probably be more advantageous to treat the aqueous solution of the manna, of which the sugar has been destroyed by fermentation, directly with animal charcoal, and to evaporate the clear solution to crystallization.

Riegel described a compound of mannite with chloride of sodium. Knopp and Schnedermann could not succeed in obtaining this compound, which was also the case with the author. When a solution of mannite is saturated with chloride of sodium, and the liquid left to spontaneous evaporation, both crystallize out together. Frequently a crystalline mass is obtained from concentrated solutions, which might be considered as a combination; but under the mi-

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* See Chem. Gaz., p. 102 of the present volume.

croscope crystals of mannite and of the salt are readily detected; besides, spirit extracts the mannite from the dried saline mass. These experiments were repeated several times with the same result.

On adding an excess of superoxide of lead to an aqueous solution of mannite, and applying heat, only a small quantity of carbonic acid escapes, and carbonate of lead is deposited. If a slight excess of sulphuric acid is added to the liquid, and the mixture submitted to distillation, an acid passes over, which reduces the salts of silver, and has the peculiar odour of formic acid. On the addition of dilute sulphuric acid to a solution of mannite and bichromate of potash, carbonic acid is given off. On the distillation of the liquid, formic acid is obtained. If mannite be added to fused hydrate of potash, at a gentle heat so that little hydrogen gas is given off, a frothy swollen mass, which does not solidify immediately, is obtained, which contains but small traces of oxalic acid. Supersaturated with sulphuric acid and submitted to distillation, an acid liquid is obtained, which, along with acetic acid and traces of formic acid, contains a new acid, whose properties and composition have been investigated by M. Gottlieb*.

Sugar.—To ascertain the quantity of fermentable sugar in the various kinds of manna, the aqueous solution was set in fermentation by means of yeast, the disengaged carbonic acid dried by being passed over chloride of calcium, and collected in a potash apparatus, to which a tube filled with fused hydrate of potash was annexed. A glass tube, whose outer extremity was drawn out to a point and sealed, reached into the fermenting fluid. When the experiment was finished, it was opened to allow of air being drawn through the apparatus, in order to expel the whole of the carbonic acid. The temperature of the fermenting fluids was maintained between 65° and 77°. In four experiments, made in this manner, 4·01–6·74 per cent. carbonic acid was obtained, corresponding to 8·94–150·3 crystallized grape-sugar.

Mucilage.—As the gummy body which remains after exhaustion of the inspissated mother-liquors with absolute alcohol cannot be purified in this way from mannite, its combination with lead was analysed. For this purpose a clear filtered solution of mannite was precipitated with acetate of lead, the light gray precipitate washed, and then dried first over sulphuric acid, and then at 266°. The organic substance exhibited in its combination with lead, the following composition:—

Carbon..........	45·31	6	450·7	45·04
Hydrogen	5·09	4	49·9	4·98
Oxygen	49·60	5	500·0	49·98

The numbers coincide with those which Mulder found for the composition of mucilage in its combinations with lead.

Resin.—If an equal volume of water be added to manna, and the mixture then shaken repeatedly with æther, this becomes yellow, and leaves on distillation an acid liquid and a yellow resin, which

* Chem. Gaz. p. 157.

may be freed from the acid by treatment with hot water. It was now dissolved in hot absolute alcohol and filtered while hot; on cooling, a small quantity of white powder separated.

The solution has a reddish-brown colour, but is perfectly clear; the odour is very disagreeable, and the taste nauseous, irritating and repugnant. Water renders this solution turbid. Ammoniacal nitrate of silver produces only after some length of time, a dark colour and a precipitate. A spirituous solution of acetate of lead produces a brown precipitate, which is increased by the addition of ammonia. The quantity of resin obtained from 6 lbs. of manna was very inconsiderable. The substance did not however appear to be pure, for two analyses made with it yielded results differing widely from each other.

Acid.—The manna likewise contains but small quantities of the acid, which is extracted along with the resin by the æther. On evaporation of the aqueous solution, a yellowish-brown resinous body separates; if the solution of the acid be diluted with water, and the filtered liquid again evaporated, a further quantity of the brown substance is obtained; so that it appears as if the acid became gradually converted into the resin. It could not therefore be procured pure this way; it was likewise found impossible to deprive it of the colouring substance by treating it with æther or alcohol. The aqueous solution of the acid cannot be obtained perfectly clear. Sulphuric and muriatic acids do not alter it; nitric acid colours it yellow on the application of heat. The carbonated and caustic alkalies give it a yellow colour, which disappears on the addition of a mineral acid. An ammoniacal solution of silver immediately produces a precipitate of metallic silver; acetate of lead, a lemon precipitate, which is insoluble in ammonia. The acid yields no precipitate with salts of zinc, consequently it contains no lactic acid. On distilling the acid, a fœtid liquid, with a very faint acid reaction, passes over, which does not reduce salts of silver.

Ash.—When the several kinds of manna are heated, they melt and swell, becoming black and giving off a combustible gas. It is very difficult to burn the ash white; it effervesces strongly with acids. The principal constituent is potash; lime, magnesia, peroxide of iron, phosphoric, muriatic and sulphuric acids occur but in small quantity; the alumina and silica which are met with are probably owing to impurification with earthy matter. The quantity of the ash amounted to 1·32–1·99 per cent.

Water.—On desiccation at 212°, the mannas acquire a brown colour, and yield a brownish-red powder, which absorbs water from the atmosphere with great intensity. They lost in weight 11·1–13·0 per cent.

Insoluble Constituents.—These remain on dissolving the mannas in water, and consist of sand, earth, bark, &c.; collected on a filter and dried at 212°, they amounted to 0·40–3·24 per cent. The following table exhibits the collective results:—

	Manna canellata.	*Man. canel. in fragments.*	*Manna calabrina.*
Water	11·6	13·0	11·1
Insoluble constituents	0·4	0·9	3·2
Sugar	9·1	10·3	15·0
Mannite	42·6	37·6	32·0
Mucilaginous body with mannite, resinous and acid substance, and also a small quantity of nitrogenous matter	40·0	40·8	42·1
Ash	1·3	1·9	1·9
	105·0	104·5	105·3

Ann. der Chem. und Pharm., liii. p. 124.

CHEMICAL PREPARATIONS.

On the Preparation of Valerianic Acid. *By* Prof. G. Righini.

In a memoir read at Milan before the Chemical Section of the Italian Scientific Association, M. Righini established that valerianic acid does not exist in valerian root in a free state, but that a temperature of 230° is required for its formation; this temperature is requisite for the development of the volatile oil, from which, as is well known, the pure valerianic acid may be extracted. It is certain, moreover, that the proximate constituents of the root of valerian, conjointly with the high temperature at which the volatile oil is developed, react upon a portion of the latter, determine its decomposition, and that valerianic acid is thus produced. In support of this assertion the author has given the following process, by which he has succeeded in preparing the acid.

20 lbs. of wild valerian root are taken (collected in the month of October or November), and after having washed them with water and cut them in very small pieces, they are piled up in a marble mortar, adding enough water to remove all the juice by means of pressure. The juice thus obtained is placed in a small pan, and heated nearly to the boiling-point; carbonate of lime in very fine powder, or lime water, is then added; valerianate of lime is precipitated, and after repose for 2–3 hours, water acidulated with muriatic acid is added to the precipitate. The latter, combining with the lime, gives rise to the production of chloride of calcium, and sets free the valerianic acid. The whole is exposed to a gentle heat; and after continuing the evaporation until a pellicle commences to be formed, the liquid is introduced into a retort, and distilled in a sand-bath to remove the valerianic acid, whilst the chloride of calcium remains in the retort. The distillation should be carried to dryness. The quantity of root mentioned above yielded by this process 160 grms. of very pure valerianic acid.—*Journ. de Chim. Méd.*, July 1845.

Preparation of Valerianate of Zinc. By G. GIRTLER.

8 lbs. of valerian root and 60 lbs. of river or rain water are put into a still provided with a perforated diaphragm; and after macerating for 12 hours, 18 lbs. are distilled over by a tolerably quick fire. The distilled liquid is poured upon 8 lbs. more valerian root, and again subjected to distillation. The acid distillate is saturated with milk of lime, filtered, well-washed, and reduced at a gentle heat to one-eighth of its volume. Oxalic acid is now added to the liquid to precipitate the whole of the lime, filtered, and freed from excess of oxalic acid by lime-water. Freshly-precipitated carbonate of zinc (obtained by decomposing sulphate of zinc with carbonate of soda) is then added to the solution of valerianic acid thus obtained until no further effervescence occurs; it is then filtered. On evaporating the filtrate in a water-bath, scaly crystals are formed, which are removed until the whole of the liquid has evaporated. The crystals are dried at a gentle heat between pieces of bibulous paper, and preserved in well-closed vessels. Should the preparation not be perfectly white, it may be purified by recrystallization.—*Oesterreichish. med. Wochenschrift*, No. 20.

Preparation of Hippuric Acid. By DR. RIECKHER.

Hippuric acid may be obtained from the urine of herbivorous animals more rapidly than in Liebig's process, by evaporating it to the consistence of a thin syrup, mixing it with an equal volume of common muriatic acid, and gradually adding chlorate of potash. The oxides of chlorine evolved do not decompose the hippuric acid, but readily the resinous and extractive matters. As soon as the liquid has become clear the addition of chlorate of potash is suspended, and the mixture is set aside to cool. The acid crystallizes in a state of tolerable purity, and by recrystallization may readily be obtained perfectly pure.—*Jahrb. für Prakt. Pharm.* vol. x. p. 244.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 14, 1845. (Prof. Brande, Vice-President, in the Chair.) The following communications were read:—

"Contributions to the Knowledge of Conjugate Compounds," by Dr. H. Kolbe, Chemical Assistant in the University of Marburg.

The author, after briefly alluding to some previous researches on the action of chlorine on sulphuret of carbon and the compounds which are thus produced, proceeds to investigate the results of the action of the caustic alkalies towards the sulphite of perchloride of carbon, a product of the previous reaction, and shows distinctly that a most interesting series of compounds are thus produced, in which the substitution of hydrogen for chlorine is most beautifully developed, and a highly important class of acid bodies submitted to investigation—hyposulphate of chloro-carbon, hyposulphate of chloro-formyle, hyposulphate of chlor-elayle, and the hyposulphate of methyle, in which we have in the second the substitution of 1 equiv. of hydrogen for chlorine contained in the first; in the third of 2 equivalents, and in the fourth the whole 3 equivalents of chlorine disappear. These compounds all form series of crystallizable salts with bases, and all agree in not uniting with oxide of ethyle to form æthers. The hyposulphate of chloro-carbon is next shown to be conjoined with the oxalate of chloro-carbon, in which $S^2 O^5$ is replaced by $C^2 O^3$; and after corroborating the investigations of Dumas and Melsens on the reproduction of acetic acid, the author states that acetic acid can be obtained by the oxidation of chloral; and shows that it bears the same relation to the oxalate of chloro-carbon as aldehyde does to acetic acid, which is the conjunct of formylic acid with perchloride of carbon; and this explains the origin of aldehyde and its conversion into perchloride of formyle and formic acid. On these data the author shows that acetic acid, which has hitherto been known only as a product of the oxidation of organic matters, can be formed synthetically from its elements, sulphuret of carbon, chloride of carbon and oxalate of chloro-carbon, being the members in conjunction with water which supply the means of transforming carbon into acetic acid; and Dr. Kolbe considers that these facts render it highly probable that the acetic acid is methyl-oxalic acid, $HO + C^2 H^3, C^2 O^3$.

"On purifying Water from Lead acquired from leaden Pipes or Cisterns," by Dr. Clark of Aberdeen. He finds simple filtration sufficient to remove oxide of lead from the water.

"On the Conversion of Cane-sugar into a Substance isomeric with Inuline and Cellulose," by Drs. Maclagan and Tilley.

After alluding to the conversion of sugar into gum, which occurs in the fermentation of the juice of the beet-root at 86° to 104° F., and into cellulose, as in the passage of fruits to the state termed "sleepy," the authors proceed to show that a similar effect continually takes place in the effervescing drinks known as lemonade, gingerade, &c.; they lose their fluidity and assume a slimy consistence; the substance to which this was owing was separated by alcohol, and when dried had the appearance of a semi-transparent horny body. With water it assumes its original appearance; the tests for starch, dextrine, sugar and gum did not indicate the presence of those bodies. On analysis it proved to be isomeric with cellulose and inuline.

"On the Action of Chloride of Lime on the Salts of Copper and Lead," by W. Crum, Esq.

In 1843 Mr. Crum first made known the formation of a rose-coloured oxide of copper; since which it has been correctly described by Klüger of Berlin as a compound of cupric acid and lime, It is formed by adding nitrate of copper to a solution of bleaching powder containing a considerable quantity of lime, and previously cooled below 32° F. A bluish-green precipitate is formed, and as the temperature rises it changes colour, and becomes of a purplish-black; it is to be washed from neutral salts with cold lime-water; exposed to the action of boiling water, oxygen gas is liberated, and brown anhydrous oxide of copper results; acids dissolve it, liberating oxygen; by exposure to the air, it is converted into green carbonate; it is decomposed in the attempt to dry it, even *in vacuo*. The analysis was conducted by taking a known weight of pure oxide of copper, converting it into the new compound, and then ascertaining the quantity of oxygen liberated by the action of sulphuric acid on it in a closed tube over mercury; the mean of six experiments on 20 grs. of pure oxide gave 1·828 gr. of oxygen; by calculation, supposing the compound to be $Cu^2 O^3$, it should have been 1·98, sufficiently near to establish the above formula.

Peroxide of lead is readily formed by the action of a solution of bleaching powder on acetate of lead, and Mr. Crum states that he has succeeded in obtaining a compound of lime with peroxide of lead, which is nearly colourless; it is insoluble in water, and when dried does not alter in the air. Nitric acid dissolves the lime, and leaves the peroxide of a deep black colour. The author has not determined the proportion of lime in this compound, but with less than 2 equiv. to 1 of oxide it is not white.

May 5, 1845.

A short notice was read by the President (Prof. Graham), "On the Presence of Phosphoric Acid in the Deep-well Water of the London Basin." This is the water from the chalk below the London clay. It is highly soft and alkaline, and remarkable for the predominance of soda salts over earthy salts among its solid constituents, as appears from their composition in the case of the well of the Castle-street Brewery, Long-acre, which gave from 100 parts—carbonate of soda, 11; sulphate of soda, 53; chloride of sodium, 22; carbonate of lime, 11; carbonate of magnesia, 2; silica, 1; phosphate of lime, 0·34; and phosphate of iron, 0·43. The author was led to look for phosphoric acid in this water from the extremely rapid growth of green confervæ often observed in it; and he suggests the inquiry, whether the value of some waters for irrigation may not depend upon their containing phosphoric acid, this constituent having been hitherto overlooked in waters.

A singular crystallized Alloy of Zinc, Iron, Lead and Copper was described by Mr. Warren Delarue.

A discussion also took place respecting the production of cyanide of potassium from the action of the nitrogen of the air upon charcoal and carbonate of potash, which has been called in question, although lately proposed as the basis of a manufacturing process*. Certain results obtained by Prof. Bunsen were communicated by Dr. Playfair, which confirm the old experiments of Mr. L. Thomson

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* See Chem. Gaz., p. 65 of the present volume.

and Dr. Fownes, that cyanogen is always produced in this way, provided the temperature be sufficiently intense to convert the iron tube in which the materials are heated into steel.

May 19, 1845. (The President, Professor Graham, in the Chair.) The following papers were read:—

"On the solubility of Oxide of Lead in pure Water," by Lieut.-Col. Philip Yorke.

It is from this property that leaden pipes and cisterns become dangerous when the water which fills them is soft and pure. The lead, however, which the water takes up may be removed by filtering the water through paper; a circumstance which has been explained by supposing that the oxide of lead is not really dissolved in the water, but merely suspended in it. The author, however, shows that the oxide of lead is taken up by the substance of the paper and combines with it, from an affinity such as subsists between the same metallic oxide and cotton fibre; the last taking the oxide from solution in lime-water, and lead being often fixed as a mordant on cloth for dyeing in this way, according to the statement of Mr. Crum. He finds also that the power of the filter may be exhausted, and that therefore it would be unsafe to trust to the action of a filter to separate oxide of lead from water for an unlimited time.

"Experiments on Ozone," by Mr. Williamson.

The name ozone was given by Prof. Schönbein to the substance which occasions the peculiar smell possessed by oxygen gas when produced by the voltaic decomposition of water, and he has made it the subject of much ingenious speculation, concluding that it is a new elementary body, and that it is derived from the decomposition of nitrogen, supposed to be of a compound nature. The last of these opinions, however, has already been disproved by Marignac*, who demonstrated that the ozone odour was produced by the decomposition of water free from nitrogen. Mr. Williamson's experiments go to prove that ozone is a compound body, and that one of its elements is hydrogen; for having excluded the last element from any other source, by obtaining the oxygen gas with ozone from the decomposition of a salt of copper, a process in which no hydrogen is generated, and passing the oxygen over metallic copper which had been reduced by carbonic oxide gas, a sensible formation of water always resulted. The bleaching power of ozone shows it to be a peroxide; and it must therefore be a higher oxide of hydrogen than water, although not the peroxide of hydrogen of Thénard, which is not volatile like ozone, but inodorous and fixed. Mr. Williamson finds also that the substance produced by the action of phosphorus on air is different from ozone, and that its effect, observed by Schönbein in decomposing iodide of potassium and liberating iodine, is the result of the joint action of phosphoric acid and free oxygen upon a solution of that salt.

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* Chem. Gaz., p. 168 of the present volume.

PATENT.

Patent granted to Sir George Steuart Mackenzie, Coul, Ross, *for Improvements in the Manufacture of Paper, and also of Fluids to be used with the improved Paper in the manner of Ink.*

The objects of this invention are,—1st, to substitute for the common black and blue inks a transparent and, as much as practicable, a colourless and innocuous fluid, which being used with suitably prepared paper will produce either black or blue characters; and 2nd, to produce a black ink which, when written with on paper or other material suitably prepared, will flow readily from the pen and be indelible, and from which copies may be taken if required on copying paper prepared for the purpose.

In the first place a dry powder is prepared, consisting of,—1st, gall-nuts in their natural state, or salts prepared from them, or from other substances containing tannin, by treating galls or such other substances with water, common spirits, alcohol, æther, vinegar, pyroligneous acid, or other means; 2nd, anhydrous ferrocyanide of potassium; 3rd, carbonate of lime or anhydrous carbonate of soda; 4th, rice-flour. The proportions of these articles and the number of them employed admit of variation, according to the varying qualities of the gall-nuts. The proportions that have been found suitable for producing dark writing are 3 parts by weight of powder of gall-nuts, 1 part anhydrous ferrocyanide of potassium, 1 part carbonate of lime and 3 parts rice-flour; for blue writing, 1 part anhydrous ferrocyanide of potassium and 6 or 7 parts rice-flour. The blue tint may be varied by the addition of a small quantity of gall-nut powder. These powders are pressed into the paper after it has been sized and before it is finished; in the case of hand-made paper the powder is pressed in by hand, assisted by a brush to remove the superfluous portions, or by a small machine; and it is applied to machine-made paper by the machinery hereafter described. Parchment is prepared in the same manner, by hand, to be written on with the black indelible ink.

The clear fluid used as ink with the prepared paper is made of permuriate of iron diluted with a large proportion of water: other persalts may be used.

The black indelible ink may be prepared in two ways,—either by rubbing down Indian ink in a pretty strong solution of permuriate of iron in water, or by making a stiff paste of the finest lamp-black with strong mucilage of gum-arabic, and diluting this paste with a strong solution of permuriate of iron in water—1 measure of permuriate of iron to 7 of water. Copies may be taken on prepared copying paper of anything which has been written with this ink.

The machinery or apparatus for applying the powder to machine-made paper consists of,—1st, rollers for drawing in the paper; 2nd, a box, having a narrow bottom of fine wire-cloth, and capable of being shaken, so that a small quantity of powder may escape from it; or, instead of the box, a revolving metal cylinder, finely perforated, may be used; 3rd, a rather open brush, having a lateral motion, to spread the powder over the paper as it passes; 4th, a close and rather hard brush, with a lateral motion, for rubbing the powder into the paper; 5th, a revolving brush, moving in an opposite direction to the paper, for sweeping off the superfluous powder; 6th, a roller to take up the paper, and to turn the under side up, in order that it may be treated in the same manner as the other side. Any other suitable machinery may be used for applying the powder.—Sealed Sept. 26, 1844.

Patent granted to Frederick Ransome, Ipswich, *for Improvements in the Manufacture of Artificial Stone for grinding and other purposes.*

This invention consists,—1st, in manufacturing artificial stone, by cementing broken or pulverized stone, sand, or earthy or metallic matters, with a solution of silica; and 2nd, in subjecting the artificial stone formed in this manner to hydraulic or other mechanical pressure in moulds.

The solution of silica or siliceous cement is made, by preference, in the following manner, but the patentee does not confine himself to this mode of preparing it:—100 lbs. of crystallized carbonate of soda are dissolved in 50 gallons of water, and the soda is rendered caustic by the addition of lime; or, instead of carbonate of soda, 50 lbs. of carbonate of potash are dissolved in the requisite quantity of water, and the potash rendered caustic, as above mentioned. The caustic alkaline solution is reduced by heat to 20 or 25 gallons; it is then put into an iron boiler or digester with 100 lbs. of finely-broken flints, or other siliceous substance, and the mixture is heated during ten or twelve hours up to a pressure of about 60 lbs. to the square inch (being frequently stirred during that period); after which it is removed from the digester and passed through a sieve, to separate any undissolved stone from it. The cement is now ready for use, or may be brought to any required consistence by the admixture of sand or finely-powdered flints, or it may be thinned by the addition of water.

Millstones are made, according to this invention, by mixing together 1 part of siliceous cement, 1 part of powdered flint or powdered pipe-clay, and 3 or 4 parts of fragments of burr, or other suitable stone; this compound is subjected to mechanical pressure in iron moulds, and after being removed therefrom is allowed to dry at the ordinary temperature of the atmosphere for twenty-four hours; it is then placed in an oven or drying-room, where the temperature is gradually raised to that of boiling water, and the stone is thus effectually dried. When artificial stone for other purposes is to be manufactured, a mixture is made of granite, common sand, or fragments of any siliceous or other hard stone or substance, with from one-fourth to one-sixth of the siliceous cement; and it is treated in the same way as that above described.

By reducing the stone or other material to very fine particles previous to adding the siliceous cement thereto, more or less fluid mixtures may be produced, for coating walls or other surfaces.—Sealed Oct. 22, 1844.

THE CHEMICAL GAZETTE.

No. LXIX.—September 1, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Acid contained in Wormwood (Artemisia Absinthium).

By Dr. E. Luck.

Braconnot obtained from wormwood a peculiar deliquescent and uncrystallizable acid, which did not precipitate solutions of either nitrate of lead or silver or protoxide of mercury, but yielded white precipitates with acetate of lead, lime water and barytic water, and combined with ammonia, forming a salt which crystallized in many-sided prisms and was insoluble in alcohol. As ultimate analyses of the acid were wanting, and M. Braconnot's experiments had not been confirmed, the author undertook the task. The dried plant was exhausted with warm water in a press, and acetate of lead added to the solution as long as a yellowish-brown precipitate continued to be formed; the liquid, which was slightly acid, was neutralized by ammonia, warmed to facilitate the separation of the precipitate, and after having been set aside for 24 hours, this was collected in a conical bag, washed and pressed.

The precipitate was now suspended in water and decomposed at a temperature of 86° to 104° with sulphuretted hydrogen. The liquid, which was strongly acid and of a brownish colour, was filtered and evaporated in a basin on the sand bath. This operation must, however, be commenced in a retort to which a receiver is adapted, on account of the evolution of acid fumes, which escape with the watery vapour. The addition of nitrate of silver to the distillate indicates merely a trace of muriatic acid. By saturation with potash and evaporation, I obtained crystals of nitrate of potash, in which the nitric acid could be distinctly detected, and which must have been partly thrown down in the lead precipitate by the other acids in the course of the operation.

The fluid remaining in the retort was carefully evaporated to the consistence of a syrup and mixed with alcohol, which caused the separation of an acid salt (of lime and magnesia). The liquid separated from this by filtration was evaporated, so as to drive off the greater part of the alcohol, mixed with water and saturated with soda. After some time a mass of crystals separated, which was accelerated by the addition of alcohol. They were much less coloured than the mother-liquor, and by two recrystallizations were obtained perfectly white. They were alkaline, fused by heat, but did not become brown or carbonaceous when the temperature was raised. They gave a yellow precipitate with nitrate of silver, which was soluble in acids, and was rapidly blackened by exposure to light; when treated with sulphate of magnesia and ammonia, and muriate of ammonia was added, they yielded a white crystalline precipitate, which satisfactorily proved them to be phosphate of soda.

The dark brown mother-liquor was now treated with a solution of acetate of magnesia, to which I had previously added some ammonia and acetate of ammonia; the mixture was digested for several days at a gentle heat, until all the phosphoric acid had separated. It was filtered, neutralized with acetic acid, and again precipitated with solution of acetate of lead. The precipitate, when decomposed by sulphuretted hydrogen in the same manner as the first, yielded a liquid which was still coloured, and on careful evaporation assumed a darker colour. Attempts to purify it by charcoal were unsuccessful, as also combining it with lead and subsequent decomposition, as a portion of the colouring matter united with the precipitate, and when this was decomposed it became again dissolved. Moreover, the lead salt being partly soluble, this precipitation caused a considerable loss. Consequently, I made use of another method of purification.

The impure acid liquid was digested in the heat with finely-divided oxide of copper, a slight excess of which was finally added; the beautiful green solution was evaporated, during which it might be perceived, by careful observation, that small brownish-black flakes were separated. The gummy residue was digested in a small quantity of water, the solution filtered, the filtrate diluted with water, and decomposed by sulphuretted hydrogen. The acid liquid, on careful evaporation, now left a pale yellow syrupy residue, which did not assume a crystalline appearance even after a considerable time. When dried over sulphuric acid, it formed a gummy mass. Æther dissolved the greater part of it, leaving a small quantity of an acid salt of lime. On evaporating the æther, the acid remained, possessing the same properties as above described. On heating the acid, dried over sulphuric acid, in a glass tube, a crystalline sublimate was formed, and a small quantity of carbon was left, which with free access of air burnt, leaving only a trace of ash. The ash did not amount to $\frac{1}{2}$ per cent. Chloride of calcium did not give any precipitate, either in the acid solution or in that supersaturated by ammonia. Alcohol precipitated a very soluble lime salt from it. Potash formed a gummy, and ammonia a deliquescent salt. On precipitating the potash salt with nitrate of silver, a white precipitate was formed, which was soluble with difficulty in boiling water, was rapidly blackened by light, and was readily soluble in acids; during this solution, that portion which was not *immediately* dissolved instantly assumed a dark colour.

The composition of this salt, dried at 212°, was*—

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* $C = 76{\cdot}43$.

	Found.	Atoms.		Calculated.
Carbon..........	13·84	4	305·740	14·010
Hydrogen	1·18	2	24·959	1·143
Oxygen	18·71	4	400·000	18·330
Oxide of silver....	66·27	1	1451·600	66·517

Acetate of lead added to the dilute watery solution of the acid or its potash salt yielded a white precipitate, which on the application of heat contracted, and finally fused to a resinous mass at the bottom of the liquid. When the supernatant fluid was poured off, in a few days, shining, colourless needles and laminæ combined into stellate groups separated, which likewise fused in water by heat. The crystallized salt lost 13·657 per cent. on drying at 212°, and contained 56·675 per cent. of oxide of lead.

The atomic weight of the acid, calculated from this, amounts to 732·21, and the amount of water in the salt to 336·03 = 3 atoms; consequently it contains per cent.—

Oxide of lead	56·675
Acid	29·668
Water of crystallization	13·657

The crystallized salt, dried at 212° (I.), burnt with oxide of copper, and the precipitated lead salt (II.) yielded—

	I.	II.	Atoms.		Calculated.
Carbon	14·37	14·17	4	305·740	14·29
Hydrogen......	1·30	1·14	2	24·959	1·17
Oxygen.........	18·62	19·98	4	400·000	18·85
Oxide of lead ..	65·70	65·70	1	1394·500	65·69

consequently the salt, dried at 212°, would be $C^4 H^2 O^4 + PbO$, and the crystalline salt $C^4 H^2 O^4 + PbO + 3aq$.

Finely divided oxide of copper was digested with the aqueous solution of the acid, filtered and evaporated; but no crystals separated, even after 24 hours. It was consequently again evaporated at a gentle heat, and the gummy salt thus obtained separated from the excess of free acid by alcohol. It formed a dark green amorphous mass, which readily dissolved in water; the solution was of a verdigris colour: it was insoluble in alcohol.

It contained 37·178 per cent. of oxide of copper. Its atomic weight from this is = 838·1. It yielded—

		Atoms.		Calculated.
Carbon	22·644	4	305·740	22·83
Hydrogen	2·665	3	37·439	2·79
Oxygen	37·515	5	500·000	37·34
Oxide of copper..	37·178	1	495·700	37·02

which corresponds with the formula $C^4 H^2 O^4 + CuO + HO$.

From these analyses, as also from the characteristic reaction of its lead salt when heated under water, this acid would certainly appear to be malic acid.

The copper salt retains an atom of water when dried. Berzelius, in his 'Lehrbuch,' mentions a copper salt which perfectly agrees with this in its external characters, but he does not give its composition. The malates of copper hitherto examined were not neutral.

The deliquescent acid which Braconnot obtained must have been a mixture of phosphoric and malic acids; and probably Braconnot, by the mixed reactions of the two acids, was led to believe that it was a peculiar acid. The carbonate of potash found in the ash of wormwood arises partly from the malate and partly from the nitrate of potash; the latter exists in it in considerable quantity.

I had arrived thus far, when Prof. Zwenger's paper came into my hands*. According to this author, Braconnot's acid is represented by an extremely small quantity of succinic acid (which however is not deliquescent); and the brownish-yellow reaction of the bitter principle of wormwood with perchloride of iron, which Mein alludes to, does not arise from this, but from succinic acid.

I was therefore induced to experiment upon a fresh quantity of wormwood, and followed Zwenger's mode of proceeding. I can confirm the separation of a brown acid resin, which Zwenger procured by treating the impure acid obtained by decomposing the lead precipitate with water, and shall subject this resin to a further examination. On treating the acid freed from the resin with æther (which contained water and alcohol), I likewise obtained a *very small* quantity of a crystalline acid, which dissolved readily in water and alcohol, but was nearly insoluble in anhydrous æther. The cold aqueous solution gave no precipitate with lime-water, but when boiled a slight precipitate. When neutralized by ammonia, it likewise gave no precipitate in the cold; but on boiling, a granular precipitate. Acetate of lead was precipitated white; the precipitate did not melt in the liquid; it was soluble in acetic acid. When heated in a glass tube, it yielded a crystalline sublimate; but I could perceive no fumes which excited coughing. Perchloride of iron produced no precipitate in the aqueous solution. I could not discover any resemblances in its properties to succinic acid.—*Ann. der Pharm. und Chem.*, April 1845.

Observations on Cetrarine.

According to the investigations of Dr. Schnedermann, cetrarine, the bitter constituent of the Iceland moss, is a mixture of three distinct substances. The first is *cetraric acid*, which alone possesses the bitter taste; it is colourless, forms small shining prisms, and is composed according to the formula $C^{34} H^{16} O^{15}$. The second constituent of cetrarine is a kind of fatty acid, which crystallizes from alcohol in shining, colourless, oblique quadrilateral prisms, melts readily, and forms with bases salts representing those of the other fatty acids. Its composition is expressed by the formula $HO + C^{29} H^{23} O^{5}$. The third body is likewise crystalline, but indistinctly so, is neither an acid nor a base, and has not yet been sufficiently examined.—*Archiv der Pharm.*, xliii. p. 41.

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* Chem. Gaz., vol. ii. p. 122.

On the Action of Chlorine on the Cyanide of Mercury under the Influence of the Solar Rays. *By* JULES BOUIS.

Gay-Lussac, in his remarkable investigation of hydrocyanic acid, observed, that on placing cyanide of mercury in flasks filled with chlorine exposed to the sun an oily yellow liquid was produced; but he merely mentioned this fact, his investigation being made with a different object.

Subsequently Sérullas studied this body, and regarded it as a mixture of chloride of nitrogen, of a liquid chloride of cyanogen and of perchloride of carbon held in solution; but he did not analyse this yellow liquid, and he proposed to return to this subject, so well deserving of attention, which he was not able to investigate except at intervals, on account of the dangerous explosions and the painful irritation of the eyes produced by the volatilization of these bodies

The following are the results which I have obtained:—When flasks containing chlorine and a saturated and boiling solution of cyanide of mercury are exposed to the solar rays, an oily yellow liquid is obtained, heavier than water, in which it is insoluble, but soluble in alcohol and æther; this liquid, which is of an excessively strong irritating odour, makes the eyes water; its taste is very caustic, and it burns with a red flame. Whether moist or dry, it deposits in the course of time crystals of Faraday's sesquichloride of carbon, and becomes partially decolorized.

Like the nitrate of methylene, this body, although explosive, may be burnt with oxide of copper at a red heat; but it is very difficult to carry on the combustion in a regular manner. Its composition is represented, according to my analysis, by $C^8 N^4 Cl^8, C^4 Cl^6$*. The formation of the first member, $C^4 N^4 Cl^8$, is very readily explained, since we place the elements of cyanogen in presence of an excess of chlorine. We may likewise suppose the formation of a second molecule of the same nature; this is now decomposed under the influence of the water, and yields carbonic acid and nitrogen, which are evolved; sal-ammoniac, which remains in solution; and sesquichloride of carbon, as indicated by the equation—

$$C^8 N^4 Cl^8 + H^8 O^8 = C^4 O^8 + N^2 Cl^2 H^8 + N^2 + C^4 Cl^6.$$

The sesquichloride of carbon, in the nascent state, combines with the product $C^8 N^4 Cl^8$, giving rise to a more stable compound $= C^8 N^4 Cl^8 + C^4 Cl^6$. If the action of the chlorine is continued, this product remains, and the liberation of nitrogen is observed, with formation at the same time of hydrochloric acid. The production of these two gases is owing to the decomposition of the chloride of ammonium. My experiments and analyses confirm this mode of view.

The yellow liquid, on decomposition by heat, deposits sesquichloride of carbon, liberates nitrogen, and appears in the form of a colourless transparent liquid, with the composition—

$$C^8 N^4 Cl^4 + 2(C^4 Cl^6) + C^4 Cl^6,$$

being in fact derived from the first product—

$$2(C^8 N^4 Cl^8) = C^8 N^4 Cl^4 + 2(C^4 Cl^6) + N^4.$$

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* $C = 6, N = 14, Cl = 35{\cdot}5.$

Nitric acid oxidizes the yellow liquid, and yields a more irritating and caustic product than the preceding, represented by

$$C^8\,N^4 \left.\begin{matrix} Cl^8 \\ O^4 \end{matrix}\right\} + C^4\,C^6.$$

Ammonia likewise decomposes the yellow liquid into several products, among which Faraday's sesquichloride of carbon always occurs.

From the preceding facts, we might admit the existence of three chlorides of cyanogen (monochlorated, bichlorated and trichlorated), acting the part of acids and combined with the sesquichloride of carbon. In the trichloride of cyanogen, 4 equiv. of chlorine are replaced by 4 equiv. oxygen. These products form the series—

$$\begin{aligned} &C^8\,N^4\,Cl^4 + C^4\,Cl^6 + 2C^4\,Cl^6. \\ &C^8\,N^4\,Cl^8 + C^4\,Cl^6. \\ &C^8\,N^4 \left.\begin{matrix} Cl^8 \\ O^4 \end{matrix}\right\} + C^4\,Cl^6. \end{aligned}$$

The sesquichloride of carbon, $C^4\,Cl^6$, being derived from ordinary æther, $C^4\,H^5\,O$, these compounds might be regarded as chlorated æthers, formed by the union of the chlorides of cyanogen with the sesquichloride of carbon.—*Comptes Rendus*, July 21, 1845.

On a new Double Salt of Carbonate of Potash and Soda.
By M. MARGUERITE.

The salt in question had formed on the concentration of a solution of yellow prussiate of potash, which had been prepared in the usual way by heating nitrogenous carbonaceous substances to redness with potash. On a superficial examination, it appeared to be bicarbonate of potash, exhibiting the reactions of potash in the moist way, effervescing with acids, and consisting of distinct non-deliquescent crystals.

On heating the salt, to convert it into neutral carbonate of potash, it fused in its water of crystallization, even on the first application of heat, a property by which it is easily distinguished from the bicarbonate of potash. Its solution yielded an abundant precipitate with salts of magnesia and lime; the latter are precipitated without the smallest quantity of carbonic acid being disengaged even on boiling. It could therefore not be a bicarbonate salt; yet although the presence of potash could be distinctly proved by tartaric acid and chloride of platinum, it could not be admitted that the salt was neutral carbonate of potash, for then it would have been deliquescent.

After some time the crystals began to effloresce slightly on exposure to the air, which led the author to suspect soda in them; it was now tested before the blowpipe, and coloured the flame so intensely yellow, that this was a sufficient reason to admit the presence of soda, not as a mere impurification. The antimoniate of potash, which Fremy proposed as a test for soda, yielded an abundant precipitate with a solution; sulphuric acid gave distinct crystals of sulphate of soda, proving the presence of soda in the compound beyond all doubt. After the author had assured himself of the absence of sulphuric and other acids, the next thing was to determine in what proportion the carbonate of potash was combined with the carbonate of soda. For this purpose, he first converted the combination into chlorides, dried them, and determined the proportions from the degree of cold which their solution produced. 50 grms. of the salt converted into chloride produced, on solution in 200 grms. water, a decrease of temperature of 10°, which corresponds to the proportion of 40·5 chloride of potassium to 59·5 chloride of sodium. This result was confirmed by the alkalimeter, for 4·807 grms. of the ignited salt required for complete neutralization, on an average, 80·5 cubic centimetres of the dilute sulphuric acid usually employed in alkalimetry = 4·029 grms. $SO^3 + HO$. It contained accordingly 1·8945 grms. carbonate of potash and 4·9125 carbonate of soda. The amount of water is easily determined by heating to redness. According to these results, the salt consists of $2NaO\ CO^2$, $KO\ CO^2$, $18HO$.

If the salt was dissolved and again evaporated, at first somewhat more potash separated with the soda, while the last-formed crystals contained more soda than those above described. On again dissolving the salt and evaporating, the crystals contained only traces of potash and 62 per cent. water. If, on the contrary, the salt was dissolved in a solution of carbonate of potash, it crystallized without having undergone any change. The salt exhibited the same behaviour towards other concentrated saline solutions. The salt may therefore be easily prepared by dissolving carbonate of soda in a solution of carbonate of potash.

It is probable that the circumstances under which this new double salt is formed frequently occur, especially in the manufacture of pearlash. So, for instance, the salt must be readily formed on reducing the plants to ash; it is on that account the carbonate of potash cannot be perfectly separated from the carbonate of soda by deliquescence.

The above double salt dissolves very readily in cold, as well as in boiling water, and forms beautiful crystals, which still contain a quantity of interstitial water; they effloresce easily *in vacuo*, but scarcely at all by exposure to the air. The salt of the above composition may however likewise be conceived as consisting of $2NaO\ CO^2 8HO$, $KO\ CO^2 2HO$. Now we know that $NaO\ CO^2 8HO$ on solution in water is converted into $NaO\ CO^2\ 10HO$, but at the same time the excess of carbonate of potash is able to deprive the carbonate of soda of some water. This explains the decomposition of the salt on solution in water. It appears therefore as if the salt did not exist in the fluid, but is first formed on the separation of crystals.—*Journ. de Pharm. et de Chim.*, 3rd series, 4 ann., p. 344.

ANALYTICAL CHEMISTRY.

Improvements in Marsh's *Method of detecting Arsenic.*

By M. Blondlot.

The author's attention has been principally directed to two points, viz. the disorganization of the animal matters which conceal the arsenic, and certain modifications in Marsh's apparatus, rendering its use more positive and convenient. As regards the first point, the author disorganizes the tissues by means of concentrated sulphuric acid, in the manner adopted by MM. Flandin and Danger*; but instead of continuing the heat, so as to obtain a dry and friable charcoal, whereby we run the risk of losing a portion of the poison, he ceases when the substance has acquired a pasty consistence; then treats this with a certain quantity of water, which forms a turbid and blackish liquid, through which a current of chlorine is passed for some minutes. The solution is filtered, and thus rendered clear and limpid, and is introduced into Marsh's apparatus, in which it produces little or no froth. The advantage of this proceeding is, that no part of the arsenic is lost, nor is there any fear of sulphurous acid being formed, as the chlorine immediately converts it into sulphuric acid, at the same time destroying or precipitating the small quantity of animal matter remaining in solution.

The modification of Marsh's apparatus enables us to control the flow of the gas, and to suspend it completely if necessary. For this purpose a three-necked Woulfe's bottle is used. One of the lateral necks gives passage to a straight tube, through which the liquid is introduced; the other, to the tube for the escape of the gas, the disposition in the arrangement of which varies according to the method adopted for decomposing the arseniuretted hydrogen. The third neck contains a cork, through which a glass rod, capable of being elevated or depressed, passes; spiral laminæ of zinc are attached to its lower extremity; these are plunged into the dilute acid. Thus the operation throughout is entirely at our command. —*Comptes Rendus,* July 1845.

On the Qualitative and Quantitative Analysis of Albuminous Fluids.

By Dr. Heller.

An evil well-known to all chemists is, that albuminous fluids, especially if the albumen has been coagulated, pass through the filter with difficulty; the paper becomes completely stopped up, so that washing the residue is almost impossible. Heller therefore makes use of the following method for estimating the quantity of albumen:—

1. When the fluids do not completely coagulate by ebullition, their specific gravity is first taken, then the quantity of solids, and the reaction ascertained. If this is alkaline, a few drops of acetic acid are added, so as to produce a slightly acid reaction. From 5–8 oz. of the fluid are now boiled for a short time in a narrow-mouthed flask, which is then closed, and the liquid when cold strained through

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* Chem. Gaz., vol. i. p. 4.

a moderately fine linen cloth. The strained fluid is thus obtained perfectly clear, the albumen remaining on the linen as a snow-white magma. By treating a small portion with nitric acid, we may be certain that the albumen is completely separated. The amount of solid residue is again ascertained from a smaller weighed quantity, and the per-centage of both results calculated; the difference gives the amount of albumen.

2. Many fluids, as the serum of blood, hæmorrhagic and other exudations, are almost completely coagulated by heat. Here a larger weighed quantity of it is coagulated, as the solids without the albumen amount to but little. The coagulum is broken up in the same vessel with a glass rod, and boiled with distilled water as long as anything is dissolved. It is well to render the first portion of water slightly acid, for if it were alkaline small portions of the albumen might also be dissolved. It is then boiled with weak spirit (equal parts of alcohol of 0·830 and water) as long as this removes anything, then in like manner with absolute alcohol, and finally with æther, to remove the fat. The residue is albumen, which after being dried is weighed. The quantity of water and solid residue is ascertained from another portion of the fluid under examination, from the latter of which the weight of the albumen must be subtracted, to find the total amount of other solid matters. The fixed salts are directly estimated by evaporating and incinerating the washed matters; for if the solid residue of the liquid and the albumen are incinerated together, the fixed salts belonging to the albumen alone are included with the others.—*Arch. f. Phys. u. Path. Chem. u. Heilk.*, Part 2.

PHARMACOLOGY.

On some Constituents of Fern Root. By Dr. E. Luck.

When the æthereal extract of the root of *Aspidium Filix mas* known by the name of *Oleum Filicis,* is allowed to repose for some time, a granular sediment is deposited, which by pressure and rapid washing with a mixture of æther and alcohol, may be for the greater part freed from the adherent fatty oil. On treating it with boiling æther, as the æthereal solution cools, indistinct crystals subside; these may be purified by repeated crystallization from æther. Under the microscope, they appear to be rhombic plates. They are insoluble in water and alcohol, but soluble, although not readily, in æther. They have a faint balsamic odour, fuse at 320°, and then solidify to a yellowish transparent mass. At a higher temperature they are blackened and decomposed; white fumes escape, which condense into a yellowish oily liquid, having the odour of rancid fat. Dilute aqueous solution of ammonia dissolves them in but small quantity, but ammonia mixed with alcohol dissolves them readily; acids throw down this body immediately after solution, in the form of a white precipitate. A concentrated aqueous solution of carbonate of soda dissolves it when gently heated; the excess of carbonate of soda is completely precipitated from the concentrated solution by absolute alcohol, and we then have the body in combination with soda in solution.

By precipitating this solution (to which a drop of acetic acid has been added, to remove every trace of carbonate of soda) with acetate of lead, we obtain the lead compound. This compound (*a*), on combustion with oxide of copper, gave—

	I.	II.	III.
Carbon*..........	65·09	64·85	64·78
Hydrogen	6·78	6·52	
Oxygen	28·13	28·63	

I. and III. were crystallized from æther, II. was precipitated from the soda compound by muriatic acid.

The lead compound contained 16·80 per cent. oxide of lead, and on combustion yielded,—carbon, 53·12; hydrogen, 5·76; oxygen, 24·32. This analysis must be repeated, as it was made only once, and that with a small quantity. If we assume the above amount of oxide of lead to be correct, we obtain the formula $C^{59} H^{38} O^{20} + PbO$. From the products of this substance, however, it is probable that it should be $C^{60} H^{36} O^{20}$. If an alcoholic solution of the substance (*a*) be subjected to spontaneous evaporation, oxygen is absorbed, and a change is produced; the liquid becomes brownish-yellow, and on the addition of an acid a new yellowish-brown substance (*b*) is obtained. This is soluble in alcohol, with an intensely yellow colour, and is deposited from it on evaporation as an uncrystallizable pulverulent mass. It combines with alkalies. It yielded—

	I.	II.
Carbon	63·62	63·50
Hydrogen	6·58	6·69

I. was precipitated by muriatic acid, II. subsided from the alcoholic solution.

The ochreous yellow lead compound, obtained by precipitating the ammoniacal compound with acetate of lead, yielded in *one* experiment—

Oxide of lead	52·44
Carbon	29·29
Hydrogen	2·85
Oxygen	15·42

Hence the formula would be $C^{10} H^{6} O^{4} + PbO$. The free substance however is not $C^{10} H^{6} O^{4}$, but $C^{20} H^{11} O^{7}$, which absorbs an atom of water on combining with bases. The formula $C^{20} H^{11} O^{7}$ requires 63·40 C and 5·80 H.

The compound (*b*), when exposed to a high temperature, also gives off the odour of rancid fat, which we have already mentioned.

After the body *a* was completely separated from the sediment by æther, alcohol extracted a substance from the residue, at the same time acquiring a brown colour; it was precipitated from it by water, dissolved with difficulty in boiling water, but readily in alkaline

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* In this and all the subsequent analyses, C = 75.

liquids. It was also obtained when the root of the fern was exhausted with alcohol; and the residue remaining after the separation of the spirit by distillation from the filtered liquor was treated with boiling water. It separated from the boiling filtered solution in the form of an uncrystalline powder, which when dry was of a yellowish-brown colour. The alcoholic solution was for the most part decolorized by zinc and dilute sulphuric acid. The portion precipitated from it by water was of a bright brown colour. It gave a grayish-green precipitate with persulphate of iron, and a yellowish-brown with acetate of lead. I shall call this *c*. It yielded—

	I.	II.
Carbon	59·430	59·300
Hydrogen	5·202	5·125
Nitrogen	1·326	1·326
Oxygen	34·042	34·249

The lead compound gave, as a mean of five experiments, 29·59 per cent. of oxide of lead; hence the atomic weight is 3319·3, and the above composition calculated per cent. to this number gives C $26\frac{1}{4}$, H $13\frac{1}{2}$, N $\frac{1}{4}$, O $11\frac{1}{4}$, and in whole numbers, $C^{105} H^{54} NO^{45}$.

When this substance, dissolved in alcohol, is treated with muriatic acid gas, we obtain a splendid red compound, the greater part of which is precipitated by water from the alcoholic solution. It forms blue compounds with alkalies, a gray one with oxide of lead, and a red lake with solution of alum. Its alcoholic solution is decolorized by deoxidizing media; in short, it has the properties of a natural red colouring matter. The lead precipitate, dried over sulphuric acid, gave 19·158 oxide of lead, and its atomic weight is 5884. On drying at 212°, it is altered, assuming a brownish-black colour, and no longer produces the beautiful red colour on decomposition by muriatic acid. It then yields 20·24 per cent. oxide of lead, and its atomic weight is 5494. I have not examined it any further. If the muriatic acid gas be allowed to act too long, we obtain a brownish-red substance, which is not soluble in alcohol.

After the substance *c* had been extracted by alcohol from the original sedimentary extract, a gray body was left; this burnt on platinum foil, evolving an odour of burnt horn. It was insoluble in all solvents except caustic alkalies, in which it dissolved with a brown colour. When digested with a caustic alkali and freshly-precipitated protoxide of iron, it was dissolved without the formation of the brown colour. When treated with alcohol and muriatic acid, it likewise yielded a red colouring matter, which differed but little in its external characters from that above mentioned. The lead compound, dried at 212°, gave 32·77 per cent. oxide of lead; hence its atomic weight was = 2860. On analysis it yielded—

Carbon	41·11
Hydrogen	3·56
Nitrogen	3·44
Oxygen	19·12

which leads to the formula $C^{24} H^{12} N O^{8} + PbO$.—*Ann. der Chem. und Pharm.*, April 1845.

Chemical Remarks on Cascarilla. *By* A. Duval.

After giving a brief history of this substance, and detailing the analyses of it made by Boulduc, Boehmer, Trommsdorf, Caventou and Felix Cadet, the author proceeds to give an account of his own analysis. He says, the following are the principal substances I have found in the officinal cascarilla:—Albumen, a peculiar kind of tannine, a bitter crystallizable principle (cascarilline), red colouring matter*, fatty matter having a nauseous odour, wax, gummy matter, volatile oil (this has an agreeable odour and a spec. grav. of 9·938), resin, starch, pectic acid, chloride of potassium, calcareous salts and woody fibre.

The most interesting of these principles is the bitter one. My process for extracting it is as follows:—I first select a bark the taste of which is strongly bitter. After having been coarsely powdered and placed in a displacement apparatus, it is treated with water. Solution of acetate of lead is added to the mixed liquids, which are filtered and freed from excess of lead by sulphuretted hydrogen. They are again filtered, evaporated to about two-thirds; a small quantity of animal charcoal is then added, and the mixture filtered. The solution is evaporated at the lowest possible temperature. At a certain period a pellicle forms. When this has acquired a moderate consistence and before the liquid becomes syrupy, the whole is allowed to cool, and the substance is carefully removed. Sometimes, however, it does not possess the crystalline aspect, but appears resinous, and adheres to the sides of the evaporating dish. It becomes harder by cooling.

To purify either of these substances, they are pulverized; the powder is placed in a tube, and as much cold alcohol of spec. grav. 0·870 is poured over it as is rather more than sufficient to moisten it. After a sufficient interval, this alcoholic liquid, which is highly coloured, is poured off. The greater part of the fatty and colouring matters with which the cascarilline was mixed is thus removed; the remaining powder is considerably decolorized. This is then treated with boiling alcohol of spec. grav. 0·835; a little animal charcoal is added; it is then filtered and allowed to evaporate spontaneously. The residue is dried on unsized paper. To complete its purification, it is powdered, again treated with cold alcohol, and subsequently dissolved in boiling alcohol, filtered, and allowed to evaporate spontaneously. The bitter matter is thus obtained in a state of purity.

In this state it is white and crystalline; the crystals, under the microscope, appear to be prismatic needles, sometimes mixed with hexagonal plates. It is inodorous and bitter, but this is not immediately perceptible on account of its slight solubility in water. When heated in a closed tube, it fuses, forming a yellow syrupy liquid with the aspect of caramel. It fuses at a lower temperature than salicine. Exposed to a great heat, it decomposes, evolving fumes which redden litmus-paper. It leaves no ash. Heated with potash in a tube,

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* This is insoluble in æther, but it is soluble in alcohol, to which it imparts a fine purple colour. It readily dissolves also in water containing an alkali.

its vapours do not restore the colour of reddened litmus. It is very slightly soluble in water, but renders it strongly bitter. The solution is neutral to litmus-paper; it is not precipitated by either neutral or basic acetate of lead, tannine or alkalies. It is soluble in alcohol and æther. Concentrated sulphuric acid dissolves and instantly reddens it; the tint is very deep and tinged with purple. A certain quantity of water causes a precipitate in the solution. The liquid then appears green; as the precipitate subsides it becomes paler. Ammonia does not dissolve the precipitate, but renders it of an ochreous-yellow colour. Nitric acid dissolves the principle, and the yellow solution thus formed is precipitated by ammonia. Muriatic acid dissolves it, acquiring a tinge of violet, which is converted into blue on the addition of a very small quantity of water. As cascarilline does not contain nitrogen, and combines with neither bases nor acids, it must be ranged among the neutral non-nitrogenous substances, with salicine, columbine, &c. Its intense bitterness, and the general analogy between cascarilla and cinchona, render it probable that it may be advantageously used in medicine.—*Journ. de Pharm. et de Chim.*, Aug. 1845.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Electro-chemical Treatment of Copper Ores.

By MM. GAULTIER DE CLAUBRY *and* DECHAUD.

THIS process requires, in the first place, the transformation of the mineral into a compound readily soluble in a liquid easily obtained at the place of working; it is only on this condition that the electrical forces are of advantage in separating the metal from its combinations; for instance, with copper ores, such as the carbonate, oxide, sulphuret or bisulphuret, which are the most common, the two first are transformed into sulphate by means of sulphuric acid, and the two latter by roasting them; an operation which is executed in great perfection in Mexico in the preparation of magistral, an indispensable agent in the amalgamation by *patio*. As soon as they have been completely converted into sulphates, the ore is washed and the solution submitted to electro-chemical decomposition in a very simple apparatus. To obtain the copper in sheets, the apparatus should be so arranged that the solution is constantly at its maximum of saturation. The authors have succeeded in performing this by the following very simple arrangements:—

When two solutions are placed one above the other in a vessel, the one saturated with sulphate of copper, the other less dense with sulphate of iron, and if a sheet of copper is placed in the first and a sheet of cast iron in the other, communicating with the first by means of a metallic conductor, a voltaic pair is formed whose action suffices to decompose the sulphate of copper; the oxygen and the acid of the sulphate act on the cast iron forming sulphate of iron, while the copper is deposited on the sheet of copper forming the negative pole.

The copper deposited at first is chemically pure, but the iron becoming more and more abundant, the copper in precipitating carries down with it some iron; it gradually becomes brittle, then pulverulent, in proportion as the solution becomes weakened. But while this solution becomes less dense, that of the sulphate of iron, on the contrary, increases in density, and there results,—1st, a normal solution of copper, occupying the lower portion of the vessel; 2nd, a solution of the same salt, somewhat less dense, floating on the first; 3rd, a very dense solution of sulphate of iron; 4th, another normal solution. To continue always in the primitive conditions, and to obtain the copper in sheet, it was requisite to remove the less dense solution of sulphate of copper and the more dense one of sulphate of iron. This is the principal perfection which the authors have made in the treatment of copper ores electro-chemically.

Their apparatus is composed of the following parts:—A wooden trough, lined with lead, then covered with wax or some analogous substance, and destined to receive the solution of sulphate of iron. This trough is provided with two apertures, a superior one for the introduction of the normal liquor, an inferior one for expelling the dense liquor by means of siphons. In the interior, at suitable distances, are sunk copper or sheet-iron cases lined with lead, the extremities and lower part of which are of metal, whilst the lateral divisions are open and furnished with sheets of pasteboard solidly fixed. A lower opening also lets off the concentrated solution of copper by means of siphons; and another, placed nearly at the superior part, allows the weak solution to flow off.

The negative metal destined to receive the deposit of copper is placed in these cases; and between each of them, as well as at the exterior of the two extreme cases, are fixed the two cast-iron plates which are to produce the voltaic action.

Metallic conductors serve to establish a communication between all parts of the battery; and the apparatus is so regulated that as much strong solution of sulphate of copper and of weak solution of iron arrives every moment as weak solution of copper and strong solution of iron flow out; the action continues without any hand work.

On the other hand, in order to facilitate the passage of the current between the two solutions in contact and separated by diaphragms of pasteboard, these are pierced with small openings above the superior level of the negative plate. With this arrangement the solution of normal sulphate of iron, occupying the superior part of the case, spreads itself over that of the copper, so that the apparatus is brought back to its first condition.

When once the apparatus is arranged, it is only necessary to take away the sheets of copper when they are of a suitable thickness, and to insert fresh metal plates when the others have been dissolved.

The movement of the liquids is effected by means of siphons connected with basins of a constant level; the quality of the metal used is of small importance; that of the worst quality succeeds equally well. The sheets of copper can immediately be sent to market; when passed through the flattening machine, they acquire the density of those of the copper obtained by the process of flattening.

All the copper precipitated is not obtained in sheets; there is hardly the three-fifths, and even the half of it; the remainder is in the state of powder, or of fragments which should be melted.

The electro-chemical process for the treatment of ores of copper with the improved method of MM. Gaultier de Claubry and Dechaud, seems to be more advantageous than the old methods; but it requires that the ores should be entirely transformed, and at a cheap rate, into sulphate. On this depends the whole question. On the other hand, the solution of copper, partly exhausted, becomes more and more charged with iron; so that in passing it afresh over the ores, in order to saturate it with sulphate, and putting it again into the apparatus, there comes a time when the quantity of iron which it contains is so great that the copper precipitate contains a certain proportion of this metal, which deteriorates the quality of it. To remedy this inconvenience, the solutions which contain too much iron should not be again passed over the ore, and the copper which they contain with iron should be precipitated.—*Comptes Rendus,* July 1845.

Description of a simple Process for detecting the Presence of free Sulphuric Acid in Vinegar. By R. Böttger.

The ordinary vinegars of commerce frequently occur adulterated with powerful mineral acids, especially with sulphuric acid, and hitherto it is only by a somewhat minute and tedious process that it has been possible to prove with certainty a sophistication of this nature; in fact, the ordinary reagents, such as the nitrate and acetate of barytes, are here of no service, since almost all the vinegars contain small quantities of sulphates, which are readily detected by the addition of the above reagents. Now the process proposed by Prof. Runge, which consists in demonstrating by means of a solution of sugar the presence of free sulphuric acid in vinegar, proves perfectly successful in the hands of an experienced chemist; but it is too long and too little certain for the manufacturer and persons unacquainted with chemistry. I believe therefore that the following process, which is as simple and easy of execution as it is certain, will be received with some interest. I observed that all the vinegars, without exception—vinegars made from wine, brandy, cider or beer, no matter which—are, notwithstanding the small quantity of sulphates they may contain, perfectly indifferent to the action of a concentrated solution of *chloride of calcium.* If, consequently, a few drops of a concentrated solution of chloride of calcium are added to any unsophisticated vinegar whatever, not the least turbidness is evident, still less the formation of a precipitate, because the total quantity of the sulphates which occur in ordinary vinegar is so small that it does not decompose a saturated solution of chloride of calcium, either at the ordinary temperature or at that of ebullition. Now the result is very different when free sulphuric acid is present in the vinegar; for instance, if to about 2 drms. of vinegar, which has been purposely mixed with scarcely a thousandth part of free sulphuric acid, a fragment of crystallized chloride of calcium about the size of a nut is added, and the vinegar then heated to boiling, it is seen, as soon as it has become perfectly cold, to exhibit a very considerable turbidness, and soon afterwards to deposit a very abundant precipitate of sulphate of lime. This never happens, as I have stated, when ordinary vinegar, which has not been adulterated with sulphuric acid, is employed for the experiment. If the proportion of the sulphuric acid in the vinegar is larger than one-thousandth (it always exceeds this when vinegar has been purposely adulterated by the greedy manufacturer or shopkeeper), this precipitate, or at least a turbidness, is found to appear in the vinegar even before it has become perfectly cold. In case a vinegar should contain free *tartaric acid* or *bitartrate of potash*, or had been purposely mixed with these substances, the same treatment with chloride of calcium would not furnish any similar reaction. It is known indeed that neither free tartaric acid nor the bitartrate of potash are able to decompose chloride of calcium even at boiling heat; thus the reaction above recommended for the detection of free sulphuric acid would be neither less manifest nor less certain, even with the presence of tartaric acid or of the bitartrate of potash in the vinegar.—*Journ. für Prakt. Chem.*, vol. xxxiv. p. 254.

Determination of the Causticity of the Soda Salts of Commerce.

By M. Barreswil.

Having had occasion to examine, with M. S. Riess, alkalimetrically some samples of commercial soda, we employed, in order to determine the caustic alkali, a new process of great accuracy, which although demanding somewhat more time than the ordinary process, is so readily executed that it may be recommended to manufacturers, and in some cases it might certainly be employed with advantage in analytical investigations of the laboratory.

This process is founded on two chemical reactions, both well known, viz.—

1. When an excess of chloride of barium is poured into a solution of carbonate of soda, the filtered liquid is not rendered turbid by carbonic acid.

2. When the least quantity of alkali is added to a perfectly neutral solution of chloride of barium, the filtered liquid is rendered turbid by carbonic acid.

The process of analysis consists in determining the amount of barytes eliminated from the chloride of barium by the caustic alkali contained in the soda salt. For this purpose, 10 grms. of the soda to be assayed are dissolved in water, and to the solution one of 25 grms. of perfectly neutral chloride of barium, that is to say, an excess, added to it. It is now filtered, the filtrate washed, and a current of carbonic acid passed into the filtered liquid, which is then heated to boiling; the precipitate collected, washed and weighed. 1 equiv. of carbonate of barytes corresponds to 1 equiv. of caustic soda. This process, which we have frequently employed, has enabled us to detect less than 1 per cent. of caustic alkali in a soda salt, and to convince ourselves that certain samples, which were said to contain from 1 to 2 per cent. of free alkali, contained not the least trace. These samples were very rich sodas of remarkable purity; submitted to the alkalimetric test by Gay-Lussac's method, they saturated 58½ measures of the test-liquor, according to which they should contain 99 per cent. of pure and dry carbonate of soda. Astonished to meet in a commercial product, made on so large a scale, so remarkable a purity, we verified with chemically pure carbonate of soda our alkalimetric liquid, which had however been made with the greatest care. It required exactly 59½ divisions of the tube for 3·185 grms. of the soda salt. With nitrate of silver and chloride of barium, we obtained scarcely perceptible precipitates in the solution of soda previously saturated with nitric acid. One single crystallization removed the last traces of impurity.—*Journ. de Pharm.*, Aug. 1845.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

May 19, 1845. (The President, Professor Graham, in the Chair.)

A Memoir, containing the results of an extensive inquiry, "On Atomic Volume and Specific Gravity," by Dr. L. Playfair and J. P. Joule, Esqrs.

This paper began with a review of the labours of those who had preceded the authors in inquiries on this subject. Gay-Lussac had proved that gases unite in multiple volumes, and that the resulting compounds stand in a simple relation to the volumes of their constituents. Schröder, Kopp and Persoz had drawn attention to a fact formerly enunciated by Thomson, that the quotients resulting when the atomic weights of certain bodies are divided by their specific gravities are often the same numbers for different elements. Kopp and Persoz extended this observation to many isomorphous compounds; and Schröder observed, that when the primary volume of the same member of a series of analogous compounds is subtracted from them, the remainder is equal for each. In these inquiries, however, there was no attempt to ascertain whether the volumes of solids were multiples of each other. The authors of the present communication have examined the volumes occupied by an extensive series of salts. They conceived that the error of previous experimenters was in comparing the specific gravities of solids with an equal bulk of water; or, in other words, referring the solid form of matter to its liquid form. To contrast the volume of a salt in its liquid state with water, the authors constructed a simple instrument, consisting of a bulb with a graduated stem; in this, by means of a tubulure, the salt was placed, and dissolved in a given weight of water, which had previously been introduced. The increase in the stem of the instrument, corrected for the expansion of the solution above that of water at a given temperature, gave the volume of the bulk in solution. The first results given by the authors were, that certain hydrated salts, such as the magnesian sulphates, occupy no space of themselves in solution, but merely the space which would have been taken up by their combined water had it been added without the salt to which it was attached. Dalton had observed this fact in some cases in the year 1840, and the authors have confirmed his observations. The case is particularly striking in alum, which contains 23 anhydrous atoms and 24 atoms of water; on dissolving alum in water, the space occupied is exactly that due to the water, the 23 anhydrous atoms taking up no space of themselves.

The authors then proceeded to examine the volumes of salts which are either anhydrous or are combined with only a small quantity of water. The stem of their volumometer was divided into grains of water, so that 9 of the graduation was equivalent to the volume taken up by 1 equivalent of water at 60° F. On dissolving an equivalent of any salt in water, they observed that the increase was in every case either 9 or a multiple of that number, the extreme difference in the observations being 2 in 45. Thus an equivalent of sulphate of potash increases the bulk of the water 18, or 9×2; chloride of potassium 27, or 9×3, &c. This law of multiple volumes they found to prevail with great uniformity in all the classes of salts which they subjected to examination. Salts which possessed the same form in the solid state possessed also the same volume in solution, with the exception of the ammoniacal salts, which affect one volume in solution more than the corresponding salts of potash. Double salts were found to have the sum of the volumes of the constituent salts. The next subject treated of by the authors was the specific gravity of solids. They had found that in every case the salt in solution occupied less bulk than it did in its solid state, the difference for each volume being as $9:11$. If the specific volume of the salts, which in solution took up no bulk of themselves, were divided by 11, the quotient indicated the number of atoms contained in the salt; several exceptions were given, in which the difference was as $9:10$, or the difference between the volume of water and of ice. In the case of anhydrous salts, or salts possessing only a small amount of water of hydration, they did not find any exceptions as to the multiple relation of the solid volumes, except those due to errors of observation, the extremes of which were stated as 3 in 44. The quotient resulting from dividing the atomic volume of the solid by 11 in most cases gives the same numbers as that obtained by dividing the liquid volume by 9. In some cases, however, a chemical union seems to take place between the salt and the water, for the salt in its solid state loses a volume in becoming liquid; thus sulphate of potash, which has a volume of 33 or 11×3 in its solid state, has in solution a volume of 18, or

9×2. The ammoniacal and corresponding potash salts have the same volume in the state of salts; in fact, all strictly isomorphous bodies have; and double salts have their volume the sum of the volumes of their constituent salts. The authors described the new mode which they had employed in taking the specific gravities of salts; the simplicity of which they conceived to have enabled them to establish the relation between the specific gravities of the salts, by enabling them to multiply their observations.

PATENT.

Patent granted to Louis Antoine Ritterbandt, Gerard-street, Soho, *for preventing and removing Incrustation in Steam-boilers and Steam-generators.*

The object of this invention is to prevent and remove incrustation in steam-boilers. In commencing his specification, the patentee states that the incrustation of steam-boilers wherein fresh-water is used arises chiefly from the heat causing the lime (which exists in the water in the form of a soluble bicarbonate) to be converted into an insoluble carbonate of lime, the particles of which, as they fall towards the bottom, carry down with them other insoluble matters that may be floating in the water; and as regards boilers wherein salt or sea-water is used, the incrustation is generally promoted by the carbonate of lime set free by the heat, which, as it floats in the water previous to subsiding, forms a nucleus for the gathering of other matter, and disposes the saline compounds, such as the sulphate of magnesia, chloride of sodium, &c., to crystallize and precipitate much sooner than they otherwise would. This invention is designed, in the first case, to prevent the formation of carbonate of lime, or to convert it when formed into a soluble salt; and in the latter case, to retard the formation of the saline crystals, and thereby also to retard the precipitation of other floating matters which would produce incrustation. To effect these objects, the patentee introduces into the water in the boiler, or into the supply tank, a quantity of muriate, acetate or nitrate of ammonia, or any other ammoniacal salt, the acid of which uniting with lime as a base, will form a perfectly soluble salt of lime, which will not be precipitated by heat, and neither incrust the boiler nor contribute to its incrustation by promoting the crystallization or precipitation of other matters.

The quantity of ammoniacal salt to be employed will depend upon the amount of lime contained in the water in the form of bicarbonate. The patentee describes the following mode of ascertaining the amount:—"Take a gallon or any other measure of the water to be examined, and evaporate it slowly in an open vessel. Collect the solid matter left at the bottom of the vessel, and weigh it carefully. Then add to it, in a glass vessel, a mixture of equal parts of muriatic acid and distilled or rain water, and let it remain during 15 minutes. Next filter through white filtering or blotting paper, or strain through clean linen or calico. Collect the solid matter left in the filter, and dry it. The difference between its weight now and before will give the amount of carbonate of lime dissolved in the muriatic acid; thus, if a gallon of water gives 10 grs. of solid matter, and after digesting with muriatic acid there are only 6 grs. left, the gallon contains 4 grs. of carbonate of lime."

If muriate of ammonia be employed to prevent incrustation, the quantity added to the water should equal the quantity of lime contained therein, or rather exceed it; as, for instance, 54 parts of the ammoniacal salt to 50 parts of carbonate of lime. When acetate of ammonia is used, the proportions must be about 40 parts of a saturated solution (prepared by adding carbonate of ammonia to acetic or pyroligneous acid, or to distilled vinegar, until no more is dissolved) to 15 parts of carbonate of lime. If nitrate of ammonia be employed, the proportions must be about 80 parts of the crystals to 50 parts of carbonate of lime. In every case the amount of water evaporated in a given time must be taken into account, as in proportion to the water evaporated will be the carbonate of lime set free and the quantity of ammoniacal salt required.

The action of the muriate of ammonia (which is preferred by the patentee on account of its cheapness) is partly chemical and partly mechanical. It is chemical, inasmuch as, after the introduction of the salt into the water, a double decomposition takes place; the muriatic acid combines by elective affinity with the lime to form muriate of lime, while the carbonic acid passes to the ammonia and forms carbonate of ammonia; the muriate of lime remains in a state of solution, and the carbonate of ammonia, volatilizing under the influence of the heat, passes off along with the steam. This decomposition, however, goes on slowly and gradually. When the ammoniacal salt is added to the water in considerable quantities at a time, part of it remains in the state of muriate of ammonia until the introduction of a fresh supply of water; it will therefore be found advantageous to add the salt in considerable quantities at a time, as one supply will then be sufficient for several days, or even weeks. The mechanical action of the muriate of ammonia (as also of the acetate, nitrate or other salt of ammonia) consists in increasing the density of the water, and thus assisting to retain in suspension any foreign matter which would otherwise sink to the bottom, and there form a solid incrustation.

To free boilers from old incrustation, muriate of ammonia, or any other ammoniacal salt (the acid of which, with lime as a base, will form a soluble compound), is used, but in much larger quantities, say double, or even treble, the proportion above mentioned. And when the old incrustation does not readily yield to these means, the patentee introduces once a week into the water in the boiler or supply-tank a quantity of muriatic or nitric acid, in the proportion of about 1 quart to 100 gallons of water; or acetic acid, in the proportion of 1 gallon to 100 gallons of water; or common vinegar, in the proportion of 2 gallons to 100 gallons of water.—Sealed Dec. 2, 1844.

THE CHEMICAL GAZETTE.

No. LXX.—September 15, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Œnanthylic Aldehyde (Hydruret of Œnanthyle, Œnanthole).

By M. Bussy.

In a memoir* on castor oil, written conjointly with M. Lecanu, it was proved that this oil was peculiar, and perfectly distinct from all other fatty bodies which had at that time been described.

We showed that on saponification it furnished peculiar acids, margaritic, ricinic and elaidic; and that the two latter were formed by distillation. We also showed that this distillation of castor oil, which took place at a temperature not exceeding 518°, was remarkable in the oil under the influence of heat becoming distinctly divided into two parts; one, the residue, is colourless, spongy, and of the consistence of soft new bread; the other, volatile, complex, passes over into the receiver, contains water, elaidic and ricinic acids, a small quantity of acroleine, and a matter having a peculiar aromatic odour, which, from its odour and volatility, we called *essential oil.*

The examinations of the essential oils of vegetables which have taken place since then, have greatly extended our information of this kind of product, and rendered it much more precise; and our knowledge of the essential oils now constitutes an important part of organic chemistry, hardly known when our first memoir appeared; consequently it became of great interest to recommence the study of this essential oil, of which only a sketch was given at the period we speak of, to establish the relations of its composition to the products which arise from it, and to assign its place in the series of organic products. Among those works which have been published within the last few years, and directly relate to our subject, is that of Mr. Tilley on the action of nitric acid on castor oil†. The author discovered a new volatile acid, to which he applied the name of *œnanthylic acid,* on account of its relation to the œnanthic acid discovered by Liebig and Pelouze in wine. From analysis, this acid, both free and combined, appeared to have its composition exactly determined by the formula $C^{12} H^{14} O^{4}$. However, the results obtained by Mr. Tilley have been called in question by M. Larivière, who having examined the volatile acid product obtained by the ac-

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* Journ. de Pharm., vol. x.

† Phil. Mag., vol. xviii. p. 417.

tion of nitric acid on castor oil with great care, deduced from the analyses of its silver and barytes salt the formula $C^{12} H^{12} O^{4}$, which would seem to show that the acid obtained is nothing more than Chevreul's caproic acid. In fact, M. Lerch, in his essay on the volatile acids of butter*, proposes to adopt the formula $C^{12} H^{12} O^{4}$ as that of caproic acid.

It is improbable that the difference in the results obtained by Mr. Tilley and M. Larivière depends upon some error in the analyses. Do there then exist two distinct volatile acids in the product of the oxidation of castor oil by nitric acid? Such an idea seems best to accord with the results of our combined researches.

Preparation.—The essential oil, which we shall call henceforth *œnanthole*, is obtained by distilling the oil of the seeds of the castor oil plant; the collected product is oily, of a yellow colour, and floats on a small layer of a watery liquid; the latter is separated, and the oily product again distilled with 5–6 volumes of pure water. The residue of the last distillation consists of the mixture of ricinic and elaidic acids. The distillate is colourless, odorous, and contains the œnanthole, a little acroleine, œnanthylic acid, and some fixed fatty acids, which have been carried over in the distillation; it is agitated with 5–6 times its weight of water, which is separated, and which dissolves the greater part of the acroleine.

The distillation with water is repeated until no more fixed oily residue remains with the water.

The product thus obtained is next shaken with a weak solution of baryta until it ceases to redden litmus-paper. After having thus separated it from any acid it might contain, it is decanted; the product is heated in a retort, and when the temperature at which it boils is constant between 307° and 316°, it is collected; thus the water and a small quantity of acroleine are separated. Anhydrous phosphoric acid cannot be used for drying the oil, because it is blackened and materially altered by contact with it; but chloride of calcium removes the water, without the product retaining any appreciable quantity of it.

Œnanthole is colourless, limpid, powerfully refractive; its density at 44° is 0·8271; it possesses a powerful, aromatic, penetrating odour, which is not disagreeable; its taste is at first sweet, then acrid and persistent; it is soluble in alcohol and æther in every proportion. Water dissolves but a very small portion of it, sufficient however to acquire its peculiar odour. When free from water, it boils between 307° and 316°; however, towards the end of the operation the temperature rises, it becomes coloured, and acquires an acid reaction: this occurs even when the distillation is conducted in an atmosphere of carbonic acid.

The analysis of the œnanthole gives the formula $C^{14} H^{14} O^{2}$. Thus it is isomeric with the butyrone which M. Chancel obtained by the decomposition of the butyrate of lime†.

Its density, calculated for this formula, would be 4·00192. Ex-

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* Chem. Gaz., vol. ii. p. 377.

† See Chem. Gaz., vol. ii. p. 341.

periments repeated many times and at different temperatures, have constantly yielded a higher density, which appears to depend upon some alteration experienced by the œnanthole from the heat, and its great affinity for oxygen.

It combines with water, forming a crystalline hydrate, the composition of which is represented by $C^{14} H^{14} O^2, HO$. On exposure to air, it absorbs oxygen and is converted into œnanthylic acid. The mere decanting it from one vessel to another is sufficient to effect this change.

Met-œnanthole (*œnanthylic meta-aldehyde*).—This is an isomeric modification of œnanthole, obtained by the action of nitric acid upon it in the cold. It is solid at 50°–53°, and below that point, is not acid, but inodorous and crystallizable. When it has been exposed for some time to a temperature higher than 59°–68°, it loses its power of solidifying, but acquires it by long exposure to a moderate degree of cold. Oxidizing agents readily cause the transformation of œnanthole into œnanthylic acid, and frequently the action is violent. On contact with chromic acid, it takes fire. When boiled with dilute nitric acid, it is decomposed into œnanthylic acid and an essential oil, which is not acid, having an odour of cinnamon. It reduces the nitrate of silver in the same way, and under the same circumstances, as alcoholic aldehyde. The vessels in which the action occurs are coated with silver, as with the latter. The analysis of the barytic and silver salt of this acid confirms the composition assigned to it by Mr. Tilley, $C^{14} H^{14} O^4$. This composition ranges œnanthylic acid with the volatile fatty acids, and places it between the caproic and capric acids of M. Chevreul. We have consequently the following series of volatile fatty acids:—

Butyric acid	$C^8 H^8 O^4$
Caproic acid	$C^{12} H^6 O^4$
Œnanthylic acid	$C^{14} H^7 O^4$
Caprylic acid	$C^{16} H^8 O^4$
Capric acid	$C^{20} H^{10} O^4$

Potash and weak solutions of the alkalies do not materially alter œnanthole; when concentrated, they remove its odour, and transform it into a viscid fatty matter, which is more or less coloured according to the energy of the action. Heated with 10 times its weight of potash and lime in a proper apparatus for collecting the gas, a quantity of hydrogen is disengaged, and œnanthylic acid formed; the latter remains in combination with the potash. The proportion of acid produced however is very small comparatively to the quantity of œnanthole employed; a resinous mass, more or less carbonaceous, according to the temperature employed, is produced at the same time.

If we endeavour to account for the mode of generation of the œnanthole, we see that it is produced under similar circumstances to those which give rise to acroleine, which is likewise an aldehyde, and with which it has considerable analogy.

Acroleine, $C^6 H^4 O^2$, is formed from glycerine by the removal of a certain quantity of water. This reaction may be expressed thus:—

Glycerine	$C^6 H^8 O^6$
Water	$H^4 O^4$
Acroleine	$C^6 H^4 O^2$

If œnanthole was also formed at the expense of the elements of the glycerine in the castor oil, the reaction should be different; in fact, it arises from the separation of a certain amount of the elements of glycerine in the form of water and oxalic acid:—

3 glycerine	$3(C^6 H^8 O^6$
Œnanthole	$C^{14} H^{14} O^2$
Oxalic acid	$C^4 O^6$
Water	$H^{10} O^{10}$
	$C^8 H^{24} O^{18}$

It must however be remarked, that œnanthole may be produced under very different circumstances; thus, when stearic and margaric acids, and several other analogous fatty bodies, are treated with nitric acid, we obtain both œnanthole and a certain quantity of œnanthylic acid, which is evidently a secondary product of the reaction of the nitric acid on the œnanthole.—*Comptes Rendus*, July 7, 1845.

On the Oil of Madia sativa. *By* Dr. Luck.

The oil was saponified with potash, which was readily effected; the soap was decomposed with common salt, again dissolved in dilute alkali, and separated by salt. The white solid soap, decomposed by tartaric acid, when distilled in small quantity, yielded no volatile acid. The fatty acid was repeatedly crystallized from alcohol; it formed fine radiating needles. The alcohol could not be perfectly removed, even by long-continued heat; it was, however, separated by again dissolving the acid in caustic potash, and precipitating it by muriatic acid, from which it was freed by repeated melting in water. The hydrated acid, on analysis with oxide of copper, and passing acurrent of oxygen through the tube towards the termination of the burning, gave—

Carbon	74·002
Hydrogen	12·290

The solution of the soap was precipitated by acetate of lead, and the precipitate treated with æther, which dissolved a trace of a lead salt. On decomposing the lead salt thus treated by muriatic acid, I obtained a fat acid, which fused between 129° and 131°, and solidified at 125° to a foliaceous mass. It yielded—

	I.	II.
Carbon	75·514	75·678
Hydrogen	12·498	12·620
Oxygen	11·988	11·702

The silver salt yielded 32·23 and 32·04 oxide of silver; average, 32·14. And—

	I.	II.
Carbon	52·684	52·76
Hydrogen	8·212	8·30
Oxygen	6·964	6·80

From the analysis of the silver salt, I calculated the formula $C^{32}H^{30}O^{3} + AgO$. Hence the hydrate should give,—carbon, 75·31; hydrogen, 12·14; numbers which differ, it is true, from those found by experiment.—*Ann. der Pharm.*, April 1845.

On the Composition of the Hydrate of Baryta and Strontia.
By M. Filhol.

Both baryta and strontia form two hydrates; one of which, consisting of 1 equiv. base and 1 equiv. water, is amorphous, while the other is crystalline. The latter, which is obtained on the cooling of a boiling saturated solution of baryta, consists, according to Thénard and Berzelius, of 9 equiv. water and 1 of base. According to the latter, the hydrate so obtained has even more than twice the weight of the anhydrous baryta employed. The author, however, on examination of this hydrate, dried at the ordinary temperature between bibulous paper, and decomposing the compound by sulphuric acid, obtained, as the mean of six analyses, 48·57 per cent. water and 51·43 baryta, which, according to the calculation, would correspond to 8 equiv. water to 1 of baryta, or 48·64 per cent. water and 51·36 baryta.

The crystals of this hydrate melt already at 212° in their water of crystallization, with which they part at a higher temperature. Their specific gravity at 61° is 2·188; according to Berzelius it is 4, but this is probably an error, and refers to the hydrate with 2 equiv. water.

The crystalline hydrate of strontia contains, according to the general statement, 12 equiv. water to 1 equiv. base; the author, however, obtained, on examination in the manner above described, 60·83 per cent. water and 39·17 strontia, therefore only 9 equiv. water, or calculated, 60·99 per cent. water and 39·01 strontia. Its specific gravity at 61° is 1·911. It is remarkable that baryta and strontia, which resemble one another so much in other respects, should form hydrates with such different quantities of water; however, similar differences in the amount of water are met with in other combinations of strontia and baryta, for instance in the chlorides, of which that of barytes contains 4 equiv. and that of strontia 12 equiv. water; and the hydrated compounds of strontia likewise contain more water than the corresponding ones of baryta.—*Journ. de Pharm. et de Chim.*, 3 ser., 4th ann., p. 271.

Researches on Rutinic Acid. By A. Borntraeger.

To obtain rutinic acid (*Rutine* of Weiss), the dried and cut plants of *Ruta graveolens* are boiled for about half an hour with ordinary vinegar, the liquid expressed, and left to stand for several weeks. In the course of this time the rutinic acid separates, mixed with several other substances, partly in the form of a sediment, partly in microscopic crystals. Still more may be obtained by evaporating the separated mother-ley.

The impure acid is washed with a little cold water, then boiled with about four times the quantity of pure acetic acid, diluted with 4 parts of water, and the solution filtered. After some days the greater portion of the rutinic acid separates in a crystalline form. On partial evaporation of the remaining solution, a further deposit takes place after some time. The whole of the acid thus obtained is washed with a little cold water, dissolved in about 6 times its weight of boiling alcohol to which some animal charcoal has been added, and filtered. This solution is mixed with about one-eighth water, the alcohol entirely removed by distillation, and the residue left for several days in a cool place for the acid to crystallize. The mother-ley is again concentrated by evaporation, for the deposition of the acid only takes place gradually, and the more readily the lower the temperature. This process has the advantage of requiring much less alcohol; for although the rutinic acid when pure is very readily soluble in alcohol, it requires a large quantity of it when mixed with other substances. The acid extract, it is true, deposits apparently a large quantity of impure acid; but it is so very much mixed with foreign matters, that but little acid is finally obtained in the pure state.

Rutinic acid, thus prepared and purified, forms a pale greenish-yellow powder, which appears crystalline to the naked eye. When magnified 200 times, it is seen to consist of concentrical aggregations of quadrilateral prisms with very acute terminal surfaces. It has no taste, but its alcoholic solution acts decidedly acid upon litmus-paper. When heated and exposed to the air, it melts, giving off an odour similar to that of burnt sugar, and burns with a flame. Heated in the oil-bath, it melts at 356° to a yellow tenacious liquid without parting with any water. On cooling, it solidifies in part to a crystalline mass; at 428° a small portion sublimes in yellow drops, and at 469° it is reduced to charcoal. It is very sparingly soluble in cold water, more readily in hot; the boiling saturated solution, however, forms no deposit on cooling, nor even on evaporation to one-sixth of its original volume. Only after much greater concentration does any crystallization take place after some days, and then proceeds only very slowly. The solution has a pale yellow colour. It is very little soluble in cold absolute alcohol, but very readily in boiling alcohol of 0·873 spec. grav. This solution, when highly concentrated, congeals to a magma in which nothing crystalline is perceptible. In fact, rutinic acid can only be crystallized from alcohol by mixing the solution previous to evaporation with about one-sixth water.

The slowness with which rutinic acid is deposited from its solutions is probably owing to the substance having a different composition in these solutions than in the crystallized state; perhaps it contains in the latter 1 atom more water, which is separated from it by the action of the hot solvent, but subsequently gradually recombines with it during crystallization. The composition of its combination with lead, in which 2 atoms of eliminated water are replaced by 1 atom of oxide of lead, appears to favour such a view.

Rutinic acid is perfectly insoluble in æther even on boiling; it dissolves readily in a dilute solution of potash with a reddish-yellow colour, likewise in caustic ammonia, in barytic, strontia and lime water; but it is impossible to obtain in any way definite or crystallized combinations with these bases. The solution in potash rapidly acquires a darker colour when exposed to the atmosphere, and the rutinic acid is soon destroyed, especially on evaporation, with formation of a brown humus-like substance. It behaves in precisely the same way in an alcoholic solution of hydrate of potash. Carbonic acid passed through this solution precipitates carbonate of potash, while pure rutinic acid remains dissolved; and, in fact, it is separated by other acids perfectly unaltered from its solutions in the alkalies, if it has not been modified by the air, although under these circumstances it is deposited very slowly. The solution in caustic ammonia leaves on evaporation pure rutinic acid free from ammonia. Oxide of lead was the only base with which a definite compound could be obtained. A solution of rutinic acid mixed with one of acetate of lead forms an orange-coloured precipitate of the same purity and brilliancy of colour as chromate of lead. For analysis, it was precipitated in a closed vessel by mixing an alcoholic solution of rutinic acid with an alcoholic solution of acetate of lead.

Rutinic acid yielded on analysis—

Carbon..........	50·34	50·27	3	50·04
Hydrogen........	5·55	5·54	2	5·54
Oxygen	44·11	44·19	2	44·42

The lead compound gave the following results:—

Carbon	30·50	30·37	12	30·34
Hydrogen	2·46	2·63	6	2·52
Oxygen	20·32	19·05	6	20·19
Lead	47·02	47·05	1	46·94

Consequently the acid combined with the oxide of lead contains 2 equiv. less water than the crystallized acid, whose composition must be expressed by the formula $C^{12} H^{8} O^{8}$, or $C^{12} H^{6} O^{6} + 2HO$. —*Ann. der Chem. und Pharm.*, liii. p. 385.

Observations on Bog Butter. By Dr. E. Luck.

This substance, which occurs in the Irish turf-moors, is very light, whitish, and of a faint, peculiar odour. It readily dissolves in alcohol, leaving small quantities of mechanically-mixed impurities. The solution solidifies to a mass of fine needles, and reacts strongly acid. When several times recrystallized, it fuses at 124°; and on being heated in a tube, the odour of acroleine is evolved, which did not appear to me to be very strong. It yielded—

	I.	II.
Carbon	73·78	73·89
Hydrogen	12·50	12·37

It formed a turbid gelatinous soap with caustic alkali, but no evolution of ammonia was perceptible; the compound was separated by common salt, and this operation several times repeated. By treating the soda soap with tartaric acid, I obtained an acid, which when purified fused at 129° and solidified at 124°, but did not acquire a crystalline aspect. It yielded C 75·57, H 12·474.

The salts which I endeavoured to form with this acid afforded no constant composition, I therefore combined it with lead, and treated the lead salt with æther; this left on evaporation a carbo-hydrogen and a trace of a lead salt. The fatty acid was obtained pure by decomposing the residuous salt of lead with muriatic acid. It now gave, —carbon, 75·051; and hydrogen, 12·56.

The silver salt gave 31·35 and 31·17 per cent. AgO (mean, 31·26); atomic weight = 3193·4.

The lead salt gave 30·35, 30·54, 30·78 per cent. PbO (mean, 30·55); atomic weight = 3170·2.

The barytic salt gave 23·23 and 22·79 per cent. BaO (mean, 23·01); atomic weight = 3201·6.

The barytic salt moreover yielded—

		Calculated for the formula $C^{33}H^{32}O^{3} + BaO$.
Carbon	59·65	59·91
Hydrogen	9·62	9·66
Oxygen	7·72	7·27
BaO	23·01	23·16

The silver salt gave—

		Atoms.	Calculated.
Carbon	53·45	33	53·50
Hydrogen	8·61	32	8·63
Oxygen	6·68	3	6·49
AgO	31·26	1	31·38

The hydrated acid, calculated for $C^{33}H^{32}O^{3} + HO$, gives—

		Found.
Carbon	75·30	75·051
Hydrogen	12·52	12·560

Ann. der Chem. und Pharm., April 1845.

Observations on the Double Chloride of Copper and Ammonium.

By Ch. Heumann.

According to Prof. Graham, equal quantities of chloride of copper and chloride of ammonia are dissolved in water for the preparation of this double salt, and the solution evaporated to crystallization.

Cap and Henry, on the other hand, add caustic ammonia to a solution of oxide of copper in muriatic acid until the precipitate first formed is redissolved to a clear deep azure-blue liquid; on gentle evaporation the salt separates in well-formed octahedrons. According to Graham, the salt is perfectly soluble in water, although less readily so than the chloride of copper, and consists of $NH^4Cl + CuCl + 2aq$; while Cap and Henry state that it is only partially soluble, even in alcohol, especially when heat is employed. The residue left on solution is, according to their statement, a green powder of difficult solution, and approaching in its composition to the protochloride of copper. The salt consists, according to their analysis, of $NH^4 + CuCl + HO$; it contains, therefore, 1 equiv. water less than according to Graham's assertion.

The various modes of preparation and the contradictions in the description of the properties of this compound which occur in the above-mentioned authors lead us to doubt the identity of the two products. When the salt is prepared according to Graham's directions, small crystals are obtained whose form is rhomboidal tablets, but which frequently appear hexagonal from the acute angles being truncated. Dried between blotting-paper, the salt has a pure light blue colour, is unaltered by exposure to the air, and dissolves readily and entirely in water, but more slowly in alcohol. In the examination of this salt, the author determined the copper by caustic lime, the chlorine by nitrate of silver, and the ammonia by chloride of platinum. The analysis gave—

$CuCl$	41·59	1 =	838·35	42·76
NH^4Cl	34·48	1	669·60	34·20
HCl	2·17			
HO............	21·76	4	449·92	23·04
			1957·87	

The excess of muriatic acid found in the examination evidently consisted of free acid which adhered to the crystallized chloride of copper, and was omitted in the calculation as not belonging to the constitution of the salt.

When caustic ammonia is added to a concentrated solution of oxide of copper in muriatic acid, a clear liquid of azure-blue colour is obtained, from which a salt separates on slow evaporation in crystalline crusts, but which the author could never obtain, as stated by Cap and Henry, in well-formed octahedrons. Dried between blotting-paper and treated with water, a small portion of it dissolves with a blue colour, while the greater portion remains as a green amorphous powder; the blue solution is rendered turbid by the addition of much water, with separation of a green precipitate; this takes place more rapidly on heating the blue solution. The solution, boiled for some time, became at last perfectly colourless, and contained only chloride of ammonium with a trace of copper; the salt was decomposed into 44·24 chloride of ammonium, and 55·76 per cent. of a basic salt of copper. The latter, as already stated, forms a greenish powder, which yields nothing to water, nor does it alter its colour. Heated in a glass tube, it parts with much water, and becomes black. It is readily dissolved by dilute acetic acid without a trace of residue, and has consequently all the properties of the oxychloride of copper. The analysis of the salt gave—

Cu	58·29	7	= 2769·90	57·40
Cl............	9·99	1	442·65	9·19
O	12·47	6	600·00	12·49
HO	19·25	9	1012·32	20·92
			4824·87	

The basic salt has consequently the formula $CuCl + 6CuO + 6aq$, and forms in combination with chloride of ammonium the blue salt which Cap and Henry considered to possess the same composition as that described by Graham.—Buch. *Rept.*, 2nd ser., xxxvii. p. 304.

On the Constituents of Polytrichum formosum. *By* Dr. A. Reinsch.

The specimens examined were collected just as the plants were about to develope their capsules; at the period therefore when they are richest in their constituents. Some ripe capsules collected in August yielded but a very small quantity of seed, which allowed merely of a microscopical examination. The seed formed a light brown dust, which with a magnifying power of 500 appeared like globules of the size of a lentil, covered with very fine points; each globule has an umbilical impression in the centre. The globules acquired under the microscope a somewhat darker colour on being moistened with tincture of iodine diluted with water, without however becoming blue, so that they appear not to contain a trace of starch. Acetic acid and caustic ammonia produce no remarkable changes. No starch could be detected in the leaves and stems; they were, however, distinctly coloured brown by tincture of iodine.

From want of material, the analysis of the moss could only be made qualitatively, which was effected by extracting it successively with æther, absolute alcohol, alcohol of 0·833 spec. grav., weak spirit, cold and boiling water, and caustic potash.

Æthereal Extract.—This is of a deep dark green colour, and brownish-red by transmitted light. On distilling off the æther, some green flocculent masses and a greenish oil separated; the residue dried to a salve-like greenish mass. This latter was boiled with water, when a somewhat turbid, nearly colourless liquid was obtained, which smelt strongly of the *Polytrichum*, was coloured faintly brown by tincture of iodine, rendered milky by absolute alcohol, and gave a greenish-brown precipitate with peracetate of iron. After drying, a light brown hygroscopic extract remained, which possessed a moss-like taste. The residue, insoluble in water, was treated with boiling spirit of 0·876 spec. grav., which yielded a dark green tincture, while a green oil remained, which on cooling resembled stearine; the quantity of greenish-brown flakes separated from the alcoholic solution had all the appearance of a kind of wax. The portion insoluble in alcohol was dissolved in æther and left to evaporate, when some dark greenish drops of oil crept up the tube, between which were deposited some faintly-coloured crystals. From want of material, a separation of these substances by a solution of caustic potash had to be omitted.

Alcoholic Extract.—On treating the plants which had been exhausted by æther with absolute alcohol, a beautiful emerald-green coloured tincture was obtained, which had the same colour by transmitted light. On evaporation of the solution, some greenish-brown flakes separated, apparently a resin, which is more readily soluble in alcohol than in æther, but to which, as well as to several of the other substances, the chlorophylle adheres somewhat tenaciously. Water and æther did not remove anything from this extract.

Extract of Alcohol of 0·833 *spec. grav.*—In this operation a pale green tincture was also obtained, which on cooling became very turbid, and deposited a quantity of greenish flakes, which after filtration dissolved in water, and appeared to be a gummy substance, as their solution yielded an abundant white flocculent precipitate with basic acetate of lead. The residue, evaporated to dryness, left a brownish-green extract, which on combustion in a platinum capsule gave off an odour of a nitrogenous substance and resin.

The cold aqueous extract was immediately coloured brown by tincture of iodine, precipitated of a dirty green by peracetate of iron, and was not altered by chromate of potash. On evaporation it formed a brown, hygroscopic, faintly astringent extract, which on combustion left a large quantity of ash. A solution of it behaved like a gummy substance with traces of tannic acid.

A light reddish-brown decoction was obtained by *boiling the residue of the moss in water*; it had neither smell nor taste; a portion of it was evaporated to dryness, when it left a somewhat tenacious, but not hygroscopic extract, which on being heated on platinum foil, swelled, diffused a very disagreeable odour, and left a large quantity of ash, which before the blowpipe yielded a bluish-green fused mass. The solution was scarcely rendered turbid by absolute alcohol, became brown by tincture of iodine, and yielded with basic acetate of lead a flocculent precipitate. On extraction with *caustic potash*, a brown liquid was obtained, which was not coagulated by acids, and after saturation was coloured brown by tincture of iodine.

According to the above results, the principal constituents of *Polytrichum* are,—a fat oil containing chlorophylle in combination with a crystalline substance, some resins, a gum having an odour of moss, traces of tannic acid, nitrogenous vegetable substances, a body which is coloured brown by tincture of iodine, probably a kind of starch, and several vegetable salts with inorganic bases.—*Jahrb. für Prakt. Pharm.*, x. p. 298.

On a new Organic Alkali called Amarine. By A. LAURENT.

I have discovered this new base by a process similar to that which M. Hoffmann and I proposed for the preparation of aniline, viz. by causing ammonia to act on the oil of bitter almonds or the oxide of benzene.

Amarine is without colour, crystallizes in needles, is insoluble in water, soluble in alcohol, and volatile without decomposition, Its composition is represented by the following formula:—

$$C^{84}\,H^{36}\,N^{4}.$$

The chloride of amarine contains 1 atom of acid and 1 atom of base, or

$$H^{2}\,Cl^{2},\ C^{14}\,H^{36}\,N^{4}.$$

On adding some chloride of platinum to some chloride of amarine, yellow crystals of a double salt are obtained, which contain

$$H^{2}\,Cl^{2},\ C^{84}\,H^{36}\,N^{4} + Cl^{4}\,Pt.$$

The constitution and the formation of amarine present peculiarities of the highest interest, which will assist in solving the questions which I have raised respecting chemical types and against the existence of mechanical types.

In my Memoir on Aniline, I showed that the organic alkalies should have the constitution of the radicals of the series to which they belong; thus the aniline $C^{24}\,H^{10}\,Ad$ corresponds to phène $C^{24}\,H^{10}\,H^{2}$.

I showed that aniline was not formed by the reaction of ammonia on phenic acid, but by the decomposition of the phenate of ammonium; in short, that when ammonia is placed in contact with phenic acid, it first gives rise to phenate of ammonia

$$\begin{array}{lr} \text{acid, it first gives rise to phenate of ammonia} & C^{24}\,H^{10}\,(H^{8}\,N^{2}) + O^{2} \\ \text{from which afterwards separates.........} & H^{4}\qquad\quad O^{2} \\ \hline \text{and there remains ....} & C^{24}\,H^{10}\,(H^{4}\,N^{2}). \end{array}$$

Amarine is produced by the action of ammonia on the oxide of benzene, but there is no proof that *benzenate of ammonium* is first formed. We must therefore admit that ammonia reduces the oxide of benzene, and that the nitrogen of the ammonia does not enter into amarine in the state of amide, as in aniline, but as a simple body. We should therefore have the following reaction:—

$$\underset{\text{Oxide of benzene.}}{(C^{84}\,H^{36} + O^{6})} + H^{12}\,N^{4} = \underset{\text{Amarine.}}{(C^{84}\,H^{36} + N^{4})} + H^{12}\,O^{2}.$$

Amarine then would not possess the constitution which I have assigned to the organic alkalies; the nitrogen would not exist in the state of amide, as M. Dumas supposes.

It might be said, it is true, that during the reaction of the ammonia on the oxide of benzene, a perturbation in the grouping of the molecules of benzene took place, which allowed the free nitrogen to enter the radical, and so combine with some hydrogen and form amide; but this would be an hypothesis. I can however easily prove that this perturbation really takes place, although it may appear impossible at first sight.

Two isomeric bodies, in fact, differ solely because the grouping of their molecules is not the same. If with the same compound, and by one and the same process, we obtain two isomeric bodies *by equivalent substitution,* it is evident that if the chemical type or grouping of the molecules is preserved in one case, it must be destroyed in the other. Now, with the oil of bitter almonds and ammonia I obtained three isomeric compounds *by equivalent substitution*; therefore only one of them can have preserved the constitution of the oil; in the two others, the type or arrangement of the molecules must have been destroyed.

The following formulæ will render this explanation clearer :—

Let us admit for nitrogen the equivalent $Az\frac{2}{3}$, proposed by MM. Millon and Bineau, and let it be represented by N, we shall have,

I. Formation of the nitruret of benzene (hydrobenzamide)—

$$\overset{\text{Oxide of benzene.}}{(C^{28}H^{12} + O^{2})} + H^{4}N^{2} = \overset{\text{Hydrobenzamide.}}{(C^{28}H^{12} + N^{2})} + H^{4}O^{2}.$$

II. Formation of the nitruret of picrene (benzhydramide)—

$$3(C^{28}H^{12} + O^{2}) + 3H^{4}N^{2} = \overset{\text{Benzhydramide.}}{(C^{84}H^{36} + N^{6})} + 3H^{4}O^{2}.$$

III. Formation of amarine—

$$3(C^{28}H^{12} + O^{2}) + 3H^{4}N^{2} = \overset{\text{Amarine.}}{(C^{84}H^{30}Im^{2}Ad)} + 3H^{4}O^{2}.$$

The nitruret of benzene has alone preserved the properties of the benzenic series; with it we can regenerate the oil, benzoic acid, &c.

The nitruret of picrene unites with the picrenic series; it is no longer possible to regenerate the oil of bitter almonds from it. Amarine, isomeric with the preceding, cannot be a nitruret; in its formation there must have been some derangement in the radical benzene; the nitrogen was able to combine with the hydrogen to form amide and imide, and to constitute an alkali which is derived from $3C^{28}H^{12}$, just as aniline is derived from $C^{24}H^{12}$.

From the preceding facts I shall draw an inevitable conclusion :—*A compound gives rise, by equivalent substitution, to two isomeric bodies*, it being impossible for these to differ from each other except by the arrangement of their molecules. It results that it is not sufficient that 1 equiv. of chlorine, of bromine, of nitrogen, &c., take the place (in weight) of 1 equiv. of hydrogen, in order to conclude that the grouping or the mechanical type is preserved.

Thus acetic acid does not belong to the same group as alcohol; bromaniloine is not constituted in the same way as aniline, as will be proved soon by experiment.—*Comptes Rendus*, vol. xix. p. 353.

CHEMICAL PREPARATIONS.

New Process for preparing œconomically Oxide of Carbon.

By Prof. Filhol.

In the memoir which M. Pelouze has recently published on lactic acid*, he has pointed out as very remarkable the following reaction :—When a mixture is formed of lactic acid and of very concentrated sulphuric acid, the latter in great excess, an abundant liberation of pure carbonic oxide results on heating gently the vessel containing the mixture.

In reflecting on the relation which exists between the composition of sugar and lactic acid, I was led to think it possible that a similar reaction would ensue if sugar were substituted for the lactic acid in the preceding mixture. Crystallized cane-sugar is represented by the formula $C^{12}H^{11}O^{11}$, while that of hydrated lactic acid

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* See Chem. Gaz., p. 29 of the present volume.

is $\frac{C^{24}H^{12}O^{12}}{2}$; thus, if we subtract the elements of 1 equiv. water from those of 2 equiv. lactic acid, we have the formula of crystallized cane-sugar. If we admit, with M. Guérin-Vary, that anhydrous starch-sugar is represented by the formula $C^{24}H^{12}O^{12}$, it would exactly contain the elements of 2 atoms of lactic acid.

I heated in a flask 20 grms. of cane-sugar with 80 grms. of concentrated sulphuric acid. On keeping the mixture at a very gentle heat, a lively reaction was soon manifested, with a very abundant disengagement of gas; the mass swelled up, became black, and very soon almost solid; I then discontinued the operation, and had collected nearly 2 quarts of gas. This gas I found on analysis to be formed of a mixture of carbonic acid and of carbonic oxide; it contained about one-fifth its volume of carbonic acid, but the composition of the mixture varies in each operation.

Deprived of all its carbonic acid by washing with lime-water, this gas is colourless, does not redden litmus-paper, is decomposed at a red heat by potassium, which absorbs the oxygen and causes a deposit of carbon. It burned with a pure blue flame, and I found by eudiometrical analysis that it consisted solely of carbonic oxide. Starch-sugar and starch furnished analogous results; thus the reaction of sulphuric acid on sugar or starch differs from that which the same acid exercises upon lactic acid only in this, that with the latter pure carbonic oxide is obtained without any mixture of carbonic acid; however, the separation of this latter is so easy, that it will always be more œconomical to employ sugar.—*Journ. de Pharm.*, August 1845.

Indelible Ink

May be prepared by adding lamp-black and indigo to a solution of the gluten of wheat in acetic acid. This ink is of a beautiful black colour, at the same time cheap, and cannot be removed by water, chlorine, or dilute acids. M. Herberger gives the following directions for its preparation:—Wheat-gluten is carefully freed from the starch, and then dissolved in a little weak acetic acid; the liquid is now mixed with so much rain-water that the solution has about the strength of wine-vinegar, *i. e.* neutralizes one-sixteenth of its weight of carbonate of soda. 10 grs. of the best lamp-black and 2 grs. of indigo are mixed with 4 oz. of the solution of gluten and a little oil of cloves added. This ink cannot be employed for marking linen, as it does not resist mechanical force.—*Jahrb. für Prakt. Pharm.*, x. p. 248.

Ready Method of procuring Perchloride of Copper.

By M. Rieckher.

When equal parts of finely pulverized sulphate of copper and culinary salt are mixed with a little water at a temperature of 122° to 140°, a beautiful dark green liquid is obtained, from which on cooling sulphate of soda separates. On slow evaporation by exposure to the air, or at a temperature of 68°, the whole of the sulphate of soda and the excess of chloride of sodium separate, on which account the liquid must be now and then poured off. When no more salt forms, the perchloride of copper separates on cooling in crystals, which are removed from the liquid by decantation. If the evaporation is carried on too quickly, the perchloride of copper and salt separate together.—*Jahrb. für Prakt. Pharm.*, x. p. 243.

Detection of Impurities in Disulphate of Quinine.

The following test for the adulteration of disulphate of quinine is recommended by Dr. Nevius of Liverpool, on account of its delicacy and simplicity:—To 1 or 2 grs. of the suspected salt add 3 or 4 drops of sulphuric acid in a white evaporating dish and twice as many drops of water. If the salt contains either fatty matter or starch, these will remain; whilst, if they are absent, the whole will be dissolved. Next apply heat to the solution, and as it becomes concentrated the acid will char any sugar which may be present, which will be indicated by a black stain round the edge of the solution, and the whole will speedily assume the same colour. By this means 1 or 2 per cent. of organic matter may be recognised in as many minutes without trouble. It is said that salicine is an occasional adulteration, and, if present, it is detected by the same proceeding. If a very minute quantity only is mixed with the quinine, blood-red points, and ultimately a general reddish colour, are produced as the concentration proceeds. It is a good plan to observe the effect of the sulphuric acid before the addition of water, as it acts upon the salicine cold, producing the blood-red colour. Thus the single test of sulphuric acid, diluted and heated, detects nearly every impurity which is found in the disulphate; for starch, fatty matters and insoluble earthy salts are left undissolved before the application of heat, and salicine, gum and sugar are shown by the effects of heat on the solution. Pure disulphate of quinine is not affected by sulphuric acid applied as above.—*Lancet.*

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 19, 1845.—"On the Gas Voltaic Battery. Voltaic Action of Phosphorus, Sulphur, and Hydrocarbons." By William Robert Grove, Esq., M.A., F.R.S., V.P.R.I., Professor of Experimental Philosophy at the London Institution.

The author, referring to a paper of his published in the Philosophical Transactions for 1843, states, that in repeating and verifying some of the experiments therein contained, he was led to those which form the subject of the present memoir. With the form of gas battery last described in that paper, by which the interfering action of the external air is excluded, he finds that deutoxide of nitrogen associated with oxygen gives a continuous voltaic current; and that the volumes respectively absorbed by the electrolyte are as four to one, indicating the formation of hyponitrous acid.

Passing to the more immediate object of the present paper, he states that having observed nitrogen procured by the combustion of phosphorus to give rise, in the gas battery, to a temporary voltaic current, he was led to believe that phosphorus, although an insoluble non-conductor, might, by means of the gas battery, be made the excitant of a continuous voltaic current, analogous to the zinc element of an ordinary voltaic combination. This expectation was verified by experiments, a series of which are given; phosphorous being suspended in various gases and voltaically associated with oxygen. The experiments were continued during several months, and the results indicated the same consumption of phosphorus with reference to the oxygen, as would occur by the formation of phosphorous acid; the phosphorus being thus burned by oxygen at a distance. Phosphorus and iodine, both non-conducting solids, being each suspended in nitrogen in the associated tubes of a gas battery, give a continuous voltaic current, and are consumed in equivalent ratios. Sulphur, suspended in nitrogen and associated with oxygen, gives a voltaic current when fused. Other volatile electro-positive bodies, such as camphor, essential oils, ether and alcohol, when placed in nitrogen and associated with oxygen, gave a continuous voltaic current.

The author observes that the gas battery which in his former experiments introduced gases, by the present experiments renders solid and liquid insoluble non-conductors the exciting constituents of voltaic combinations, and enables us to ascertain their electro-chemical relations: it also introduces the galvanometer as a test of vaporization.

A new form of gas battery is described, in which an indefinite number of cells are charged by the hydrogen evolved from a single piece of zinc; the oxygen of the atmosphere supplying the electronegative element. The charge of the battery is self-sustained, in a manner somewhat similar to the Doebereiner light apparatus.

"Contributions to the Chemistry of the Urine, on the variations in the Alkaline and Earthy Phosphates in the healthy state, and on the Alkalescence of the Urine from fixed Alkali." By Henry Bence Jones, M.A. Cantab., Licentiate of the Royal College of Physicians.

The author, having observed that in some states of disease there occurs in the urine a great excess of the earthy phosphates, was induced to investigate the subject; and as a preliminary inquiry, to ascertain the variations in the amount of these phosphates at different times in the same person in a state of health, and to trace the causes which determine an excess or a deficiency of these salts in the urine; noting, at the same time, the variations in the quantity of the alkaline phosphates contained in it, with a view of discovering whether these variations are influenced by the same, or by different causes. The principal results to which his experiments have conducted him are the following. The quantity of the earthy phosphates in the urine voided soon after taking food is considerably greater than in that voided at other times; and this happens whether the meal consists of animal food or of bread only. After long fasting, the proportion of earthy phosphates is considerably diminished. On the other hand, the alkaline phosphates are present in greatest quantity when the food consists of bread alone: when meat alone is taken, the deficiency in those salts is still more marked than the excess in the former case. Exercise occasions no change in the quantity of the earthy phosphates, but causes an increase of nearly one-third in the amount of alkaline phosphates; but its influence is, on the whole, less than that of diet. The earthy phosphates are increased in quantity by chloride of calcium, sulphate of magnesia, and calcined magnesia taken into the stomach.

The author next examines the conditions in which the urine is alkalescent, and which he considers to be of two kinds; the one, long known as *ammoniacal*, and arising from the presence of carbonate of ammonia; and the other, which has not hitherto been distinctly recognised, arising from fixed alkali, and appearing most frequently in urine secreted during a period of from two to four hours after breakfast, in persons suffering only from defective digestion. Under these circumstances, it may be, when voided, either turbid from amorphous sediment, or clear and alkaline when tested, or free from deposit and slightly acid. If in either of these last cases it be heated, an amorphous precipitate falls down, which is soluble in dilute hydrochloric acid, or in a solution of biphosphate of soda. Healthy urine may at any time be made to yield a precipitate of earthy phosphates by heat, even though it be acid, by having a portion of this acid neutralised by any alkali, or by phosphate of soda, the fluid becoming more acid when boiled. A solution of earthy phosphates in biphosphate of soda also gives a precipitate on boiling, if some of its acid reaction is removed by any alkali. The fluid when boiled becomes more acid to test-paper, indicating the formation of a more basic earthy phosphate. A result precisely similar is obtained when common phosphate of soda, phosphate of lime, and a little biphosphate of soda exist together in solution; and by varying the quantities of each of these substances, the various phænomena which the urine occasionally presents may be imitated. The time at which the alkalescence of the urine from fixed alkali generally occurs, indicates the existence of some alkaline phosphate, or of some carbonated alkali in the food.

"On the Compounds of Tin and Iodine." By Thomas H. Henry, Esq.

Different properties have been assigned by different authors (as Sir Humphry Davy, Gay-Lussac, Boullay and Rammelsberg) to a combination of tin with iodine. With a view to explain these discordances, the author instituted the series of experiments detailed in this paper, and which have led him to the conclusion that the substance obtained by heating tin with twice its weight of iodine is a mixture of two salts, differing from each other in their composition. One of these is soluble in water to a slight extent without suffering decomposition, while the other is immediately decomposed on coming into contact with water; the former being the real proto-iodide described by Boullay, and the latter being a biniodide, a salt of which no particular description had hitherto been given, but which was probably the compound noticed by Sir Humphry Davy as being of a brilliant orange colour. The author found that this biniodide sublimes at a temperature of 356° F., while the proto-iodide, if protected from the contact of air, may be heated to redness without subliming. The author did not succeed in obtaining a combination of tin and iodine corresponding to the sesquioxide, although Boullay supposes that such was the composition of some yellow crystals which were formed by the mixture of solutions of proto-chloride of tin and of iodide of potassium. A more detailed account of the properties of the iodides of tin is reserved for a future communication.

PATENT.

Patent granted to William Newton, Chancery Lane, *for certain Improvements in treating and preparing Oily or Fatty Matters.*

These improvements in treating and preparing oily or fatty matters relate more particularly to the treatment and preparation of palm oil, and are intended to render the same more applicable to the various purposes for which it may be employed. The invention may be divided into two heads; the first being an improved method of treating palm oil, for the purpose of separating the liquid from the solid parts, or the oleine from the stearine and margarine; and the second, an improved method of bleaching solid fatty matters.

The essential feature of novelty of the first head of the invention is the separation of the liquid from the solid constituents of the palm oil, without employing the process of saponification, as is ordinarily the case. The manner in which the operations are carried on is described by the inventor as follows:—

The principle of this invention or discovery, and the mode of proceeding to effect the separation of the liquid from the solid portions of the oil, is founded upon a fact that has hitherto escaped the observation of manufacturers, and has never to my knowledge been usefully and advantageously applied to the arts. This fact is, that the liquid and solid constituents of the palm oil exist naturally in a state of chemical separation in the palm oil of commerce, although their particles are in mechanical contiguity, and that therefore nothing else is requisite to effect their complete separation but a purely mechanical process, unassisted by any ingredients which would effect a chemical change in the oily or fatty matters, as is the case when saponification takes place.

The process which forms the subject of the present invention consists in causing the solid fats to crystallize by first heating and then gradually cooling the raw material; then submitting it to pressure, to remove a certain portion of the oleine; after which it is again heated and cooled, so as to cause it to crystallize a second time, when a fresh quantity of oleine may be expressed or removed, by a second pressure. By this means the separation of the solid and liquid fat is effected, without resorting to the process of saponification, and is conducted as follows:—I take the raw palm oil, as it is imported from Africa (or, if thought more advantageous, palm oil, previously bleached, may be taken), and a large quantity of the palm oil, whether bleached or unbleached, is put into iron or other vessels, and heated to about 212° F., at which temperature it is maintained for about one hour; after which it is run off into wooden or other convenient vessels, where it is allowed to cool very slowly, and to remain until it begins to crystallize. The congealed mass is then to be packed in cold woollen cloths, in quantities varying from 16 to 30 lbs. each bundle, according to the capacity or size of the press. Hydraulic pressure is preferred, and the mass of congealed fatty matters is, in the first instance, submitted to a light or gentle pressure, whereby about one-third part of the mass is made to run off in a liquid state, and which will be found to be nearly pure oleine. The other two-thirds of the mass remain in a solid state between the woollen cloths.

The liquid obtained, as above mentioned, from this first pressure of the materials, when cold, is pure or nearly pure oleine; but as palm oil is generally considered to contain about 69 per cent. of oleine, and 31 per cent. of stearine and margarine or solid matter, it follows that one-half of the former is yet contained in the solid cakes or masses that have been submitted to the first pressure above-mentioned.

In order to facilitate the further separation of the remaining portion of the oleine from the stearine, the cakes of fatty matters must be again heated in a boiler or vessel to about 212° F. for from 3 to 4 hours; after which it is again run off into a wooden or other convenient vessel, where it is left to cool slowly and crystallize a second time.

The fatty matters are then again packed in small parcels of from 16 to 30 lbs. weight each in woollen cloths; and each parcel is to be placed in a horse-hair bag or sack, and between pressing-plates, when the fatty matters are submitted to a second pressure with a powerful hydraulic press. For this second pressing operation, the woollen cloths, the horse-hair bags and the pressing-plates are to be warmed before packing the mass in bundles in the press.

It will be found that a small portion of the solid fats will run off, during the second or warm pressing operation, with the liquid oleine. Such being the case, the oleine or liquid matter thus obtained is added to a mass of fresh palm oil that has not yet been operated upon, and is about to undergo the first pressing operation. The cakes that remain in the cloths, after the second or warm pressing operation, will be found to consist of the solid constituents or parts of palm oil, namely, stearine and margarine. It has been found that from 100 lbs. weight of the raw palm oil of commerce, 30 per cent., or nearly so, of stearine may be obtained by my process, and about 68 per cent. of oleine. This latter substance, when obtained by the above process, is not diminished in value, as it would be if the old process of saponification were employed; but will be found to be quite as good, and equally applicable to the purpose of making soap as the raw palm oil itself, as it undergoes no chemical action.

If the oleine is to be converted into white soap, it must of course be bleached, which may be done in the usual way. The cakes of stearine that remain in the woollen cloths, after the second and warm-pressing operation, are then to be bleached, if the palm oil, from which they were obtained, has not been previously operated upon for that purpose.

The operation of bleaching the stearine or solid fat, and which forms the second part of the invention, is not conducted in the usual way, by means of chlorine, manganese or sulphur, but upon an entirely different, and what I conceive to be a new plan. The cakes of stearine, obtained as above, are placed in a tub or vessel, and melted, the temperature being maintained at about 212° F. When the mass has been reduced to a perfectly liquid state, it is to be run out into a trough or conduit, which is kept supplied with a running stream of clear cold water, in the proportion of about 2 parts of water to 1 of stearine, so that the latter always meets a quantity of water about double its own bulk; and by this means it becomes almost instantaneously solidified, and converted into minute particles or crystals. The water, carrying the stearine and margarine in this state with it, is run into a vessel, from whence the stearic and margaric crystals are removed, and exposed to the action of the air and the light of the sun, whereby they become perfectly white in a very short time. The bleached solid fats, or stearine and margarine, are then to be remelted in a bath of water, that is to say, they are placed in a vessel containing water, and are mixed therewith. The water is then heated by means of steam-pipes, or in any other convenient manner, and a small quantity of sulphuric acid is added, in the proportion of about 2 lbs. by weight of acid to 100 lbs. by weight of the stearine or fatty matter, for the purpose of clearing the latter from all particles of iron, or any other foreign or extraneous matters, which might have gone over or become mixed therewith during the different processes of boiling. After the mass has been cleansed in this manner, it is removed to another vessel, where it is again melted in water, with the addition of the white of 5 eggs to every 100 lbs. weight of stearine or fatty matter. The whole must boil for some time (about 1 hour), and be kept well-stirred; after which it should be left to itself, for the purpose of allowing all the dirt and other impurities to settle at the bottom of the vessel. The stearine and margarine is then run off into moulds, and when solid will be found to be a fine white crystallized fat, consisting of stearine and margarine, ready for use.

This improved process of bleaching may also be employed for bleaching wax, or other materials of which candles may be manufactured; and is also applicable to bleaching stearine, obtained from other substances than palm oil.

If it is proposed to use the stearine for the manufacture of candles, it will be found desirable to prepare the candle-wicks in the following manner, as their burning will be thereby very much improved:—Dissolve 1 part of boracic acid (well-ground) in 24 parts of alcohol or of dilute sulphuric acid (but alcohol is preferable); let the wicks that are intended to be used remain in this liquid for 12 hours; after which press them gently, to remove any superfluous liquor, and use the remaining portion of the liquor for another operation.—Sealed Sept. 12, 1844.

THE CHEMICAL GAZETTE.

No. LXXI.—October 1, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Respiration. *By* Prof. MAGNUS.

IN a paper read before the Royal Academy at Berlin, the author first enumerated the different views on the nature of respiration which had been proposed, and especially urged against all those theories which suppose that a chemical combination takes place in the lungs between the oxygen and the blood, that they do not explain how it is that blood, after having been darkened by agitation with carbonic acid, is again rendered of a bright red by oxygen or atmospheric air, and is capable of again assuming its former arterial colour, if its arterial tint depends upon oxidation; for carbonic acid cannot deoxidize the blood, and how can it be conceived that blood which has once been oxidized can be again oxidized a second or third time, and so on, without having been deoxidized? This objection appears to the author so conclusive, that he considers it sufficient to refute any theory which supposes chemical combination of oxygen with the blood to occur.

He then alluded to the theory which he had proposed in 1837, according to which the inspired oxygen does not combine chemically with the blood, but is only absorbed, and thus arrives in the capillary vessels, where it is applied to the oxidation of certain substances, converting them into carbonic acid, and perhaps also into water. The carbonic acid, instead of oxygen, is then absorbed by the blood, and reaches the lungs with it, to be removed by contact with the atmosphere; a fresh quantity of oxygen is then absorbed instead of it, and undergoes the same changes.

The quantities of oxygen which were then separable from the blood by the air-pump were but small. The author has now endeavoured to procure larger quantities from it, and has been occupied with an examination of the general absorbent properties of the blood, especially with regard to oxygen. With this object, the blood was agitated with continually renewed portions of atmospheric air, and to ascertain subsequently how much air it contained from absorption, it was placed in a vessel filled with mercury, and which was closed with an iron stop-cock. This was then screwed upon a second vessel, likewise closed with a stop-cock, and containing carbonic acid. On opening the cock, the mercury fell out and the carbonic acid ascended to the blood. The vessels were then separated, and the blood continually agitated with the carbonic acid. The vessel was then screwed upon another completely filled with mercury, and the gas was allowed to collect in this. Carbonic acid was then in the same manner again mixed with the blood, which was then agitated and the gas also conveyed into this vessel; and this process was repeated several times. Finally, the collected gas was examined, the carbonic acid being absorbed by caustic potash, the oxygen being detonated with hydrogen, and the remainder considered as nitrogen.

Although these experiments appear so simple, it was at first impossible to carry them out, because the time which it was requisite to allow for the subsidence of the froth after each agitation was so great that decomposition commenced in the blood before the completion of the experiment.

This difficulty was subsequently removed by adding a drop of oil, which when placed on the surface of the blood soon caused the disappearance of the froth.

Numerous and repeated experiments, made in this manner, on the blood of calves, cattle and horses, have yielded tolerably uniform results, the minimum of oxygen being 10 per cent. and the maximum 12·5 per cent. of the volume of the blood, and the minimum of nitrogen being 1·7 per cent. and the maximum 3·3 per cent. reduced to the temperature of 32° F. and the mean barometric pressure.

The proportion in which the oxygen and nitrogen found in the gas obtained from the blood are, affords another indirect proof that no air had entered the vessels from without during the experiment. Had this been the case, the quantities of the two gases found would have been more nearly in the proportions existing in the atmosphere, whilst the oxygen ordinarily amounted to 3 and frequently 4 and 5 times as much as the nitrogen.

Although the difference between 10 and 12·5 per cent. is not inconsiderable, still it might appear remarkable that the experiments agree so well with one another, especially as they do not liberate the whole of the absorbed gas; but the more frequently fresh carbonic acid is added to the blood, the greater must be the quantity of gas. This is also true in practice; but after renewing the carbonic acid 3 or 4 times, the increase in the quantity of gas was found to be so small, that it fell within the limits of error of observation. Moreover, all the experiments were carried out under the same conditions. About 400 cubic centimetres of blood were usually employed; a smaller quantity was only used for some experiments. Too small a quantity could not be applied, as the amount of gas obtained is very small. The volume of carbonic acid, which was each time shaken with the blood, was never less than that of the blood itself; nor could much larger quantities be taken, because the vessels when completely filled with mercury would be managed with too much difficulty, and would be readily broken. Even in their present size containing about 700 cubic centimetres, they must be made of exceedingly strong glass. They are tall and cylindrical, with a narrow neck, and are graduated in cubic centimetres.

The quantity of oxygen which, as shown by these experiments, the blood was capable of absorbing, is, as the author has proved, sufficient to allow of the supposition that the whole quantity of air inspired is absorbed by the blood; but it is doubtful whether the arterial blood contains as much oxygen as that repeatedly shaken with atmospheric air, and whether the quantities obtained were but a small portion of the oxygen really absorbed.

To decide this, the experiments were varied, so that the blood was first agitated with constantly renewed quantities of carbonic acid, to remove the whole of the oxygen and nitrogen absorbed. The blood was then repeatedly shaken with measured quantities of atmospheric air, and the remaining air was again measured, and the quantity of carbonic acid, oxygen and nitrogen ascertained by the method previously described, when the quantity of oxygen and nitrogen absorbed was found. From numerous experiments conducted in this manner, the minimum amount of oxygen absorbed amounted to 10 per cent. and the maximum to 16 per cent. of the volume of the blood. In several experiments as much as 6·5 per cent. of nitrogen was absorbed.

In one of these experiments calves' blood was uninterruptedly shaken with atmospheric air; it was then repeatedly agitated with carbonic acid. By this treatment it yielded 11·6 per cent. of its volume of oxygen, but absorbed 154·9 per cent. of carbonic acid. This blood was then shaken with separate portions of a measured quantity of atmospheric air; it thus absorbed 15·8 per cent. of oxygen, yielding at the same time 138·4 per cent. of carbonic acid. Finally, it was again shaken with carbonic acid, and again yielded 9·9 per cent. of oxygen, whilst it absorbed 92·1 per cent. of carbonic acid.

It is thus evident that by agitation with carbonic acid we can separate almost the whole of the oxygen absorbed by the blood, which would be the most striking proof that the oxygen is not chemically combined with the blood, but exists in it merely as absorbed.

These experiments show that the blood is capable of absorbing 1½ times its volume of carbonic acid, a result which has also been obtained by other observers. They moreover show that it is capable of absorbing from 10 to 12·5 per cent. of its volume of oxygen from the atmosphere, consequently 10 to 13 times more than water under the same circumstances, and that the absorption of nitrogen amounts to 6·5 per cent.

Moreover, experiments similar to those above described were instituted on the real arterial blood of horses which were of advanced age. By agitation with carbonic acid there was obtained—

Oxygen.	Nitrogen.
10·5	2·0
10·0	3·3

whence it is evident that the oxygen exists in at least as great quantities in the arterial blood of horses.

The author then shows, that from some observations upon the quantity of the inspired air and of the blood which flows into the lungs in a given time, we may conclude that the blood does not absorb more than half the oxygen which the experiments above detailed have shown to exist in it. This portion is each time consumed in the capillary vessels, and the remainder, amounting to the other half, remains in the venous blood.

On the Atomic Weights of Sulphur and Gold. By J. Berzelius.

The atomic weight of sulphur has been admitted to be 201·16, based on the experiments performed in 1818 by M. Berzelius. In the course of last year, Erdmann and Marchand*, from an analysis of vermilion, have considered themselves justified in taking it exactly at 200; but as the atomic weight of mercury from which they calculated it is one of the most difficult to determine with perfect accuracy, and these chemists moreover have a certain inclination to round off the atomic weights to equal multiples of 12·5, the atomic weight of hydrogen, M. Berzelius felt himself inclined to ascertain by experiment whether this rounding off was admissible or not.

The former experiments, in which the atomic weight was deduced from the sulphate of lead, have been again carefully compared, and the mean deduced from the best of them. Owing to a certain correction in the atomic weight of the lead, that of sulphur becomes 200·8.

Since the atomic weight of the chloride of silver has been determined with great accuracy by Marignac's experiments, M. Berzelius considered it best to convert a weighed quantity of chloride of silver into sulphuret by gently heating it in sulphuretted hydrogen gas, and from thence to calculate the atomic weight of the sulphur. The experiments, which differed very little among one another, gave as the atomic weight of sulphur 200·75, which agrees most closely with the mean result of the author's former experiments. This slight variation in the atomic weight of sulphur has influence on that of arsenic, fluorine, tantalium, thorium, zirconium, aluminum, magnesium and calcium, as they have all been deduced from combinations with sulphur or sulphuric acid.

The former atomic weight, 201·16, had been deduced from a single one of the former experiments, which had been regarded as the most trustworthy.

The atomic weight of gold was determined from the quantity of gold which a certain weight of mercury precipitated from the perchloride; it was found from these experiments to be 2486·026; but since the atomic weight of mercury can no longer be depended upon, M. Berzelius selected for a new determination the composition of a potassio-perchloride of gold, $KCl + Au^2Cl^3$, well-purified by crystallization, which leaves, when reduced by hydrogen, chloride of potassium and gold, which may be separated with quantitative accuracy. The weight of the chloride of potassium to that of the gold

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* Chem. Gaz., vol. ii. p. 399.

is then as KCl : Au. The mean of these experiments gave 2458·33. —Poggendorff's *Annalen*, 1845, No. 6.

On a new Product resulting from the Decomposition of Urea.
By FR. WÖHLER *and* J. LIEBIG.

When perfectly pure dry urea is submitted to slow distillation, the greater portion of it is converted, not into cyanuric acid, but into a new body, which may be regarded as cyanurate of ammonia from which the elements of 2 equiv. carbonic acid have separated. In its behaviour it belongs to the series of the mellon compounds. On exhausting the residue of the distillation with a large quantity of boiling water, this product of the decomposition remains undissolved. In its dry state it forms a shining white powder, and is perfectly insoluble in boiling water, readily soluble in alkalies and acids, from which it is precipitated on neutralization. On the further action of these solvents, it is decomposed into ammonia and cyanic acid. Heated when dry, it leaves a lemon-coloured residue, which on strong ignition is decomposed into cyanogen gas and nitrogen. The formula for this compound is $C^6 N^4 H^4 O^4$.—*Ann. der Chem. und Pharm.*, liv. p. 371.

On two new Oxyacids of Sulphur. By E. M. PLESSY.

The acids described in this memoir were obtained in investigating the action of sulphurous acid on the chlorides of sulphur in the presence of water. It is known that water decomposes these chlorides, the chlorine forming hydrochloric acid, while a certain quantity of sulphur which the oxygen of the water has not been able to act on is deposited. When sulphurous acid is present in this reaction, no sulphur separates; its affinities are satisfied equally with those of the chlorine, and it enters into solution. This is most evident with the perchloride of sulphur, which disappears as it were instantaneously and totally on agitation with water charged with sulphurous acid, giving rise to the formation of a new compound of sulphur and oxygen, the preparation of which we shall now describe.

Sulphurous acid is passed into 1500 grms. of distilled water to complete saturation, and about 30 grms. of perchloride of sulphur are added to the acid liquid; when the perchloride has become dissolved by agitation, sulphurous acid is again passed into the liquid, and more chloride added. After having repeated this operation three or four times, the acid liquid is evaporated over the open fire to about one-half; and when it has become sufficiently cool, it is completely saturated with pulverized and sifted carbonate of lead. It is then filtered through linen, and as the precipitated chloride of lead retains a large quantity of liquid, it should be submitted to strong pressure. The filtered liquid now contains a salt of lead, which is decomposed by a quantity of dilute sulphuric acid just requisite to precipitate the base. It is seen that a sufficient quantity of acid has been added when the sulphate of lead separates from a clear liquid.

The eliminated acid is lastly submitted to evaporation over an open fire with certain precautions, and reduced until it indicates 12° to 15° on Baumé's areometer; it then occupies for the proportions above mentioned a volume of about 2 decilitres. When cooled, it is saturated with carbonate of barytes, filtered, and the solution precipitated by absolute alcohol and æther.

The crystalline precipitate thus obtained, after having been pressed between folds of blotting-paper, is dissolved in water; the solution precipitated by absolute alcohol, yields a well-crystallized salt, which leaves on calcination about 52·4 per cent. residue. Should the amount of residue be greater, the salt must be redissolved and recrystallized until it invariably yields 52·3 per cent. residue of sulphate of barytes; it is only then that it can be considered as representing the new combination in the state of purity.

The salt first precipitated by alcohol and æther sometimes leaves as much as 60 per cent. residue; but this contains chloride of barium, which is removed by the treatment with water, and subsequently with alcohol; the presence of a chloride may be detected in the salt itself by means of acetate of lead, the chloride of lead being very sparingly soluble. A salt of silver cannot be employed as a test, because it would form a yellow precipitate in which the chloride of silver could not be detected.

I am at present able to state that the prolonged ebullition to which the acid is subjected removes the acids of MM. Langlois, Fordos and Gelis, which are not very permanent. The change in behaviour which the liquid presents after boiling is a certain index of their destruction. Before ebullition the liquid yields a white precipitate with corrosive sublimate, and a blackish-yellow one with protonitrate of mercury; after boiling it no longer precipitates the first, and forms with the second a beautiful permanent yellow precipitate, which an excess of nitric acid does not change into black.

We have seen that water removes nothing more from the barytes salt, which yields 52·3 per cent. residue. The preciseness of the reactions of this salt, and its crystalline form, all lead us to regard it as a pure salt. To determine its composition, it was decomposed by chlorine, which converts the sulphur into sulphuric acid. The chlorine requisite for this transformation furnishes the amount of oxygen in the salt.

1 grm. of salt treated with chlorine yields 2·613 sulphate of barytes, that is to say, a weight 5 times greater than that obtained by calcination, which proves that for 1 equiv. of base, which the salt yields on calcination, it contains 5 equiv. of sulphur. From 1 grm. of salt there was also obtained 5·802 chloride of silver, which answers for 5 equiv. of sulphur, found by experiment, to 9 equiv. oxygen; the salt contains therefore 6. From the preceding numbers the following per-centage composition is deduced for the new salt:—

Sulphur	37·87
Base	34·12
Water and oxygen	30·01

which leads to the formula $S^5 O^6 BaO, 2HO$; consequently the new acid which results from the decomposition of the *perchloride of sulphur* will be represented by the formula $S^5 O^6 + \text{aq}$.

The acid separated from the barytic salt by means of sulphuric acid may be boiled, but it undergoes a slight decomposition; it does not appear to be decomposed at the ordinary temperature; it is not affected by cold concentrated sulphuric acid; nitric acid, on the contrary, determines a precipitation of sulphur; it yields no precipitates in solutions of zinc, copper or iron. It forms in the protonitrate of mercury a beautiful persistent yellow precipitate, and none in the solution of corrosive sublimate; but after some minutes a deposit of sulphur is gradually formed. With the nitrate of silver a beautiful yellow precipitate is obtained, which passes somewhat rapidly into a chocolate-brown. These reactions do not allow of confounding the acid yielding them with any of the oxygenized compounds of sulphur hitherto known. We have seen that they are singularly altered by the addition of a sulphated or bisulphated hyposulphate. The salt of M. Langlois, even in very small quantity, turns the yellow precipitate obtained with the protonitrate of mercury perceptibly black. With respect to the salt of MM. Fordos and Gelis, its presence is proved only by corrosive sublimate, with which it affords a white precipitate.

The protonitrate of mercury is a very delicate test for M. Langlois's acid, and has been of great service, as this acid is frequently mixed with the new compound, since it results in some measure from its decomposition, as will be seen subsequently. As we have already stated, it is to destroy the acid of M. Langlois that the acid liquid, such as it is obtained after decomposing the chloride of sulphur by sulphurous acid, is boiled, because under this circumstance it is the least stable; in other cases, on the contrary, it is readily generated, especially in the presence of a base.

We shall presently describe the products of the decomposition of the acid $S^5 O^6$ in presence of a base; but among those products must evidently be classed the oxygenized compound which we have obtained with the protochloride of sulphur, water and sulphurous acid.

Action of Sulphurous Acid on the Protochloride of Sulphur in the Presence of Water.

Sulphurous acid is passed into 1500 grms. of water until completely saturated; and as the protochloride dissolves but slowly, about 100 grms. are added at once, and sulphurous acid continued to be passed into it so as to mix the two liquids by the current of gas. When the chloride of sulphur has lost its fluidity and has become pasty, the passage of sulphurous acid is discontinued and the reaction regarded as terminated; the acid liquid, separated from the chloride by decantation, is submitted to ebullition for some minutes, and then saturated with carbonate of lead as previously. The barytic salt, thrown down by absolute alcohol and æther, yields 61 per cent. residue. We will here observe, that the salt obtained under the same circumstances, but with the perchloride, yields the same quantity of sulphate of barytes on calcination; and as the two salts behave similarly towards reagents, it appears at first as if the product obtained with the protochloride of sulphur and that which results from the decomposition of the perchloride were identical; but if the salt of barytes obtained with the protochloride of sulphur is dissolved in water and then precipitated by alcohol from its solution; if, in fact, it be submitted to the same treatment by means of which we were able to obtain the salt of the acid $S^5 O^6$ in the pure state, it always retains the same composition, constantly yields 61 per cent. residue, and does not alter. Thus, in the first place, a barytic salt which left 60 per cent. residue, after having been dissolved in water and thrown down by alcohol a certain number of times, leaves no more than 52·3 per cent. sulphate of barytes. In the second place, on employing protochloride of sulphur, a salt of barytes is obtained, which yields 61 per cent. sulphate of barytes on calcination, and on which water and alcohol have no action. It may also be observed, that the barytes salt, prepared with the protochloride and precipitated by æther, contains no chloride of barium, while the corresponding salt, *i. e.* that precipitated under the same circumstances and prepared from perchloride, contains some. This difference may be partly attributed to the quantity of chloride of lead which was able to dissolve.

When perchloride is employed, there is formed relatively much more hydrochloric acid, and consequently more chloride of lead, so that it is requisite to add much more water to render complete the saturation with carbonate of lead and not to lose too much of the new product. If the quantity of dissolved chloride of lead is greater, the proportion of chloride of barium will have increased subsequently after concentration and saturation with carbonate of barytes, and will be precipitated by æther and absolute alcohol.

The composition of the salt of barytes yielding 61·4 per cent. residue was determined by means of chlorine. The following is the mean of several analyses:—

Sulphur	33·84
Base	41·29
Water and oxygen	24·87

These results lead to the following formula, $S^4 O^5 BaO, HO$, which is the composition of the bisulphated hyposulphate of barytes minus 1 equiv. water. However, the acid we have obtained with the protochloride of sulphur exhibits too much analogy with the compound furnished by the perchloride to be confounded with the acid of MM. Fordos and Gelis, or to be regarded as isomeric with it.

The present formula must evidently be doubled. But should the acid which it contains be regarded as a bibasic acid with the formula $S^8 O^{10} + 2HO$, would it not be preferable to represent it as derived from the acid $S^5 O^6$ in the following manner? 1 equiv. of this acid, on parting with 1 equiv. hyposulphurous acid, $S^2 O^2$, would form the hypothetical acid $S^3 O^4$, which finding some undecomposed acid $S^5 O^6$, would combine with 1 equiv. to form the acid $S^8 O^{10}$. The following equation will explain this transformation:—

$$2(S^5O^6) - S^2O^2 = S^8O^{10} = \left.\begin{matrix}S^3O^4?\\ S^5O^6\end{matrix}\right\} = S^8O^{10} = 2(S^4O^5).$$

I have vainly endeavoured hitherto to obtain salts of the acid S^3O^4; but whatever be the case, in order that the hypotheses just made be of some value, it is necessary to be certain that the acid on which they repose differs from that with which it appears identical as regards its per-centage composition. This certainty has been acquired in the following way:—The acid, which we may henceforth call the acid S^8O^{10}, offers very different reactions to those which MM. Fordos and Gelis have assigned to their acid, which, for instance, yields a yellow precipitate with the nitrate of mercury, a precipitate of the same colour with the nitrate of silver, but which very soon passes into a chocolate-brown. The acid S^8O^{10} does not produce any precipitate in corrosive sublimate, but after some time it is decomposed with a deposit of sulphur. Moreover, the barytes salt of the new acid differs by 1 equiv. of water from the bisulphated hyposulphate of barytes.

Lastly, the acid S^8O^{10} is completely distinguished from the acid of MM. Fordos and Gelis by the remarkable decomposition which the salts undergo under the influence of heat when their solution is very concentrated. When the solution of a salt of the new acid is kept at a temperature of 104° to 122°, it deposits sulphur without any perceptible disengagement of sulphurous acid. After some time the tests prove in it the presence of acids with 5 equiv. oxygen to 3 and 4 of sulphur. Thus under this circumstance the very reverse happens, as it were, from what is produced by the action of heat on the free acid. On experimenting with a combination of the acid S^8O^{10} with potash, M. Langlois's salt was obtained in beautiful crystals by the addition of a small quantity of alcohol while hot, and allowing it to cool. A bisulphated hyposulphate is likewise formed by the decomposition of a salt of the acid S^8O^{10}. This salt is distinguished from that of M. Langlois's by means of corrosive sublimate; in a dilute solution this test first acts on the bisulphated hyposulphuric acid, with which it yields a white precipitate; it then attacks the acid of M. Langlois, and decomposes it with a deposit of sulphur. From what has been stated respecting the decomposition of the salts of the acid obtained by the protochloride of sulphur, it may be represented by the following equation:—

$$S^8O^{10} = \left.\begin{matrix}S^5O^6\ 2BaO\\ S^3O^4\ 2HO\end{matrix}\right\} = S^3O^5BaO,\ Aq + S^4O^4BaO,\ Aq + S.$$

This transformation takes place in the cold, and in the absence of water most precisely but slowly; when effected at the boiling-point, sulphate and sulphurous acid are produced.—*Comptes Rendus*, Aug. 25, 1845.

On the Artificial Production of Diaphanous Quartz.
By M. EBELMEN.

When either of the two silicic æthers which I have recently described* is exposed to the continued action of a moist atmosphere, the liquid finally solidifies to a transparent mass. This product, very delicate and fragile in the first days after its solidification, contracts more and more under the influence of the moist air still remaining diaphanous. Two or three months are requisite in operating on 5 or 6 grms. of æther, for the substance to cease to lose in weight and for its molecular movement to terminate. The substance prepared as above is hard, faintly scratches glass, and possesses great cohesion; its lustre, its fracture and transparency are perfectly comparable to the most beautiful rock crystal. Its density is 1·77. It is a hydrate, which contains twice as much oxygen in the silica as in the water, the formula of which is consequently $(SiO)^2 HO$.

It is essential, in order that the product may not become fissured during the contraction it experiences before attaining the definite formula $(SiO)^2 HO$, not to allow the moist air to enter except by an aperture of very small diameter. During the whole of the experiment the flask containing the silicic æther exhales an alcoholic odour, which persists a long time after the solidification, proving that only a portion of the organic matter had separated from the silica when the solidification took place. The contraction proceeds the more slowly the less easily the moist air is renewed in the apparatus, and this slowness appears indispensable to the success of the operation.

From the properties of the hydrate of silica, we may be allowed to hope that it may be turned to advantage in the construction of optical instruments. It is my intention to make some experiments in this direction.—*Comptes Rendus*, Aug. 25, 1845.

On the Artificial Production of Hydrophane. By M. Ebelmen.

By slightly modifying the process for the preparation of hydrate of silica, described in the preceding paper, there is obtained, instead of a diaphanous product, an opake substance, which becomes entirely transparent when placed in water, in a word, true hydrophane. It suffices for this purpose that the silicic æther employed retain a little chloride of silicium, which happens when an excess of alcohol has not been employed in the preparation of the æther. On exposing this æther, still somewhat acid, to the action of moist air, there is obtained a solid mass, which is at first transparent, but ends by becoming opake after some weeks' exposure to the air. The translucidity of this substance is so much the less the greater the proportion of the chloride of silicium in the æther. Some of the fragments have the semi-transparency of opal. They all become entirely transparent in water.

We are therefore able artificially to reproduce hydrophane, this rare variety of quartz, and the curious property of which had struck mineralogists.

A very small proportion of foreign substances suffices in fact to

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* See Chem. Gaz., vol. ii. p. 462.

modify the translucidity and the appearance of the hydrate of silica; thus a small flask containing silicic æther having been closed by mistake with a cork, which belonged to a bottle full of creosote, the æther, on becoming coagulated under the action of moist air, yielded a slightly yellowish silica, and merely translucid like chalcedony; the product thus obtained was not hydrophanous.

I propose to continue and to vary these experiments, which appear to me of great importance and of considerable interest.—*Comptes Rendus*, Sept. 1.

Discovery of some new Earths in Zircons. By L. SVANBERG.

At a recent sitting of the Royal Swedish Academy, M. Svanberg stated that he had, in company with E. C. Norlin, submitted zircona to a more minute examination; whence it had resulted that zircona is not a simple earth, but, like what recent investigations have shown with respect to the oxide of cerium, of yttria and tantalic acid, consists of a mixture of several earths; and these earths occur in unequal quantity in the various zircons according to their locality (for instance, Siberia, Norway, Ceylon), and those varieties to which the name of hyacinth has been applied from Expailly in France. On the quantitative determination of the relative proportions between earth and acid in a quantity of sulphates which had been prepared in different ways, (by fractional precipitations with oxalic acid from solutions of chloride of zirconium as well from the hydrated chloride of zirconium, which crystallized out at different periods, and likewise from that which was just about to crystallize from its solution of muriatic acid, and in which the earths of zircons from various localities were employed in the experiments,) it was found that very considerable differences occurred in the proportions, which could not be otherwise explained than by admitting that there were present several earths with different amounts of oxygen.

On determining the atomic weights, under the supposition that all the earths found were constituted according to the formula $2R+3O$, they were found to vary in general between the numbers 938 and 1320; but for certain of these earths, with some little differences, they were included between 1100 and 1150.

The atomic weight hitherto adopted for zircona, 1140, is nearly in the middle of the two extremes of the new numbers, which might induce the opinion that the zircona was composed of equal atoms of the earths, now separated in a state of greater purity. However, M. Svanberg is not of this opinion, although he has not examined the subject as yet in sufficient detail. Hitherto he has not succeeded in discovering sufficiently accurate qualitative differences upon which to found an analytical process for the separation of the different earths. However, it is perfectly certain that there are more than two present.

Although it was found that the oxalate of the one earth was far more insoluble in acids than that of the others, and although the chloride of the radical of the one earth is likewise less soluble in muriatic acid than those of the radicals of the others, yet this afforded no method of separation sufficiently accurate to purify the one earth entirely from the others. It was likewise found that on adding a somewhat larger quantity of free sulphuric acid to the sulphate of the one earth, it crystallized far more readily and in a different form from that of the others. Their behaviour towards carbonated alkalies is likewise dissimilar. It was moreover found that, on heating the sulphates, the salt of the one earth, after the mechanically intermixed sulphuric acid had been previously expelled, lost at a higher temperature a portion of its sulphuric acid, and was left as a definite basic salt, while the sulphates of the other earths behave quite different under the same treatment at the same temperature. In addition, there exist double salts of dissimilar properties between the chlorides of the earthy radicals, as well as between them and those of the radicals of the alkalies; proving satisfactorily the existence of several distinct earths which have hitherto been comprised in the common name zircona, but which it has not been possible as yet to separate.

Already the considerable difference in the specific weight of the zircons from different localities might have led us to imagine an essential difference in their internal constitution; the same equally applies to the hardness of some zircons. The differences in both respects are too great to be ascribed to the one kind of zircons containing some per cents. of peroxide of iron more than another.

The first cause which gave rise to the more accurate examination of the substance in question was the observation made many years ago by M. Svanberg, that the zircons occurring in the neighbourhood of Stockholm had a much lower specific gravity, = 4·03, and less hardness (being readily scratched by quartz) than other zircons; and in endeavouring to make himself acquainted with the properties of zircona, he found that the earth extracted from these zircons differed entirely from all the statements hitherto made concerning it. As the author could not procure a sufficient quantity of Stockholm zircons for this examination, he worked principally with zircons from Norway; and therefore proposes for the earth, which differs from zircona, the name of *noria*, from *Nore*, the old name of Norway; the radical of the earth would therefore be *Norium*. M. Svanberg asserts however that the northern zircon is not the only one in which the new earth occurs.

On the Chemical Constituents of the Flores Chamomillæ Romanæ *and* Anthemis nobilis.

M. Schendler has separated a peculiar acid from the Roman chamomile, which greatly resembles valerianic acid, if it be not identical with it. He however only obtained 2½ drms. from 24 lbs. of dry flowers, while the same quantity yielded from 4 to 6 ozs. of the most beautiful essential oil, therefore far more than is usually stated. From flowers which had been kept for a long time much less essential oil is obtained than from fresh. The author, on distilling the flowers of *Anthemis nobilis*, obtained 1·17–1·10 per cent. oil and 0·81 per cent. of a peculiar volatile acid, while Wyss obtained only traces of it in his analysis.—*Archiv der Pharm.*, xci. p. 32.

On some Salts of Uric Acid. By A. BENSCH.

Berzelius adopts the formula $C^5 N^2 H^2 O^3$ for uric acid, while Liebig and Wöhler take it double; consequently the same salts, which according to the one formula are considered to be acid, are according to the other neutral. From the author's investigations, the formula in his opinion is somewhat different, viz. for the hypothetically anhydrous uric acid, as it is contained in the neutral salt of potash, $C^5 N^2 HO^2$, and for the crystallized uric acid $C^5 N^2 HO^2 + HO$.

To separate the uric acid from the excrements of serpents, they were reduced to powder, dissolved in dilute caustic potash (1 part KO to 20 parts HO), and boiled with it until the odour of ammonia had disappeared; a current of carbonic acid was passed through the filtered solution until the precipitate, at first gelatinous, had assumed a granular state, and readily subsided, or, what is the same, until the liquid was nearly neutral. The precipitate is bi-urate of potash; it is filtered and washed with cold water until what passes through, on mixing with the first filtered ley, becomes turbid. The potash salt so obtained is of a pure white colour, and on being dissolved in dilute caustic potash and decanted while hot into dilute muriatic acid, yields a perfectly pure acid. The separation of the urate of potash from the alkaline solution by carbonic acid is so complete, that on adding some muriatic acid to the mother-ley, it is a long time before a very small quantity of uric acid is deposited.

To ascertain the solubility of uric acid in water, some pure acid was well-washed with hot water, then boiled in a flask for half an hour with water so that some undissolved acid still remained, the liquid filtered through a hot filter, which had likewise been previously washed with hot water, into a glass vessel provided with a good ground stopper, weighed, evaporated in the water-bath, and the residue perfectly dried at 230°. It was found that the uric acid required from 1800 to 1900 parts of boiling water for its solution. In determining its solubility in cold water, the washed acid was boiled with water, and the liquid, after having stood for 8 days at a temperature of 68°, filtered; the acid required, according to these experiments, from 14,000 to 15,000 parts of water at 68° for its solution.

Neutral Urate of Potash.—Uric acid dissolves readily in solution of potash; the clear solution, when a sufficient quantity of caustic potash is present, deposits during the evaporation a heavy crystalline powder, which washed with alcohol yielded on analysis nearly 2 equiv. potash to 10 equiv. carbon. As the carbon and hydrogen were found too high on combustion, it was prepared in a different manner. Uric acid, which had been previously moistened with water, was added in the cold to a dilute solution of potash (1 part potash to 15 water) perfectly free from carbonic acid, as long as this dissolved readily; the clear solution was then heated to boiling in a flask, and 2 volumes of boiling alcohol of 0·863 spec. grav. added to it. The liquid remained clear, but soon after deposited some acicular crystals arranged in fascicular groups as soon as some strong caustic potash was added. When the liquid had cooled, the crystals were separated from the supernatant alcohol by a siphon, and the alcohol renewed several times, after which they were brought on to a filter and washed with æther, freed from æther under the air-pump, and were completely dried in a current of air wholly deprived of carbonic acid. The salt was washed under a bell-glass closed by water, as the carbonic acid of the atmosphere decomposes it. It forms a white crystalline powder, having strongly alkaline properties, dissolves in from 30 to 40 parts of boiling water, is very sparingly soluble in alcohol, and not at all in æther; when muriatic acid is added to it, it gives off no carbonic acid, is converted by the action of carbonic acid and water into an acid salt, becomes brown at 302°, black at a higher temperature, fuses, and after long-continued ignition the residue is perfectly white. The analysis gave the following results:—

	I.	II.	III.	IV.	V.	VI.	VII.		
KO	37·874	38·022	...	...	...	...	...	1	38·519
C*	...	...	24·273	24·015	24·365	24·346	...	5	24·486
N	...	...	...	...	...	...	22·780	2	23·120
H†	...	...	0·928	0·896	0·930	0·904	...	1	0·816
O	...	...	...	...	...	...	...	2	13·059

which leads to the formula $KO + C^5 N^2 HO^2$, and the atomic weight of the hypothetically anhydrous uric acid = 941·572 = $C^5 N^2 HO^2$.

When the salt dried at 212° was moistened with water, and exposed for several days in an atmosphere of carbonic acid, and then dried at 212°, 100 parts of the salt had increased by 13·425. If 2 equiv. salt take up 1 equiv. carbonic acid and 1 equiv. water, 100 parts should increase 12·65; consequently 2 equiv. $KO + C^5 N^2 HO^2$ become, after treatment with water and carbonic acid, 1 equiv. carbonate of potash and 1 equiv. $KO + 2(C^5 N^2 HO) + HO$; the former may be readily removed by water, while the latter is left as a very sparingly soluble salt. This explains the circumstance that many chemists have asserted the potash salt to become less soluble after drying; but if all carbonic acid is excluded during desiccation, the salt retains its primitive solubility.

Bi-urate of Potash.—When a solution of uric acid in potash-ley, or the solution of the neutral salt, is saturated with carbonic acid, this salt, as above observed, is deposited in a granular state; it was washed with water, and again dissolved in boiling water, when it separated on cooling as a flocculent precipitate, but which on filtration dried to a hard amorphous mass. The salt dissolves in 70 to 80 parts boiling, in 780 to 800 parts of water at 68°; it is insoluble in alcohol and æther, and absorbs no carbonic acid; its aqueous solution is neutral, tasteless, is precipitated by chloride of ammonium, salts of barytes and bicarbonated alkalies, and by salts of lead and silver, but not by sulphate of magnesia. Dried at 212° the salt yielded—

* Carbon = 75·00

† Hydrogen = 12·5.

KO........	22·439	22·161	..	..	1	22·815
C	..	..	28·467	28·69	10	29·007
N	..	..	..	..	4	27·387
H	..	..	1·62	1·65	3	1·450
O	..	..	..	..	5	19·337

which leads to the formula $KO + 2(C^5 N^2 HO^2) + HO$.

Neutral Urate of Soda.—This was prepared in the same way as the neutral potash salt, except that only 1 volume of boiling alcohol was taken instead of 2; it separates in verrucous masses, without however any crystalline appearance. Washed with alcohol, and finally with æther, the salt forms a white, tolerably hard powder, dissolves in 80 to 90 parts of hot water, is insoluble in æther and very sparingly soluble in alcohol. Its aqueous solution is strongly alkaline, absorbs carbonic acid from the atmosphere, and becomes turbid from the deposition of bi-urate of soda. It is decomposed at 302°, fuses at a higher temperature, and leaves a black residue, which after long ignition acquires a white colour. The analysis of this compound yielded—

NaO....	27·177	27·003	..	..	..	1	27·05
C	..	..	26·403	26·380	..	5	25·95
N......	..	..	..	..	25·150	2	24·51
H......	..	..	1·809	1·778	..	2	1·73
O	..	..	..	..	..	3	20·76

At 284° the salt parts with water; consequently the salt dried at 284° is represented by the formula $NaO + C^5 N^2 HO^2$, and that dried at 212° $= NaO + C^5 N^2 HO^2 + HO$; the calculated atomic weight of uric acid is 941·572.

When the neutral salt dried at 212° is moistened with water and exposed to an atmosphere of carbonic acid, it is converted, like the potash salt, into an acid salt, the soda of the one equivalent being changed into carbonate, while the uric acid combined with it unites with the other equivalent of soda.

Bi-urate of soda is readily prepared by passing carbonic acid into an aqueous solution of the neutral salt; it is then obtained in very minute warty concretions; but if a boiling solution of uric acid in caustic soda be treated with bicarbonate of soda, the salt separates in delicate acicular crystals, which collected on a filter and washed with cold water form after drying a very light white powder. The salt dissolves in 123 to 125 parts of boiling water, and in 1100 to 1200 parts of water at 59°; the aqueous solution is neutral, is precipitated by carbonated alkalies as well as by salts of barytes, lead and silver; it is insoluble in æther and alcohol, and absorbs no carbonic acid. Dried at 212° and submitted to analysis, it gave—

NaO..	15·325	15·239	15·643	..	..	1	15·642
C	..	..	..	29·903	30·078	10	30·012
N	..	..	..	..	..	4	28·337
H	..	..	..	2·130	2·145	4	2·000
O	..	..	..	..	..	6	24·009

The salt dried at 212° lost, on being heated to 338°, 1 equiv. water; and on being burnt with chromate of lead yielded—

NaO	..	..	1	16·379
Carbon	31·345	31·337	10	31·427
Nitrogen	..	..	4	29·673
Hydrogen	1·797	1·714	3	1·571
Oxygen	..	..	5	20·951

We have accordingly for the salt dried at 338° the formula $NaO + 2(C^5 N^2 HO^2) + HO$, and for the salt dried at 212°, $NaO + 2(C^5 N^2 HO^2) + 2HO$.

Bi-urate of Ammonia.—When an excess of solution of ammonia is poured over uric acid, it swells on being warmed: the precipitate, well-washed on a filter and dried over lime, forms a white, hard, amorphous mass, which dissolves entirely but with difficulty in water; its solution has an acid reaction. Warmed with muriatic acid, the dried precipitate swells, and after some time uric acid separates in the form of a heavy crystalline powder. The salt, dried over lime, was completely desiccated at 212°, and yielded on analysis—

Carbon	32·550	32·649	..	10	32·291
Nitrogen	..	..	37·645	5	38·111
Hydrogen	3·879	3·918	..	7	3·767
Oxygen	..	..	..	6	25·833

which leads to the formula $NH^3 + C^{10} N^4 H^4 O^6 = NH^4 O + 2(C^5 N^2 HO^2) + HO$.

If uric acid be suspended in boiling water, and during ebullition ammonia added in excess, slender acicular crystals, entirely different from those of uric acid, are formed; collected on a filter and dried over lime, they formed a very light powder. These crystals, heated to 284°, were submitted to analysis, and yielded—

Carbon	32·542	32·321	..	..	10	32·291
Nitrogen	..	..	37·856	37·924	5	38·111
Hydrogen	3·822	3·847	..	..	7	3·767
Oxygen	..	..	..	..	6	25·833

When the salt was heated with muriatic acid until the uric acid had subsided as a heavy powder, the liquid, after having stood 24 hours in the cold, was filtered, the weight of the uric acid determined, the filtered solution evaporated with some perchloride of platinum, and from the double salt thus obtained the amount of oxide of ammonium calculated. There was found—

Oxide of ammonium	13·722	1	14·08
Uric acid	80·08	2	81·08
Water	..	1	4·84

If uric acid be boiled with an excess of ammonia, and a large quantity of ammonia and the liquid filtered, a white caseous mass, without any crystalline structure, separates on cooling. To ascertain whether this precipitate was the acid salt in the moist state, or whether it was converted into this by drying, the proportion of the uric acid to the oxide of ammonium was determined in the following manner:—The moist precipitate was heated with muriatic acid, the uric acid separated by filtration, and the oxide of ammonium in the solution estimated by perchloride of platinum. There was found in the moist precipitate, for 1 equiv. oxide of ammonium, 2·26–2·28 equiv. uric acid; whence it results that the salt separating from the hot aqueous ammoniacal solution is acid. Dried over lime in an atmosphere of ammonia, 100 parts yielded on combustion—

Carbon......	32·265	10	NH^4O	13·609	1	14·080
Nitrogen	..	38·1455	$C^5N^2HO^2$	79·040	2	81·077
Hydrogen ..	3·909	7	HO	..	1	4·843
Oxygen	..	6				

From these results it is evident that the uric acid forms with ammonia, under all circumstances where it comes into contact with much water, an acid salt represented by the formula $NH^4O + 2(C^5N^2HO^2) + HO$.

A boiling solution of uric acid, to which an excess of ammonia has been added, may be evaporated to within one-sixth of its volume without becoming turbid; during the ebullition ammonia escapes, the liquid begins to acquire an acid reaction, and finally to froth very much. If the water be renewed during the boiling, it is possible to remove the whole of the ammonia, when the uric acid separates during the boiling in distinct crystals, which under the microscope have the appearance of perfectly transparent quadrilateral prisms. If the water is not renewed, uric acid separates along with urate of ammonia in verrucous masses, and it consequently appears as if the salt were decomposed very slowly: indeed when the liquid is very concentrated, and it begins to froth, no ammonia escapes, this only recommences when more water is added.

It was to be supposed that the hydrated uric acid would absorb dry ammonia; however, on passing ammoniacal gas over it at 212° and at 338°, no increase in weight occurred. An excess of ammonia added to uric acid which had been previously dried at 212°, and then again dried at 212°, was found to have increased 10·021–10·336 per cent. in weight. According to the formula $NH^4O + 2(C^5N^2HO^2) + HO$, 100 parts should increase 10·176, 1 equiv. ammonia entering into combination with 2 equiv. of the hydrated acid. To determine the solubility of the urate of ammonia in water, uric acid was boiled with water and an excess of ammonia; after the liquid had stood in the cold for 24 hours, it was filtered, muriatic acid added to the solution, and the amount of ammoniacal salt calculated from the weight of uric acid. According to these experiments, 1 part urate of ammonia requires 1608 parts water at 59° F. for solution; consequently a boiling saturated solution of uric acid in water should not become opake on cooling when saturated with ammonia, which was confirmed by experiment.

[To be continued.]

On the Cyanate of the Oxide of Ethyle and Methyle.

By Profs. Liebig *and* Wöhler.

On saturating alcohol or æther with the vapour of the hydrate of cyanic acid, there is formed, besides the so-called cyanuric æther, which is deposited in a crystalline state, a second combination of cyanic acid with the oxide of ethyle, which remains dissolved in the residuous liquid; it contains the elements of 1 equiv. hydrate of cyanic acid and 1 equiv. alcohol, or of cyanate of the oxide of ethyle + 2 equiv. water : $CyO, AeO + 2Aq$. This new substance crystallizes in large transparent laminæ and tablets, which are very soluble in water, alcohol and æther, fuse readily, and are extremely volatile. The oxide of methyle forms a similar combination with cyanic acid.—*Ann. der Chem. und Pharm.*, liv. p. 370.

PATENTS.

Patent granted to John Swindells, *of Manchester, for Improvements in the Preparation of various Substances for Dyeing.*

These improvements in dyeing and producing colour consist, in the first place, in preparing (when madder, madder root, and munjeet is used) the madder in the following way:—Take any given quantity of madder and reduce it to a fine powder, then mix it with as much of a solution of caustic ammonia, potash or soda, as will thoroughly carbonize the yellow or fawn colouring matter therein: different kinds of madder will require varying proportions. The best French madder will require one-eighth part of its weight of caustic alkali, or of ammonia, as much of the solution as will be equivalent in saturating a given weight of an acid, as one-eighth of potash. The powdered madder, when mixed with any of these solutions, is exposed to a heat not exceeding 175° Fahr.; it is then dissolved in water, and is ready to be used in dyeing, or forming madder lakes or pinks.

If preferred, the madder may be first treated with sulphuric acid, as in making garancine, and the alkali afterwards applied. By this method the operation of heat upon the alkalies will not be required, but they may be dissolved in a solution of any of the alkalies, or their carbonates, or other salts thereof: for these purposes the patentee prefers the caustic solution of ammonia, as producing the best effects.

Cotton and linen fabrics which are required to be dyed with the prepared madder, or with the common kinds, or even with other vegetable matters, are prepared in the following manner:—After the fabrics are bleached, and thoroughly cleansed from impurities, they are steeped in a solution of gelatine or albumen, of a specific gravity of 1·04, for several hours; they are then removed, and steeped in a strong solution of tannin for twelve hours; after which they must be wrung out and thoroughly dried. This process may be repeated, or not, according to the depth of colour required; and the usual process of dyeing may be proceeded with in the ordinary way.

The second part of the invention consists in preparing, for dyeing blues and similar colours, the compounds of cyanogen and ammonia, as follows:—

Instead of horn and hoof, and other animal matters commonly employed for this purpose, the patentee grinds to a fine powder common coal, cannel coke, or charcoal, or other carbonaceous matter, and mixes therewith a solution of gelatine or albumen, or both combined; and after thoroughly drying the compound, he uses it in the same way as the horn and hoof are used. Another method of producing the compounds of nitrogen, viz. cyanogen or prussiates and ammonia, consists in combining nitrogen gas or the oxides of nitrogen with carbon, as follows:—When nitrogen is to be used, it may be obtained by passing atmospheric air, or any of its compounds or mixtures, through heated carbonaceous matter; but charcoal or coke is preferred, so as to convert oxygen, if it be atmospheric air, into carbonic acid. In order to accelerate the process, the mixed nitrogen and carbonic acid is forced through lime, either in a semi-fluid or hydrated state; or it may be passed through an alkaline solution, or through alkaline earth, which will take up the whole of the carbonic acid, and any aqueous vapour that may be present, leaving the nitrogen gas moderately free from other gases. The nitrogen gas is then passed through charcoal, previously saturated with potash or soda, and kept to a full red heat in a close retort, until the required quantity of cyanide is produced. If ammonia is required to be obtained, nitrogen gas is passed, together with one-fourth its volume of steam, through charcoal kept at a red heat; the ammonia so produced is condensed by the usual process. Or atmospheric air may be used, and passed with steam through carbonaceous substances kept at a red heat, either in open or close vessels. When the protoxide, deutoxide, or nitrous vapour is employed for producing cyanogen, the same process may be used as that described in operating with nitrogen gas. In forming ammonia, or its compounds, from the oxides of nitrogen or nitrous vapour, they are passed with their own volume of steam through charcoal, at a red heat, either in close or open vessels; but if cyanogen is to be produced, the apparatus containing the charcoal must be air-tight, in order to exclude oxygen, carbonic acid, and aqueous vapour.

The third part of the invention, viz. improvements in the application and use of several chemical compounds for the purpose of dyeing or producing colour, consists in operating upon a class of salts not hitherto used in producing colour.

The cyanides, ferrocyanides, or other salts of cyanogen, are employed for the above purpose, by separating the acid, which is required to produce the colour, from its combination with barium, strontium, or calcium: the patentee prefers to operate on a salt of barium; and he precipitates the barium by its equivalent quantity of sulphuric acid, diluted with as much water as may be necessary to produce the required strength of acid to be used in dyeing. The chromates and bichromates of barytes, strontia or lime, are also treated with sulphuric acid and water, to separate their bases from the chromic acid. The manganates of barytes, strontia or lime, are likewise treated in the same manner. The acid solutions thus obtained are employed for raising, dyeing, and oxidizing various coloured fabrics.—Sealed June 12, 1844.

Patent granted to George Brown, *of Glasgow, for certain Improvements in the Manufacture of Soda.*

The object of this invention is to transform the sulphuret of sodium, produced in the manufacture of soda, into sulphate, sulphite, or hyposulphite of soda, and so make soda free from those impurities which render it less fit than it otherwise would be for soap-making, bleaching, and other uses. The patentee proposes to effect this by fluxing the soda, containing sulphuret of sodium, with a sufficient quantity of nitrate, chlorate, or chlorite of soda, or other body possessing an oxidizing power; but in most cases he prefers to use the nitrate of soda.

One mode of carrying this invention into effect is as follows:—The liquor drawn from crude soda is boiled down in a pan or furnace, until about four-fifths of the salt are precipitated; the whole is then removed from the furnace, and the wet pasty salt allowed to remain for some time in a vessel to drain; by this means the greatest proportion of the liquor that remained in the mass (commonly known as red liquor) will be separated from it. The red liquor (which consists chiefly of caustic soda and sulphuret of sodium, with a certain proportion of neutral salts, such as sulphate of soda and common salt) is put into a metal pan, and evaporated to about the consistency of tar; then the proper quantity of nitrate of soda is added, and heat applied to expel the remaining water, and flux the mass. The application of heat causes copious fumes of ammonia to be exhaled, and the mass froths and bubbles up, which serves as a guide to the operator in adding the nitrate of soda; as when no ebullition is produced by the addition of a fresh portion of nitrate of soda, it is a proof that the proper quantity has been added. When the mass is brought to a quiet flux, it is run into moulds; and when removed therefrom, is ready for use.

Another mode of proceeding is to boil down the whole quantity of crude soda liquor; and during the boiling, when the liquor is brought to about the consistency of tar, to add the nitrate of soda, or other oxidizing body; and, the evaporation being completed, flux the soda containing the sulphuret of sodium.—Sealed February 20 1845.

THE CHEMICAL GAZETTE.

No. LXXII.—October 15, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Suboxide of Antimony and Antimoniuretted Hydrogen.

By Prof. R. F. Marchand.

The suboxide of antimony may be very readily prepared in large quantity by decomposing a tolerably concentrated solution of tartar-emetic by a Grove's or Bunsen's battery. Under a lively evolution of gas a black powder separates on the positive pole, which soon covers the platina plate, from which it falls off and collects at the bottom of the vessel. Should the solution become too concentrated by the decomposition of the water, tartar-emetic is precipitated along with the suboxide; and the precipitate must therefore be purified by washing with boiling water. After desiccation over sulphuric acid, the compound forms a heavy velvety black powder, which exhibits under the microscope a perfectly homogeneous appearance, and takes a metallic lustre under the polishing steel.

It is decomposed by boiling with hydrochloric acid into metal and oxide which dissolves; the black colour disappears, although only after considerable boiling, and gray spangles with metallic lustre separate. The compound is likewise decomposed by boiling with bitartrate of potash into metal and oxide, which dissolves. The powder retains some moisture with considerable tenacity; heated in the air, it burns like tinder to oxide of antimony without giving off any perceptible vapour if the temperature be not too high; when heated more strongly, it forms antimoniate of the oxide of antimony.

For the examination of the black powder, a tolerably strong narrow glass tube, sealed at the lower part, was filled one-fourth with the powder, and the suboxide brought into a state of fusion over the spirit-lamp. The metallic antimony unites at the bottom of the glass tube to a small regulus, above which the fused oxide of antimony forms a layer.

If the glass tube is 4 or 5 inches long, the sublimate of the oxide of antimony does not ascend more than half-way up, so that it can occasion no loss in the weight. After weighing, which gives the loss of water, the regulus of antimony can be separated perfectly from the glass and the oxide by a gentle blow of the hammer, and determined by weight. The author found in this way—

Antimony....	92·91	92·51	3 =	2418	92·37
Oxygen......	..	..	2	200	7·63
				2618	

This composition differs essentially from that of the suboxide of arsenic (As^2O); it is possible that the compound obtained by electrical decomposition has a different composition to that prepared by a different method, especially as the suboxide separated electrically from arsenious acid is not converted under water into arsenious acid; it is also possible that a like difference occurs in this case as between the antimoniuretted and arseniuretted hydrogen.

When a concentrated solution of sal-ammoniac is decomposed with a very powerful battery, the negative pole of which is formed of a bar of antimony, a gas may be obtained under certain circumstances, which is probably inflammable antimoniuretted hydrogen. For this purpose, a bar of antimony, which should be so thick as not to be entirely covered by the liquid, is placed in a round shallow porcelain vessel with perpendicular sides, the bottom of which is covered with a concentrated solution of sal-ammoniac. It is best to place the bar so near to the margin of the vessel, that some liquid is shut in between it and the metal. The metallic bar is now connected with the negative pole of the battery, and a thick platinum wire, which is connected with the positive pole, inserted into the inclosed liquid near to the antimony, and so that a tolerably long piece of wire lies quite close to it. During the liveliest evolution of gas, some black flakes, probably hydruret of antimony, are seen to separate from the antimony; and if the battery acts with sufficient power, faint detonations very soon begin to be heard, which increase in loudness the greater the bursting bubbles become; these burn with a brilliant lustre and a white flame, like antimoniuretted hydrogen gas. The separation of white fumes renders it highly probable that the phænomenon is produced by inflammable antimoniuretted hydrogen.—*Journ. für Prakt. Chem.*, xxxiv. p. 381.

Observations on Caffeine. By Dr. F. Dœbereiner.

The author recommends extracting the caffeine by means of the displacement apparatus. In this way he obtained from a pound of moderately good raw coffee from 98 to 100 grs. of caffeine, while Robiquet and Boutron procured only 32 grs. from the same quantity of the very best kinds of coffee. The large amount of sugar of the coffee examined was remarkable, and also the circumstance that a considerable quantity of mannite was found in it, which hitherto had not been detected in coffee. The author believes that the sugar and mannite, as well as the caffeine, act some part in the dietetic use of coffee, and that moreover another nitrogenous body occurs in the roasted coffee, which passes into solution, but which he has hitherto not succeeded in obtaining pure, since when once isolated it appears to be in a very altered condition, being then perfectly insoluble in the ordinary solvents. The odour of this body when heated in the air is peculiar, for even when separated from the worst kinds of coffee it diffused the odour of the best coffee in the act of roasting. —*Archiv der Pharm.*, xciii. p. 27.

On Human Gall-stones consisting of Biliary Colouring Matter. *By* Prof. SCHMIDT.

Biliverdine has been several times found in the gall-stones of ruminant animals, but not in those of man. Those examined by the author were removed from a woman aged 50, who died of dropsy. They had the ordinary rounded polygonal form, were numerous, but very small, and weighed altogether 4 grms. When treated with water, they appeared of a dark green colour, had a strong fatty lustre, and were iridescent like the elytra of *Cetonia aurata.* When dried in the air, they were readily pulverizable, and yielded a dark reddish-brown amorphous powder. Water extracted 19 per cent.; the solution was yellow, soon became putrid, and contained merely dried bile. The powder, after treatment with water, partly dissolved in alcohol with a green colour, as also in æther, and to a greater extent in solution of potash, leaving merely microscopic fragments of a dark yellow colour, and columnar bodies (six-sided prisms with six-sided summits); these ultimately disappeared.

The alkaline solution, when treated with nitric, sulphuric or muriatic acid, yielded a precipitate of dark green flakes, the liquid assuming a yellowish colour. On supersaturating the liquid with nitric acid, it at first became green, then speedily blue and violet; after some time it turned red, and finally yellow. This play of colours, as is well known, is afforded by bile, serum of blood, and other animal fluids. Its cause is unknown, but it certainly does not arise from the precipitated green flakes.

When the potash solution was treated with muriatic acid until flakes ceased to be deposited, after filtering, washing and drying the precipitate, a dark greenish-yellow brittle mass, with a spermaceti lustre, remained. This was readily soluble in potash and ammonia. The colour of the solution was at first greenish-yellow; subsequently, dark yellowish-brown, with a tinge of green. On the addition of acids, a precipitate, consisting of dark green flocks, was again produced. Nitric acid readily dissolved the mass, yielding a yellowish-red solution, muriatic and sulphuric acids with difficulty, forming a green solution. Alcohol dissolved a small quantity, forming a green solution; æther exerted the same action, but in a less degree.

At a temperature of 212° the biliary calculi lost 11·9 per cent. of water. Heated over a spirit-lamp in a platinum spoon, they puffed up, leaving a black metallic-looking coal, evolved ammoniacal vapours, took fire, and left after a continued red heat 7·7 per cent. of an ash consisting of carbonate with a little sulphate and phosphate of lime.

Biliary calculi of the same kind were found in another individual. They formed irregular-clustered lumps of more than 3 lines in diameter. They were dull on the external surface; when fractured, they had a spermaceti lustre.—*Archiv der Pharm.*, xli. p. 291.

Concretions composed of Cholepyrrine from Human Bile.
By H. WACKENRODER.

These concretions consisted of several bodies, the size of which varied from that of a lentil to that of a pea. They were clustered, of a dark brown, almost black colour, inodorous, and void of any peculiar taste. Their surface was uneven; when fractured they appeared granular, and in parts filled with irregular cavities. They were readily pulverizable, and yielded a dark ochrey-yellow powder. When heated in a glass tube, they evolved at first white, subsequently yellow pungent vapours, a brown empyreumatic oil and a tolerable amount of ammonia, leaving a porous, alkaline cinder, containing sulphuret of calcium, carbonate of lime and iron.

On digestion with alcohol of 0·851 spec. grav., they yielded a dark green neutral solution, which gave with acetate of lead, a dirty white precipitate soluble in acetic acid; with nitrate of silver, a flocculent precipitate soluble in ammonia; with perchloride of iron, a flocculent precipitate soluble in acetic acid; and with sulphate of copper, a flocculent dirty green precipitate. Caustic and carbonated alkalies, tannic acid, bichloride of mercury, protochloride of tin and chromate of potash produced no turbidness; nitric acid converted the green colour into a hyacinthine red. On evaporating the solution, green flakes were deposited. When the green residue was heated on platinum foil, at first an odour resembling that of caramel was evolved; subsequently a disagreeable one, resembling that of burning feathers.

The mass, after treatment with alcohol, yielded merely a small quantity of sulphate of lime to water; æther removed some greenish fat.

On digesting the undissolved green substance with dilute nitric acid, it assumed a pale red and yellow colour, copious effervescence ensuing at the same time: a small portion remained undissolved. The solution contained principally lime, a trace of magnesia, and peroxide of iron. The remainder dissolved completely in potash, forming a brownish-green solution, and yielded with a little nitric acid dark green flocks, which were at first coloured red, and then yellow, by strong nitric acid. Protochloride of tin threw down brownish-green flakes; acetate of copper produced a strong greenish-gray precipitate, protosulphate of iron a dark greenish-gray, and perchloride of iron a brown precipitate.

Consequently these concretions consist of biliary colouring matter, with small quantities of fat, carbonate and sulphate of lime and carbonate of magnesia and iron.—*Archiv der Pharm.*, xli. p. 294.

Chemical Examination of Stapelia hirsuta. *By* FR. J. BERNAYS.

The juice of *Stapelia hirsuta*, as well as several other species of this genus, contains a peculiar bitter substance, which tastes very much like aloes. The author made an incision on a specimen, and obtained in a few minutes a watch-glass full of a mucous limpid juice, which soon dried in a warm place to a clear gum, full of fissures, and had an acid reaction in its fresh state.

This dry juice of the *Stipelia hirsuta* is amorphous, like gum-arabic, transparent, shining, pulverizable, not altered by exposure to the air, is void of smell, and has a very permanent bitter taste. Alcohol dissolves out the greater portion, leaving white tasteless flakes as a residue, which dissolve in water for the greater part. The alcoholic solution on mixture with water becomes milky, and leaves on evaporation a bitter substance shining like varnish, and of which the author swallowed from 3 to 4 grs. without any evil consequences being observed.

Æther dissolves from one-fifth to one-sixth of the juice; and on driving off the solvent, a yellowish, transparent, easily-pulverizable substance, of very bitter taste, remains. This bitter principle of *Stapelia* fuses readily on the application of heat, and burns with a smoky flame without residue, diffusing an odour resembling very much that of burning horn; from which, according to Buchner, we may suppose the presence of nitrogen.

What the æther leaves undissolved is for the greater part taken up by alcohol, and on evaporation of the alcohol a resinous shining residue is left, the external characters of which scarcely differ from that prepared with æther; but this constituent, insoluble in æther and soluble in alcohol, does not melt on being heated, but puffs up, and leaves an ash on combustion. The bitter principle not only dissolves in æther and alcohol, but also in water. The aqueous solution has a neutral reaction, and yields with solution of potash a flocculent precipitate.—Buch. *Rept.*, xxxviii. p. 95.

On some Properties of Asparagine. By M. Piria[*].

I have continued my researches on asparagine[†], and have had occasion to confirm my former results respecting its conversion into succinic acid. I have, moreover, found that it displaces acetic acid from its combination with oxide of copper when heated to boiling with an aqueous solution of acetate of copper. It then forms a crystalline precipitate of an ultramarine colour, which contains $C^8N^2H^7CuO^6$. Sulphuretted hydrogen again separates the asparagine with all its properties.

A more important fact is, that asparagine and aspartic acid are two amides of malic acid; they are to malic acid what oxamide and oxamic acid are to oxalic acid. If we double the formulæ of this last series, we have in fact—

$C^4N^2H^8O^8$ = oxalate of ammonia.	$C^8N^2H^{12}O^{10}$ = malate of ammonia.
$-H^4O^4$	$-H^4O^4$
$C^4N^2H^4O^4$ = oxamide.	$C^8N^2H^8O^6$ = asparagine (malamide).
$C^4NH^5O^8$ = binoxalate of ammonia.	$C^8NH^9O^{10}$ = bimalate of ammonia.
$-H^2O^2$	H^2O^2
$C^4NH^3O^6$ = oxamic acid.	$C^8NH^7O^8$ = aspartic acid.

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[*] In a letter to M. Dumas.

[†] See Chem. Gaz., vol. ii. p. 457.

In fact, aspartic acid and asparagine are very readily decomposed at the ordinary temperature in contact with nitrous acid; pure nitrogen is disengaged, and the liquid contains malic acid. The very deliquescent acid noticed by M. Liebig in treating asparagine or aspartic acid with concentrated hydrochloric acid, is only aspartic acid retaining a trace of hydrochloric acid, which renders it exceedingly soluble and deliquescent.

I regret not being able to announce at the same time the synthesis of asparagine, as the analogy with oxamide appears to indicate; but hitherto I have not been able to obtain the malic acid, and must await the favourable season to prepare it.

I have also obtained some remarkable products with urea, among which a crystalline compound with corrosive sublimate, that gives with potash a white precipitate, which appears to correspond to the amide, and, what is remarkable, explodes when heated like the amiduret of mercury.—*Comptes Rendus*, Sept. 15, 1845.

On some Salts of Uric Acid. *By* A. Bensch.

[Continued from p. 417.]

Bi-urate of Magnesia.—A hot saturated solution of bi-urate of potash, on being mixed with sulphate of magnesia, remains for a long time clear; but in the course of 2 or 3 hours, silky crystals, grouped in verrucous masses, which frequently float on the surface, separate. These crystals were washed with water, then dissolved in hot water, of which they required a far greater quantity than that from which they had separated; on the cooling of the hot solution, acicular crystals separated in considerable quantity. When washed with cold water and dried, they form a light powder, which becomes brownish at 356°, and burn at a higher temperature, leaving a white residue. The crystals are insoluble in spirit and in æther, dissolve in 150 to 170 parts boiling, and 3500 to 4000 parts cold water. The solution has a neutral reaction. The salt yielded on analysis—

MgO	8·557	8·731	8·695	..	..	1	8·82
Carbon	..	..	..	25·550	25·836	10	25·61
Nitrogen	..	..	..	..	..	4	24·18
Hydrogen	..	..	..	3·926	3·998	9	3·84
Oxygen	..	..	..	..	..	11	37·55

which leads to the formula $\text{MgO} + 2(\text{C}^5\,\text{N}^2\,\text{HO}^2) + 7\text{HO}$. There was no potash in the salt.

The urate of magnesia, dried at 212°, lost at 338° 19·195 per cent. or 5 equiv. water; accordingly the salt, dried at 338°, is represented by the formula $\text{MgO} + 2(\text{C}^5\,\text{N}^2\,\text{HO}^2) + 2\text{HO}$.

Bi-urate of Lime.—This salt is obtained by mixing a solution of chloride of calcium with a hot solution of bi-urate of potash; it separates as a white amorphous precipitate. If the urate of potash is somewhat alkaline, it frequently happens that acicular crystals in verrucous groups are obtained (probably a double salt). The bi-urate of lime is very difficult of solution in water; it is much less so if the water contains chloride of potassium. For analysis, the precipitate was taken after it had been well-washed with hot water. Dried at 212°, 100 parts gave—

CaO	13·796	13·609	..	..	1	13·615
Carbon	..	..	29·354	29·408	10	29·176
Nitrogen	..	..	..	..	4	27·547
Hydrogen	..	..	2·692	2·626	5	2·431
Oxygen	..	..	..	..	7	27·231

These numbers correspond to the formula $CaO + 2(C^5 N^2 HO^2) + 3HO$.

Bi-urate of Baryta is obtained by mixing a hot solution of bi-urate of potash with a solution of chloride of barium in excess; it is deposited as a white amorphous powder. Washed with hot water and dried at 212°, the salt gave—

BaO	30·006	30·165	..	..	1	30·114
Carbon	..	..	23·727	23·764	10	23·604
Nitrogen	..	..	..	..	4	22·286
Hydrogen	..	..	2·121	2·250	5	1·967
Oxygen	..	..	..	..	7	22·030

which corresponds to the formula $BaO + 2(C^5 N^2 HO^2) + 3HO$.

The urate of baryta is insoluble in water, and likewise in alcohol and æther, and burns readily without fusing. Carbonate of baryta, boiled with uric acid, gives rise to an abundant disengagement of carbonic acid.

Bi-urate of Strontia is obtained by mixing a solution of chloride of strontium with a hot solution of bi-urate of potash; it forms a white amorphous powder, is somewhat soluble in boiling water, insoluble in alcohol and æther, and burns easily. The analysis gave—

SrO	22·808	22·767	..	..	1	22·570
Carbon	..	..	26·142	26·192	10	26·152
Nitrogen	..	..	..	..	4	24·692
Hydrogen	..	..	2·347	2·388	5	2·179
Oxygen	...	..	..	..	7	24·408

These numbers answer to the formula $SrO + 2(C^5 N^2 HO^2) + 3HO$.

Uric Acid and Oxide of Lead.—When an excess of acetate of lead is added to a saturated solution of bi-urate of potash, a white heavy precipitate immediately subsides, which forms, after being well-washed with hot water and dried, a light powder insoluble in water, alcohol and æther, which burns readily, leaving behind a mixture of metallic lead and oxide of lead. The determination of the oxide of lead was made by dissolving the salt in dilute nitric acid, adding to it alcohol and sulphuric acid, and washing the separated sulphate of lead with alcohol. On combustion, 100 parts dried at 212° yielded—

PbO	40·185	40·087	..	1	39·812
Carbon	..	..	21·387	10	21·413
Nitrogen	..	..	..	4	20·218
Hydrogen	..	..	2·532	4	1·427
Oxygen	..	..	..	6	17·130

corresponding to the formula $PbO + 2(C^5 N^2 HO^2) + 2HO$; it may however also be looked upon as a mixture of neutral urate of lead with uric acid $= (PbO + C^5 N^2 HO^2 + HO)$ and $(C^5 N^2 HO^2 + HO)$.

The salt, dried at 212°, heated to 322°, does not lose in weight.

Uric Acid and Oxide of Copper.—When a solution of sulphate of copper is added to one of bi-urate of potash, a green precipitate is formed, which could not be obtained free from potash by long-continued washing with cold water. When boiled with water, it acquired a brown colour; the filtered water had an acid reaction, and deposited uric acid on cooling. As soon as the hot water which passed through no longer possessed any acid reaction, the precipitate was dried over sulphuric acid, when its brown colour changed into a violet; it was easily reduced to powder, and exhibited no crystalline structure under the microscope. Dried at 284°, and submitted to analysis, it yielded—

CuO	42·857	42·718	..	3	41·378
Carbon	..	..	21·513	10	20·855
Nitrogen	..	..	..	4	19·692
Hydrogen	..	..	1·530	4	1·390
Oxygen	..	..	..	6	16·723

The salt, dried over sulphuric acid, lost at 284° 5·57 per cent., or 3 equiv. water; consequently, the formula for the salt dried over sulphuric acid is $3CuO + 2(C^5 N^2 HO^2) + 5HO$, while that dried at 284° may be represented by $3CuO + 2(C^5 N^2 HO^2) + 2HO$, or as a mixture of 2 equiv. hydrate of uric acid with 3 equiv. oxide of copper.

Urate of Silver.—If a solution of bi-urate of potash be mixed with an excess of nitrate of silver, a white gelatinous precipitate separates, which however soon acquires a dark colour. If the solution be previously warmed and an excess of silver salt employed, the precipitate immediately becomes black; but with an excess of urate of potash, the precipitate retains its white colour even on drying. From the gelatinous nature of the precipitate, it is very difficult to wash, the more so as no hot water can be employed without decomposing it. After long-continued washing, it was dried and submitted to analysis, but yielded for 23·73 per cent. oxide of silver 9·008 per cent. potash. The preparation of this salt was attempted several times, but it always contained a considerable amount of potash.—*Ann. der Chem. und Pharm.*, liv. p. 189.

On a peculiar Colouring Substance in some kinds of Mosses.

When dried *Bryum stellare* is moistened with some water in a watch-glass, after some time the brownish colour is observed to become of a lively green, then to grow darker, and to become finally of a blue-green. This change in the colour may be very easily observed under the microscope; it generally begins near the granules of chlorophylle, situated close to the margin of the cells, extends very rapidly, and forms around the granules of chlorophylle a dark blue band, while the granules themselves retain their green colour.

After a longer time the moss becomes entirely of a dark blue colour, which it retains even on being dried. This phænomenon has some resemblance to the formation of indigo in the leaves of the indigo plant; and the author was led to imagine that a similar colouring principle might likewise be contained in the moss. However, fresh *Bryum stellare* does not exhibit this phænomenon, but retains its green colour on being softened in water; the colouring principle therefore is first formed under the influence of the atmosphere during desiccation. A specimen, which had become blue on being moistened with vinegar, changed into yellowish-green; it differed therefore from litmus. If, on the contrary, it was soaked in water to which a drop of caustic ammonia had been added, it immediately became blue, green, and very soon dark blue. This colouring principle therefore most resembles hæmatoxyline, which is coloured blue by alkalies and yellow by acids.—*Jahr. für Prakt. Pharm.*, x. p. 245.

On the Composition of the Oriental Bezoar.

By THOMAS TAYLOR, ESQ.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,

Upon looking over the numbers of the 'Chemical Gazette,' published during my absence from London, I perceive with some satisfaction that Prof. Wöhler has confirmed my assertion with regard to the composition of the oriental bezoar. The circumstance of the oriental bezoar being composed of ellagic acid was described by me in the 'London and Edinburgh Philosophical Magazine' for May 1844, and also in a Report addressed to the Museum Committee of the Royal College of Surgeons in 1841, besides having been mentioned in conversation to several chemists, among others to Prof. Liebig.

Permit me also to take this opportunity of stating, that the atomic constitution of the phosphate of lime contained in the Beluga stone had been printed in the College Catalogue many months prior to the analysis of Prof. Wöhler; and it gives me pleasure to find that the results obtained by that excellent chemist coincide in every respect with my own.

I am, Sir,
Your obedient Servant,
September 30, 1845. THOMAS TAYLOR, Surgeon.

[We regret having accidentally omitted to notice the labours of our correspondent at the time Prof. Wöhler's paper was inserted. The passage referred to in the 'Phil. Mag.' is the following:—"Several intestinal concretions have been discovered, consisting of the insoluble acid obtained by Braconnot from the infusion of gallnuts, and termed by him ellagic acid. The constituent of these concretions has been described by John under the name of *Bezoarstoff*. It forms also the *ligniform matter* of Berthollet; and I have also no doubt that it is the *peculiar acid* from the oriental bezoar described by M. Lippowitz, and termed by him bezoaric acid."—W. F.]

On a remarkable Change which Morphine undergoes by the Action of Sulphuric Acid. By A. E. Arppe.

When morphine is dissolved in an excess of sulphuric acid, and the liquid evaporated to incipient decomposition, a white body is separated by adding water to the brownish mass, which is not sulphate of morphine, and does not contain a trace of morphine.

This white body is most readily obtained in the following manner:—Crystallized sulphate of morphine is treated with a slight quantity of dilute sulphuric acid, the mass evaporated and heated to 302°–322°. The brown mass thus obtained is boiled with water, so that the precipitate which had formed on the addition of water is entirely redissolved. The solution is filtered as hot as possible, when the white body again separates if the solution was sufficiently concentrated. That portion of the brown mass which was not taken up by the water is again treated in the same manner; a few drops, however, of sulphuric acid should be added, in order to produce a perfect solution on boiling. When a sufficient quantity of sulphuric acid has been used, and the stated temperature has not been exceeded during the evaporation, the precipitate formed is perfectly white, while the supernatant liquid is nearly colourless, and the filter is only coloured by a minute quantity of a light brown body. The white substance, collected on a filter, may be easily washed with cold water from the excess of sulphuric acid; it is then freed from adherent moisture by means of blotting-paper, and finally dried at a very gentle heat. The mother-ley contains a little more of the substance in solution, but it only yields a very impure preparation on evaporation.

The following are the properties of this body:—Its colour is white, and after drying always more pure than in the moist state, yet frequently with a brownish tint, which is generally not to be removed by the ordinary means. Suspended in the liquid, it separates readily in large caseous flakes, and on evaporation shrinks extremely. As seen under the microscope with a magnifying power of 200, it consists of round shining globules, which are perfectly homogeneous, but not in the least crystalline. Exposed to the air, it gradually becomes greenish on the surface; it is slightly soluble in water, but the solution is decomposed on boiling, and acquires an intense emerald-green colour. It is not dissolved or altered by alcohol or æther. In acid liquids, especially if sulphuric or muriatic acid is present, it is dissolved with the greatest ease without change; the substance separates unaltered on evaporating the dilute solutions, but it is decomposed by the concentrated acids with formation of a brown body. Alkaline fluids, especially when caustic and concentrated, act in a similar manner to the concentrated acids; they destroy the substance, and give rise to the formation of a brown product of decomposition.

Potash and ammonia produce in the acid solutions very considerable precipitates, which are readily soluble in an excess of the precipitant. Carbonate of ammonia likewise yields a precipitate, but does not redissolve it. These precipitates are especially characterized by the circumstance, that they soon acquire, when exposed to the air, a more or less dark green colour, being converted into another body which contains only two-fifths of the sulphuric acid of the white substance. The amount of sulphuric acid of this white substance is greater than that of the sulphate of morphine, but only a portion of the sulphuric acid is separated from a solution in muriatic acid by chloride of barium, while the other portion can only be detected after decomposition by chlorine. The analysis of the body, dried in a current of carbonic acid gas, yielded—

	Found.		Calculated.
Sulphuric acid	14·66	14·14	14·63
Carbon	61·12	61·22	61·41
Hydrogen	5·88	5·58	5·84
Nitrogen	3·96	..	4·11
Oxygen	..	..	14·01

The organic constituent of this compound is, judging from its equivalent, equal to 4 atoms of morphine; it may consequently be expressed by the formula $4(C^{35} H^{20} NO^{6}) + 5SO^{3}$. If we set out from the supposition that the morphine is a conjugated compound of ammonia, its sulphate, which contains, like the salts of the organic bases in general, 1 atom water, can be expressed by the formula $C^{35} H^{17} O^{6} + NH^{4} O,SO^{3}$, *i. e.* it contains 1 atom of oxide of ammonium instead of the ammonia. On being heated with sulphuric acid, the whole of the water is expelled, and the peculiar sulphates of ammonia discovered by H. Rose are formed, in which the ammonia is conjugated with the sulphuric acid. Of these compounds the neutral is $NH^{3} SO^{3}$, and the acid one which Jacquelain analysed, $3NH^{3} + 4SO^{3}$. If these two salts were formed in the substance examined, it is directly evident that the above composition must result, and the rational formula would accordingly be $(C^{35} H^{17} O^{6} + NH^{3}) + SO^{3} + 3(C^{35} H^{17} O^{6} + NH^{3}) + 4SO^{3}$. The fact that anhydrous sulphuric acid passed over effloresced morphine produces this body, speaks in favour of this view; nevertheless the change which the morphine undergoes must be more considerable, since it can no longer be separated from the compound. Moreover, the circumstance that a portion of the sulphuric acid is precipitated by chloride of barium, while in the above ammonia salts none of it is thrown down, cannot be brought into perfect union with the view abovementioned; it might however be explained by a decomposition being perhaps effected by the acid employed to dissolve it.—*Ann. der Chem. und Pharm.*, lv. p. 96.

Researches on the Density of the Vapour of the Perchloride of Phosphorus. By A. CAHOURS.

Being at present engaged on an investigation of the perchloride of phosphorus, I endeavoured at first to explain an anomaly which this compound presents, and which is quite similar to that which I have met with in the different acids of the acetic group, and also in some essential oils.

It is known, from the experiments of Mitscherlich, that the density of the vapour of perchloride of phosphorus, taken at 365°, is represented by the number 4·85, which leads us to conclude that the molecule of this compound, reduced to vapour, affords 6 volumes, a mode of grouping which is not very probable, and which might result from the determination of the density of this substance in its gaseous form having been made at a temperature too near that of its boiling-point. I have recently proved, in fact, that for certain substances it is requisite to go far beyond the point of ebullition in order to obtain a density no longer variable; in operating thus, the exceptions disappeared; and it was always found that a compound molecule reduced to vapour yielded 2 or 4 volumes, never 3 or 6, and that this latter mode of grouping rests on purely fortuitous circumstances.

To throw light upon this difficulty, I have taken the density of the vapour of the perchloride of phosphorus at various temperatures. I then found that at about 284 degrees beyond the boiling-point, the vapour of this compound no longer presented the mode of condensation admitted by Mitscherlich; and that from this term the numbers representing the density remain constant, as will be seen from an inspection of the results contained in the following table:—

Temperatures.	Densities.	
374°	4·99	
392°	4·85	
406°	4·73	
446°	4·30	
482°	3·99	
525°	3·84	
550°	3·67	Mean, 368.
552°	3·69	
572°	3·654	
620°	3·656	

Whence it is seen that the perchloride of phosphorus, like many other compounds, forms, when examined in the gaseous state, a curve, the ordinates of which (densities) decrease in proportion as the abscissæ (temperatures) increase up to a certain limit, when they remain constant. Now it results, from the inspection of this constant number, that the molecule of the perchloride of phosphorus yields 8 volumes of vapour; in fact, we have—

1 volume of vapour of phosphorus	4·420
10 volumes of vapour of chlorine	24·420
	28·840

$$\frac{28{\cdot}840}{8} = 3{\cdot}61$$

In considering the perchloride of phosphorus as formed by the union of 1 vol. of vapour of phosphorus and of 10 vol. of chlorine condensed into 8, we should have a kind of molecular division which has never yet been met with. From the very manner in which the perchloride of phosphorus behaves towards certain reagents, would it not be more suitable to consider it as a compound resulting from the union of equal volumes of chlorine and of protochloride of phosphorus, with condensation of half the elements? a mode of combination which is quite usual: we should then, on this hypothesis, have—

1 volume of vapour of protochloride of phosphorus .. 4·80
1 volume of chlorine............................ 2·44

$$\frac{7{\cdot}24}{2} = 3{\cdot}62$$

The same is probably the case with the constitution of the perchloride of antimony, which, as is well known, is partially decomposed every time it is distilled, yielding free chlorine and protochloride of antimony.

This mode of viewing the constitution of the perchloride of phosphorus appears to me perfectly conformable to observed facts. Indeed Serullas has shown that by acting with dry sulphuretted hydrogen on this compound, 2 molecules of chlorine are eliminated and replaced by 2 of sulphur, the new-formed product corresponding entirely to the perchloride of phosphorus; we have, in fact, $PhCl^5 + 2SH^2 = 2ClH + PhCl^3 S^2$.

I hope soon to be able to show that other simple or compound bodies may be substituted for the molecules of chlorine in the perchloride of phosphorus, giving rise to new products of an analogous molecular grouping.—*Comptes Rendus*, Sept. 15, 1845.

On the Action of Sulphuric Acid upon Carbon.
By Prof. R. F. Marchand.

According to Knezaureck, there is formed, in the action of sulphuric acid upon carbon, besides sulphurous acid, carbonic acid; which is in contradiction to the statements of most works on chemistry, that in this reaction no carbonic acid is produced, but only carbonic oxide. The author however found, on examining the mixture of gas, that both carbonic acid and carbonic oxide were disengaged, and besides these also a small quantity of carburetted hydrogen; that these gases are formed in very variable proportions, and in by far too small a quantity for the sulphurous acid to be produced solely by the formation of carbonic acid and carbonic oxide.

The quantitative analysis was made by shaking the gaseous mixture with superoxide of manganese, according to Gay-Lussac's method, till no more of it was absorbed; the carbonic acid was then determined by means of potash, and the carbonic oxide removed by fusing potassium.

100 volumes of the gaseous mixture contained—

	CO^2.	$CO(+CH)$.
1	10·1	11·6
2	11·4	10·4
3	9·2	7·8
4	11·8	6·8
5	11·3	6·9
6	15·8	6·8
7	16·1	6·8
8	16·3	4·8
9	16·5	4·4
10	17·0	3·8
11	17·1	3·0
12	18·1	2·9

From the difference in the results, it is probable that the differences of temperature produce essential modifications. Consequently, in the present instance, charcoal does not behave as carbon, but as an organic compound, like woody fibre, sugar, &c.

The action of sulphuric acid upon *graphite* only commences at the boiling-point of the former. The gaseous mixture, freed from the sulphuric acid which had distilled over, likewise presented a variable composition, according to the duration of the action. At the commencement the sulphurous acid greatly predominated, but the amount of the carbonic acid increased considerably towards the end of the reaction, and had finally attained very nearly the proportion of 1:2 towards the sulphuric acid. It amounted to 10·5 CO^2:23·0 SO^2. Carbonic oxide was not formed. On the whole, the quantity of gases were small, although the sulphuric acid was distilled almost entirely from the graphite before the reaction was interrupted.

The appearance of the residuous graphite was not altered, and it was readily and completely edulcorated; when fused with a mixture of nitrate of potash and carbonate of soda, chloride of barium precipitated sulphate of barytes from the muriatic solution. According to this determination, the graphite contained in one experiment 3 per cent., in another 1·8 per cent. sulphur; evidently the product had a different composition according to the length of the reaction. When ignited in the platinum crucible, the graphite puffed out considerably in a spiral form even at a gentle heat. The liberated acid vapours threw the greater portion out of the crucible, so that small flakes were scattered about in the air. The shining graphite was converted into a dull gray, very light mass, which by gentle pressure reacquired its former appearance. No sulphuric acid could be extracted from the graphite by boiling with caustic potash.

It was not possible to obtain, by the long-continued action of sulphuric acid, a constant chemical combination, which is probably mixed, as it were, in the graphite in the form of carbo-sulphuric acid.—*Journ. für Prakt. Chem.*, xxxv. p. 228.

ANALYTICAL CHEMISTRY.

On the Solubility of the Basic Ammonio-phosphate of Magnesia, and on the quantitative Determination of Phosphoric Acid and Magnesia by means of this Salt, together with Observations on the Constitution of Crystallized Phosphate of Soda. By Dr. R. Fresenius.

The incorrect views respecting the solubility of the basic ammonio-phosphate of magnesia contained in most works have led chemists to regard the determination of magnesia in the form of this salt as inaccurate, and have prevented many from estimating the phosphoric acid by means of it.

On the supposition that the double salt in question, which is not wholly insoluble in water, is only then not taken up by it when this contains phosphatic salts, no one ventured to wash completely the precipitate, and the method proposed by Otto for the determination of phosphoric acid was not considered accurate.

It is my intention to prove that the presence of phosphates has no influence on the solubility of the basic ammonio-phosphate of magnesia, and that it is to free ammonia only that the double salt is indebted for its insolubility in the liquids which are obtained on precipitating a solution of magnesia with phosphate of soda, with addition of sal-ammoniac and ammonia. This being established, it will result that henceforth the estimation of magnesia in the form of this salt, as well as that of phosphoric acid, correctly executed, must yield perfectly satisfactory results.

1. *Solubility of the Basic Ammonio-phosphate of Magnesia in pure Water.—a.* Freshly precipitated double salt, after having been perfectly edulcorated with water, was digested with water at about 59° for 24 hours, being frequently shaken. 84·42 grms. of the filtered solution left 0·0047 grm. pyrophosphate of magnesia. *b.* The same precipitate, digested in the same way for 3 times 24 hours. 84·42 grms. of the filtered solution left 0·0043. Average of the two experiments = 0·0045, which corresponds to 0·00552 anhydrous double salt. 1 part therefore dissolves in 15293 parts pure water at the ordinary temperature. The evaporation was effected here, as in the following experiments, in a platinum dish weighed accurately to 0·0001 grm.

A cold saturated solution yielded with ammonia, after standing for a short time, a distinct crystalline precipitate; with phosphate of soda it remained perfectly clear, even after two days; but phosphate of soda and ammonia gave rise to as considerable a precipitate as ammonia alone.

2. *Solubility of the Salt in Water containing Ammonia.—a.* Pure basic ammonio-phosphate of magnesia was dissolved in as little nitric acid as possible, a large quantity of water added, and then an excess of ammonia. After 24 hours the solution was filtered; its temperature was 58°. 84·42 grms. left 0·0015 pyrophosphate of magnesia, corresponding to 0·00184 anhydrous double salt. 1 part of the latter requires therefore 45880 parts of water containing ammonia.

b. Some of the pure double salt was digested with ammoniacal water for 4 weeks, being frequently agitated; the liquid (temp. 58°) was then filtered; 126·63 grms. left 0·0024 $PO^5\,2MgO$, corresponding to 0·00296 double salt. 1 part of the latter requires therefore 42780 parts ammoniacal water. Mean of the two experiments, 44330; consequently, 1 part of magnesia in the form of the double salt dissolves in 120760 parts, and 1 part phosphoric acid in 70000 parts. It is evident therefore that the double salt may be washed for some length of time with water containing ammonia, before 1 milligrm. of magnesia or phosphoric acid is washed away.

3. *Solubility of the Salt in Water containing Chloride of Ammonium.*—Some of the freshly precipitated salt was digested with a cold solution formed of 1 part chloride of ammonium to 5 of water. 18494·5 grms. of the filtered solution left 0·0020 grm. PO^5, 2MgO,

corresponding to 0·00245 double salt; 1 part dissolves therefore in 7548.

4. *Solubility of the Salt in Water containing Chloride of Ammonium and Ammonia.*—Freshly precipitated salt was digested at a mean temperature in a solution consisting of 1 chloride of ammonium to 7 ammoniacal water. 23·1283 grms. solution left 0·0012 pyrophosphate of magnesia, corresponding to 0·00148 double salt; consequently 1 part of the latter requires 15627 parts of an ammoniacal water nearly saturated with chloride of ammonium; and therefore 1 part magnesia (in the form of the double salt) 42600, and 1 phosphoric acid 24700 parts.

It results from the experiments in paragraphs 3 and 4, that the presence of chloride of ammonium increases considerably the solubility of the double salt in pure as well as in ammoniacal water; but it is also evident that the precipitate is nevertheless still sufficiently insoluble, even in an almost saturated solution of chloride of ammonium, ammonia being present, as not to interfere with the accuracy of the method.

5. *Estimation of the Magnesia.*—In order to attain the greatest possible accuracy in the determination of magnesia, care should be taken not to add too large quantities of ammoniacal salts to the liquid, and to wash the precipitate with water containing ammonia. The edulcoration should be continued until a drop leaves not the least residue on platinum foil. Two analyses made with these precautions yielded the following results:—

a. 1·0587 grm. pure anhydrous sulphate of magnesia gave 0·9834 grm. pyrophosphate of magnesia.

b. 0·9672 sulphate of magnesia gave 0·8974 pyrophosphate of magnesia, or in 100 parts of the sulphate of magnesia—

Calculated.	Found.	
	a.	*b.*
34·01	34·06	34·02

6. *Estimation of the Phosphoric Acid.*—For this purpose perfectly pure air-dried crystallized phosphate of soda was employed, and for safety the amount of water determined by ignition with the greatest care. 1·3123 substance left 0·4899 grm. pyrophosphate of soda, or 62·67 per cent. The formula $2NaO, HO, PO^5 + 24aq$ requires 62·71 per cent.

a. 1·9847 grm. of the air-dried crystallized phosphate of soda was dissolved in water and precipitated with sulphate of magnesia, with the addition of the requisite quantity of chloride of ammonium and excess of ammonia. The precipitate, washed completely with ammoniacal water, weighed, after ignition and deduction of ashes for the filter, 0·6336 grm., corresponding to 0·3945328 phosphoric acid. According to this, the phosphoric acid in the crystallized phosphate of soda is, in 100 parts,—

Calculated.	Found.
19·90	19·87

It is evident from this, and from the experiments given in No. 5, that the greatest possible accuracy may be attained by the above method. I can vouch for the coincidence of the found numbers with those calculated not being accidental; it results directly from the methods, which are as good as perfectly free from sources of error.

To convince myself that this mode of determining the phosphoric acid might be employed with the same favourable result in the analysis of the perphosphate of iron and of phosphate of alumina, I dissolved 3·0676 grms. of the same crystalline phosphate of soda in water, added muriatic acid, then perchloride of iron and solution of alum to it, and thus formed a liquid similar to what would have been obtained by dissolving phosphate of iron and phosphate of alumina in muriatic acid. I now added tartaric acid, and finally ammonia, until the whole of the precipitate which at first formed had redissolved, and then precipitated with sulphate of magnesia. The precipitate, filtered after 12 hours, was washed so completely with ammoniacal water, that a drop of what finally passed through left not the least residue on platinum-foil. I mention this purposely, because nevertheless I could not succeed in obtaining a precipitate as white as it ought to have been; it exhibited to the very last a faint tint of yellow, and on ignition the whole mass became slightly blackish. After deducting the ashes of the filter, it weighed 0·9786 grm., corresponding to 0·6181 phosphoric acid = 20·14 per cent.; calculated, 19·91. The 0·23 per cent. excess owe their origin to a trace of carbon and to a small quantity of peroxide of iron; the first separated on dissolving the residue in muriatic acid, the latter was distinctly indicated in the solution by sulphocyanide of potassium.

From what I have above stated respecting the edulcoration, it is evident that the error was not in the mode of execution; we must rather admit that the basic ammonio-phosphate of magnesia retains tenaciously a trace of the double tartrate of iron, from which it cannot be freed absolutely by washing.

Now, although it results from this circumstance that the phosphoric acid cannot be determined by magnesia when iron is present with quite the same accuracy as when it is absent, the above analysis nevertheless proves that results obtained in the above manner are still far more accurate than those by other methods; so that in analyses of ashes and soils (in which phosphate of iron is always present) this process will certainly deserve the preference, being at the same time far more simple.

7. *Composition of the ordinary crystallized Phosphate of Soda.*—Various views prevail respecting the amount of water of this salt. While the numbers found by Graham, Clark and Berzelius, certainly lead to the formula $2NaO\ PO^5 + 25aq = (2NaO, HO, PO^5 + 24aq)$, Malaguti draws from his results the formula $2NaO, PO^5 + 27aq = (2NaO, HO, PO^5 + 26aq)$. From the numbers above-mentioned it is absolutely certain that the first formula is the correct one. I will here arrange together the numbers obtained by the several chemists who have analysed this salt:—

	Calculated.	Fresenius.	Berzelius.	Graham.	Clark.	Malaguti.
2NaO ..	17·39	..	17·67	37·1	37·48	16·71
PO^5	19·90	19·87	20·33			18·80
25Aq....	62·71	62·67	62·00	62·9	62·52	64·25

The phosphate of soda employed by me was obtained in the form of a crystalline powder by agitating during the crystallization. After washing with a little cold water, it was pressed till perfectly dry between blotting-paper, and was then left exposed to the air for half an hour; it had not effloresced in the least.—*Ann. der Chem. und Pharm.*, July 1845.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Observations on the Theory of M. Peligot *and* M. Baudrimont *respecting the Manufacture of Sulphuric Acid. By* Dr. Kœne.

In the 'Comptes Rendus,' vol. xix. No. 9, is a treatise by M. Peligot*, the object of which is to prove,—1st, that in the manufacture of sulphuric acid, the sulphurous acid acts *incessantly* and *exclusively* on the nitric acid, with formation of sulphuric acid and hyponitric acid; 2nd, that the formation of sulphuric acid is quite independent of the presence of the crystals in the lead-chambers.

This investigation has given rise to a dispute as to priority between the above chemist and M. Baudrimont, who likewise supposes that the hydrated nitric acid (*azotate hydrique*) is absolutely requisite for the formation of the sulphuric acid.

Both these chemists therefore agree that the sulphurous acid reduces the nitric acid merely to the state of hyponitric acid.

But from my investigations concerning the nature of the crystals which form in the lead-chambers, it results that the sulphurous acid reduces the hyponitric acid to nitrous acid. This result, which led me to consider the theory of M. de la Provostaye as incorrect, induces me also to show that that of M. Peligot is erroneous.

M. Baudrimont adopts, with the followers of the theory of M. Gaultier de Claubry, that the crystals, or at least an analogous compound, is indispensable to the formation of sulphuric acid; but this theory does not answer to the facts; for, as M. Peligot has proved, sulphurous acid is capable of deoxidizing nitric acid in the presence of a considerable quantity of water. This proves that the compound ($SO^3 NO^3 + SO^3 HO$) is not absolutely requisite, as was hitherto supposed, for the formation of sulphuric acid.

The sulphurous acid acts under these circumstances, deoxidizing precisely like hydrochloric acid, with which it possesses the same property in respect to nitric acid, and in almost the same degree. As long as the latter is not too diluted, the first two convert it into nitrous acid, which is decomposed into nitric oxide and nitric acid, if there is sufficient water present; but in the manufacture of sulphuric acid the quantity of water is seldom large enough for this change to take place, for it is not to the interest of the manufacturer to exclude from action one of the generators of his product, nor to convey more water into his lead-chamber than requisite for the for-

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* See also p. 271 of the present volume of this Journal.

mation of the acid; nor is it more requisite that he should introduce dilute acid into his large chamber at the commencement of the operation; it suffices, if there be a sufficient quantity of aqueous vapour present to prevent the formation both of crystals as well as of nitric oxide. The reaction goes on regularly, and the product only contains traces of nitric acid; but then follows the reaction between sulphurous acid, nitric and hyponitric acid; for the hyponitric acid, which is produced by contact with sulphurous acid, instead of being oxidized and converted into a hydrated acid, forms under these circumstances, on the one hand nitrous acid, and on the other sulphuric acid, as my experiments have shown.

In a leaden chamber in operation, the sulphurous acid therefore reduces the nitric to nitrous acid without the formation of crystals, the quantity of water being too large for the compound ($SO^3 NO^3 + SO^3 HO$) to be produced, and too small for the nitrous acid to be decomposed into nitric oxide and nitric acid.

When the latter case occurs, which happens sometimes under circumstances that must be regarded as accidental, the product is impurified with larger or smaller amounts of nitric acid, from which it is freed by passing sulphurous acid through it. This operation can never fail to succeed, because such an acid contains sufficient water for the nitrous acid to be decomposed into nitric oxide, which escapes, and into nitric acid, which is again destroyed by the influence of the oxidizing agent.

In the opposite case, when the sulphuric acid is too concentrated, the nitrous acid undergoes no further decomposition from the sulphurous acid: nor is it possible, by means of this acid, to free the commercial sulphuric acid at the ordinary temperature from nitric acid, but perfectly well from nitrous acid. The first of these acids is decomposed during the concentration into oxygen and nitrous acid, as I have shown, by allowing hydrochloric acid gas to act on the monohydrated sulphuric acid which had been employed for concentrating commercial nitric acid. No chlorine was disengaged, and thence follows, contrary to the opinion of M. Peligot, that the concentrated sulphuric acid contains neither nitric nor hyponitric acid. Nor can there be any nitric oxide contained in it, this not being perceptibly soluble in this acid; but it may contain nitrous acid, the presence of which may be readily proved, on the one hand by means of hydrochloric acid, and on the other by means of the protosulphate of iron and metallic copper.—Poggendorff's *Annalen*, 1845, No. 6.

PATENTS.

Patent granted to Robert Oxland, Plymouth, Devon, *for Improvements in the Manufacture of Chlorine.*

This invention consists in a method of manufacturing chlorine by the decomposition of hydrochloric acid by atmospheric air. The hydrochloric acid gas and atmospheric air are mixed in the proportion of 1 measure of the former to 2 of the latter; and the mixture is passed through an air-tight furnace, kept at a bright red heat.

The hydrochloric acid is best obtained by decomposing common salt by sulphuric acid in a furnace or retort so heated that the products of combustion do not mix with the acid gas evolved; and the acid gas should be dried (previous to mixing it with the air) by passing it through a vessel filled with pieces of fire-brick, over which a small stream of sulphuric acid is constantly flowing. The requisite supply of atmospheric air is kept up by pumping it into an iron reservoir, furnished with a stop-cock or valve for regulating the discharge of the air. The decomposing furnace, through which the mixture of hydrochloric acid and air is passed, resembles an ordinary reverberatory furnace in form; but it is so constructed as to admit of the fire passing over the arch and under the bed; by which means the furnace is heated without the fire passing into it. The furnace is filled with pieces of porous pumice-stone, and the gas and air enter at the end furthest from the fire, and pass out at the other end through a pipe at the upper part of the furnace. That part of the furnace nearest the fire should be kept at a bright red heat by a fire acting externally, the smoke passing through flues over the furnace into the chimney.

The products resulting from the admission of hydrochloric acid and atmospheric air into the decomposing furnace consist of chlorine associated with undecomposed muriatic acid, and any excess of atmospheric air and nitrogen. This mixture is cooled by passing it through a series of earthenware tubes surrounded by water; after which the hydrochloric acid is effectually separated by passing the mixture through water; and, finally, the chlorine is obtained, and chloride of lime produced, by passing the residuary mixture into the ordinary lime condenser, where the chlorine is absorbed, and the nitrogen and atmospheric air remaining are allowed to pass into the atmosphere.—Sealed Feb. 20, 1845.

Patent granted to William Oxley English, Kingston-upon-Hull, *for Improvements in the distilling of Turpentine and Tar, and rectifying Volatile Spirits and Oils.*

This invention consists, first, in distilling turpentine and tar at a low temperature; and, secondly, in rectifying the spirits of turpentine and tar, and other volatile spirits and essential oils, at a low temperature.

The following is the process employed by the patentee in carrying out his improvements:—The turpentine or tar which is to be distilled is placed in an ordinary retort, having a worm and receiver attached thereto; and the air is exhausted from the retort by an air-pump, applied either to the retort, the worm or the receiver, as may be most convenient. By thus working in vacuum, it will be found that the spirit flows over at a lower temperature than when distilling after the usual method. A similar application of the air-pump to exhaust the air from the apparatus employed in the rectification of spirits and oils is stated to be equally advantageous, and forms the second head of the invention, as above mentioned.—Sealed Nov. 25, 1844.

THE CHEMICAL GAZETTE.

No. LXXIII.—November 1, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Glycerine. By J. Pelouze.

In a paper published in 1836, I endeavoured to deduce the composition of glycerine from the analysis of the sulpho-glycerates, a new class of salts which I had obtained by saturating with bases the product resulting from the action of sulphuric acid on glycerine. My analyses related principally to the sulpho-glycerate of lime, for which I had found the formula $CaO, (SO^3)^2, C^6 H^7 O^5$. This salt, on decomposition by an excess of lime, regenerated perfectly pure glycerine; and as this was composed in its free state of $C^8 H^8 O^6$, I assigned the formula $C^6 H^7 O^5, HO$ to the free glycerine, and the formula $C^6 H^7 O^5$ to glyceric æther, or the anhydrous glycerine, such as it may be supposed to exist in the sulpho-glycerates—salts which are in every respect analogous to the sulpho-vinates.

The ingenious views of M. Chevreul upon the constitution of the neutral fatty bodies, which he had proposed to assimilate to the compound æthers, received in some measure a fresh confirmation from the existence of sulpho-glyceric acid.

It was allowable to consider that glyceric æther should have in the neutral fatty bodies the same composition as in the sulpho-glycerates, and for a long time this opinion was held by the various chemists who have attended to this important question. Nevertheless the highly complicated molecule of the fatty bodies left some doubt as to the true formula of anhydrous glycerine, which has increased since the researches of Dr. Stenhouse on palm oil. In fact, anhydrous palmatic acid, $C^{32} H^{34} O^3$, whose composition was deduced by M. Fremy and Dr. Stenhouse from the analysis of the hydrated acid, and a large number of its salts, is combined in palmatine with ½ an equivalent of glycerine from which the elements of 3 equivalents of water have been subtracted, being represented by the formula $C^{32} H^{31} O^3 + \frac{C^6 H^7 O^5 - H^3 O^3}{2}$. According to Dr. Playfair, myristine presents an analogous composition. If these latter facts were exact, it would result that glycerine does not exhibit the same composition in the neutral fatty bodies as in the sulpho-glycerates, or we must admit that it has not been correctly analysed in the latter compounds. It is especially to verify my former results that I have undertaken the present investigation; I have confirmed their accuracy both on the subjects of my former experiments, as well as by extending them to a new series of compounds.

Perfectly colourless glycerine, leaving an ash too slight to be appreciated, was dried in an oil-bath at a temperature between 248° and 266°. It was burnt with oxide of copper with the following results:—

	Found.			Equiv.		Calculated.
Carbon ..	38·95	39·00	39·15	6	450	39·1
Hydrogen	8·72	8·80	8·75	8	100	8·6
Oxygen ..	52·33	52·11	52·10	6	600	58·3

The formula $C^6 H^8 O^6$ agrees therefore as well as possible with the experiments, and I have no doubt that the composition of free glycerine is such as I found it to be ten years ago.

With respect to the glycerine in the vinic salts, the following are the results to which I have come:—1·00 grm. of sulpho-glycerate of lime, dried at 248°, left a white residue, which was ignited with distilled sulphuric acid, and the weight of which amounted to 0·353; the formula $CaO(SO^3)^2, C^6 H^7 O^5$ requires 0·355 for the same quantity of salt. These two numbers agree therefore perfectly. As the preparation of the sulpho-glycerate of lime is very long and difficult, and as moreover I had every reason to consider the composition which I had given as perfectly correct, I endeavoured to obtain another class of glyceric salts by substituting phosphoric for the sulphuric acid.

When glycerine is mixed with solid phosphoric acid (anhydrous or hydrated), the temperature of the mixture rapidly rises beyond 212°, provided the operation be made on about 30 grms. of material. The mixture contains a large proportion of a new substance, which I shall call *phospho-glyceric acid*; after having diluted it with water, it is neutralized with carbonate of barytes, and finally with barytic water. The liquid contains a large quantity of the base in the state of phospho-glycerate; the precipitate consists of phosphate of barytes. The liquid, decomposed accurately with sulphuric acid, yields the phospho-glyceric acid. This acid combines with the several bases, forming with nearly all of them salts soluble in water, and insoluble or very sparingly soluble in alcohol. Like many other acids, it can only be concentrated to a certain degree, beyond which it is decomposed even in the cold.

It forms with lime and barytes salts which are precipitated by alcohol in a state of purity. That of lime is very sparingly soluble at 212°, but very soluble, on the contrary, in the cold, so that it is almost wholly deposited from its aqueous solution when this is boiled; in this respect it behaves like the phospho-vinate of barytes. It is not altered by being heated to 320° or 338°, but preserves its whiteness and its solubility. Dried at this temperature and calcined in a platinum crucible, taking care to destroy the last traces of carbon by pure nitric acid, it leaves a residue of phosphate of lime ($2CaO, PhO^5$), the mean weight of which amounted to 60·1 per cent. of that of the dry salt. [The results found were 60·3, 60·1 60·5, 59·85, 59·80 per cent.] Burned with chromate of lead, it yielded—

Carbon	16·95	17·05
Hydrogen	3·40	3·45

These numbers lead to the formula $C^6 H^7 O^5$, PhO^5, 2CaO, which gives—

$2CaO\ PhO^5$	1600·0	60·66
C^6	450·0	17·06
H^7	87·5	3·32
O^5	500·0	18·96
	2637·5	100·00

On the other hand, 1·916 grm. sulpho-glycerate of barytes, after being dried at about 302°, left 1·246 phosphate (2BaO, PhO^5) or 73 per cent., being identical with that which the formula 2BaO, PhO^5, $C^6 H^7 O^5$ requires. Lastly, the phospho-glycerate of lead, dried at 248°, left on calcination 77·5 phosphate of lead; theory requires 78·0 per cent.; all the analyses therefore detailed in this paper lead to the formula $C^6 H^7 O^5$, HO for the free glycerine, and show that it loses like alcohol in its vinic salts 1 equiv. water.

A circumstance which will greatly interest chemists and physiologists, and which will impart a high degree of importance to phospho-glyceric acid, is the existence of this acid in the animal kingdom.

M. Gobley, in endeavouring to ascertain in what form the phosphorus exists in the yolk of egg, found, after a long and laborious investigation, that it is in the state of phospho-glyceric acid combined partly with soda and partly with ammonia. He obtained from the yolk of egg this acid in a state of purity by means of simple solvents; he has analysed it most carefully, and his numbers agree completely with those which I have myself found for the acid prepared artificially.

The egg, as is well known, contains besides phosphorus a somewhat considerable proportion of sulphur. It would be curious to ascertain whether a certain quantity of this element does not exist in it in a state of sulpho-glyceric acid.—*Comptes Rendus,* Sept. 29, 1845.

On the Chemical Composition of the Yolk of Egg. By M. GOBLEY.

When the yolk of egg, deprived of the greater part of the water it contains, is treated with boiling æther or alcohol, there is obtained by the evaporation of the liquid,—1st, a fixed oil, which is known by the name of *oil of egg*; 2nd, a substance of soft and viscous consistence, which I shall call *viscous matter.* It is in this matter that the oleic, margaric and phospho-glyceric acids occur, to which I shall now draw attention.

The viscous matter has no action upon litmus; it leaves on calcination an acid ash, which cannot be incinerated on account of the phosphoric acid which surrounds it; it mixes with water, forming a kind of emulsion which does not become acid by long-continued boiling. It dissolves in æther and boiling alcohol of 88°, from which the greater part subsides on cooling.

It is essentially formed of oleic, margaric and phospho-glyceric acids, which are combined with ammonia and form a true soap; this soap is, as it were, enveloped by a nitrogenous organic substance, which for a long time prevented me from ascertaining its nature. It is undoubtedly with ammonia that the acids are combined, for the viscous matter, triturated with solution of potash, disengages a very perceptible quantity of ammonia; moreover, 4 grms. of the substance, dried at 248°, left on calcination scarcely 0·40 residue, which contained no perceptible traces of potash or of soda.

The presence of a soap with ammonia as base in the yolk of egg, is deserving of the attention of physiologists, for hitherto the oleic and margaric acids have only been found in combination with soda in the human body.

The oleic and margaric acids are separated from the viscous matter by agitating it with dilute hydrochloric acid in a flask and heating in the water-bath. Three layers are formed,—an upper oily one, an under aqueous and slightly coloured one, and one intermediate, which is very thin and formed by small grayish pellicles.

The oily layer may be separated by means of æther, and the gray pellicles by filtration. The fatty matter consists of oleic acid, margaric acid, and of a small quantity of oil of egg which had remained mixed with the viscous matter, and from which the fatty acids may be separated by boiling alcohol. The fatty acids were purified in the usual manner; the margaric acid, treated by Gusserow's process, melted at 140°, and presented a similar composition to that found by M. Varrentrapp for the same acid purified by the same process; the oleic acid presented all the properties and the composition assigned by M. Chevreul to this body.

The gray matter is formed of the fragments of the net-work which serves to connect the viscous matter; it contains nitrogen and sulphur, dissolves in hydrochloric acid, imparting to it a blue or violet colour, and appears to differ from vitelline.

The liquid contains no phosphoric acid, but a *phosphated body*, which may be separated by means of neutral acetate of lead; the precipitate which forms under this circumstance is a combination of the phosphated substance with oxide of lead. This compound may also be obtained by treating the viscous matter with hot solution of potash, decomposing by acetic acid, separating the fatty acids and the azotized matter by filtration, and then adding neutral acetate of lead to the liquid.

To obtain the phosphated acid, the lead precipitate is decomposed after edulcoration by sulphuretted hydrogen; the filtered liquid always contains, besides the phosphatic substance, a small quantity of acid phosphate of lime, derived from the phosphate of lime contained in the viscous matter. The two substances are separated by means of lime-water, which is added to complete saturation. After separating the phosphate of lime by filtration, a liquid is obtained which contains only the phosphatic acid combined with lime.

The lime may be separated by means of oxalic acid, and the phosphatic acid obtained by evaporating the liquid. It may be concentrated to a certain degree, beyond which it contains phosphoric acid, which arises from the decomposition of the phosphatic matter. By concentrating the liquid *in vacuo* over lime, the acid may be procured in the form of a thick, viscous, uncrystallizable liquid, of a strongly acid taste, very soluble in water and alcohol. It contains no phosphoric acid, and leaves an acid cinder on calcination. It has considerable analogy with the phosphovinic acid; like it, when diluted with several times its volume of water, it may be boiled for a long time without undergoing decomposition, but it is decomposed when at its maximum of concentration. It contains no nitrogen. The acid was not analysed direct, but its composition deduced from its combination with lime.

The *lime salt* is obtained by evaporating its solution; it is one of that small class of salts which are more soluble in cold than in boiling water. Separated from the boiling liquid, it forms beautiful white micaceous laminæ; it has no odour; its taste is slightly acrid; it is not decomposed at a temperature of 302°. When calcined, it becomes black; and by continuing the heat and assisting the decomposition by means of nitric acid, a white residue of phosphate of lime is obtained. Alcohol does not dissolve it; on the contrary, it precipitates it from its aqueous solution.

The composition of this salt is very remarkable; the coincidence of the numbers obtained by determining the carbon and hydrogen by means of chromate of lead, and by the capacity of saturation of the lime salt, checked by the conversion of the phosphate of lime derived from the calcination of the salt into the bone earth phosphate of lime, leads me to consider the phosphatic acid combined with the lime as containing the elements of glycerine and of phosphoric acid. The decomposition of this acid by lime into glycerine and phosphoric acid places this beyond all doubt, and justifies my considering the phosphatic acid of the yolk of egg as phospho-glyceric acid. Moreover, my analyses agree perfectly with those of the phospho-glycerate of lime prepared artificially by M. Pelouze.

The presence of oleic and margaric acids in the yolk of egg is not in the least surprising, since these bodies have been found in almost all parts of the animal organization, in the brain, the blood, and in the bile, but not so with the phospho-glyceric acid.

How can this be explained without admitting that the phosphoric acid present deprives a portion of the margarine and oleine of all the glycerine to form phospho-glyceric acid and oleic and margaric acids? for the quantity of glycerine in combination with the phosphoric acid appears to be that which the fatty acids require to form neutral fats. This fact supports the opinion advanced respecting the constitution of margarine and oleine, which are considered as margarate and oleate of glycerine.

What part is the phospho-glyceric acid destined to act in the constitution of animals? Does it enter into the animal organization without experiencing decomposition, or is it decomposed? With a view to solve this question, I have undertaken some experiments, the results of which I shall make known as soon as they are terminated. —*Comptes Rendus*, Sept. 29, 1845.

On the Composition of the Oil of Amber. By Dr. O. Dœpping.

Among the products of distillation of amber in the preparation of succinic acid, we find empyreumatic oils and resins in great number; and again among the former, products which must be referred to the large group of neutral or indifferent bodies. When the brownish-black, more or less thick fluid masses which collect in the recipient in the distillation of succinic acid are submitted to repeated rectification, there is finally obtained a very fluid, faintly-yellow coloured oil, of a penetrating, peculiarly disagreeable odour and slightly acid reaction, which dissolves in strong spirit, æther, oil of turpentine and the fat oils, may be set fire to by a lighted body, and burns with a very smoky flame.

To free this oil as much as possible from the intermixed electro-positive and electro-negative substances, the author treated it with caustic potash and dilute sulphuric acid. The oil separated from the acid was left for a long time in contact with fused potash, being frequently shaken, and finally the decanted oil left for several weeks with chloride of calcium; the potash had removed from the oil a small quantity of a brownish-red substance, which, after neutralization with an acid, separated on the surface of the liquid, had a thickish consistence, and possessed very distinctly the odour of creosote. The quantity of this substance was too small to admit of further examination. The sulphuric acid had removed nothing from the oil. The oil thus purified was submitted to distillation; it began to boil at 284° F.; however, the boiling-point was not constant, but gradually rose to 338°, and the residue in the retort had acquired a darker colour and thicker consistence.

The oil thus obtained disengaged a small quantity of gas when brought into contact with potassium, and the surface of the metal became dull. Since it is highly probable that the cause of this inconsiderable disengagement of gas was owing to a small amount of water which had not been removed from the oil by the above treatment, it was left in contact with small pieces of burnt lime for eight days, being frequently shaken. The oil was again rectified, when it began to boil at 338°, and gradually rose to 374°. There again remained in the retort a dark-coloured thick residue.

The oil which passed over between 356° and 374° yielded on analysis the following results:—

Carbon*	88·34	88·45
Hydrogen	11·55	11·51
	99·89	99·96

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* C = 75·85.

The analyses were made with oxide of copper, over which a current of oxygen was passed during the combustion.

In this state of purity the oil possessed the following properties:—Potassium remained in it long before it changed; but subsequently the metallic surface became coated with a yellow resinous mass, which however did not appear to be formed by the direct influence of the elements of the oil on the metal; for when the potassium was carefully freed under the liquid from the adherent mass, it still exhibited its metallic surface perfect; in contact with atmospheric air, it retains for weeks its colourless and fluid consistence; it does not absorb pure oxygen gas, at least not the slightest diminution of space was perceptible when it was confined with this gas in a tube closed by mercury; it dissolves readily in æther, with more difficulty in alcohol of 0·863 spec. grav.; it has neither an acid nor alkaline reaction; it does not dissolve in hydrochloric and cold dilute nitric acid, but is coloured yellowish-brown after some time by the latter; dilute nitric acid acts on it with the assistance of heat, giving off nitrous acid, and converts it into a yellow resinous mass (so-called artificial musk), which at last dissolves entirely when boiled for some time with the acid; concentrated nitric acid acts already in the cold violently upon the oil, and exhibits a similar behaviour towards it on the application of heat; it is insoluble in caustic ammonia and potash, both dilute and concentrated, and on the application of heat; sulphur is abundantly dissolved by it with the assistance of heat, and crystallizes from it on cooling; amber is but very sparingly dissolved by it, even with the assistance of heat; caoutchouc is dissolved in large quantity by the oil. Its specific gravity at 50° was found to be 0·9928.

If it be correct to conclude, from the variation in the boiling-point of a liquid, that it is a mixture of several having different boiling-points, it results from what has been above stated that the crude amber oil is a mixture of heterogeneous bodies, and that the purified oil includes a series of carburetted hydrogens, characterized by an equal relative number of their elements and different boiling-points. The admission of the above principle does not appear to hold good in all cases; and the circumstance that liquids possess a variable boiling-point, must frequently be ascribed to a series of metamorphoses which they undergo under the influence of heat, their atoms being extremely mobile. The possibility of this explanation is perhaps supported by the fact, that a fixed quantity of a liquid whose boiling-point gradually rises, which has been distilled over within certain limits, must in a second distillation be heated far above the highest observed temperature in order to redistil it, and then most frequently very altered residues are left in the retort.

The composition of oil of amber in 100 parts, resulting from the above analysis, agrees so closely with that of oil of turpentine (C 88·46 and H 11·54 per cent.), that the differences are within the error of observation; and since several of the above-mentioned properties of the amber oil likewise belong to the latter, the author is inclined to regard it as isomeric with the oil of turpentine.

By passing muriatic gas into the amber oil, it was not decomposed in a similar manner to the oil of turpentine; it absorbed but a small quantity of the gas, and after the operation had been continued for a length of time, became of a dark colour, which again disappeared by agitation with water.

Since Pelletier and Walter only purified the oils which they submitted to analysis, and which boiled at different temperatures, by rectification, their results cannot be well compared with the preceding. Nevertheless, the difference in the results of the analyses is very slight; and as this principally relates to the carbon, should perhaps only be ascribed to an admixture of their oils with a small quantity of a compound richer in carbon, removable by potash. Differing far more widely from the above results is the analysis of the oil of amber made by Elsner*. The oil examined was left in contact with chloride of calcium and then rectified; the analysis gave 84·00 per cent. C., 8·60 H., and 7·40 O.

According to this, Elsner's oil contains a considerable amount of oxygen, which is entirely wanting in those analysed by Pelletier and Walter and the author. Since such a difference widely exceeds the limits of probable error of observation, it must be supposed that some error occurred in the analyses, or that under certain circumstances products make their appearance in the distillation of amber, which contain oxygen, which seems to be most probable.

Action of concentrated Sulphuric Acid on Oil of Amber.—When several times the volume of concentrated sulphuric acid is gradually added to rectified oil of amber which has been purified with potash, so that it does not become heated, and the mass shaken after each addition of acid, it assumes a red colour and tenacious consistence, as described by Elsner, and separates after standing some time into two layers, of which the upper is very fluid and yellow or faintly reddish, the lower thick and of a brownish-red colour. If care has been taken to prevent the mass becoming heated during the mixing, no odour of sulphurous acid is perceptible at first; but if the oil is left for several days in contact, it makes its appearance. The disagreeable penetrating odour of the oil of amber disappears entirely after the treatment with sulphuric acid, and in its stead a peculiar and agreeable one is perceptible. If the oil floating on the tenacious dark mass is removed, and mixed anew with concentrated sulphuric acid, it again becomes coloured red, although only after some time. This reaction may be repeated until the quantity of the supernatant oil becomes so small that it can no longer be separated from the acid. The time requisite for the two substances to act on each other is greater in proportion as the experiment is repeated.

If the oil floating on the acid be removed by means of a pipette, and agitated with water for further purification, the white mass separates after some time into two layers, the lowest of which is heavy and turbid, the upper one perfectly clear. The milky fluid appeared under the microscope to be a mixture of drops of oil and water, and

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* Chem. Gaz., vol. i. p. 32.

after evaporation separated into a layer of oil and a subjacent stratum of water. The author however did not succeed in obtaining from it the crystalline body resembling paraffine, which Elsner states he procured.

The oil removed from the milky liquid was left for several weeks with caustic potash, and then with caustic lime, being frequently shaken, and subsequently purified by distillation. The boiling-point of the oil was 374°. The first portion of the oil which distilled over contained some water; it was therefore removed, and a recipient adjusted at 392°. The oil which passed over at this temperature yielded, on combustion with oxide of copper and oxygen, similar results to the former, viz.—

Carbon	88·24	88·32
Hydrogen	12·06	11·98
	100·30	100·30

This oil exhibited in its chemical properties no remarkable difference from that previously obtained; but its physical properties, as odour, specific weight, refracting power, boiling-point, &c., are widely different. It is, however, scarcely worth while to describe them, as they vary according to the temperature at which the oil distilled over. The portion which passed over between 410° and 428° had a yellow colour and the consistence of oil of poppies, and contained—

Carbon	88·69	88·84
Hydrogen	11·64	11·88
	100·30	100·72

The odour of this oil resembled very much that which had passed over at 392°; the portions subsequently obtained by interrupted distillation gradually lost their odour, and a yellow mass, which solidified on cooling and possessed no smell, was left in the retort.

When the reddish-brown mass formed by the action of sulphuric acid upon oil of amber is treated with hot water, the greater part of the acid is removed; and a thick tarry mass of blackish-brown colour separates on the surface of the liquid, which may be entirely freed from still adhering acid by repeated washing with water. If this thick mass is conveyed into a retort and submitted to distillation, a slightly yellow-coloured very fluid liquid passes over, which soon separates into two layers, the inferior one of which is water, the upper an oil which appears to contain sulphur. The odour of this oil was different from that of the two preceding, but approached nearest to the oil first described with respect to its being extremely penetrating and disagreeable.—*Ann. der Chem. und Pharm.*, liv. p. 602.

On Urinary Deposits. By W. HEINTZ.

Uric acid deposits separate in two forms, one of which appears in distinct crystals; the other subsides from the urine as a very fine amorphous powder, which is dissolved by boiling, but again deposited on cooling, and is usually of a reddish, more rarely a white colour. Although the latter deposit has been much examined, we are still in considerable doubt as to its nature; the usually received view is, either that it consists of uric acid and ammonia, and contains in addition a small quantity of a colouring matter, or that it is amorphous uric acid. Since uric acid, according to Liebig, is soluble in phosphate of soda, it might equally be supposed that a portion of the uric acid would be deposited on cooling, as that the acid phosphate of soda formed should remain in solution, whilst acid urate of soda was deposited. The decision of this question is rendered much more difficult by the ordinarily small quantity of the deposit which is formed; on washing this, the greater part is redissolved; and finally, it cannot be freed from the adhering colouring matter without great difficulty, if at all. In its examination, the author proceeded as follows:—

The fresh urine was immediately filtered, or, when the deposit had already formed, was warmed and filtered hot. The reddish-coloured powder, which subsided on cooling, was filtered and washed until the liquid which passed through ceased to contain any urinary ingredients. The powder thus obtained was treated with potash in a watch-glass whilst still moist. A glass rod, moistened with muriatic acid, and held over it, gave distinct clouds of muriate of ammonia in *every* case, so that the presence of ammonia in these deposits may be regarded as proved. Another portion of the sediment was incinerated. The amount of ash was rather variable, amounting to from 2·98 to 8·02 per cent. This was exhausted with a small quantity of boiling water, the alkaline solution filtered and evaporated to dryness. The residue was heated with a few drops of water, then warmed, and a few drops of muriatic acid added. The author constantly observed an effervescence, although slight;—a proof that the dissolved bases before the combustion of the substances were combined with organic acids. In the residue of the evaporated liquid, soda was distinctly detected by the blowpipe; potash was undoubtedly detected twice by chloride of platinum, although in very small quantity.

That portion of the ash insoluble in water was treated with muriatic acid, in which it dissolved with effervescence, the solution was rendered ammoniacal, and a solution of oxalic acid added to the liquid which had remained clear; this constantly caused a precipitate of oxalate of lime. The liquid filtered from this yielded in one case with phosphate of soda a slight precipitate of ammonio-phosphate of magnesia. Neither muriatic, sulphuric nor phosphoric acid were ever detected in the ash.

From these experiments, it is evident that the above sediment constantly contains the bases ammonia, soda and lime, sometimes also potash and magnesia; these are combined with an organic acid, which is evidently the uric. The organic acid could not be the lactic, because this forms more soluble salts. The quantity of the red colouring matter, even supposing it to be an acid, would not be sufficient to saturate such an amount of base; moreover, the author found the largest quantity of ash (8·02 per cent.) in a deposit which was quite white. The next question is, whether in this deposit the whole of the uric acid is combined with bases, or is partly free. This question cannot be decided by a simple analysis, because we cannot completely free the deposit from the colouring matter.

Becquerel, who with Quevenne considers this urinary deposit as amorphous uric acid, gives the following reasons for so doing:—When the sediment is separated by filtration from the urine, washed several times with water, and finally with alcohol, and treated on an object-glass with muriatic acid, its form is not in the least altered, whilst if it were a urate, uric acid should be separated in crystals. Becquerel has observed this to occur several times, but only partially, and then he says it was mixed with urate of ammonia.

The author however found, that when dried urate of ammonia, which was crystallized in fine needles, was treated under the microscope with dilute muriatic acid, at first no change could be perceived; gradually the needles became somewhat broader, without however the uric acid which separated assuming the ordinary form which it exhibited when it subsided immediately from the liquid. If muriatic acid diluted with alcohol be used instead of that diluted with water, the acid acts still more slowly; the uric acid, however, then subsides in the amorphous form. The sediment from the urine behaves in the same manner, as also the artificially prepared amorphous salt of urate of soda and ammonia. Consequently we can place no value on Becquerel's statement, that this sediment is composed of amorphous uric acid.

The author could not succeed in proving with certainty that the amorphous deposit does not contain any free uric acid as well as urates, but this may be supposed with great probability.

When a urine in which an amorphous deposit has formed is filtered, and a little pure uric acid added to the liquid, which is then warmed, a considerable quantity of it is dissolved, and subsides on cooling in the form of amorphous urate of ammonia.

The question then is, How can it be explained, that when urine is repeatedly boiled with uric acid, some of it is each time dissolved, and on cooling a urate is deposited? If we suppose that the artificial deposit, which has subsided after the first ebullition of the urine with uric acid, has converted the phosphate of soda contained in it almost completely into acid phosphate, this cannot certainly as such yield any amount more of its base to uric acid. But as the urine contains urea, which yields ammonia on its decomposition either at the ordinary temperature or by ebullition, phosphate of soda and ammonia must be formed, which is now capable of again dissolving uric acid. If there were not in the urine a constant source of the formation of this base, the above experiment would be of considerable importance in the decision of this question.

We know that when uric acid is precipitated from a solution of its salts by means of an acid, we constantly obtain crystalline uric acid, however quickly the precipitation occurs. Now, since the deposit from the urine subsides but slowly, we cannot see why the uric acid is here precipitated in an amorphous form. It might be urged, that the urinary colouring matter prevented the crystallization; but we very frequently find crystalline uric acid, which is likewise coloured by the colouring matter, and forms a sediment in the urine. Nay, even in the amorphous sediment we frequently find a few crystals of uric acid. Finally, when the uric acid is separated from the urine, or in favourable circumstances by an acid from the deposit, it falls in a crystalline state, and hence is coloured.

Although it has been sufficiently proved, by what we have stated, that the uric acid does not separate in the amorphous form, we have to inquire why the urate of ammonia, which can likewise be obtained in the crystalline state, does so. As regards the urate of lime, this subsides in a state of purity from water in this form. Dr. Bence Jones has advanced an explanation of this point, which is confirmed for the most part by the experiments of the author. Thus he found that when urate of ammonia is dissolved in water, and treated with a solution of other salts, as acetate or muriate of ammonia, it subsides in an amorphous form. It likewise separates from chloride of sodium in an amorphous form, but is dissolved in larger quantity by it than by the former saline solutions. Bence Jones considers the salt which separates from solution of chloride of sodium as urate of ammonia. The author however found both soda and ammonia in it, and hence at first supposed that the uric acid had formed a double salt of soda and ammonia, a corresponding amount of muriate of ammonia being produced.

To examine this salt more accurately, the author added sulphuric acid to it, heated it to redness, and estimated the residue as sulphate of soda. But the quantity of soda obtained from it varied in five specimens from 12·73 to 14·79 per cent. A salt, which was obtained in the form of fine needles by boiling an ammoniacal solution of common salt with uric acid, and allowing the filtered liquid to cool, yielded only 4·79 per cent. of soda.

To ascertain the true composition of this compound, the author adopted the following method:—A weighed quantity of the salt, which had been dried at 212°, was treated with hot dilute muriatic acid, and the solution evaporated at a moderate heat to a small bulk. After it had cooled, about 5 times its volume of absolute alcohol was added, so as to produce a liquid in which uric acid is completely insoluble, whilst chloride of sodium and ammonium are dissolved by it. The uric acid was filtered, washed with alcohol, dried at 212°, and weighed.

The muriate of ammonia was precipitated from the filtered solution by chloride of platinum, the liquid filtered, evaporated, and heated to low redness, to separate the platinum. The heated mass was then treated with water, the solution evaporated, and the residue heated to redness and weighed. Moreover, the author controlled these analyses by ascertaining the increase in weight of the salt evaporated with the water acidulated with muriatic acid, and by a nitrogen analysis. No ammonia was evolved on drying at 212°. The analyses yielded—

	I.	II.	III.	IV.		
Uric acid ..	81·20	81·82	81·75	81·81	2	80·73
Ammonia ..	0·09	0·95	0·60	1·41	1	14·96
Soda	14·92	14·27	14·41	12·64		
Water	3·79	2·96	3·24	4·14	1	4·31

The above-mentioned salt, which crystallized in needles, and had yielded 4·81 per cent. of soda, consisted of—

Uric acid..........................	88·35
Ammonia	6·31
Soda	4·74
Water	0·60

Consequently this composition cannot be expressed by a simple formula, since it contains much more uric acid than the quantity of bases obtained is sufficient to combine with. It must however be remarked that almost all the water escapes from this salt at 212°, whilst in the above-mentioned compound 1 atom remains. There is however no doubt, from the analysis of this salt, that its composition is different from that of the above-mentioned soda salt. Should it be required therefore to prepare the amorphous salt again, uric acid must not be heated with an ammoniacal solution of chloride of sodium, but urate of ammonia, with the saline solution. The stronger the solution of chloride of sodium used, the more soda is contained in the compound which separates. The author also succeeded in procuring this compound by digesting a solution of common salt, which had been triturated with finely-powdered uric acid, for several days in the cold with dilute solution of ammonia. The whole of the uric acid is thus converted into an amorphous powder, and when the amount of liquid is increased, contains the uric acid, soda, ammonia and water in somewhat larger globules. This constantly happens in the urine; consequently both salts must separate from it in the above forms.

The salt obtained by digestion in the cold contained—

	I.	II.
Uric acid	81·43	80·73
Ammonia	0·35	
Soda	13·79	14·96
Water.......................	4·43	4·31

Golding Bird dissolved phosphate of soda in water, added uric acid to the solution, and dissolved it in it by the application of heat. After filtering, a salt separated on cooling consisting of prisms united into stellæ and bundles, which were not soluble in boiling water, and left a residue on incineration. The author's experiments yielded the same results; the crystals were not altered in form by muriatic acid, but became slightly opake; some of them disappeared without any crystals of chloride being formed. His results, on analysing the ash of this compound, were entirely different. According to Golding Bird, the residue obtained by digesting the crystals with muriatic acid and incinerating in a platinum spoon, consisted of phosphate of soda. The author, however, on incineration of the pure well-washed salt, obtained a white fused residue, which dissolved in water, effervesced with acids, and at the same time evolved the odour which is set free when a cyanate is treated with an acid. It contained no phosphoric acid; consequently the salt was not a compound of uric acid with phosphate of soda, as Golding Bird supposes, but a soda salt of this acid.

When the author heated the liquid filtered from the above compound several times with uric acid, and filtered it whilst hot, a slight deposit subsided, which when washed and incinerated likewise left an ash containing soda, but in small quantity. When this was repeated with the liquid, which had been again filtered, tolerably pure uric acid was at last obtained, which left barely a trace of a fixed salt when incinerated. The form of the crystals was most similar to that in which uric acid usually occurs in the urine.

The phosphate of soda and ammonia acts in the same way as the phosphate of soda, as stated by Golding Bird, except that the deposit first formed consists of urate of ammonia, with but little urate of soda. Finally, however, almost pure uric acid subsides. Hence phosphate of soda and of soda and ammonia are partly decomposed by uric acid, so that on cooling the base remains in combination with the uric acid, which separates; but when a certain amount of the base has separated from the solution, on the application of heat the uric acid dissolves, and on cooling again subsides as free uric acid; consequently a deposit of pure crystallized uric acid must occur in the urine when it contains very acid phosphates, of course supposing that sufficient of the acid exists in the urine. In fact, the urine is always very strongly acid when it contains a deposit of crystallized uric acid. The less acid the phosphate dissolved in it, so much the more base will the uric acid which subsides contain; until at last the deposit continuing to crystallize when the proportion is 2 equiv. of base to 1 phosphoric acid, contains the largest quantity of base.

Since a urine, as we have stated above, which has deposited the amorphous sediment, when warmed with uric acid and then filtered, can deposit a similar sediment, which contains considerable amounts of fixed bases, it is evident that the amorphous deposit must be formed in the urine when more than 2 equiv. of base are combined in it with 1 equiv. of phosphoric acid. In fact, an experiment showed that when a solution of phosphate of soda was boiled for some time with urate of ammonia, and the liquid, which was then neutral or slightly alkaline, was filtered, after some time a deposit was formed, which was completely amorphous: it however adhered to the bottom of the vessel, and appeared under the microscope as consisting of tolerably large globules. This salt evidently corresponds to the amorphous urinary sediment which we often find in urine, particularly when ammoniacal. Another mode of formation of this salt may still be given. Thus, if crystals of uric acid have subsided from an acid urine, and if this urine speedily becomes alkaline from the rapid decomposition of the urea, the crystals are gradually formed in the above globules. They may also be artificially produced, by rendering the urine, in which crystals of uric acid have been deposited, slightly ammoniacal.

It has been stated above, that when pure uric acid is treated with solution of chloride of sodium and a little ammonia, an amorphous salt, in smaller or larger globules, is formed, which has exactly the same composition as that which is formed when urate of ammonia is dissolved in a similar solution of chloride of sodium. Hence it appears that the amorphous deposit occurring in the urine, which likewise forms large globules, consists of an admixture of urate of ammonia and urate of soda. The author endeavoured to purify the deposit which occurs in the urine by adding to it a small quantity of acid (by which it is not dissolved except after a considerable time, whilst the phosphates mixed with it are immediately dissolved), and then, after the deposit has subsided, pouring off the clear fluid, and rapidly filtering and washing. In most cases the filtration was prevented by the mucus, so that the deposit had time to dissolve completely; twice only could it be purified in this way. It contained a large quantity of ammonia, and gave on incineration 1·75 to 1·72 per cent. of ash, which contained a little phosphate of lime as well as soda. As the finely-pulverulent deposit forms in acid urine only, it appears allowable to suppose, that for this such a degree of saturation of the phosphoric acid occurring in the urine is necessary, that more than 2 but less than 3 atoms of base are combined with it, whereby the acid reaction can be readily explained by means of the uric acid dissolved in it. The author endeavoured to procure such a fluid, by dissolving uric acid and urate of ammonia at the same time in phosphate of soda, or by adding a very small quantity of muriatic acid to the mixture of the urate of ammonia with a solution of this salt, and filtering the warm liquid. In these cases, however, large globules mixed with uric acid were constantly formed. When chloride of sodium was now added to the liquid, the author frequently obtained a powder exactly similar to the amorphous sediment, and which always adhered somewhat firmly to the sides of the vessel, as we frequently find in urinary deposits.

The common occurrence of uric acid and urates in the urine is explained from the fact, that crystals and an amorphous powder frequently subside together, as in the above case. This may occur when but little more than 2 equiv. of base are combined with 1 of acid. However, urine, which at first is strongly acid, and deposits uric acid, may be so soon neutralized by the decomposition of the urea, that the amorphous deposit is formed.

The author only obtained the amorphous precipitate with certainty when he added a drop of very dilute acid to the globular deposit. As we know, many urines behave in the same manner, from which no deposit spontaneously subsides. In this case the acid added extracts a portion of the base from the phosphate of soda, so that it cannot dissolve any more uric acid; but this, if too much acid be not added, subsides in the form of urate.

When urate of ammonia was dissolved in a solution of chloride of sodium and phosphate of soda, to which a drop of a dilute solution of chloride of calcium had been added, the filtered, slightly acid liquid on cooling constantly deposited an extremely fine amorphous powder, which readily dissolved when heated, but on cooling subsided in the same form, and which contained lime as well as ammonia and soda. The above-mentioned pulverulent urinary deposit has the same properties and is composed of the same ingredients; and the cause of its separation as a fine amorphous powder is sufficietnly explained by this experiment. It depends upon the simultaneous precipitation of these three salts; the lime salt always separates in the form of an amorphous powder; the ammonia and soda salt do so frequently when chloride of sodium is present.—Liebig's *Annalen.*

On the Milk of the Carnivora. By M. DUMAS.

The author, in analysing milk, recommends its evaporation under the air-pump over sulphuric acid, as when evaporated in the salt water-bath with free exposure to the air, the extractive matters become coloured. When dried, it is treated with boiling æther until the fatty matter is removed; the æthereal solution is to be evaporated in a counterpoised capsule with a gilt margin, to prevent the fatty matter from ascending; this yields the proportion of fat. The residue, treated with boiling water acidified with a few drops of acetic acid, yields the extractive matter, sugar when present, and either the whole or a portion of the salts; the proportion of these substances may be ascertained by evaporating the aqueous solution to dryness. When the sugar is abundant, it crystallizes in the midst of the gummy matter, which is soluble in water; and it may be separated by pressure between folds of blotting-paper, and subsequent moistening with water. When it is but small in quantity, it is better isolated by treating the gummy extract with a small quantity of cold alcohol, and exhausting the residue with water, so as to cause it to crystallize after the separation of the earthy phosphates; however, by proceeding in this manner, the alcohol always dissolves a small quantity of sugar. The residue of the treatment with æther and acidulated water is the caseine, which frequently contains some insoluble salts.

If we require merely to ascertain the presence or absence of the sugar, we need only coagulate the boiling milk with a few drops of acetic acid, and test the solution for it, after filtration and evaporation nearly to dryness; the extract, which continues for some time in a gummy state, in general ultimately terminates by yielding crystals; this evaporation is best performed *in vacuo.*

M. Dumas found no sugar in the milk of a dog which had been fed for 15 days exclusively upon horse-flesh, nor could a trace of butyric acid be detected in it. In another, fed for the same time, and on bread soaked in fat broth, it contained sugar. He also found the caseine became diminished in quantity when a diet of bread succeeded a diet of meat; and the sugar, which could not be detected when the food contained no starch, was distinctly present when starch predominated in the food. In the milk of another dog, fed for 6 days on bread, no sugar could be detected. This M. Dumas considered as probably arising either from the too short continuance of the diet, or from the sugar being mixed with some product preventing its crystallization. When the same animal was fed on meat for 15 days, sugar was detected in the milk; the animal had during this period eaten some hay, which was detected in its excrements; when subsequently fed on meat for 15 days, and prevented from access to foreign substances, the milk contained no sugar. In a fourth dog, fed upon meat, no sugar was present. In a fifth, fed upon bread, it was detected abundantly.

The author found the caseine in dog's milk identical in composition with that in the milk of herbivorous animals; but the former is coagulated by heat, unless the milk be previously diluted with water.

M. Dumas believes that the globules in milk are surrounded by a caseous coating; he found that, if milk be shaken with pure æther, the two liquids, which are at first mixed, separate by repose, and the milk preserves its ordinary appearance, whilst the æther dissolves scarcely anything. If, however, acetic acid be added to the milk, and this is then boiled, the whole of the butter may be removed by subsequent agitation with æther; the milk is then no longer opalescent. Moreover, if the milk be saturated with chloride of sodium, when filtered, we obtain a perfectly limpid serum containing the soluble caseine, the sugar and salts; the globules remain on the filter. No amount of washing with salt water will remove the whole of the caseous matter mixed with the butter of the globules.—*Comptes Rendus*, Sept. 1845.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Experiments on the Employment of the Ammonio-Phosphate of Magnesia as Manure. *By* M. BOUSSINGAULT.

THE numerous analyses which I had occasion to make in my researches on the rotation of crops, have exhibited a remarkable relation in the association of several of the elements which enter into the constitution of plants. Thus magnesia, an earth which is generally believed to be so injurious to vegetation, is constantly met with in the ashes of plants, and its proportion is always in a certain relation to that of the phosphoric acid; and we are thus forced to admit that the mineral constituents of wheat, maize, and of the *Leguminosæ* very frequently contain phosphate of magnesia.

Again, on examining with attention the aggregate composition of an alimentary vegetable substance, an evident relation is perceived between the nitrogen and the phosphoric acid, which appears to indicate that in the vegetable organization the phosphates belong more particularly to the nutritive azotized principles, and that they follow them even into the organism of those animals which assimilate them. These considerations, upon which I have already insisted in my 'Economie Rurale,' have induced me to make some experiments on the value of the ammonio-phosphate of magnesia as a manure.

In fact, this salt contains the elements which appear the most necessary to the development of plants—the phosphoric acid, which in the state of phosphate forms part of all seeds; the magnesia, which occurs nearly always in the ashes; and the ammonia, which contributes with the nitrogen of the atmosphere to the production of the azotized substances. Moreover, the ammonio-phosphate of magnesia possesses one of the properties peculiar to gypsum, and which renders its employment free from fear of injury; it is its very sparing solubility. A sparingly soluble salt which is naturally useful, cannot become injurious by its proportion, because the water which must be absorbed by the roots never takes up but a very minute quantity.

On the 1st of May I placed some arable soil in several stone vessels, each of which held 15 cubic centimetres. These vessels were divided into two series; into the first I added to the soil of each vessel 16 grms. of ammonio-phosphate of magnesia and an already germinated seed of maize. All the plants were exposed in the open field; and when the dryness of the season required, they were watered with the same volume of water.

In the 15 days which followed their appearance above-ground, all the plants presented the same aspect and the same strength; but from the 25th day a difference became perceptible, which was constantly preserved from that period.

On the 25th of July, the plants of the first series, those which had been manured with phosphate, had attained twice the height and a diameter of stem thrice that of the maize grown in the normal soil. On the 25th of August, these relations were no longer the same; the maize of the first series had acquired once and a half the height and twice the diameter of the maize of the second series. All the plants flowered and perfected their fruit at the same time; those which had been developed under the influence of the double salt bore 2 complete ears and 1 abortive, the others 1 complete ear and 1 abortive. I may add, that the maize cultivated in the open ground generally occurred this year in the latter condition. The grain of the first plants weighed $2\frac{1}{4}$, that of the second plants being 1.

I attach generally but little importance to agricultural experiments made on a small scale; however, when it is a question of a new manure, I am accustomed to test it first, as I have done in the present case, before proceeding on a larger scale; nor should I have communicated the present results if they had not been so remarkably decided. I have already experimented, both on a small and on a large scale, upon many manures; but I have never yet obtained such striking differential effects.

Next year I propose to make experiments on a large scale (in the open ground), the only ones which are definitively capable of furnishing œconomic data. For this purpose I have entered into an agreement with M. Schattenmann, who directs the manufacture of chemical products at Bouxwiller. In the manufacture of bone-glue, a very considerable quantity of phosphate of lime, already dissolved in hydrochloric acid, is obtained, and from which consequently it is easy to isolate the phosphoric acid. When the acid is extracted, the preparation of the double salt no longer presents any serious difficulties in an establishment in which ammoniacal salts are prepared, and which is moreover situated in the neighbourhood of very considerable beds of dolomite. If, moreover, as I am very much inclined to think, the double phosphate presents a real advantage over the other ammoniacal salts as manure, it will be very easy to convert the guano into ammonio-phosphate of magnesia, by introducing magnesia, one of the most widely distributed substances on the surface of the globe.—*Comptes Rendus*, Sept. 29, 1845.

REVIEWS.

On the Analysis of the Blood and Urine in Health and Disease, and on the Treatment of Urinary Diseases. By G. O. Rees, M.D., F.R.S., F.G.S., &c.

We at all times hail with pleasure the appearance of any works tending to simplify the study or application of chemistry, for, when properly executed, they cannot fail to render this science more extensively useful, interesting and important. The work before us, and which appears especially intended for the medical profession, has for its object the exhibition of "a concise view of those plans of analysis which may be performed simply, usefully, and at a small expense, requiring for their execution care and patience rather than skill and perfection in manipulation." Such a work cannot fail to be of great value to those who are engaged in active practice, and who have neither time nor opportunities for studying the larger and more comprehensive treatises. We need not urge the importance of an accurate knowledge of the exact condition of the animal fluids, either in health, to enable us to ascertain at the earliest period the deviations from their normal condition, or in disease to enable us to treat them on sound principles. Dr. Rees's work fully carries out its original design, and will be found most materially to assist in the fulfilment of these conditions. With regard to the field of original investigation, we do not think this work will much assist us. A more minute detail of the properties of the various components of the animal fluids is requisite, but this is not its object. We also object to it, in this light, as tending to confine our experiments to proximate rather than ultimate analysis; and all those who have devoted much time to these investigations must have observed how little light is frequently thrown by the former compared with the latter.

In comparing the present edition with the first, we certainly feel somewhat disappointed that more new matter has not been added; moreover, some views therein detailed, and which have been completely disproved since, are retained unaltered. Thus, among the constituents of the blood, no allusion is made to the oxides of proteine; in the detection of bile no mention is made of Pettenkofer's test, which is certainly of great value; and xanthic oxide is still considered as a doubtful substance *sui generis*. We might enumerate other such omissions and rather antique notions. A plate containing figures of some of the components of the urine is added, but it cannot be praised; for although well-executed, the forms represented are not those most commonly occurring, nor are many detailed with sufficient accuracy to render them of value. No figures of either the oxalate or nitrate of urea are given; this is rather a grave omission; and we differ from the opinion, that in treating the blood in the ordinary way for the detection of urea, after the addition of nitric acid and repose, "if crystals exist at all, they must be nitrate of urea, since no principle of the blood that can possibly exist in the (last) tested fluid possesses the property of becoming less soluble by the addition of nitric acid." A different statement is made by Simon; and we had frequently been puzzled on this point, and discovered the cause long before Simon's work appeared. We object also to the work being confined to the blood and urine.

A second part enters upon the treatment of urinary diseases. This is rather unsatisfactory, which may probably depend upon the limited space allotted to it. The author's views on the pathology of diabetes do not appear to us so clear as the present state of our knowledge admits. Nevertheless, taking the work as a whole, we consider it well-adapted to assist in the examinations of the compounds of which it treats, and feel convinced that its careful perusal will prove highly beneficial to medical practitioners, who are in general apt to treat these matters with too great indifference; we must also remember that we are considerably indebted to Dr. Rees for the publication of the former edition of the work, which appeared when this field had been but little trodden.

The Pharmaceutical Latin Grammar. By ARNOLD JAMES COOLEY.

This work professes to be "a short and self-explanatory introduction to Latin grammar and construing, adapted more immediately to the wants of dispensing chemists and druggists, and others connected with the preparation or administration of medicine." It is a very useful little book, and we shall be glad to find it replace a number of other works which have been compiled with a somewhat similar object. The method in which the interpretation of prescriptions is usually taught or explained is much too artificial, and is quite independent of any real knowledge of Latin. The plan of the present work is on an entirely different principle; in it a knowledge of the rules of grammar are primarily detailed, the examples being of two kinds;—one, the easier, from the London Pharmacopœia; the other, more difficult, but at the same time more elegant, from the classic authors. Thus the rules are impressed upon the mind by the examples, which are in general more easily recollected, and a good foundation is laid for a more extensive knowledge of the language. We can highly commend Mr. Cooley's work, which is very carefully compiled and arranged; but we would suggest that in a future edition the "exercises" be somewhat extended, the examples selected being more difficult; and that either an uncontracted Latin version be annexed, or difficult passages or contractions be referred numerically to the rules previously detailed.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Azobenzide and Nitro-benzinic Acid, and on the Artificial Production of a new Organic Alkali. By Dr. N. Zinin.

Pure azobenzide dissolves readily in alcohol which has been saturated with ammonia forming an orange-red liquid, which is gradually decolorized on saturation with sulphuretted hydrogen, finally becomes pale yellow, and yields on cooling a large quantity of white laminar crystals, which re-dissolve in the liquid when the whole is heated, and impart a dark brown colour to it. On boiling, a considerable quantity of sulphur separates in a pulverulent form; at the same time the brown colour disappears, and passes into a light reddish-yellow one. The fluid is decanted boiling hot from the sulphur and left to cool, when whitish-yellow silvery laminar crystals separate, which are formed of fine needles. The liquid above the crystals is of an orange colour. The crystals gradually become of a deeper yellow, even when preserved in closely-stoppered vessels; and with the lens we are able to distinguish a number of minute orange-red acicular crystals and a small number of dull yellow granules. To purify the yellow body, it is dissolved in boiling alcohol, and tolerably dilute sulphuric acid added to the hot solution until nothing further is thrown down. The white pulverulent precipitate, which is almost insoluble in alcohol and water, is well-washed with spirit until this latter passes through quite colourless, and the white silky powder dissolved in dilute ammonia. On the cooling of the filtered liquid, brilliant white scales of a silky lustre form in it.

The body thus purified and dried over sulphuric acid no longer changes on preservation, and dissolves very sparingly in cold, more readily in hot water, so that the hot saturated solution solidifies to a solid paste on cooling; it is far more soluble in alcohol, and still more so in æther. It possesses no odour, but its solutions have a very strong, hot, peppery, bitter, alkaline taste. At 212° it is not altered, but loses somewhat of its lustre; at 226° it melts to a nearly colourless liquid; and solidifies at 232° to a white crystalline mass, having a slight tint of brown; on the further application of heat it becomes brown, and begins boiling, being partially decomposed; another portion distils over unaltered in the form of a liquid, which is coloured brown by the resinous products of the decomposed portion, and a carbonaceous residue is left in the retort.

This new organic base, to which the author applies the name of *benzidine*, combines with acids, forming white, beautifully-crystalline salts, which are perfectly permanent, and are decomposed by ammonia and other alkalies, as also by their carbonated salts, with separation of the base.

Benzidine, purified by recrystallization from aqueous solutions, and dried at 212°, yielded on analysis—

	I.	II.	III.				
Carbon	77·79	78·07	78·20	12	=	900·00	78·12
Hydrogen	6·60	6·70	6·69	6		75·00	6·51
Nitrogen	..	14·78	14·79	1		177·04	15·37

The sulphate of benzidine is almost entirely insoluble in boiling water and spirit, so that a trace of the base may be detected in a cold aqueous solution by means of sulphuric acid. When the solution of the base or its salts is not very dilute, a pulverulent dull precipitate is formed on the addition of the sulphuric acid; but when it is very dilute, the precipitate has a silky lustre, and consists of microscopic scales. Concentrated sulphuric acid dissolves the dry base in the cold, or when heated with a yellow colour; the solution remains liquid on cooling, and solidifies as soon as it is mixed with water to a white pasty mass; but when only a very little water is added to the solution, or the base is treated with dilute sulphuric acid, there is obtained on the application of heat a clear liquid, which however solidifies on cooling to a radiately-crystalline mass. The analysis gave—

Carbon................	50·64	12	=	900·00	50·97
Hydrogen	5·00	7		87·50	4·95
Nitrogen..............	..	1		177·04	
Oxygen	..	1		100·00	
Sulphuric acid..........	28·47	1		501·16	28·38
				1765·70	

which leads to the formula $C^{12} H^6 N + SO^3 + aq.$

The base forms a white salt with ordinary *phosphoric acid*, which is almost as insoluble as the sulphate. In dilute aqueous solutions of the base silvery scales are formed on the addition of phosphoric acid; but from concentrated solutions, a powder which has scarcely any crystalline appearance, is thrown down.

The *muriate of benzidine* is readily soluble in water, more easily in alcohol, but is almost insoluble in æther, and crystallizes from aqueous and alcoholic solutions in silvery-white, thin, rhombic laminæ, which are not altered in the dry, nor even in the moist state. In contact with æther, especially with access of air and presence of free acid, the salt is decomposed, acquires a dirty green colour, and loses its crystalline form. It is not changed at 212°. The analysis gave the following results:—

Carbon	56·12	12 =	900·00	55·99
Hydrogen	5·64	7	87·50	5·44
Nitrogen	..	1	177·04	
Chlorine	27·28	1	442·65	27·54
			1607·19	

leading therefore to the formula $C^{12} H^6 N + HCl$.

Perchloride of platinum produces in alcoholic and aqueous solutions of the muriatic salt, a yellow, shining, crystalline precipitate, which is sparingly soluble in water, and almost insoluble in alcohol and æther; it may be warmed with water, but not boiled without decomposition; with alcohol, especially on the application of heat, it passes speedily into a dark violet powder; in contact with æther this change proceeds more rapidly. The atomic weight, determined from this salt dried *in vacuo* over sulphuric acid, was found to be 1159·78, which number corresponds very well with the calculated, 1152·04.

The double salt with mercury is readily soluble in water and alcohol, and crystallizes in white, shining laminæ or flat needles.

The base is easily dissolved in dilute nitric acid by heat; from the cooled solution, the *nitrate* crystallizes in thin, quadrilateral rectangular plates, which are not altered in the air. The base dissolves in concentrated nitric acid with a brownish-red colour; on the application of heat nitrous acid is disengaged, and the solution becomes brighter. Water produces in this a reddish-brown flocculent precipitate, which is scarcely soluble in alcohol; the supernatant brownish-yellow liquid is coloured blood-red by ammonia, and deposits on being mixed with an excess much more of the brown precipitate.

The base forms a white salt with *oxalic acid*, which crystallizes in very minute silky, radiately-grouped crystals. It is somewhat sparingly soluble in water and alcohol, and permanent in the air at the ordinary temperature, as well as at 212°. Its formula is $C^{12} H^6 N + C^2 O^3 + HO$.

The *tartrate* crystallizes in tolerably large, white, shining plates, and is excessively soluble in water. The *acetate* is formed by dissolving the base in boiling acetic acid; it crystallizes in thin, flat, white needles or plates of considerable lustre, and is easily soluble in water and alcohol. The *benzoate* forms white aggregations of needles, and is far more soluble in water than the base and benzoic acid.

The base and its salts are decomposed in their aqueous and alcoholic solutions by chlorine; the liquid frequently acquires a transitory indigo-blue colour; it then changes into red-brown, becomes turbid, and deposits a considerable quantity of a vermilion-coloured amorphous powder, which is almost insoluble in water, but soluble in alcohol.

The formation of azobenzide has hitherto remained unexplained; perhaps the elimination of the oxygen from the nitrobenzide in its transition into azobenzide might be attributed to the deoxidizing power of the alcohol in the presence of caustic potash; but this process is not so simple, for the origin of azobenzide is accompanied by the formation of other products; for instance, in the distillation of the alcoholic solution of nitrobenzide with caustic potash, a large amount of carbonaceous matter remains in the retort, and in the recipient there occurs along with the azobenzide a hitherto unexamined liquid substance, which the author suspects to be aniline.

When 1 volume nitrobenzide is dissolved in 8 to 10 volumes strong spirit, and a quantity of powdered caustic potash, equal in weight to the nitrobenzide, added to the solution, the yellow liquid becomes dark brownish-red, and so heated that it boils. If the vessel be well-shaken, and heated to keep it boiling for a few minutes, there is frequently formed, on cooling, at the bottom of the vessel an aggregation of acicular yellowish-brown crystals; the supernatant liquid is decanted and distilled until it separates into two layers. The upper one is a dark brown oily fluid; after decantation and washing with water, in which it is insoluble, it solidifies in a few hours into a mass of acicular crystals; the inferior stratum is an aqueous solution of caustic potash, carbonate of potash, and a brown salt of potash almost insoluble in alcohol. The acicular crystals which had formed from the oily liquid, and in the solution of the nitrobenzide in tincture of potash, are well-pressed between paper and recrystallized from alcohol, or what is better, purified by chlorine. When, for instance, the once recrystallized body is dissolved in hot spirit, and a current of chlorine gas passed through it, the brown colour disappears and changes into a pale yellow one. The body crystallizes from the decolorized liquid in yellow, shining, quadrangular needles; they may be obtained by spontaneous evaporation from æther an inch long and more than half a line in diameter. 3 parts by weight of nitrobenzide yield about 1½ part of the perfectly pure body. The crystals have the hardness of sugar, are readily pulverized, void of taste and smell, easily soluble in alcohol, still more so in æther, and insoluble in water. This body, which the author calls azoxybenzide, melts at 97° to a yellow liquid, which strongly refracts the light, and which on cooling immediately solidifies to a radiately-crystalline mass. Muriatic and dilute sulphuric acid, solution of potash and of ammonia have no action upon it. It also crystallizes unaltered from an alcoholic solution of potash, and from alcohol which has been saturated with ammonia or with hydrochloric gas. In the fused state, and likewise in alcoholic solutions, it resists the action of chlorine; ordinary nitric acid acts slightly upon it even on boiling, but fuming nitric acid dissolves it readily at the ordinary temperature with a dark pomegranate colour; the solution becomes heated, disengages red vapours, and solidifies on cooling to a soft mass. It is brought on to a funnel stopped with asbestos, and the acicular crystals which had been dried on a porous tile are dissolved in boiling alcohol. On cooling, the solution becomes filled with very fine, dull yellow needles, aggregated in bundles. If the decanted alcoholic liquid is left to spontaneous evaporation, a peculiar body crystallizes in it in the form of long, tolerably thick four-sided prisms, which are very easily soluble in æther and alcohol. Both products resulting from the action of the nitric acid upon azoxybenzide are no longer altered by it; they dissolve readily in fuming nitric acid, and may be boiled with it and separate unaltered from the cooled solution.

Azoxybenzide dissolves in concentrated sulphuric acid on gently warming it with a dark yellowish-red colour; if this solution be mixed with water, a small quantity of a greenish oil separates from it, which soon solidifies, and is unaltered azoxybenzide contaminated with a green resinous body. The aqueous liquid appears to contain a peculiar organic acid, conjoined with an oxide of sulphur.

If fused azoxybenzide be heated to boiling, it acquires a greenish-brown colour, and disengages a yellow vapour, which condenses to a brownish-red liquid, that congeals in the recipient to a kind of butter. The last portion of the distillate solidifies to a crystalline mass, but that which passed over first remains fluid; we find in the retort a black carbonaceous voluminous substance. By a carefully-repeated distillation, the liquid portion of the butyraceous mass may be separated from the solid. The body thus obtained is azobenzide, which can be purified by pressure and recrystallization. The fluid which first passes over has a brownish-red colour, and contains azobenzide in solution, which however may be very readily separated by any dilute acid. If, for instance, the liquid be treated with a sufficient quantity of dilute boiling sulphuric acid, it dissolves rapidly; the azobenzide melts, and collects at the bottom of the vessel. The decanted aqueous solution has a slightly-yellowish colour, and on cooling becomes filled with white silvery laminæ; they are obtained perfectly pure by recrystallization from water. Alkalies decompose them, and separate the liquid body; on distillation with caustic potash, a colourless oil passes over, which has all the properties of aniline. The analysis of the sulphate confirmed the formula $C^{12}H^7N, SO^3HO$.

The analysis of the azoxybenzide yielded—

Carbon	72·57	72·72	12 =	900·00	72·60
Hydrogen	5·27	5·25	5	62·50	5·04
Nitrogen......	13·99	13·99	1	177·04	14·28
Oxygen	..	..	1	100·00	8·08
				1239·54	

According to the formula $C^{12}H^5NO$, azoxybenzide should form from the nitrobenzide by 3 equiv. oxygen being eliminated from the latter; the author however was not able to detect any of the known products of the oxidation of alcohol among the products of the action of caustic potash on the alcoholic solution of nitrobenzide. The two peculiar bodies which originate in this process, viz. a brown acid insoluble in water but soluble in alcohol, the potash salt of which behaves quite the reverse to those solvents; and an indifferent dark brown powder, very sparingly soluble in alcohol and water, are never formed in large quantity, which has hitherto prevented their being examined more minutely.

Azobenzide dissolves readily in cold fuming nitric acid; the reddish-yellow solution soon acquires a dark blood-red colour, becomes heated, and solidifies under evolution of red vapours to a paste of yellowish-red acicular crystals, which dissolve with difficulty in boiling nitric acid. By treatment with strong alcohol, the residue freed from the excess of nitric acid can be separated into two distinct bodies, one of which dissolves with tolerable ease in alcohol and æther, and crystallizes on the cooling of the solution in delicate straw-coloured dull needles; the other dissolves with difficulty in boiling alcohol and æther, and crystallizes on cooling in small rhombic tables, which have a beautiful pomegranate colour and a strong almost metallic lustre.

When an alcoholic solution of nitro-benzinic acid, saturated with ammonia and sulphuretted hydrogen, is boiled, it first acquires a dark olive-green colour, then becomes turbid, and deposits a large quantity of sulphur, when it again becomes clear. To effect the complete decomposition of the nitro-benzinic acid, the liquid decanted from the sulphur must be mixed with the alcoholic sulphuret of ammonium which distilled over during ebullition, the mixture again saturated with sulphuretted hydrogen and distilled, and this operation repeated two or three times until no more sulphur separates. The residuous alcoholic liquid is now boiled with water to remove as completely as possible the alcohol and sulphuretted hydrogen, and the liquid concentrated to the consistence of a syrup. The liquid is now cooled and supersaturated with strong acetic acid, when it congeals to a thick yellowish paste. This is allowed to drain on a filter, then pressed and dried, upon which it is dissolved in distilled water, the solution decolorized with animal charcoal, filtered boiling hot, and set aside to cool. Small white globular masses crystallize from it, which are formed of thin, short, radiately-grouped needles. This substance is a nitrogenous acid, for which the author proposes the name of *benzaminic acid*. It dissolves readily in boiling water, from which it crystallizes unaltered on cooling; in alcohol and æther it is still more soluble. It is void of smell, and has a sweetish acid taste. In all solutions it is decomposed in the course of time, especially in contact with the air, and is converted into a brown resinous substance. It is but slightly attacked by common nitric acid even on boiling, but the fuming acid dissolves it with a blood-red colour; the solution becomes heated, disengages red vapours on boiling, and acquires a pomegranate colour; it is now no longer precipitated by water. Neutralized with ammonia, it yields with salts of lead an ochreous yellow, with salts of copper a yellowish-green, and with salts of silver a reddish-brown precipitate. Benzaminic acid forms with concentrated sulphuric acid a colourless solution, which on the application of heat becomes pale yellow, but on the addition of water is again decolorized, and after neutralization yields with salts of oxide of copper a malachite-green precipitate. When heated on platinum-foil or in a retort, the acid melts to a clear colourless fluid, puffs up, gives off a white irritating vapour, and leaves a voluminous readily-combustible cinder; at the same time a portion of the acid sublimes undecomposed. In aqueous and alcoholic solutions, the acid is readily decomposed by chlorine, and converted into a brownish-black resinous substance, which dissolves in alcohol of a dark violet colour, but is insoluble in water. This substance forms with the metallic oxides sparingly-soluble saline compounds.

Benzaminic acid has a strong acid reaction, and combines readily with bases, entirely neutralizing their alkaline properties. It expels carbonic acid from its combinations. The alkaline and earthy salts are very soluble in alcohol and in water, and could not be obtained in a crystalline form. With oxide of lead it appears to form three different salts; one is pulverulent, almost insoluble in water; the second is sparingly soluble, crystallizing in needles; and the third is more soluble, and crystallizes in shining laminæ: all three salts are white. With oxide of copper it affords a malachite-green salt, insoluble in water and alcohol, but readily soluble in strong acids. Salts of silver produce in a solution of benzaminate of ammonia a white caseous precipitate, which soon changes into a crystalline powder. In boiling water this becomes brownish-white, and modified but not dissolved; heated in the dry state, exposed to the air it becomes black, fuses, puffs up, and leaves a porous coal, which may be readily burnt to pure silver. The analysis of the pure acid gave—

Carbon	61·02	61·09	14	=	1050·00	61·24
Hydrogen	5·12	5·14	7		87·50	5·10
Nitrogen	10·01	10·01	1		177·04	10·32
Oxygen	..	..	4		400·00	23·34
					1714·54	

That of the silver salt—

Carbon	34·12	34·19	14	=	1050·00	34·38
Hydrogen	2·45	2·54	6		75·00	2·45
Nitrogen	..	..	1		177·04	
Oxygen	..	..	4		400·00	
Silver	44·10	44·20	1		1351·60	44·26
					3053·64	

Benzaminic acid has consequently the same composition as anthranilic acid, but it is not identical, as it yields no aniline on distillation. The formation of benzaminic acid may be conceived in two different ways. If, for instance, we express with Mulder the composition of nitro-benzinic acid by the rational formula $C^{14} H^4 O^4 + NO^3 + HO$, we find in our hydrated acid the same radical, $C^{14} H^4 O^4$, combined with ammonia; we must therefore assume that in the transition of the first acid into the latter the equivalent of nitrous acid is separated from the compound by an equiv. water. But if we represent the composition of nitro-benzinic acid by the formula $C^{14} H^4 O^3 + NO^4 + HO$, in order to explain the formation of the benzaminic acid, we need only admit the substitution of NH^4 for NO^4 without elimination of water. The empirical formula of the benzaminic and anthranilic acids is likewise identical with that for the oxalate of benzidine.—*Bullet. de l'Académ. Impér. des Sciences de St. Pétersb.*, vol. iv. No. 90.

On the Formation of Chloral.

M. Städler has observed the formation of chloral, by causing chlorine to act in its nascent state on a large number of organic substances, and in particular on starch. It is obtained, mixed with formic acid and an oily body, which the author is still engaged in investigating, when a mixture of starch, binoxide of manganese and hydrochloric acid is submitted to distillation.—*Comptes Rendus*, Oct. 6, 1845.

On Urostealite, a new Substance, found in a Urinary Calculus.

By Dr. Heller.

The author thus designates a peculiar substance which formed a urinary calculus in a man; it was removed by carbonate of soda, in which it was soluble. The urine, before the use of the carbonate of soda, was of a pale yellow whey-like colour and inodorous; it was slightly turbid, and contained a deposit of large crystals of ammonio-phosphate of magnesia, which speedily subsided. By the microscope, globules of fat were perceptible; the reaction was neutral, and the spec. grav. 1017·5. Ammonia caused a copious precipitate of earthy phosphates without altering its colour. No uric acid could be detected in it. It contained in 1000 parts—

Water	965·800
Solids	34·200
Urea	12·631
Fat	0·320
Extractive and muriate of ammonia	8·569
Fixed salts	12·680

The latter consisted of 2·040 earthy phosphates, 0·163 chloride of sodium, 2·296 sulphate of potash, 8·181 basic phosphate of soda and peroxide of iron.

After the patient had taken 2 drms. of carbonate of soda, the urine was neutral, of a spec. grav. of 1009. After a few hours' repose, it became alkaline and somewhat turbid. No trace of lithic acid could be discovered in it at this time. Ammonia now produced a reddish-brown colouring of the urine, which had not occurred previously. The constituents of the urine were essentially the same in quantity as those stated above. After 24 hours' use of the carbonate of soda, the urine was exactly similar to the first, but contained in the deposit a calculus of urostealite of half the size of a hazel-nut. Ammonia produced a reddish-brown colour. The same phænomenon was also perceived on the next day.

To separate the urostealite from the urine, a large quantity of it was evaporated, treated with a little sulphuric acid, and exhausted by boiling with æther. This left on evaporation a violet residue of urostealite. The urine possessed the same composition as before, except that it contained more fat and urostealite, as also fixed salts. It never yielded a trace of lithic acid, and was always either neutral or very slightly acid.

Urostealite is most readily detected by the effects of heat and combustion. A small piece, placed on platinum foil and heated, remains for some time solid, then commences to fuse without melting, burns rapidly, and diffuses at first a tolerably strong vapour and very peculiar and agreeable odour, which most resembles that of shell-lac and benzoin. The odour is so strong, that the smallest piece is sufficient to allow of its being distinctly perceptible. With a stronger heat, the urostealite inflames and burns with a bright yellow flame. If the remaining voluminous cinder be completely incinerated, a small alkaline residue is left.

When boiled with water, urostealite becomes soft, swells slightly, is compressible and friable. Warm alcohol dissolves it, but with difficulty; when the alcohol is evaporated and the residue incinerated, the above-described agreeable odour becomes perceptible. Æther dissolves it with tolerable ease; if the æther be evaporated, the urostealite is left in the amorphous state; on continuing a gentle heat, it becomes coloured of a tolerably deep violet. Solution of caustic potash dissolves it readily by heat with a brownish-yellow colour; if the watery part of the solution be allowed to evaporate, a quantity of brown flocks are deposited, which are again dissolved on the fresh addition of the solvent. The product is a brown soft soap, which can be kneaded like wax, and is soluble in water. Its clear alkaline solution is decomposed by acids, and the urostealite again separates as an amorphous fat. The carbonates of soda and potash act in the same manner as the caustic potash, except that their action occurs more slowly. When the soap is treated with ammonia, this does not assume so brown a colour as when the urostealite is dissolved in urine. Even boiling ammonia has but little action on it; it swells, becomes soft, and saponifies but very imperfectly, the liquid becoming very slightly brownish. When heated with nitric acid, it yields a solution which is almost colourless, nitrous acid being slightly evolved. If the product is evaporated and the residue treated with ammonia, it assumes a dark yellow colour, similar, but in a less degree, to that produced by caustic potash.—*Archiv für Physiol. und Path. Chem.*, 1845.

On the Ammoniacal Oxide of Mercury. *By* E. Millon.

When we examine the formulæ employed to express the combinations of the binoxide of mercury and the mercurial persalts with ammonia, we are led to suspect that, notwithstanding recent investigations undertaken by well-known chemists, analysis has not attained in this class of compounds that certainty and precision which may be expected at the present day. These combinations, which for the greater part furnish therapeutics with such useful resources, are highly remarkable both as regards the mode of their chemical constitution and their characteristic reactions.

It has been asserted of these compounds, that several are of such great stability that they resist the action of a boiling concentrated solution of potash. With respect to the discordant formulæ assigned to the greater number of the ammonio-mercurial compounds, they must appear perfectly extravagant, since the researches of M. Reiset on the ammoniacal protoxide of platinum have enabled us to represent nearly all the combinations of the metallic oxides with ammonia as complex bases formed of 1 equiv. metallic oxide united to 1, 2 or 3 equiv. of gaseous ammonia.

I have endeavoured to ascertain the reason of the apparent anomalies which these combinations exhibit; and I hope I have succeeded, with respect to the essential points, in making them disappear entirely.

The principal facts of constitution, to which I have been led by analysis, are explained by means of a single ammonio-metallic grouping. It is true, it is of a new kind; but, once admitted, the most simple rules of chemistry suffice to explain everything, formulæ and reactions.

This peculiar arrangement is fortunately not hypothetical; it occurs in the formation of the ammoniacal binoxide of mercury. Notwithstanding repeated attempts, the constitution of this curious substance was wholly unknown, and the methods employed for its preparation yielded it in very variable states.

The difficult circumstances which occur in these investigations explain the discrepancies and mistakes.

The ammoniacal oxide of mercury was discovered by Fourcroy and Thenard; it is obtained by pouring liquid ammonia upon binoxide of mercury. If the mercurial oxide is in the form of the yellow modification, the combination is immediate; if, on the contrary, the red oxide is employed, the combination is not complete until after three or four days' contact. In all cases the oxide becomes of a deep yellow; it is only white when the ammonia contains some carbonate, but then the ammoniacal oxide of mercury is impure. As soon as combination has taken place, the substance may be washed, pressed and preserved without change, provided it is protected from contact with the air; but if, without pressing it strongly, it is immediately transferred into an atmosphere dried by means of sulphuric acid, the yellow compound soon darkens, and goes on changing until it has become perfectly brown. The oxide has become dehydrated; it now remains stable in its constitution and unalterable by exposure to the air. By heating the brown oxide, it loses more water between 212° and 266° without changing in appearance or colour.

The composition of the yellow oxide, which was ascertained by determining the mercury, water and nitrogen, is very accurately expressed by 4 equiv. binoxide of mercury, 1 equiv. gaseous ammonia and 2 equiv. water, $4HgO + NH^3 + 2HO$; 2 equiv. water are lost over sulphuric acid, when the oxide becomes brown, and a temperature between 212° and 266° removes another equivalent of water, with some traces of ammonia too slight to be taken into consideration; so that to represent the constitution of this compound by an arrangement which indicates to a certain point the modifications which it undergoes on parting with its water, and likewise on entering into combination, the elements may be grouped in the following manner:—

Yellow ammoniacal oxide........	$3HgO+HgNH^2+HO+2HO$.
Brown oxide formed over sulphuric acid.................	$3HgO+HgNH^2+HO$.
Brown oxide at 266°............	$3HgO+HgNH^2$.

This compound, formed by the union of 4 equiv. oxide of mercury, 1 equiv. ammonia and 2 equiv. water, is nothing less than a base. It answers to all the tests capable of demonstrating its basic nature in the most decided manner. It is an energetic base which displays the strongest affinities, which displaces ammonia from its salts as readily as do lime and baryta. It is itself expelled from its combinations by the caustic alkalies, but without losing any of its elements, however large the addition of soda or of potash, excepting when the alkaline solution is very concentrated and kept boiling for some time.

It is this stability of the ammoniacal oxide of mercury as an intimate combination of ammonia and of binoxide of mercury, that led to the belief that the white precipitate and the ammoniacal turpeth do not yield to the decomposing action of caustic potash. The ammoniacal salt of mercury does not resist in reality, but the potash merely separates the acid; the ammonio-mercurial oxide is simply eliminated in the state of the yellow hydrate. A syrupy solution of boiling potash is requisite to decompose partially the hydrated base and to expel any ammonia. The brown anhydrous base is still more stable; it remains unaltered in the presence of the most concentrated solution of potash, even when boiled. Potash, in the state of fusion, decomposes it into nitrogen, metallic mercury and binoxide of mercury.

I now come to the determination of the equivalent of this base, which is without doubt the most remarkable point in its history. It combines directly with oxalic and sulphuric acid whatever their degree of concentration; it thus forms an oxalate and a sulphate of definite composition; it very rapidly absorbs carbonic acid while in its hydrated state, and its carbonate, which is very permanent, possesses a constant composition corresponding to that of the oxalate and sulphate; but the acids, weak or strong, even when employed in large excess, always combine in the proportion of 1 equiv.

This complex oxide, formed of 4 equiv. oxide of mercury and of 1 equiv. ammonia, combines with 1 single equiv. of carbonic, oxalic or sulphuric acid. The combination takes place instantaneously, and the hydrated base absorbs carbonic acid from the atmosphere and from the carbonate of ammonia, just as lime and barytes. It is indeed almost impossible to obtain the base absolutely free from carbonate, and this rapid absorption of carbonic acid has led to the ammoniacal oxide of mercury being described as at first a whitish substance, a property which belongs solely to the carbonate.

The constitution of the salts formed directly by the ammoion-mercurial base soon led me to remark, that several compounds obtained by the action of ammonia on mercurial salts, as for instance the bichloride, biniodide, sulphate, nitrate, bromate, are related in the most simple manner to the complex compound which I have investigated.

The ammoniacal turpeth does not differ in the least from the salt obtained by the direct combination of sulphuric acid with the ammonio-mercurial base. M. Soubeiran described a nitrate which may be represented accurately by 1 equiv. of nitric acid and 1 equiv. of the same base. M. Rammelsberg has published an analysis of the ammonio-mercurial bromate, which strictly agrees with the preceding formulæ. And lastly, we find among the ammoniacal products which are derived from the bichloride and biniodide of mercury, compounds in which 1 equiv. oxygen of the new base is replaced by 1 equiv. chlorine or iodine.

We are thus able to construct the following series, which enables us to judge of the simplicity and extent of these relations:—

Hydrated base	$3HgO+HgNH^2+HO+2HO$.
Base dehydrated over sulphuric acid	$3HgO+HgNH^2+HO$.
Anhydrous base at 266°	$3HgO+HgNH^2$.
Carbonate	$CO^2+3HgO, HgNH^2+HO$.
Carbonate at 275°	$CO^2+3HgO, HgNH^2$.
Oxalate	$C^2O^3+3HgO, HgNH^2$.
Sulphate	$SO^3+3HgO, HgNH^2$.
Nitrate of Soubeiran	$NO^5+3HgO, HgNH^2, HO$.
Bromate obtained by Rammelsberg	$BrO^5, 3Hg, HgNH^2$.
Chloride obtained by washing the white precipitate with water	$2HgO, HgCl, HgNH^2$.
Iodide obtained by Rammelsberg by boiling ammonia repeatedly with bichloride of mercury	$2HgO, HgI, HgNH^2$.

This grouping evidently admits of arranging with regularity the most anomalous formulæ of the ammonio-mercurial products. Among those which do not allow of being represented simply as a salt of the new base, there are some which may be regarded as double salts formed of an ammonio-mercurial salt in combination with a salt of ammonia. We find, in fact, by direct experiment, that the ammoniacal binoxide of mercury and the salts which it forms dissolve readily in several ammoniacal salts, for instance the sulphate, nitrate and hydrochlorate. M. G. Mitscherlich has analysed the double nitrates thus formed, and their composition agrees perfectly with that of a double salt, a supposition moreover which corresponds in every respect to the general affinities of the ammonio-metallic salts.

Thus one of the double nitrates obtained by Mitscherlich is represented by the formula $NO^5 + 2HgO + NH^3$. By doubling its composition, it may very well be expressed by

$$\underbrace{NO^5, NH^3, HO}_{\text{Nitrate of ammonia.}} + \underbrace{NO^5, 3HgO, HgNH^2.}_{\text{Nitrate of the new base.}}$$

The other nitrate has for formula $3(NO^5, NH^3, HO) + 4HgO$. This formula, which has hitherto been unique in the constitution of salts, may be arranged in the following manner:—

$$\underbrace{2(NO^5, NH^3, HO)}_{\text{Nitrate of ammonia.}} + \underbrace{NO^5, 3HgO, HgNH^2, 2HO.}_{\text{Nitrate of the base.}}$$

The nitrate of the base comprised in the preceding formula contains without doubt only 1 equiv. of water, like the nitrate of M. Soubeiran. By treating the sulphate of the binoxide of mercury with a large excess of caustic ammonia, the salt is dissolved; and on evaporating over lime in a close atmosphere, large efflorescent prismatic crystals are obtained in the course of time, which in the anhydrous state have the following composition:—

$$\underbrace{NO^3, NH^3, HO}_{\text{Sulphate of ammonia.}} + \underbrace{SO^3, 3HgO, HgNH^2.}_{\text{Sulphate of the base.}}$$

All the ammonio-mercurial salts, I confess, do not come within the systematic arrangement which I have proposed; thus ammoniacal gas appears to combine simply with 1 or 2 equiv. either of bichloride of mercury or of the biniodide. Some other formulæ require further discussion, but I hope to make these formulæ derive very naturally from those which it appears suitable to assign, as well to the mercurial compounds as to the ammonio-metallic combinations in general.

The above system of compounds already constitutes a very well-defined class; it is moreover characterized by a molecular arrangement of so peculiar a nature, that I have been induced to separate it from the researches which I have undertaken on the mercurial compounds in general, and to submit it to the public at present.—*Comptes Rendus*, Oct. 6, 1845.

On the Nature of the Fluid of Ranula. By Dr. GORUP-BESANEZ.

It has always been a question, whether the fluids constituting ranula arise from an obstruction of the Whartonian duct and contain altered saliva, or whether they belong to the class of cystic tumours. The latter view has been adopted by Sir Charles Bell, Stromeyer, Julius Vogel, Petrequin, &c. Gmelin examined them twice, and found the liquid of a pale yellow colour, containing neither ptyaline nor alkaline sulpho-cyanate, but copiously albuminous. The fluid examined by the author was yellowish-white, semi-transparent, alkaline and unusually glutinous. On agitating it with thrice its volume of water, it dissolved, forming an opalescent frothy solution, which was not rendered turbid, but became still clearer by boiling. Nitric acid caused a precipitate, which soon disappeared by mere agitation; excess caused no change; hence ordinary albumen was not present. Acetic acid produced a copious white flocculent precipitate, which was not soluble in excess even after ebullition. Ferrocyanide of potassium gave rise to no change in the solution poured off from the precipitate. Alum produced a precipitate readily soluble in excess; caustic potash, no change; perchloride of iron caused a yellowish-white precipitate, which was soluble in excess. Thus the liquid reacted very much like a dilute solution of chondrine.

When evaporated to dryness, it left a brownish-yellow, brittle, semi-transparent, shining residue. A scum rapidly formed on the surface of the solution when evaporated. The powdered residue was repeatedly boiled with alcohol of 0·833 sp. gr., then treated with cold and luke-warm water. On evaporation, the greater part of the substance became insoluble. The alcoholic solution yielded distinct crystals of common salt and traces of fat on evaporation; the aqueous extract left a brownish residue, which was not altered by acetic acid and ferrocyanide of potassium, gave a whitish-yellow precipitate with tannic acid, insoluble in excess, and with alum a slight troubling, which soon disappeared. The residue left undissolved by water and alcohol, dissolved in caustic potash producing a yellow solution, and in muriatic acid producing a brownish-red solution, but did not dissolve in acetic acid. The alkaline solution yielded a white flocculent precipitate with acetic acid, which was soluble in excess; ferrocyanide of potassium caused a copious yellowish-white precipitate in the acid solution. On the addition of a drop of acetate of lead, a dark brown colour (from sulphuret of lead) was instantly produced.

The microscope detected in the fluid some blood-corpuscles and globules, which were at least twice as large as the corpuscles of mucus and saliva, and most resembled Gluge's inflammation-globules. Thus both microscopically and chemically this liquid differed completely from saliva. It yielded on analysis—

Water	95·029
Solids	4·971

consisting of alcoholic extract, fat and chloride of sodium, 1·062; aqueous extract (gluten?), 0·923; albuminate of soda, 2·986.—Heller's *Archiv für Phys. und Pathol. Chem.* 1845.

On the Composition of the Nitrate of Urea. By Dr. Fehling.

According to Regnault's experiments, the nitrate of urea consists of $C^2 N^2 H^4 O^2 + NO^5 + HO$, and contains 48·9 per cent. of urea. This composition was subsequently adopted in all analyses of the urine. Lehmann* found in dry nitrate of urea 52·9 per cent. urea and 47·1 nitric acid, according to which its composition would be $NO^5 + C^2 N^2 H^4 O^2$. Marchand† has lately asserted that the compound contains 2 or 1½ equiv. of nitric acid to 1 of urea. I am therefore induced to publish some analyses, part of which were made some time since, when preparing urea and its nitrate; the others have been recently made with artificial urea from ferrocyanide of potassium. All the analyses which were performed on the combinations dried on a porous tile or at a gentle heat, gave the same composition as found by Regnault.

(I. II.) *Nitrate of urea from urine,* once recrystallized from water and dried at 86° F.; another portion (III.) recrystallized from nitric acid:—

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* Erdmann's Journ. xxiv. p. 13.

† Chem. Gaz., vol. iii. p. 275.

	Calculated.		Found.		
			I.	II.	III.
C^2	151·7	9·8	9·9		
H^5	62·4	4·1	4·3		
N^2	354·0	42·3			
O^3	300·0				
NO^5	677·0	43·8	43·8	44·4	43·7
	1545·1	100·0			

Two analyses of urea, prepared from cyanate of potash and crystallized from nitric acid, yielded exactly 43·9 per cent. of nitric acid.

When nitrate of urea is dried at 212°, in the course of several hours it only loses from 1 to rather more than 2 per cent. of water, whilst 1 equiv. of water amounts to 7·2 per cent.; on further drying, the loss continues to increase until it has amounted to more than 12 per cent.; the compound then fuses at 212°, and distinctly evolves bubbles of gas. This decomposition ensues more rapidly at 248° F.; the gas at first consisted of carbonic acid, with one-half to one-third of a volume of nitrogen, but after a short time it was formed almost entirely of carbonic acid. No nitrous oxide was evolved.

Nitrate of urea, which had lost about 7 per cent. in weight, yielded 37 per cent. of nitric acid; another, 40·1 per cent. I shall more minutely examine the product which is here formed. But I think it important in analysis, that the nitrate of urea should be dried merely in the air, or but a very short time at 212°.—*Ann. der Chem.*, Aug. 1845.

ANALYTICAL CHEMISTRY.

On a simple Method for determining the Free and Combined Ammonia and Water in Guano and other Manures. By DAVID FORBES, Esq.*

THE want of a simple, accurate, and at the same time expeditious method for determining the amount of ammonia in guano, has, I think, been felt by most chemists who have been engaged in the analysis of that manure for commercial purposes, where time necessarily becomes a matter of importance; and as the following method, which I have introduced into the laboratory of Dr. G. Wilson, Edinburgh, where several analyses of guano are daily in progress under my direction, seems to me to possess these advantages, I beg leave to place it before the notice of chemists who may be similarly circumstanced.

The quantity of free ammonia in the guano is first determined, along with that of the water, by the following process:—A common test-tube (about 5 inches long and ½ wide) is taken, and in it a determinate quantity of the guano under examination is placed; from 25 to 50 grs. will be found most convenient. To the test-tube is then joined, by means of a cork, a tube of the same diameter, but only

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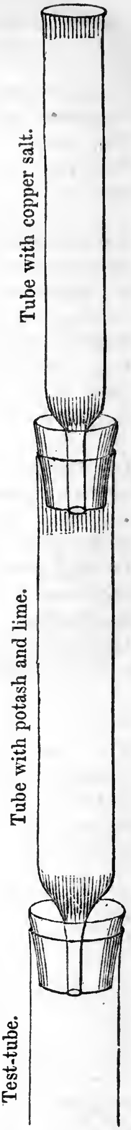
* Communicated by the Author.

about 4 inches long, having one of its ends contracted and drawn out, so as to pass through the cork and leave a small communicating aperture for the escape of gas from the test-tube. A few fragments of asbestos are then placed in the contracted end of the tube, to prevent the aperture being choked up during the process; and the tube is then filled with fragments of caustic potash, either alone or mixed with fragments of lime, which I prefer. To the top of this tube is then joined another tube of precisely similar construction, but being only about 3 inches long, and which, the asbestos being placed as before, is filled with coarsely-pounded sulphate, nitrate, or chloride of copper, previously well-dried. A few fragments of asbestos are now placed on the top of each of these tubes, so as to prevent any of their contents falling out. The tubes are then weighed separately. The three tubes are then connected, and the test-tube which contains the guano is placed in a water-bath until all moisture has been expelled. The tubes are now disconnected, and again weighed, when the quantity of ammonia contained in the guano in a free state is directly determined by the increase of weight which it is found that the tube containing the copper salt has suffered, whilst the quantity of water is shown by the increase of weight in the tube containing the potash and lime. The quantity of combined ammonia has now to be ascertained, which is done by adding to the guano contained in the test-tube about an equal bulk of caustic lime in fine powder, and mixing well by agitation; then connecting the apparatus as before, and exposing the test-tube to a low red heat, all the ammonia is expelled and combines with the copper salt contained in the upper tube, and, as before, it is determined by direct weighing. It is very easy to judge when all the ammonia is expelled and when the operation should be concluded, as the ammonia, in combining with the copper salt, gives it, as it proceeds up the tube, a magnificent blue colour, which, when it does not extend any higher up the tube, indicates the conclusion of the operation. In the case of any other manure, where the ammonia has to be found, the operation is precisely similar to the example of guano which I have here taken. I have no doubt that with some modifications the condensation of ammonia by a salt of copper would be found of use in organic analysis for the determination of the nitrogen; and in one or two cases where I have tried it, the results closely approximated to those obtained by calculation.



13 *Rankeillour Street, Edinburgh, Oct.* 24, 1845.

Action of the Bicarbonated Alkalies on the Vegetable Bases in presence of Tartaric Acid. By C. OPPERMANN.

In examining for the organic bases or alkaloids, the chemist is necessarily obliged to make use of their generic and specific characters, and among others that of their being displaced by the powerful inorganic bases and the alkaline carbonates. Under the latter circumstance they frequently give rise secondarily to combinations between the displaced alkaloid and the separating base of such a nature that these reactions afford the means of distinguishing certain of them; as some dissolve in an excess of the precipitating base, while others are insoluble.

The phænomenon of the precipitation of bases by one another when in the state of a salt is however by no means constant. We know, from the experiments of Lassonne and Rose, that several organic substances, such as tartaric acid, sugar and albumen, prevent the displacement and precipitation of an oxide, so as to prevent its being detected by a great number of tests. M. Persoz having observed that certain organic bases possess, like alumina, the property of being masked by tartaric acid, I have endeavoured to ascertain how far this phænomenon was peculiar to the class, for the importance of such a fact in the investigation of the vegetable alkalies will be readily conceived. I have made numerous experiments to ascertain whether tartaric acid, albumen, and other fixed organic substances, do or do not possess the property of preventing the displacement and precipitation of a vegetable alkali. I shall only detail here the results of my researches on the behaviour of salts of morphine, narcotine, strychnine, brucine, quinine, cinchonine and veratrine, in the presence of tartaric acid, and of the fixed alkaline bicarbonates. The solutions of the above salts were made in the proportion of 1 part of salt to 200 or 500 water (the reactions are precisely the same whether we operate on these solutions or on decoctions and extracts of the plants which contain the vegetable bases, provided they are sufficiently concentrated), to which tartaric acid is added until they exhibit a very decided acid reaction; they are then supersaturated with one or the other of the fixed bicarbonates. It is unnecessary to add that the acid tartrates of the alkaloids furnish the same results.

The salts of morphine are not thrown down by the alkaline bicarbonates, but the salts of narcotine immediately yield a very considerable pulverulent white precipitate. To be certain of the complete absence of narcotine in a neutral solution, sulphocyanide of potassium may be employed. This test, which does not produce any turbidness in the neutral solutions of morphine, immediately yields a deep red precipitate in those which contain narcotine even in an imponderable quantity. It must however be observed that a slight excess of the sulphocyanide redissolves the precipitate formed.

The salts of strychnine, under the same circumstances, either yield pulverulent precipitates or furnish crystals of considerable dimensions, according to the quantities of tartaric acid, bicarbonate of soda or potash employed, and according to the degree of concentration. If the solution is very dilute, there is no precipitate; if it is somewhat less dilute and contains much tartaric acid, no immediate precipitate is produced by the two bicarbonates, but at the end of a quarter of an hour, very long and fine crystals are perceptible, which increase until all the strychnine contained in the solution has separated. It is easy to ascertain that the solution contains no more strychnine or salt of strychnine, by treating it in the manner described by M. Marchand, with peroxide of lead and a mixture of sulphuric and nitric acids*; the blue colour, which the smallest trace of strychnine gives rise to in presence of these substances, is, as is well known, the most certain sign of the presence or absence of this base; for chlorine, which M. Pelletier recommended as a specific test for strychnine, acts in an identical manner on veratrine, as I have ascertained by direct experiment. If the solution of strychnine is concentrated and contains but a small quantity of tartaric acid, the bicarbonates immediately produce a white crystalline precipitate, and the liquid no longer contains a trace of strychnine.

Brucine, and the solutions of the salts of this base, differ entirely in this respect from the salts of strychnine; the alkaline bicarbonates do not produce the least turbidness in them.

The salts of quinine and of cinchonine may equally be distinguished by this means and separated from each other, quinine not being precipitated in presence of tartaric acid, whilst cinchonine is thrown down by the two alkaline bicarbonates.

In the solutions of the salts of veratrine acidified with tartaric acid, bicarbonate of soda alone produces a precipitate, bicarbonate of potash none.

We see therefore that by turning to account the property which tartaric acid possesses of masking certain alkaloids in their behaviour towards the alkaline bicarbonates, we establish two very distinct groups; the first of which comprises those which are precipitated by bicarbonate of soda, viz. *cinchonine*, *narcotine*, *strychnine* and *veratrine*; the second group those which are masked, *i. e. quinine*, *morphine* and *brucine*.

Tartaric acid likewise prevents the reaction of the infusion of galls towards all these bases, with the exception of cinchonine and strychnine, but it precipitates the five others abundantly as soon as the acid has been neutralized by ammonia; we should however observe that an excess of the latter base redissolves the tannate of brucine.

We see, moreover, what appears to me worthy of attention, that of two bases which are met with in the same plant, one is constantly masked by tartaric acid, whilst the other is not; the employment of this property is therefore highly valuable, as it allows of a very exact separation of the two bases.—*Comptes Rendus*, Oct. 6, 1845.

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* See this Journal, vol. i. p. 629, and vol. ii. p. 288.

On the Separation of Lime from Magnesia. *By* M. Backs.

It had been proposed in order to separate lime from magnesia to calcine the moist mixture of chloride of magnesium and chloride of calcium so as to obtain magnesia, the chloride of calcium remaining unaltered and capable of extraction by water. Berzelius has already asserted this method to be inaccurate, as on calcining the mixture a little lime always separates, hydrochloric acid gas being at the same time given off. It was however possible that the quantity of lime thus eliminated was too slight to interfere with the employment of the method in approximative analyses. The experiments however of M. Backs on this point show that it is so faulty that it cannot even be used in the latter case.—*Journ. de Pharm.*, Oct. 1845.

PATENTS.

Patent granted to Thomas Drew, St. Austell, Cornwall, *and* Edward Stocker, *for certain Improvements in the Production and Manufacture of Naphtha, Pyroligneous Acid, or other inflammable Matter.*

The improvements in the manufacture of pyroligneous acid, naphtha, or other inflammable matter, protected by this patent, consist in obtaining these matters by the destructive distillation of peat, peat-moss, or bog-earth (which has been previously dried, or deprived of the greater portion of its moisture), in retorts made of iron, stone, fire-brick or clay. Each retort is connected by a short pipe with a series of pipes, which form the apparatus employed for condensing the volatile products driven off from the retorts. The heat applied to the retorts may vary from a scarcely visible dull red to a bright red.

With regard to the condensing or refrigeratory apparatus, the patentees prefer, where locality will allow, not to pass the volatile products from all the retorts into one pipe, but to conduct them separately through one line of pipes, having at certain intervals (commencing at about 10 feet from the retort) descending pipes, through which the condensed products may pass into a receiver beneath. Each line of pipes should be placed in "shutes," about 2 inches wider and 2 inches deeper than the diameter of the pipe at the joint; the pipes should have a fall of about 1 inch in 5 feet, in the direction from the retort towards the end of the condenser; the shutes should have an inclination to the same extent in the opposite direction; by this arrangement, on cold water being caused to run through the shutes, it will meet with the coolest part of the pipes first, and will therefore be most advantageously employed for absorbing the heat.

The products of this distillation will consist of water, naphtha or pyroxylic spirit, acetic or pyroligneous acid, ammonia, tar, oil, charcoal, and an incondensable inflammable gas; these matters may be separated from each other as in the treatment of the like products of the destructive distillation of wood.—Sealed March 18, 1845.

Patent granted to Henry Jones, Broadmead, Bristol, *for a new Preparation of Flour for certain Purposes.*

This invention consists in mixing with the flour such acids and carbonated alkalies, or carbonated alkaline earths, and sugar and salt (all in a dry and finely powdered state), as will, when the flour is made into bread, biscuits, and similar baked food, flavour the same, and cause the dough to rise without the employment of any fermenting matter.

The flour is made from wheat or other grain, of fine quality, and in a perfectly dry state; after grinding and dressing, it is left to ripen for a month or six weeks; then 10½ oz. avoirdupois of tartaric acid, as dry as possible, and in fine powder, are added to each hundred-weight of flour. The mixture of flour and tartaric acid is passed through a flour dressing machine, and allowed to remain untouched for two or three days, that the water of crystallization, always more or less present in the tartaric acid, may be absorbed by the flour, and so form around the particles of acid a coating of flour; which coating will prevent the particles of alkali from coming into immediate contact with the acid, and thus preserve its power of action from being reduced. After this dressing process, an addition is made to the flour and acid of 12 oz. of bicarbonate of soda, 24 oz. of muriate of soda or common salt, and 8 oz. of loaf-sugar, all in a finely powdered and dry state; and when the mixture has been passed through a flour dressing machine, it will be ready for use.

The quantities of the acid and alkali used may have to be slightly varied, according to their quality, but the point to be attained is a neutralization of both. Other articles, such as bicarbonate of potash and citric acid, are stated to make excellent bread, but in general they are too expensive.

When the flour, prepared as above, is employed in the manufacture of bread, biscuits, or similar food, it only requires to be made into dough with water in the proportion of 10 oz. of water to 1 lb. of flour for bread, and 6 oz. of water to 1 lb. of flour for biscuits, and baked at once in a well-heated oven.—Sealed March 13, 1845.

THE CHEMICAL GAZETTE.

No. LXXV.—December 1, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Bezoaric and Glaucomelanic Acids.

By F. Merklein *and* F. Wöhler.

In a chemical point of view the concretions known as bezoars may be divided into three kinds,—1st, such as consist of phosphate of lime and ammonio-phosphate of magnesia; 2nd, those consisting of lithofellinic acid; and 3rd, those consisting of a peculiar substance, bezoaric acid.

The latter compound is the object of our examination. We were long ago occupied in an investigation of it, and had succeeded in procuring it in a pure crystalline state and recognised its properties as an acid, when Lipowitz published some experiments which had led him to the same result; but he did not ascertain its composition*.

The bezoars containing it, and which constitute the true oriental bezoars, are of a dark olive-green, sometimes brownish or mottled colour, usually of an egg or kidney-shape; the surface is smooth, as if polished; they are brittle, and exhibit internally a laminated, concentric structure, having generally some dull surfaces of stratification of a somewhat different colour. The surface of transverse fracture exhibits an indistinctly crystalline splintery texture. All the bezoars we have examined contain within them a foreign substance, which is frequently loose, and has evidently formed a nucleus. In some cases this was composed of the chewed bark of a tree; in one it was a fruit, which Prof. Grisebach determined to be that of a leguminous plant. These bezoars have a faint, agreeable smell, like that of musk or ambergris, which is particularly evident when they are bruised or dissolved in solution of potash. They somewhat resemble the bezoars consisting of lithofellinic acid, but are easily distinguished from them by a fragment of the latter readily fusing, whilst the bezoaric acid is infusible, and is converted into a cinder, which becomes covered with shining yellow crystals.

We find the following to be the best method of obtaining pure bezoaric acid:—The bezoars, separated from the nucleus, are finely pulverized; the powder is covered with a moderately strong solution

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* Chem. Gaz., vol. ii. p. 121.

of caustic potash in a vessel which can be closed air-tight, and which is completely filled: it is then shaken until it is dissolved*. The amount of potash must be so regulated that neither bezoarate of potash is left undissolved, nor too great an excess of potash remains. Heat must not be applied, nor must the solution be set aside too long, nor air admitted, otherwise the substance will be decomposed. The solution is of a deep saffron-yellow colour. When clear, it is carefully removed by a siphon filled with water from the sediment, which is usually but small and consists of foreign matters; a copious current of washed carbonic acid is then immediately passed through it, which precipitates nearly the whole of the bezoaric acid in the state of a neutral potash salt. The precipitated salt, which is at first almost white, subsequently becoming pale greenish-gray, is separated by filtration, washed repeatedly with cold water without agitation, and pressed between bibulous paper. The yellowish or greenish-brown filtrate is immediately precipitated by muriatic acid; the precipitated bezoaric acid is brown, but may be purified by a repetition of the above process.

The precipitated potash salt is purified by solution in water which has been boiled, and is at an almost boiling temperature, and filtration, by which it is separated from a heavy pale green or yellow powder, which is the anhydrous salt, and is formed in greater abundance in proportion to the length of time and the intensity with which the liquid has been heated with the undissolved portion of the potash salt. On the subsequent addition of warm water, the whole is perfectly but slowly dissolved. On cooling and subsequent repose, the potash salt subsides in voluminous crystalline masses, which are filtered, washed with water, pressed and dried. The acid is separated by redissolving the salt in hot water and pouring the solution into dilute muriatic acid, at the same time agitating the vessel, and allowing the muriatic acid to remain in slight excess. The precipitated acid is washed with cold water and dried.

The pure bezoaric acid forms a light pale yellow powder. When magnified, it is seen to consist of transparent prisms. Its specific gravity at 65° F. is 1·667. It is tasteless. At a higher temperature a portion sublimes, condensing in sulphur-yellow crystals on the cinder like indigo, but the mass does not fuse; a large portion however is decomposed. It is but little soluble in cold water, and insoluble in æther. Alcohol dissolves it slightly, acquiring a pale yellow colour; the solution is slightly acid. It dissolves in concentrated sulphuric acid, becoming yellow, but is precipitated unchanged on dilution with water. If the sulphuric solution is exposed to the air, the acid is deposited unaltered in long, delicate, almost colourless prisms. It is immediately dissolved by caustic potash, assuming a saffron colour.

Crystallized bezoaric acid gives off on an average 10·88 per cent. of water by heat. This is equal to 2 atoms (10·64 per cent.). It be-

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* Judging from the properties of the soda salt, which we shall detail presently, solution of soda would be preferable.

gins to escape even at 212°. If heated to 392° and upwards, it subsequently remains anhydrous when exposed to the air; but if the water be expelled by a heat of 248°, it gradually absorbs the water from the air. When precipitated by water from its sulphuric solution, it also contains the same amount of water, although the yellow colour, produced on treatment with the concentrated acid, results from its abstraction.

The acid, dried at 392°, was analysed with the employment of oxygen gas; it yielded—

	I.	II.	III.	Calculated according to $C^{14}H^{3}O^{8}$.
Carbon ……	55·67	55·34	55·65	55·67
Hydrogen….	2·16	2·11	2·13	1·98
Oxygen……	42·17	42·55	42·22	42·35

Its atomic weight was found from the potash salt precipitated by carbonic acid, as a silver salt could not be prepared, and the lead salt was not constant in its composition. It yielded—

	I.	II.	Calculated according to $KO+C^{14}H^{2}O^{7}$.
Potash …………	24·32	24·63	24·93
Carbon …………	43·99	44·56	44·44
Hydrogen ………	1·39	1·27	1·05
Oxygen …………	30·30	29·54	29·58

Hence the acid dried at 392° F. contains 1 atom of basic water, which is replaced in the potash salt by an atom of potash. The equivalent of the anhydrous acid is therefore $C^{14}H^{2}O^{7}$, or 1776·64, and the crystallized acid is $= (HO + C^{14}H^{2}O^{7}) + 2HO$.

From this composition, and the properties we have above detailed, we arrive at the remarkable fact, that this substance, as previously suspected by Th. Taylor*, is nothing more than ellagic acid, or the acid which was first procured by Chevreul from galls, and more accurately examined by Braconnot. To remove any doubt, we prepared ellagic acid from galls, and compared its properties with the bezoaric acid, and found them perfectly identical. Pelouze, in his analysis of dried ellagic acid, obtained $C = 55{\cdot}31$ and $H = 2{\cdot}66$ †, and gave the formula $C^{7}H^{2}O^{4}$, which differs from ours by one atom more of hydrogen. Since we constantly found in our analyses more carbon and less hydrogen than Pelouze, we consider our formula as the correct one ‡.

Bezoarate of Potash.—The preparation of this salt has been described above. When dried, it forms a loose, light, papery mass, appearing under the microscope as an interlacement of transparent prisms, frequently combined into fan-shaped bundles, generally of a pale greenish-gray or greenish-yellow colour. It is but little soluble in cold water, considerably more so in hot, forming a greenish solu-

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[*] Lond., Edinb. and Dublin Phil. Mag., 1844, May, p. 354.

[†] $C = 75{\cdot}12$.

[‡] The authors consider it advisable to retain the name bezoardic acid, as the German name "Ellagsäure," besides being ill-formed, is by no means harmonious; a change which few chemists, in our opinion, will be inclined to approve of.—W. F.

tion, from which it subsides on cooling in prisms united into flakes. The amount of water was not ascertained; it parts with it so readily, that even on boiling in a saturated solution it becomes anhydrous and yellow. On heating to redness, it is decomposed, burning, like tinder, without evolving any odoriferous products, leaving a residue of carbon and carbonate of potash. A second salt is formed by adding a solution of hydrate of potash in alcohol to the acid or neutral salt and digestion; it speedily decomposes. It forms a dark citron-yellow powder, consisting of microscopic, yellow transparent prisms. It is insoluble in alcohol. It must be preserved from access of air, filtered, washed with alcohol, pressed and dried *in vacuo* over sulphuric acid. It becomes blackish-green, and is converted into the neutral salt and carbonate of potash by exposure to the air. It is readily soluble in water, forming a deep yellow solution, which is easily decomposed. It contains 34·0 per cent. of potash. Hence it appears to consist of $3KO + 2C^{14} H^2 O^7$, which requires 33·2 per cent. of potash. If it consisted of 2 atoms of potash to 1 of acid, it would require nearly 40 per cent. of potash.

Bezoarate of Soda.—The neutral salt is precipitated from a solution of the acid in caustic soda by carbonic acid, in the form of a bright yellow crystalline powder, which appears to be more difficultly soluble than the potash salt. It yielded on analysis 17·3 per cent. of soda. The formula $NaO + C^{14} H^2 O^7$ requires 17·99 per cent. On dissolving bezoaric acid in a boiling solution of caustic soda, the deep yellow solution, if preserved from contact with air, deposits on cooling a voluminous, beautiful lemon-yellow mass of concentric, delicately-radiated, warty aggregations. It is soluble in pure water, and may be recrystallized from a boiling solution, although a considerable quantity of it is decomposed. In the solid state it immediately becomes blackish-green on exposure to the air.

Bezoarate of Ammonia.—Caustic ammonia does not dissolve much of the acid, but the latter absorbs some ammonia. On mixing neutral bezoaric acid with muriate of ammonia, the bezoarate of ammonia is thrown down in the form of a bright olive-green precipitate. By exposing the anhydrous acid to a current of dry ammoniacal gas, it absorbs it, heat being evolved, and assumes a bright greenish-yellow colour. In one experiment, 0·508 grm. of the ammoniacal salt was obtained from 0·449 grm. of the acid; hence the compound appears to consist of $2NH^4 O + 3C^{14} H^2 O^7$. However, when the readily-dehydrated acid was treated with ammonia, its weight was but little altered, although water was copiously evolved. 0·6170 of the ammoniacal salt was obtained from 0·6195 acid. This appears to be neutral bezoarate of ammonia, $NH^4 O + C^{14} H^2 O^7$.

Bezoarate of Baryta.—When the acid is treated with barytic water, it immediately assumes a deep lemon-yellow colour, without dissolving. The air turns it of a pistachio-nut green colour; at the same time it absorbs carbonic acid. The dried salt yielded 45·35 baryta. It is composed therefore of $3BaO + 2C^{14} H^2 O^7$, which according to calculation should contain 44·6 per cent. of baryta. The neutral salt would contain 35 per cent., and the acid salt 51 per cent. of baryta. The *lime salt*, prepared in the same manner as the barytic salt, has exactly the same properties.

Bezoarate of Lead.—When a solution of bezoaric acid in alcohol is mixed with an alcoholic solution of acetate of lead, a yellow amorphous precipitate is formed, which becomes olive-green on drying. It appears essentially to consist of $2PbO + C^{14} H O^{7}$. It gave 63 per cent. of oxide of lead. The formula requires 61 per cent.

Glaucomelanic Acid.—We wish to designate by this name, from the bluish-black colour of its salts, an acid which is formed by the action of the air on the basic alkaline bezoarates.

If bezoaric acid be dissolved in a tolerably strong solution of caustic potash, and the deep yellow solution exposed to the air, it immediately assumes a deep reddish-yellow, frequently almost blood-red colour, which in a short time becomes paler, the surface of the solution becoming at the same time covered with delicate black crystals, which gradually increase, enlarge, and fall to the bottom; their quantity however is always very small. This is the glaucomelanate of potash. If the solution be exposed to the air too long, bezoarate of potash also separates from the action of the carbonic acid. The solution is decanted, the black crystalline powder is collected on a filter, and washed at first with a weak solution of potash to remove the bezoarate, and then with cold water.

Glaucomelanate of potash forms a black, shining, crystalline powder, tinged with blue. When magnified 200 times, it appears to consist of thin broad prisms, which are transparent and of a blackish-blue colour. It is but little soluble in cold water, considerably more so in hot; but in the latter case it is completely decomposed, so that on cooling the black salt is not again deposited, but bezoarate of potash as a grayish-green crystalline powder. The black salt is dissolved by hot concentrated solution of potash, forming a deep verdigris-coloured solution, which soon becomes deep yellow by exposure to the air. It is insoluble in alcohol. Heated in a tube, the black salt gives off water and then carbonizes, without evolving any empyreumatic products. It leaves a mixture of carbon and carbonate of potash. By warming the salt with muriatic acid, pure bezoaric acid is separated. Nitrous acid vapour colours the black salt of a beautiful purplish-red, a reaction which bezoaric acid also exhibits.

Glaucomelanate of potash contains water of crystallization, three-fourths of which are removed *in vacuo*. The whole is evolved at 212°, without the salt being the least altered in appearance. In two experiments the water amounted to 16·96 and 16·72 per cent.

The salt, dried at 392°, when burnt in the same manner as the bezoarate of potash, gave—

	I.	II.	Calculated according to $KO + C^{12}H^{2}O^{6}$.
Potash	26·83	28·68	27·88
Carbon	41·72	40·96	42·54
Hydrogen	1·29	0·98	1·18
Oxygen	30·16	29·38	28·53

Thus the water in the salt amounted to 4 atoms or 17·53 per cent. In both analyses the residuary carbonate of potash contained some unburnt carbon, which was calculated for. The potash was estimated by chloride of platinum. The difference in the numbers is explicable from the fact that the salt begins to part with water even at the ordinary temperature. An analogous black salt may be obtained with soda, but it is procured with much greater difficulty.

The authors suggest that the conversion of gallic into bezoaric acid may probably occur when a solution of an alkaline gallate mixed with excess of alkali is exposed to the action of the air, by which the gallic acid is so rapidly decomposed with the well-known changes of colour. At a certain period of the action of the air, the solutions may contain bezoaric acid; its formation may have hitherto escaped observation, because, as has been shown above, it is so speedily changed; on the other hand, it must be remarked, that as soon as a concentrated solution of bezoaric acid in potash comes into contact with the air, it exhibits the same alteration of colour to a blood-red as a solution of gallic acid in potash.

Considering the relations of bezoaric to gallic acid, it appears highly probable that the animals in which these kinds of bezoars occur, feed upon plants containing tannic acid; this tannic acid is converted by digestion into bezoaric acid, but is not subsequently acted upon by the digestive process, and forms the bezoars.—*Ann. der Pharm.*, Aug. 1845.

On the Acids of the Fir. By A. LAURENT.

I have ascertained from recent researches that the natural acid of the fir is the pimaric acid. This compound is converted, either by time or under the influence of certain agents, into two isomeric compounds, the pinic and sylvic acids. It is erroneously stated, in all treatises on chemistry, that the sylvic acid crystallizes in quadrilateral prisms; its form is highly remarkable, and alone suffices to distinguish this acid at first sight; its crystals have the form of triangular tablets. It is this error which prevented me from recognizing the identity of the sylvic and pyromaric acids. With respect to the amorphous pimaric and pinic acids, they are probably identical; the pinic and sylvic acids which are met with in the commercial resin are derived from modifications which the natural or pimaric acid has experienced with time, or under the influence of heat and light.—*Comptes Rendus*, Oct. 13, 1845.

On the Composition of the Yolk of Egg. By M. GOBLEY.

In a preceding memoir* I pointed out the presence of oleic, margaric and phosphoglyceric acids in the yolk of egg; at present I believe I am able to conclude from my experiments that the yolk of egg moreover contains water, an albuminous substance, or

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* See Chem. Gaz., vol. iii. p. 443.

vitelline, oleine, margarine, cholesterine, salts, two colouring substances, osmazome, traces of lactic acid and traces of iron.

The quantity of water was determined by heating the yolk of egg in the water-bath until it ceased to lose in weight. Before submitting it to this operation, it must be entirely deprived of the albumen which surrounds it. This process is very simple; it consists in placing the yolk of egg on a piece of linen, and sliding it to and fro until it ceases to moisten it.

The albuminous substance or vitelline has much analogy with albumen, from which it differs especially by its composition. It was obtained entirely free from all fatty matter, by treating the yolk of egg, deprived of albumen and dried by exposure to the air on plates, with boiling alcohol. These alcoholic digestions were continued until the vitelline was entirely decolorized. The yolk of egg yields on an average 16·557 per cent. Submitted to analysis, the vitelline prepared by the process just described gave results which agreed with those of MM. Dumas and Cahours.

The yolk of egg is not an ordinary emulsion, that is to say, a liquid in which a fixed fatty matter is held suspended in water by means of the albuminous matter, as is generally believed. An ordinary emulsion may be diluted with water without any separation of its elements resulting; while a separation does really occur when a large quantity of this liquid is added to the yolk of egg. Among the properties of the yolk of egg, one of the most remarkable which it possesses is that of dissolving in dilute vegetable acids; the liquid merely preserves a faint opakeness.

The oil of egg is formed in great part of oleine and margarine, but it moreover contains cholesterine and some colouring matter; neither phosphorus nor sulphur occurs in it, as is generally believed. Soon after its preparation, it deposits a solid matter, the quantity of which is the more considerable as the temperature is low. This deposit, which has hitherto been considered as formed of stearine mixed with a small quantity of oleine, is composed of margarine, oleine, cholesterine and colouring substance. To separate these ingredients, it must be treated with weak boiling alcohol, which removes the cholesterine and the colouring substance, as well as a small quantity of oleine. The decolorized oil consists of oleine and margarine; on saponification with potash, it yields glycerine and oleic and margaric acids, which presented all the properties and the composition assigned to these bodies by M. Chevreul.

Cholesterine was discovered in the yolk of egg by M. Lecanu, and correctly characterized by that chemist. There was still some doubt as to the identity of this product with that which M. Chevreul obtained from biliary calculi; in fact, the cholesterine of M. Lecanu fuses at 293°, while that of M. Chevreul melts at 279°. It was therefore important to ascertain whether the cholesterine of the yolk of egg was identical with that from biliary calculi. On submitting the cholesterine from the yolk of egg to analysis, I obtained numbers which agreed perfectly with those of M. Chevreul. I then sought to explain the difference in the points of fusion; for that purpose I experimented with the two cholesterines in the same bath, and I found that both authors were perfectly correct, only that M. Chevreul had noted, as he states in his 'Traité sur les Corps gras,' the moment when the melted substance solidifies, and M. Lecanu that at which it begins to melt. The cholesterine from the yolk of egg is therefore identical with that from biliary calculi. 100 parts of yolk of egg contain about 0·438.

The cholesterine cannot be kept in solution in the yolk of egg by means of the oily substance only; the soapy portion must likewise assist, for the oil of egg cannot hold it all in solution at the ordinary temperature. Wagner observed that an aqueous solution of 4 parts of soap dissolved 1 part of cholesterine; now since this proportion is still higher in the yolk, it is allowable to think that the cholesterine is partly dissolved by its mediation. Is this the case with respect to the blood and bile? May it not be on account of the quantity of soap not being sufficiently considerable in the bile, that a portion of the cholesterine separates to form biliary calculi? According to this hypothesis, the soap preparations would prove very useful to individuals affected with this disease.

Turmeric and litmus-paper do not change colour when brought into contact with the yolk of egg; blue litmus-paper appears, on the contrary, to assume a faint rosy tint. The yolk would consequently appear to be neutral or very slightly acid. However this may be, it is certain that on boiling it in water an acid liquid is obtained, which becomes more acid on concentration, and when absolute alcohol is added to it. The precipitate which this latter causes consists of earthy phosphates and animal matter, which appears to prove that the acidity of the liquid was concealed by the phosphates. The filtered liquid contains a certain quantity of the indefinite substance to which M. Berzelius has given the name of extract of meat, and yields to æther, after having been evaporated, an acid which exhibits the properties of lactic acid.

The composition of the liquid obtained on treating the yolk of egg with water is highly remarkable, for we find in it all the principles which chemists have met with in the gastric juice; lactic acid, chloride of sodium, chloride of potassium, muriate of ammonia, sulphate of potash, phosphate of lime, phosphate of magnesia and animal matter.

The presence of lactic acid in the yolk of egg is of considerable importance in a physiological point of view. The solvent property which it possesses leads to the belief that it is the principal agent of digestion in the young chicken, and that it is through it, that a part of the phosphates penetrate into the body of the young animal.

To obtain the saline matters of the yolk of egg, this is first treated with boiling water, which removes the soluble salts and a portion of the earthy phosphates. The residue from the first operation is then treated with water acidulated with acetic acid, which yields on evaporation and calcination the phosphates of lime and magnesia. On treating the salts obtained with ammonia, the chloride of sodium, chloride of potassium and sulphate of potash are dissolved, and the phosphates of lime and magnesia remain. 100 parts of yolk yield on an average chloride of sodium and potassium, 0·268; sulphate of potash, 0·09; phosphates of lime and magnesia, 0·402. One of the elements of the yolk has hitherto not been deprived of all the phosphates it contains; this is the vitelline, which does not yield it either to water or to acetic acid. To ascertain how much it held back, the residue of the two preceding observations was exhausted by boiling æther and alcohol; 0·934 of the substance gave 0·035 of phosphate by calcination, so that the yolk of egg does not contain more than 1 per cent. of earthy phosphate. Besides the above, the yolk contains muriate of ammonia.

Prout imagined that eggs just on the point of being hatched contained more lime and magnesia than fresh eggs. According to his experiments, the former contained 0·382 per cent., and the latter only 0·099. Not knowing to what to attribute this great difference, he supposed that the excess of lime and magnesia was either derived from the shell, or was produced entirely by the vital force at the expense of other substances—hypotheses which he himself however has qualified as untenable. Undoubtedly the process of analysis which he followed was defective, since I have obtained from the yolk of egg alone more lime and magnesia than he from the entire egg and young chicken. The proportion of saline matter existing in fresh eggs should be the same as that which occurs in eggs which have been set on; the state of combination of these salts may change under the influence of incubation, but I do not think that their quantity can vary.

The yolk of egg presents, as is well-known, an orange-yellow colour; M. Chevreul thought that it was owing to the union of two colouring principles, the one yellow, the other red; and then by an ingenious deduction he assimilated the first to the yellow matter of the bile, and the second to the red matter of the blood. In the various treatments to which I have submitted the yolk of egg, I have verified the existence of these two principles; but I have not succeeded in separating them accurately; the red colouring principle seemed to me more soluble in alcohol than the yellow one. I found some iron in the red colouring principle, and the yellow colouring principle appeared to me to possess analogy with the yellow matter of the bile. Thus are confirmed in some measure the previsions of M. Chevreul.—*Comptes Rendus*, Nov. 3, 1845.

On the Production of Iodoform. By E. Millon.

Iodoform is obtained by the combined action of iodine and the alkalies upon alcohol. The analogy of composition existing between this compound and chloroform renders it probable that it might also be prepared by substituting for the alcohol, acetone, pyroligneous æther, or any product of the methylic series. I have not attempted this mode of production, but I have recently found, in seeking to obtain a quick method of preparing iodide of potassium, that several substances give rise to the production of iodoform when simultaneously acted upon by iodine and carbonate of potash, or more advantageously by the bicarbonate.

Cane, grape and milk-sugar, gum, dextrine, and several albuminoid substances, are thus circumstanced. Iodoform is abundantly produced with these different substances, without however advantageously replacing the alcohol, at least under the conditions in which I experimented.

Equivalent quantities of iodine and of bicarbonate of potash should be employed, and a very small quantity of the organic substance; the iodine is added last and by degrees; heat is applied, when the iodoform becomes almost immediately perceptible. The quantity of water will vary more or less; with sugar, 4 or 5 parts of water to 1 part iodine do very well.

When an albuminous substance (albumen, fibrine, caseine, gluten, legumine) is treated in this manner, it is well to employ at first a little caustic potash; the nitrogenous substance is thus readily dissolved, and the froth which is subsequently formed by the disengagement of carbonic acid is rendered less persistent.

The production of iodoform is somewhat limited, notwithstanding the instances above quoted; I have not succeeded in forming it with the resins, the fats, nor with the essential oils, among which I place the alcohol of amyle, as having furnished me with a negative result.

If we bring together the organic products, excluding the products of ultimate decomposition, which are common to the decomposition of the sugars, gum and alcohol, we only find the acetic and formic acids; we must at present add to them iodoform.

With respect to the products of decomposition which are derived both from the hydro-carbonaceous substances, such as the sugars, gums, &c. and the albuminoid substances, they are already sufficiently numerous. Acetic acid exists in the products of distillation of all; an energetic oxidation gives rise to oxalic acid; formic acid was pointed out by M. Mulder among the number of principles which potash liberates from albuminous substances; we likewise owe to M. Mulder the remarkable discovery of humic products in the reaction of hydrochloric acid on the albuminoid substances; the same hydrochloric acid likewise forms humic compounds at the expense of hydro-carbonaceous substances; iodoform presents a new member common to these two classes of substances, which acquire each day a more considerable part in organic phænomena.—*Comptes Rendus*, Oct. 6, 1845.

On the Action of Prussic Acid, the Cyanides, Alkaline Chlorides, Bromides and Iodides on Mercurial Compounds, especially on the Protochloride of Mercury. By Dr. E. Riegel.

Several cases have recently occurred in which the cotemporaneous internal use of the protochloride of mercury with water containing prussic acid has been accompanied by highly injurious consequences. The reason of this was owing to the prussic acid, and waters which contain it, decomposing the protochloride of mercury, and forming percyanide of mercury and hydrochloric acid, with separation of metallic mercury. Bérenger recently found, after Scheele, and subsequently Soubeiran and Regimbeau had observed the decomposition of calomel by bitter almond-water, that on mixing prussic acid with protochloride of mercury, percyanide of mercury was constantly found. By mixing 100 grs. of calomel with 25 oz. of cherry-laurel water, there were obtained, according to Béranger, 90 grs. undecomposed calomel, 5 grs. cyanide of mercury, and 5 grs. metallic mercury. Béranger has however not stated what became of the hydrochloric acid which was formed in his experiments, as this could not escape. According to Mialhe, on pouring an excess of prussic acid upon protochloride of mercury, there is formed, first percyanide of mercury, muriatic acid and metallic mercury; as soon however as this reaction is over, muriatic acid and percyanide of mercury act so upon each other that perchloride of mercury and hydrocyanic acid result; however, this decomposition is only partial. A little ammonia and formic acid occur as accessory products. Æther readily extracts the prussic acid and corrosive sublimate, and leaves undissolved the cyanide of mercury.

The behaviour of prussic acid towards the protiodide and protobromide of mercury, as well as to the protosalts of mercury, is quite analogous to that with calomel. Corrosive sublimate is likewise decomposed by prussic acid, a certain amount of cyanide of mercury is formed and a corresponding quantity of hydrochloric acid. In some recent experiments with cherry-laurel water, Béranger observed indeed the formation of cyanide of mercury, but was unable to detect the formation of perchloride of mercury and hydrochloric acid, as iodide of potassium produced no precipitate in the water digested with calomel. This phænomenon is explained from the fact that the calomel which is set free by the decomposition of the chloride combines, according to Béranger, entirely, or for the greater part, with the benzoyle, forming chloride of benzoyle. On evaporation of cherry-laurel water which has been digested with calomel, there is obtained, besides crystallized cyanide of mercury, a yellow oily fluid, soluble in water but not in æther, of a strong odour of oil of bitter almonds and sharp burning taste; it becomes hard on drying, and resembles gum-arabic. Mixed with pure lime, and exposed to red heat in a glass tube, decomposition occurs, dense suffocating vapours are given off, resembling those of benzoic acid, and the chlorine combines with the lime; accordingly the reaction of the cherry-laurel water should be distinguished from that of the pure prussic acid.

When, according to the author, 6 oz. of cherry-laurel water of the Prussian Pharmacopœia are poured over 1 oz. of calomel, immediate decomposition results, the formation of metallic mercury being directly perceptible. If the mixture is digested at the ordinary temperature for 8 days, and the liquid filtered from the gray sediment, the solution exhibits no essential change with reference to its original odour; it possesses a metallic taste and faintly reddens blue litmus-paper. Hydrosulphuret of ammonia produces in it a black precipitate, iodide of potassium a yellowish-white one, which soon becomes dirty red, but finally assumes a beautiful scarlet-red, nitrate of silver a white precipitate insoluble in nitric acid; lime water and caustic potash produced no change. When the liquid is evaporated, it loses its original odour and acquires one similar to that of balsam of Peru. A crystalline powder separates, and on the bottom of the vessel a yellowish oily substance.

When a mixture of calomel and cherry-laurel water in the above proportions is digested for 5 or 6 hours between 176° and 194°, being frequently agitated, the reaction appears to be far more energetic, the protochloride of mercury becomes black, and the filtered liquid possesses an insupportable metallic taste, strongly reddens blue litmus-paper, and no longer blackens calomel. It yields with hydrosulphuret of ammonia an abundant black precipitate, with iodide of potassium a white one, which soon becomes yellowish, and finally scarlet, and with nitrate of silver a precipitate insoluble in nitric acid. A slip of copper immersed in it becomes immediately coated with a film of mercury. When the liquid is diluted, it is rendered turbid, and finally exhibits some yellow oily drops. On cooling, two distinct layers are perceptible, an upper aqueous one, and an under oily one of the colour of cinnamon oil. By evaporating the former, a residue is obtained consisting of percyanide of mercury, perchloride of mercury, chloride of ammonium and benzoic acid, as well as some muriatic acid.

The above-mentioned oily substance possesses a yellow colour, great resemblance to the oil of cinnamon, and the odour of the hydruret of benzoyle; it boils at about 250°, when a colourless fluid of somewhat less specific gravity passes over, which solidifies on cooling, and is a combination of hydruret of benzoyle and perchloride of mercury. The unrectified fluid undergoes no apparent change in low temperatures; it dissolves in every proportion in æther, in 30 parts water and 10 parts alcohol; it was found impossible to deprive this body of the perchloride of mercury by treatment with water or chloride of sodium; but the whole of the corrosive sublimate may be removed by repeated mixing with a solution of chloride of ammonium, when the substance appears to become only somewhat specifically lighter. Hydrocyanic acid could not be detected in it by reagents.

This oily body is not formed when a solution of percyanide or perchloride of mercury in cherry-laurel water is evaporated; it is however obtained when a corresponding quantity of hydrochloric acid is added to the solution of the percyanide. The presence of hydrochloric acid appears to cause the formation of this body, which is independent of the action of the cherry-laurel water upon calomel, for it is only produced upon evaporation and at a certain concentration of the liquid. When, instead of evaporating this, it is saturated with chloride of sodium and treated with æther, the latter leaves on evaporation oil of bitter almonds, which contains some hydrochloric acid.

Prenteloup found that the chloride of benzoyle never assumes a solid state, at least at the ordinary temperature, and that it is rapidly decomposed on boiling with water. The dried mixture, which presents, according to Béranger, a gummy appearance, should be considered, according to Prenteloup, as an oxide, and consists of benzoic acid, traces of hydruret of benzoyle and perchloride of silver. This explains why a mixture from the evaporated residue, derived from the action of cherry-laurel water upon calomel, yields at a red heat with lime an odour similar to that of benzoic acid and chloride of calcium.

On treating calomel with dilute prussic acid, phænomena analogous to the above occurred, with the exception that no formation of the oily body resulted even on evaporation. Bromide and iodide of mercury behave precisely like calomel. The action of the alkaline chlorides upon the protochloride of mercury constitutes an exactly similar phænomenon. According to Mialhe, calomel in the presence of chloride of ammonium, potassium, or of sodium and pure water, is converted partially into perchloride of mercury with separation of some pure metal; the protiodide of mercury likewise passes under the same circumstances into periodide. According to the experiments of Cattanel di Moma, calomel in contact with chloride of ammonium, or common salt, at 104°–118° undergoes no change; but according to Abbene corrosive sublimate is formed at 212° from calomel under the above circumstances. Larroque arrived at the same results from his experiments. The latter thinks that the protochloride of mercury cannot be converted into the perchloride without the separation of some metallic mercury. Mialhe attributes the formation of perchloride solely to its affinities for the alkaline protochlorides. The formation of the perchloride is less when the air is excluded than when this is not the case. The alkaline protochlorides form, in the presence of calomel and atmospheric air, 3 times as much corrosive sublimate as without the latter, since at the ordinary temperature calomel is capable of absorbing a certain quantity of air, as was shown by Guibourt; at a higher temperature the absorption is greater, and it is likewise hastened by the presence of the alkaline chloride. Each equivalent of peroxide of mercury formed by this absorption of oxygen yields, by double decomposition with the alkaline protochloride, 1 equiv. perchloride and 1 equiv. alkaline oxide. It is remarkable that the perchloride is not decomposed by the alkali; Mialhe explains this from the great affinity between the perchloride and the alkaline chlorides; at least magnesia precipitates corrosive sublimate alone, but not in combination with an alkaline protochloride; whence it follows that the alkaline solution of protochloride can decompose calomel into corrosive sublimate with excess of air, without the liberation of metallic mercury. According to this the chlorides of the alkalies convert the calomel in the cold partially into perchloride without separation of metallic mercury; but on the application of heat corrosive sublimate is formed and metallic mercury set free.

Since the perchloride of mercury does not occur in the above mixture alone, but in combination with the alkaline oxide, or as basic perchloride, æther according to Mialhe does not remove anything from it. Larroque, on the contrary, asserts that when a mixture of 1 part calomel, 1 of an alkaline protochloride and 42 parts water are kept boiling for some time, the perchloride can be detected in the filtered liquid by iodide of potassium, protochloride of tin and sulphuretted hydrogen; when chloride of ammonium is employed, the application of heat is not even necessary to give rise to the production of perchloride, which may be extracted by æther.

Selmi found that calomel in contact with animal albumen was partially converted into corrosive sublimate, not only when the reaction was alkaline, but even in the presence of some free acetic acid. If 4 grs. chloride of sodium are dissolved in 3 drms. albumen, and shaken for 15 minutes with 3 grs. of calomel, metallic mercury is formed, while 10 grs. of chloride of sodium, dissolved in 2 drms. of water, give no reaction with 3 grs. of calomel. Chloride of ammonium acts more powerfully under the same circumstances than chloride of sodium, about as $\frac{2}{3} : \frac{1}{2}$. According to Grimelli, the albumen itself, from the sulphur it contains, acts on the calomel, on which account the albumen of eggs which have been sat on exhibits a stronger reaction than that of fresh eggs.

It results, from the experiments of the author, that when 1 part calomel is mixed with 2 parts of an alkaline chloride and 10 parts water at the ordinary temperature, no perceptible reaction occurs. After digestion for several days, the protochloride of mercury became somewhat gray, and most so when chloride of ammonium was employed. The quantity of perchloride of mercury remaining on evaporation was however very inconsiderable. On heating a mixture of an alkaline chloride with calomel and water, a dark gray colouring of the sediment immediately results, arising from the separation of metallic mercury, and the presence of perchloride of mercury may very readily be detected in the filtered liquid. On evaporating the liquid, and treating the residue with æther, the entire quantity of the perchloride formed is extracted. When calomel is shaken for 10 to 15 minutes with the chloride of an alkali and albumen, the separation of metallic mercury and formation of corrosive sublimate is immediately perceptible.

The alkaline bromides and iodides have likewise a decomposing action on calomel; it is entirely decomposed by an excess of alkaline protiodide, especially on the application of heat; the mixture becomes gray, yellowish-red, melts and becomes brownish-black; metallic mercury and periodide of mercury sublime in consequence of the decomposition of the protiodide in the presence of alkaline protiodides. The residue is whitish, entirely soluble in water, and consists of alkaline protochloride and alkaline protiodide. The alkaline and other soluble protiodides, as those of ammonium, magnesium, iron and zinc, decompose calomel, which at the moment of contact assumes a grayish-green colour, which on trituration of the mass becomes dark green. Under the influence of light, the mixture acquires a yellowish, and finally red colour; at the same time globules of metallic mercury are observed, protiodide of mercury and alkaline protochloride being formed. On treating the protiodide or protobromide of mercury with a chloride of the alkalies in the presence of water, no apparent change of the protobromide or protiodide appeared to occur at the ordinary temperature; but if the mixture is exposed to the temperature of 212°, some periodide or perbromide is dissolved in the liquid.—*Journ. für Prakt. Pharm.*, x. p. 8.

On the Relations of Oil of Mustard to Oil of Garlic.

By T. Wertheim.

In a former communication, I stated as my opinion, that oil of mustard might be considered as a sulpho-cyanic compound of allyle. In a paper on the oil of mustard*, which appeared about the same time, Dr. Will attempted to establish the same view. I have at last succeeded in obtaining the most direct proof of it, as will be seen from the experiments which I shall now proceed to describe.

1. If oil of mustard be exposed to the action of soda and lime in a hermetically-sealed glass tube for some time, at a temperature of about 248°, when this is opened the intensely-pungent odour is no longer perceptible, but is replaced by an aromatic smell resembling that of leeks. If this experiment be modified, by bending the tube at a right angle before fusing it, and the apparatus be now placed perpendicularly in the oil-bath, so that any unaltered oil may constantly flow back into the mixture of soda and lime, and if, when the reaction is complete, it be placed horizontally, so as to collect the distillate in the empty part of the tube, on applying a continued heat a perfectly colourless oily liquid collects in it in tolerable quantity. If 50–60 drops of the oil have been used, after 12 hours' heating in the perpendicular position the distillation may be commenced. The distillate possesses the odour and general properties of oxide of allyle, as obtained by decomposing the nitrate of silver and oxide of allyle with an alkali. The substance for analysis was dehydrated in the distillatory apparatus itself, by inclosing a piece of fused chloride of calcium, by means of a wire-gauze, in the empty limb previous to sealing it. This prevented the chloride of calcium from falling into the other end of the tube while in the perpendicular position. 2 portions of the substance separately prepared gave with chromate of lead—

Carbon	67·17	65·71
Hydrogen	9·30	9·14

If we calculate the quantities of hydrogen, which are in the same proportion to the quantities of carbon thus obtained as in the oxide of allyle, they are as follows:—

	I.	II.
Carbon	67·17	65·71
Hydrogen	9·21	9·01

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* Chem. Gaz., vol. iii. p. 253.

Thus the results of analysis are perfectly consistent with the idea that the analysed substance contains the radical allyle.

The filled extremity of the tube contains sulphocyanide of sodium, as when treated with a few drops of solution of perchloride of iron and neutralized with muriatic acid, it instantly assumes an intensely blood-red colour. Sometimes it is requisite to add considerably more chloride of iron, as sulphuret of sodium is formed by the secondary action of the excess of alkali on the sulphocyanide of sodium formed, so that the first portions of the perchloride are reduced to the state of protosalt.

The above decomposition is easily explained, if we regard oil of mustard as sulphocyanide of allyle. By double decomposition we obtain from—

$$(C^2 N S^2) + All \text{ and } NaO,$$
$$(C^2 N S^2) + Na \text{ and } AllO.$$

We obtain further proof of this in being able to procure the beautiful crystallized silver compound obtained by mixing an alcoholic solution of nitrate of silver with oxide of allyle, as I have elsewhere described*. On mixing the distillate with an alcoholic solution of nitrate of silver, this compound was produced in abundance; and although there was no doubt of its identity, to be perfectly certain I analysed it, and obtained—

		Calculated.	Found.
6 atoms	carbon	16·57	16·17
5 ...	hydrogen	2·27	2·29
1 ...	silver	49·22	49·61
1 ...	nitrogen	6·45	
7 ...	oxygen	25·49	

The calculation corresponds to the formula $AgO + AllO + NO^5$, *i. e.* nitrate of silver and oxide of allyle.

2. If oil of mustard be mixed with sulphuret of potassium, obtained by subjecting neutral sulphate of potash with charcoal to a white heat, and under the same conditions as with the soda and lime, corresponding changes are produced. The distillate possesses the odour and properties of oil of garlic; the residue, in the filled portion of the tube, contains sulphocyanide of potassium. The metamorphosis readily occurs; the temperature need scarcely exceed 212°. The distillate, mixed with an alcoholic solution of chloride of platinum, yields a beautiful yellow precipitate of the double sulphochloride—

$$(PtCl^2 + AllCl) + 3(PtS^2 + AllS),$$

the properties of which I have previously described†.

If, in this operation, a more highly sulphuretted compound be substituted for the sulphuret of potassium, after long application of heat, a tolerably copious supply of crystals which have a powerful odour of assafœtida are formed in the empty end of the tube. These are probably a higher sulphuret of allyle. The same peculiar odour

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* Chem. Gaz., vol. iii. p. 181.

† Chem. Gaz., vol. iii. p. 179.

occurs in the higher sulphurets of cacodyle described by Bunsen. The explanation of the reaction of sulphuret of potassium is equally as simple as that of soda and lime; thus by double decomposition, we obtain from

$$(S^2C^2N) + \mathrm{All} \text{ and } S + K,$$
$$S + \mathrm{All} \text{ and } (S^2C^2N) + K.$$

3. It now only remained to ascertain whether, *vice versâ*, a decomposition could not be produced, and oil of mustard formed, by treating any suitable compound of allyle with sulphocyanide of potassium. This succeeded perfectly. I have described a compound*, which is formed by mixing alcoholic solutions of oil of garlic and bichloride of mercury, and the composition of which is expressed by the formula—

$$2(HgCl) + AllCl + 2(HgS) + AllS.$$

If this is mixed with excess of sulphocyanide of potassium, and the mixture is warmed to 248°–266° in a small distillatory apparatus, by which the sulphocyanide of potassium is fused, the mass is immediately blackened, the intense odour of oil of mustard is perceptible, and drops of it collect in the receiver. If the distillate be mixed with solution of ammonia in excess and evaporated at a gentle heat, we obtain crystals, there actions and external properties of which distinguish them indisputably as the combination of oil of mustard with ammonia. I considered it unnecessary to analyse them. These crystals, before being washed several times with alcohol, as also the mother-liquor from which they separated, had a strong odour of oil of garlic, which was particularly distinct when the excess of ammonia was neutralized by an acid. If the process which ensues here be analysed, all the phænomena are easily accounted for; for whilst the double sulpho-chloride,

$$2(HgCl) + AllCl + 2(HgS) + AllS,$$

reacts upon an excess of sulphocyanide of potassium, there is double decomposition, on the one hand between the groups $2(HgCl) + AllCl$, and 3 equiv. $S^2C^2N + K$ on the other; 3 equiv. of chloride of calcium, 2 equiv. of sulphocyanide of mercury and 1 equiv. of sulphocyanide of allyle, *i. e.* oil of mustard, are formed; at the same time the connexion of the members of the other groups is destroyed, they being resolved into 2 equiv. of sulphuret of mercury and 1 equiv. of sulphuret of allyle, which passes over into the receiver with the oil of mustard. The blackening of the residue arises from the sulphuret of mercury which separates; the odour of the oil of garlic is perceptible when the penetrating odour of oil of mustard is removed by the addition of ammonia.

I have a tolerable quantity of oil of mustard which I prepared in the above way; the intimate connexion of oil of mustard with oil of garlic, as different compounds of one and the same radical, is thus placed in the clearest light.—*Ann. der Pharm. und Chem.*, Sept. 1845.

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* Chem. Gaz., vol. iii. p. 18

On a new Method of preparing Urethane. By A. CAHOURS.

M. Dumas, in his beautiful researches on the compound æthers, has shown that ammonia in the gaseous state forms, on acting upon certain of these products, a series of remarkable bodies, constituting a peculiar class, that of the *amethanes.* In the case of chloroxycarbonic æther, the aqueous solution of ammonia behaves precisely in the same manner as the dry gas. The action is violent, accompanied with disengagement of heat, production of chloride of ammonium, and formation of an amethane. The reaction takes place between 1 equiv. chlorocarbonic æther and 2 equiv. ammonia. We have—

$$\underset{\text{Chlorocarbonic æther.}}{C^6 H^5 Cl O^4} + 2N H^3 = Cl H N, H^3 + \underset{\text{Urethane.}}{C^6 H^7 N O^4}$$

The new substance received from M. Dumas the name of urethane, on account of its composition; in fact, $2(C^6 H^7 N O^4)$ may be decomposed into—

$$2(\underset{\text{Carbonic æther.}}{C O^2, C^4 H^5 O} + \underset{\text{Urea.}}{C^2 O, N^2 H^4}),$$

which would exhibit this substance as a combination of urea and carbonic æther. On considering the intimate analogies existing between carbonic and oxalic æthers, as well as the manner in which this latter behaves towards dry ammonia, I thought that this gas would also produce urethane by acting on carbonic æther. My suppositions have been entirely confirmed by experiment.

The best mode of operating is the following:—Pure carbonic æther is placed with its volume of liquid ammonia in a stoppered flask, and left until the æther has entirely disappeared. On evaporating the alkaline liquid *in vacuo*, a well-crystallized substance, presenting all the properties and the composition of urethane, is obtained. On analysis it yielded—

Carbon	40·37	..	12	40·45
Hydrogen	8·08	..	14	7·87
Nitrogen	..	15·96	2	15·73
Oxygen	..	..	4	35·95

The formation of urethane by means of carbonic æther is readily conceived. 1 equiv. of the hydrogen of the ammonia acts in this case on 1 equiv. oxygen of the carbonic æther, giving rise to the production of water, and consequently of alcohol, which is eliminated. We have therefore—

$$2(C O^2, C^4 H^5 O) + N H^3 = C^4 H^5 O, H O + C^6 H^7 N O^4,$$

another example of an identical substance being produced by two bodies essentially different.—*Comptes Rendus,* Sept. 12, 1845.

Preparation of the Chloride of Zinc.

M. Martiny proposes the following process for the preparation of pure chloride of zinc:—Commercial zinc is dissolved in crude muriatic acid, an excess of zinc left for some days in contact with the solution, the liquid heated with nitric acid, some recently precipitated oxide of zinc added to it, a current of chlorine passed through it, filtered and evaporated. When the saline mass is nearly dry, a small portion of recently formed nitromuriatic acid is added to it, after which it is dried. The chloride of zinc is of a brilliant white, and dissolves entirely in water. Buchner is of opinion that the above process may be considerably shortened; the addition of nitric acid appears superfluous if chlorine is passed into the solution, and then recently precipitated hydrate of the oxide of zinc added to separate the iron as peroxide; the *aqua regia* might likewise be dispensed with if in the drying of the chloride of zinc too high a temperature be avoided.—Buch. *Rep.*, xxxviii. p. 248.

ANALYTICAL CHEMISTRY.

On a Simple Method of detecting the least Traces of Sulphurous Acid.

By W. HEINTZ.

IN 1792, Pelletier, senior, published a tolerably sensitive test for sulphurous acid. In 1835, Girardin again directed the attention of chemists to this method, which had become almost forgotten. It is based on the action of protochloride of tin on this acid, and is indeed very applicable when the quantity to be detected is not too small. When, for instance, crystals of protochloride of tin are immersed in the liquid under examination, to which hydrochloric acid has been added, or protochloride of tin dissolved in hydrochloric acid and poured into the unmixed fluid, it becomes after a time yellow, turbid, and the yellow precipitate gradually acquires a brown colour when sulphurous acid was present. But if only extremely small traces are to be detected, this method no longer suffices; it then gives no result at all. This has led MM. Fordos and Gelis to recommend another one*, which in fact detects much smaller quantities of sulphurous acid. They employed it principally in examining the purity of muriatic acid. According to them, the acid is poured upon zinc, and the hydrogen evolved passed through a solution of a lead salt (they used basic acetate of lead). The sulphuretted hydrogen formed from the sulphurous acid throws down from the solution of lead sulphuret of lead. It is evident that this method may be employed, not merely in examining muriatic acid, but almost in every case where the absence of sulphuretted hydrogen has been proved. It is only requisite to add muriatic acid to the substance under examination, and to act with this liquid upon zinc.

However, notwithstanding the sensitiveness of this method, it has many inconveniences. In the first place, it is always necessary to have a peculiar, even though simple, apparatus for disengaging the gas; and, in the next place, the greatest care must be taken that the zinc contains no sulphur.

I have been led to a more simple and quite as sensitive a method,

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* See Chem. Gaz., vol. i. p. 264.

which indeed is identical with that first described by Pelletier, only the means by which I render the reaction more evident is new. The following is my process:—A solution of protochloride of tin in dilute muriatic acid is added to the liquid under examination, or to the substance dissolved in water or in muriatic acid, and the mixture heated to incipient boiling. This would produce decomposition, causing the precipitation of sulphuret of tin if there were any quantity of sulphurous acid present; but if the quantity is diminished to within a certain limit, no sulphuret of tin is deposited; the liquid however smells of sulphuretted hydrogen, and acquires a faint yellowish tint without becoming turbid. The smell would therefore already indicate a smaller quantity of sulphurous acid than requisite to produce a precipitation of sulphuret of tin. But since the smell, when only minute traces of the acid are present, might be concealed by the vapours of the muriatic acid, the presence of the sulphuretted hydrogen may easily be rendered perceptible by adding a few drops of a solution of sulphate of copper to the cold liquid. Sulphuret of copper is immediately thrown down, which from its intense colour indicates the presence of the most minute trace of sulphuretted hydrogen, consequently in this case also of sulphurous acid. A solution of chloride of bismuth in muriatic acid may likewise be employed instead of the solution of sulphate of copper; but acetate of lead cannot be used for the purpose, as no black precipitate, but a white one, would be obtained, consisting of chloride of lead.

The reaction is not quite so certain if the sulphate of copper is first added to the liquid into which some protochloride of tin has been conveyed, and the whole then heated; for in this case the protochloride of tin first reduces the oxide of copper. If therefore more of the copper solution has been added to the liquid than can be converted into the protoxide of copper by means of the protochloride of tin used, there remains in such a case none of the latter to convert the sulphurous acid into sulphuretted hydrogen. It is true, that when care has been taken to use an excess of the protochloride of tin, a reaction is also obtained in this way, the oxide of copper being first reduced to protoxide of copper, and the sulphurous acid being converted into sulphuretted hydrogen by the excess of the protochloride of tin, which produces a precipitation of sulphuret of copper.

The action of protochloride of tin on sulphurous acid and a solution of copper, and the liquid so obtained, may be rendered more intelligible by the following equation:—

$$2SO^2 + 6SnCl = SnS^2 + 2SnO^2 + 3SnCl^2$$
$$\text{and } SnS^2 + 2CuO = SnO^2 + 2CuS.$$

The reaction which occurs between the sulphurous acid, protochloride of tin and solution of copper might be exhibited by the following equation:—

$$SO^2 + 4SnCl + 2CuO = SCu + 2SnCl^2 + 2SnO^2.$$

Poggendorff's *Annalen.* 1845. No. 9.

On a new Eudiometrical Process. By M. LASSAIGNE.

On experimenting recently with the protosulphate of iron, advised by M. Dupasquier, and repeating the process which he has published *, I have been led to turn to account a reaction which is well-known to chemists, but which has never, as far as I am aware, been applied to the analysis of the air.

This method is founded on the facility with which metallic copper shavings become oxidized in contact with air in presence of liquid ammonia, and on the formation of a blue ammoniuret of deutoxide of copper. Several experiments having proved that this reaction, when effected in a limited volume of air, determined in a very short time the total absorption of the oxygen contained in it, leaving the nitrogen free, I was immediately led to apply this property to the analysis of the air, and the result has turned out as I expected it would.

The application of this new method is very simple; it does not require the employment of any peculiar apparatus. A common graduated tube, from 14 to 15 centimetres long and 12 millimetres in diameter, and a small bottle with ground stopper from 30 to 35 cubic centimetres' capacity, are the only requisite vessels. The process consists in introducing into the small bottle from 3 to 4 grms. of copper shavings, then half-filling the bottle with distilled water, upon which it is filled to the top with a concentrated solution of ammonia. This bottle, thus accurately filled, is closed with its glass stopper, and is inverted in a pneumatic trough, taking care that the copper shavings do not fall upon the mouth of the bottle. This being done, a volume of air is measured in the graduated tube, filled with water, and passed by means of a small glass tube into the bottle, which has been unstoppered under water; this done, the bottle is immediately stoppered, removed from the pneumatic trough, and agitated for 8 or 10 minutes. In less than 1 or 2 minutes the ammonia acquires a bluish tint, which gradually becomes darker from the formation of the ammoniuret of deutoxide of copper. This blue tint soon arrives at its maximum of intensity on experimenting with 15 to 20 cubic centimetres of air; it gradually diminishes when the whole of the oxygen of the volume of air has been absorbed; the successive decoloration, which serves as an index of the close of the operation, is dependent on the reaction of the excess of copper on the ammoniuret of the deutoxide, which becomes transformed into the colourless ammoniuret of the protoxide. When we have proceeded thus far, the residue of gas is passed into the graduated tube in order to measure it, taking the precautions indispensable in this kind of operations. In the various experiments which I have made with the use of this method, the gaseous residue contained after the action of the copper and the ammonia no trace of oxygen; for when phosphorus was introduced into it, there was no phosphorescence in the dark nor any diminution in volume.

The volume of nitrogen gas determined by this process has always

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* Chem. Gaz. vol. ii. p. 145.

been from two to three-tenths of a degree higher than that obtained by the action of phosphorus upon the air; the relation was : : 79 : 79·22. This last number, deduced from our experiment, approaches closely to 79·17, which MM. Dumas and Boussingault arrived at from their analysis of the air by weighings.

In the analysis of an artificial mixture, composed of 41·5 air and 57·5 nitrogen, a mixture in which the proportion of nitrogen was consequently 90·2, the new method indicated 90.

The simplicity of this operation, and the promptitude with which this process may be carried out, will undoubtedly allow of its being employed in various circumstances.—*Comptes Rendus*, Oct. 13, 1845.

On a Sensitive Test for Manganese. By Walter Crum.

In the formation of green manganate of potash, we possess a test for manganese which leaves nothing to be desired. It is however only applicable with the dry substance. The following is a method for detecting this metal in a liquid, which is by no means inferior in sensitiveness to that in the dry way; it depends on the formation of permanganic acid and the intensely red colouring of the manganiferous solution produced by it. When peroxide of lead is heated with dilute nitric acid, and a solution of manganese then added to it, the liquid acquires, even when very little of the latter has been employed, the intensely purple-red colour of permanganic acid, which is very readily perceptible as soon as the excess of peroxide has subsided.

10 grs. of unslacked lime, dissolved in nitric acid and heated with dilute nitric acid and peroxide of lead, produced a purple colour, which was as intense as that formed under the same circumstances with $\frac{1}{100}$ gr. protosulphate of manganese. This lime consequently contained approximatively $\frac{1}{3000}$ of its weight manganese. White marble was likewise found to contain manganese by means of this test.—*Ann. der Chem. und Pharm.*, August 1845.

On the Quantitative Determination of Lithia. By C. Rammelsberg.

When lithia and soda, as is usually the case, occur together, there is, as is well-known, no other mode of estimation than precipitating the first in the form of phosphate of soda and lithia, or the arithmetical method of indirect analysis first employed in chemistry by Richter. Both processes are undoubtedly imperfect, especially the first, as will be seen from some experiments to be subsequently related; and the method of calculation, considering the very slight difference in the atomic weights of the two bodies, presupposes a degree of accuracy in the analytical operations such as it is frequently impossible to attain in the examination of minerals when these alkalies are the last to be determined.

The author found, after numerous experiments on various salts, that a mixture of alcohol and æther might be employed for the separation of the chloride of sodium and chloride of lithium with very satisfactory results. When anhydrous chloride of lithium is treated with ordinary æther, two strata of liquid are formed which do not mix; the upper consists of æther, and contains but a very small quantity of the salt; the heavier stratum is a concentrated solution of chloride of lithium in the water which the æther contained. The greater portion of the salt however naturally remains undissolved; on the other hand, chloride of lithium, even when it has been previously fused, dissolves entirely in a mixture of equal parts of anhydrous alcohol and æther, while only a trace of chloride of sodium accompanies the salt of lithia.

0·977 grm. of pure strongly-ignited chloride of sodium and an undetermined quantity of chloride of lithium were treated with the above mixture and placed aside for some days, being frequently agitated. After filtration and washing with æther and alcohol, 0·964 chloride of sodium were left. Of 100 parts of this salt therefore 98·67 per cent. had been re-obtained.

This method was employed in the subsequent analyses of the phosphate of soda and lithia, and the chloride of sodium was always obtained free from lithia.

The phosphate of soda and lithia is undoubtedly one of the most interesting of all the salts of lithia, because from its sparing solubility it affords the means of detecting lithia where others no longer answer. Berzelius first described this compound, and the mode of precipitating it from solutions containing lithia. He concluded from analysis that the salt consisted of equal atoms of neutral phosphate of soda and neutral phosphate of lithia. M. Rammelsberg endeavoured by numerous experiments to ascertain in how far this double salt is really suited for the quantitative estimation of lithia, and whether its constitution was, under all circumstances, identical with that assigned to it by Berzelius. He found that it was perfectly useless for quantitative purposes, and that the phosphate of soda and lithia is a salt of very variable composition. The following was the method of analysis:—The salt was heated to redness, when it lost scarcely anything in weight, and is therefore anhydrous. It was then dissolved in hydrochloric acid, and the phosphoric acid precipitated by a mixture of chloride of calcium and ammonia. The precipitate was constantly $3CaO, 2PO^5$, as was evident on decomposition by sulphuric acid. The liquid, freed from lime by means of oxalic acid, was evaporated, the chlorides remaining after volatilization of the sal-ammoniac weighed, treated with a mixture of alcohol and æther, and placed aside for some days in a well-stoppered bottle. The residuary chloride of sodium was then brought on to a weighed filter, and its weight determined after perfect desiccation, by which the quantity of chloride of lithium was found.—Poggendorff's *Annalen,* No. 9, 1845.

On the Estimation of Fluorine. By F. WÖHLER.

The author recommends the following process for ascertaining the quantity of fluorine:—The weighed substance is intimately mixed with pure silica, unless it already contains some; the mixture is placed in a small flask, which can be weighed on the balance; very concentrated sulphuric acid, which has been boiled, is added, and the flask quickly closed with a cork, through which a small tube, filled with fused chloride of calcium, and drawn out to a fine point, passes. The whole apparatus is now weighed, and then exposed to a proper heat as long as gaseous fluoride of silicium is evolved. The last portions are removed by exhaustion under the air-pump. The loss in weight which it experiences is fluoride of silicium, from which the amount of fluorine is calculated. 1·395 parts of fluoride of silicium are formed for each part of fluorine. To test this method, the author estimated the amount of fluorine in fluor spar, and the results were accurate to the first decimal place.—Poggendorff's *Annalen*, vol. xlviii.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Nov. 3, 1845. (The President, Professor Graham, in the Chair.) The following communications were read:—

"On the Oxygen Compounds of Nitrogen," by Dr. Schönbein.

Of the five compounds of nitrogen and oxygen whose existence is generally admitted by chemists, two are entirely hypothetical, viz. the hyponitrous and nitric acids; protoxide and binoxide of nitrogen, and the so-called hyponitric acid (NO^4), can be isolated and exhibited in a separate state. It is also a received opinion that the acid of the nitrates can only have existence in combination with water or base. Under these circumstances, observes Dr. Schönbein, it appears most philosophical to view the supposed compounds of hyponitrous and nitric acids in another light, so as to avoid the necessity of creating hypothetical substances. The hydrate of nitric acid, for example, instead of containing $NO^5 + HO$, or $NO^6 + H$, may be regarded as a compound of hyponitric acid and peroxide of hydrogen $NO^4 + HO^2$, and a normal nitrate of $NO^4 + MO^2$. This view of the subject is confirmed by the behaviour of hydrate of nitric acid and nitrate of lead under the influence of heat, the former dividing into NO^4, HO, and O, and the latter into NO^4, PbO and O.

Hyponitrous acid may also be supposed to contain hyponitric acid (NO^4) in combination with binoxide of nitrogen, and a normal hyponitrite of binoxide of nitrogen in combination with the peroxide of the metal, as $NO^2 + PbO^2$. These views of the constitution of hyponitrous and nitric acids are strengthened by the phænomena presented by the action of water on hyponitric acid.

"On the relation of Ozone to Hyponitric Acid," by Dr. Schönbein.

In this paper Professor Schönbein proceeds to state his views respecting ozone, which he considers as a body isomeric with the peroxide of hydrogen of Thenard, or HO^2, and that it is formed in combination with NO^2 when hyponitric acid or its vapour is brought into contact with water or atmospheric air containing watery vapour, and that it is to this production of ozone that the oxidizing effects of such mixtures are to be attributed. The author next shows that these oxidizing properties are not effected by the ozonized air being charged with the vapours of carbonate of ammonia. The same compound is considered also to result from the contact for a short time of diluted, pure nitric acid, and with many metallic bodies, as zinc, iron, lead, copper, mercury, silver, &c., the acid acquiring the same oxidizing properties as ozone. Tin however is an exception, and this metal even destroys the property which the acid may have previously obtained.

"On certain Impurities in commercial Sulphate of Copper," by Mr. S. Piesse.

One source of impurity of the sulphate of copper of commerce arises from the treatment of brass and German silver articles, technically called dipping, and which consists in plunging them for a short time into a mixture of nitric and sulphuric acids, which removes the coat of oxide from the surface of the metal, and leaves the latter in a clean state proper for the reception of varnish or other finishing. In time this dipping liquid becomes in great measure saturated, and after neutralization with old copper yields on evaporation in leaden pans a large quantity of sulphate of copper in crystals. According to the author, not less than 100 tons of dipping liquid are thus disposed of annually at Birmingham by the makers of buttons and other articles. The crystallized sulphate of copper so obtained is often largely contaminated with sulphate of zinc, which may sometimes be seen in the form of slender white needles on the surface of the dark blue crystals, and in some of the applications of this salt may prove injurious. Sulphate of nickel, sulphate of lead, arsenic and chlorides are also sometimes present.

"A Report on the Composition of the Fire-Damp of the Newcastle Coal Mines, and the Means of preventing Accidents from its Explosion," by Professor Graham.

The author had some years ago examined the gas of these mines, with the same result as Davy, namely, that it contains no other combustible ingredient than light carburetted hydrogen. But the analysis of the gas of the coal mines in Germany, subsequently published, showing the presence of other gases, particularly of olefiant gas, rendered a new examination of the gas of the English mines desirable. The gases were,—1st, from a seam named the Five-Quarter seam, in the Gateshead Colliery, where the gas is collected as it issues, and used for lighting the mine; 2nd, the gas of Hepburn Colliery, which issues from a bore let down into the Bensham seam—a seam of coal which is highly charged with gas, and has been the cause of many accidents; and 3rd, gas from Killingworth Colliery, in the neighbourhood of Jarrow, where the last great explosion occurred. This last gas issues from a fissure in a stratum of sandstone, and has been kept uninterruptedly burning, as the means of lighting the horse-road in the mine, for upwards of ten years, without any sensible diminution in its quantity. The gases were collected personally by Mr. J. Hutchinson, with every requisite precaution to ensure their purity and prevent admixture of atmospheric air. The usual eudiometrical process of firing the gases with oxygen was sufficient to prove that they all consisted of light carburetted hydrogen, with the exception of a few per cent. It was observed that phosphorus remains strongly luminous in these gases mixed with a little air, while the addition of one four-hundredth part of olefiant gas, or even a smaller proportion of the volatile hydrocarbon vapours, destroyed this property. Olefiant gas itself, and all the allied hydrocarbons, were thus excluded. Another property of pure light carburetted hydrogen, observed by Mr. Graham, enabled him to exclude other combustible gases, namely, that the former gas is capable of entirely resisting the oxidating action of platinum black, and yet permits other gases to be oxidated which are mixed with it even in the smallest proportion, such as carbonic oxide and hydrogen, the first slowly and the last very rapidly, air or oxygen gas being of course also present in the mixture. Now platinum black had not the smallest action on a mixture of the gas from the mines with air. The gas was also inodorous, and clearly contained no appreciable quantity of any other combustible gas than light carburetted hydrogen. The only additional matters present were nitrogen and oxygen, or air; the specimen collected in the most favourable circumstances for the exclusion of atmospheric air, namely that from the Bensham seam, still containing 0·6 per cent. of oxygen. The gases also contained no carbonic acid. Attention was directed to the result that nothing oxidizable at the temperature of the air was found in a volatile state associated with the perfect coal of the Newcastle beds. The remarkable absence of oxidability in light carburetted hydrogen appears to have preserved that alone of all the combustible gases originally evolved in the formation of coal, and which are still found accompanying the imperfect lignite coal of Germany, of which the gas has been examined. The fact is of geological interest, as it proves that almost indefinitely protracted oxidating action of the air must be taken into account in the formation of coal; air finding a gradual access through the thickest beds of superimposed strata, whether these strata be in a dry state or humid. In regard to measures for preventing the explosion of the gas in coal mines, and of mitigating the effects of such accidents, Mr. Graham confined himself to two suggestions. The first has reference to the length of time which the fire-damp, from its lightness, continues near the roof, without mixing uniformly with the air circulating through the workings. He found that a glass jar, of 6 inches in length and 1 inch in diameter, filled with fire-damp, and left open with its mouth downwards, continued to retain an explosive mixture for 20 minutes. Now it is very desirable that the fire-damp should be mixed as soon as possible with the whole circulating stream of air, as beyond a certain degree of dilution it ceases to be explosive. Mr. Buddle has stated, "that immediately to the leeward of a blower, though for a considerable way the current may be highly explosive, it often happens that after it has travelled a greater distance in the air-course, it becomes perfectly blended and mixed with the air, so that we can go into it with candles; hence, before we had the use of the Davy lamp, we intentionally made 'long runs,' for the purpose of mixing the air." It was recommended that means be taken to promote an early intermixture of the fire-damp and air; the smallest force is sufficient for this purpose, as a downward velocity of a few inches in the second will bring the light gas from the roof to the floor. The circulating stream might be agitated most easily by a light portable wheel, with vanes, turned by a boy, and so placed as to impel the air in the direction of the ventilation, and not to impede the draft. The gas at the roof undoubtedly often acts as an explosive train, conveying the combustion to a great distance through the mine, while its continuity would be broken by such mixing, and an explosion, when it occurred, be confined within narrower limits. Secondly, no effective means exist for succouring the miners after the occurrence of an explosion, although a large proportion of the deaths is not occasioned by fire, or injuries from the force of the explosion, but from suffocation by the after-damp, or carbonic acid gas, which afterwards diffuses itself through all parts of the mine. It was suggested that a cast iron pipe, from 8 to 12 inches in diameter, be permanently fixed in every shaft with blowing apparatus above, by which air could be thrown down, and the shaft itself immediately ventilated after the occurrence of an explosion. It is also desirable that, by means of fixed or flexible tubes, this auxiliary circulation should be further extended, and carried as far as practicable into the workings.

PATENT.

Patent granted to James Muspratt, Liverpool, *for Improvements in the Manufacture of Manure.*

The object of this invention (which is a communication from Professor Liebig) is to prepare manure in such a manner as to restore to the land the mineral elements taken away by the crop which has been grown thereon and removed, and at the same time render the alkaline matters used in making the manure less soluble, so that they may not be washed away from the other ingredients by the rain falling on the land. The improvements consist in combining carbonate of soda or carbonate of potash, or both, with carbonate of lime, and combining carbonate of soda and carbonate of potash with phosphate of lime, in such a manner as to diminish the solubility of the alkaline salts used in the preparation of the manure. And although, in carrying out this invention, various materials are combined with the alkaline salts, no claim is made thereto separately; and such materials are varied according to the matters which the land requires to have returned to it, in addition to the minera substances before-mentioned.

The mode of manufacturing the manure is as follows:—Carbonate of soda or potash, or both, is or are fused in a reverberatory furnace with carbonate or phosphate of lime; other ingredients are mixed with these fused compounds, as hereafter mentioned; and the composition, when cold, is ground to powder, and applied to land as manure. In order to apply the manure with precision, the analysis and weight of the previous crop ought to be known, so as to return to the land the mineral elements in the same weight and proportion as they have been removed by the crop.

Two compounds are first prepared, one or the other of which is the basis of all the manures made under this invention. The first compound is formed by fusing 4 or 5 parts of carbonate of lime with 2 parts of potash of commerce (containing on an average 60 parts of carbonate of potash, 10 of sulphate of potash and 10 of chloride of potassium in 100 parts), or with 1 part of potash and 1 part of carbonate of soda. The second compound is made by fusing together phosphate of lime, potash of commerce and soda-ash in equal proportions. Both compounds are ground to powder, and other salts or ingredients are mixed with them (or those which are not of a volatile nature may be added when the compounds are in a state of fusion), so that the manure may represent, as nearly as possible, the composition of the ashes of the preceding crop; or if a crop of a different description is to be grown, the manure must be prepared accordingly.

The ingredients composing the manure, and the relative proportions thereof, will vary according to the nature of the soil to which the manure is to be applied; but the patentee has given the following general proportions as a guide to the farmer:—Manure, suitable for land on which a crop of wheat has been grown, and removed therefrom, is made by mixing together 6 parts by weight of the first compound above described, 1 part of the second, 2 of gypsum, 1 of calcined bones, a quantity of silicate of potash (containing 6 parts of silica), and 1 part of phosphate of magnesia and ammonia. This manure may be also used after growing barley, oats and plants of a similar character. For land on which a crop of beans has been grown, the manure is composed of 14 parts of the first compound, 2 of the second, 1 of common salt, a quantity of silicate of potash (containing 2 parts of silica), 2 parts of gypsum and 1 of phosphate of magnesia and ammonia. This manure may also be applied to land after growing peas and plants of a similar character. The manure for land on which turnips have been grown consists of 12 parts of the first compound, 1 of the second, 1 of gypsum, and 1 of phosphate of magnesia and ammonia. This manure may also be used after growing potatoes and plants of a similar character.

When the straw of wheat and other plants, which require much silicate of potash, is returned to the land as manure (which mode the patentee considers to be the best for restoring the silicate of potash), the silicate of potash is omitted in the preparation of the manure.—Sealed April 15, 1845.

THE CHEMICAL GAZETTE.

No. LXXVI.—December 15, 1845.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Oxygen on the Blood and its Constituents.

By Prof. R. F. Marchand.

Eight years ago, Prof. Magnus pointed out that the blood contained free oxygen and nitrogen, as well as free carbonic acid. In some recent experiments[*] upon the blood of calves, cattle and horses, he found that it never contained more or less than 10–12·5 per cent. of oxygen, and 1·7–3·3 per cent. nitrogen of the volume of the blood. The quantity of oxygen which this experiment shows the blood to be capable of absorbing, is sufficient to admit of the supposition that the whole of the inspired air is absorbed by the blood. When the blood was previously deprived of all the air it contained, and then agitated with atmospheric air, the oxygen absorbed amounted to 10–16 per cent., that of the nitrogen to 6·5 per cent. of the volume of the blood. The oxygen could be completely removed by carbonic acid (a proof that it is not chemically combined in the blood), the blood at the same time absorbing 1½ vol. of carbonic acid. If the quantity of air inspired be compared with the amount of blood which passes through the lungs in the same space of time, it is found that the blood does not absorb more than half of the oxygen which the above experiments have shown it to contain. Thus this portion is each time consumed in the capillaries; the rest remains in the venous blood.

The author, in his experiments on respiration[†], observed that animals which inspire pure hydrogen or oxygen, in the former case expire oxygen and nitrogen as well as carbonic acid, in the latter of course only nitrogen, provided that the remaining air had previously been removed from the lungs as perfectly as possible. Hence it appears proved that oxygen, nitrogen and hydrogen are contained in the blood.

It has been objected to Liebig's view, of the evolution of carbonic acid arising from bicarbonate of soda, that the existence of the carbonate of soda in blood is problematical; still it cannot be denied that there is a certain resemblance between the condition of the carbonic acid in the blood and that of the second equivalent in

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[*] See page 401 of the present volume.

Ib. pp. 145. 160.

the carbonates when in solution, as seen on exposure *in vacuo,* the application of heat, and on passing currents of indifferent gases through them. Magnus has already found that carbonic acid could be removed from the solution of the bicarbonate by the above gases; and it appeared probable, from the experiments of H. Rose, that the salt might in this manner be completely converted into the neutral one. With a view of clearing up this point, the author passed a strong current of moist atmospheric air through a solution of pure bicarbonate of soda, which was perfectly saturated at 32°, and the volume of which amounted to 140 cubic centimetres, the fluid, which was placed in a tall glass cylinder, being surrounded with melting ice. After a million and a half of cubic centimetres of air had passed through, it was found, on estimating the carbonic acid and the soda, that the bicarbonate was converted into the sesquicarbonate. When the solution, saturated at 32°, was heated to 100° F., and two millions of cubic centimetres of air were passed through it at this temperature, the evolution of carbonic acid then ensued much more rapidly than before. In addition to the bubbles of the air passed through, numerous minute bubbles ascended, and the air evolved a distinct odour of carbonic acid. On quantitative analysis, there were found 390 parts of soda to 290 of carbonic acid; 275 parts of the latter would have corresponded to the neutral salt. If the transmission of the air had been continued, this result would probably have been attained. Hence oxygen might cause the evolution of carbonic acid from the blood, when this gas exists in it in the free state, or at least not held with greater affinity than the second equivalent in the bicarbonate.

The next question is, whether the carbonic acid formed in the capillaries is merely mechanically separated in the lungs, or whether it is produced by the immediate influence of the air on the constituents of the blood. The following experiments were made to determine this point. Liebig has urged, as an objection to the experiments of Magnus, in which free oxygen was found in both kinds of blood, that fibrine combines directly with oxygen. The author therefore first examined the venous blood of a dog, as to whether it contained oxygen. This analysis, which was merely qualitative, was made by collecting the blood from the vein under mercury, in a bottle filled with mercury, and in which there was a small quantity of pure carbonic acid and oil. The blood was thus preserved from contact with the air. The mercury had been previously agitated with carbonic acid, to remove the air which it contained. The bottle, which was perfectly closed under mercury, was now strongly agitated, to coagulate the fibrine, and then a steel cock, which passed through the cork, was provided with a tube for conducting gas, which dipped into a globe filled with mercury. The cock was opened, and the apparatus placed upon the plate of the air-pump. On exhaustion, the blood frothed slightly, and the gas which was evolved passed under the globe containing the mercury, and thus separated from the blood, was collected. The quantity of gas was however inconsiderable, and not enough for an analysis. A perfectly colourless solution of ammoniacal protoxide of copper was therefore conveyed into the globe by a siphon. This was immediately coloured deep blue, so that the presence of oxygen was indisputable. When carbonic acid was collected over the mercury instead of the air pumped out of the blood, the ammoniacal protoxide of copper was not coloured blue, so that in the former case the oxygen could not arise from an accidental admixture.

To examine the action of oxygen on the constituents of the blood more accurately, beaten horse's blood was completely deprived of its gaseous contents. For this purpose, the glass which contained the beaten blood was closed with a cork, which was twice bored. Two tubes, bent at right angles, were inserted in these apertures, one of them reaching to the bottom of the bottle. The other terminated immediately below the cork. A small quantity of oil was first put into the bottle, which was otherwise completely filled with the blood. A second prepared empty bottle, which contained a few drops of oil, was connected to this by the short tube. To the first bottle was attached a cock, which was perforated perpendicularly, and on one side, and to the lateral aperture of which a glass tube dipping into mercury was connected; the third aperture was connected with a hydrogen apparatus, from which pure dry hydrogen gas was evolved. The hydrogen gas was now passed through the blood for some time; this slightly frothed, and a small quantity passed into the second bottle. When a third bottle, filled with barytic water, was placed after the second, it was immediately rendered turbid. A powerful air-pump was now connected with the second bottle, the cock of the former closing behind the first bottle, so that the hydrogen was compelled to escape by the lateral tube; the blood was continuously exhausted for a quarter of an hour; some hydrogen was then admitted, and the exhaustion again applied, and so on, until the hydrogen which passed through yielded no more carbonic acid to the barytic water.

The hydrogen apparatus was now replaced by a gasometer containing pure oxygen. This was passed through solution of potash, and then over solid caustic potash before it came into contact with the blood. As soon as the change in colour from the previous perfectly dark into the bright red was perceptible, a very slight troubling of the barytic water appeared. As a little carbonic acid might possibly have been still contained in the blood, hydrogen was again passed through it, and by means of the air-pump this was continued as long as the barytic water was troubled. After passing the hydrogen through for a quarter of an hour, and no admixture of carbonic acid being apparent, oxygen was again passed through it. No more carbonic acid was evolved, however long the stream of oxygen was continued.

When venous blood was treated with hydrogen, its dark red colour became somewhat brownish, but never of a brighter tint, as stated by some. The reaction is however much more distinct when hydrogen is allowed to act upon arterial blood: after some time a dilute ordinary dark colour ensued, which was again rendered red by the transmission of oxygen.

According to Scherer, fibrine has a great tendency to combine with oxygen, and to produce carbonic acid. Scherer's experiment however was continued for eight days, in which time 24 cubic centimetres of moist fibrine yielded 202 cubic centimetres of carbonic acid from 246 cubic centimetres of oxygen; whilst the volume of gas had diminished one-tenth. On repeating this experiment, the author found that no carbonic acid was formed in 16–20 days at a temperature of 39°–41°. The same substance, moistened with a little water as in the previous experiment, at 53° evolved but little carbonic acid; but when it was kept very moist the formation of carbonic acid was incomparably greater. Notwithstanding this observation, it must remain doubtful whether the same process occurs in the blood. A reaction, which requires fourteen days to appear distinct and positive, is not analogous to the effects which ensue so rapidly, and with which it has been compared. In several other experiments it was distinctly evident that no carbonic acid was evolved until putrefaction had actually commenced. Blood which had been freed from fibrine evolved no carbonic acid on the transmission of oxygen; just so with the serum, as Scherer also found, and albumen of eggs; the carbonic acid contained in the latter must however be previously separated by hydrogen, &c. The experiments were finally extended to a solution of the corpuscles in pure water, and to hæmatine prepared according to Mulder's process. Neither constituent of the blood evolved any carbonic acid on the continued transmission of oxygen gas.

Magnus was not able to separate the absolute quantity of oxygen which the blood had absorbed by carbonic acid; hence it might be supposed that this oxygen in the blood had been applied, not to the formation of carbonic acid, but Mulder's binoxide and tritoxide of proteine. However, it may be objected to this view, that the formation of these products cannot be proved to occur on first inspiration, and that if the fibrine were so readily metamorphosed into them, it could not exist undecomposed in the presence of so much free oxygen.

From the above facts we may conclude, that the mere absorption of the oxygen by the blood does not cause any chemical change, certainly no formation of carbonic acid, and perhaps none at all; but that this change is caused through the agency of animal cells, and hence commences even in the lungs. Immediately after the gaseous absorption a chemical reaction must occur and heat be evolved. Brechet and Becquerel found arterial blood 0·84–1·01 C. warmer than venous blood, but they also found a difference of 0·900 C. in the temperature of the blood in the right and left cavities of the heart of an Indian cock. John Davy found a similar difference with the thermometer; he also observed, that on agitating venous blood with oxygen its temperature rose 1–2° F. This observation, however, does not prove that the red colour is produced by a chemical combination, but that in this absorption of gas, as in all others, an elevation of temperature occurs.

The author observed, that the temperature of the blood, which he treated with a large current of carbonic acid, rose 0·9° C. After some hours, when the blood had acquired the temperature of the room, oxygen was passed through it, and the temperature then rose only 0·1° C. When carbonic acid was again passed through it, the temperature remained unchanged: the same occurred with atmospheric air. The production of cold by evaporation was always prevented. In another experiment the temperature rose 0·5° C. only. When carbonic acid was passed through a similar quantity of water the temperature rose 0·3° C. only. However, this is explicable by both substances having very dissimilar solvent powers for carbonic acid, and the blood dissolving this gas much more rapidly.

Observations have been recently made on the colour of the blood by Scherer and Von Bruch. As regards the colour of the blood after mixture with water and treatment with oxygen and carbonic acid, the experiments of the author agree with those of Bruch. Beaten blood, mixed with an equal volume of water, and which had thus become completely black, was agitated with oxygen, which was conducted into a bottle containing the solution of blood. No essential difference was perceptible by reflected light, whilst the liquid appeared bright and transparent by transmitted light. Carbonic acid rendered the blood again black. Blood which has been agitated with oxygen when mixed with water becomes far less black than ordinary blood; after agitation with carbonic acid it becomes much darker. Putrid blood, in which the corpuscles were barely perceptible, reacted in the same manner. In the blood mixed with water, the corpuscles, deprived of their colouring matter, are barely perceptible, but may readily be discovered after the addition of a mixture of hydriodic acid and iodine. Neither blood which has been mixed with water, nor that which has not, exhibits any perceptible difference in the form of its corpuscles after treatment with carbonic acid and oxygen. If blood be mixed with sulphate of soda it becomes bright red, even that which has been mixed with water; the corpuscles, which were at first not perfectly circular, but somewhat angular, become more distinct and appear as circular flattened discs, their diameter being somewhat diminished.

If ordinary beaten blood is mixed with sulphate of soda, it becomes bright red; if it has been previously agitated with carbonic acid, not so bright; but if previously agitated with oxygen, much brighter. If the blood has been heated for a short time to 104° F., and then exhausted in the air-pump, the gases, carbonic acid and oxygen are evolved; this blood becomes brighter than usual with sulphate of soda, because the carbonic acid which blackens it is absent. If blood is retained at 122° F. for a considerable time it becomes black, and the corpuscles appear dissolved; this ensues more rapidly and completely when the blood is dissolved at the same time. Hematine (free globuline and the corpuscles) is not chemically altered by gases and salts. The change in colour appears therefore to depend upon a physical and not a chemical cause.—*Journ. für Prakt. Chemie,* xxxv.

On the Red Protoxide of Tin. By Dr. ROTH.

The red protoxide of tin was accidentally obtained in the preparation of a solution of proto-acetate of tin, by adding a solution of crystallized protochloride to one of carbonate of potash, washing the hydrated protoxide, and then digesting it with so much concentrated vinegar, in a glass flask over a water-bath, that only a portion of the hydrated protoxide was dissolved. After the flask had been set aside for some days, it was found, on decanting the solution of proto-acetate, that the white sediment was mixed with a number of small red crystals, and the sides of the flask coated with a red crust. The white sediment was readily separated by suspension from the red crystals, which on examination were found to be pure protoxide of tin. The author succeeded twice in preparing the red oxide of tin artificially, by placing freshly-precipitated hydrate of the protoxide of tin after edulcoration upon a paper filter, adding to it a solution of proto-acetate of tin, which still contained some free acetic acid, and had a specific gravity of 1·06, placing in an evaporating stove and filtering at a higher temperature. The crystals were increased each time that the liquid which had passed through was again poured upon the filter, until the greater portion of the hydrate had undergone this change. They were then purified by suspension, and dried in the dark.—*Archiv für Prakt. Pharm.*, x. p. 381.

On a peculiar Acid in Chamomile Water. By M. PINETTI.

Recently prepared chamomile water has no acid reaction, which is the case however after it has been preserved some length of time. The acid which is formed under these circumstances yields with lime a crystalline salt. The author proposes for it the name *acidum parthenicum.—Journ. de Chim. Méd.*, 1845, p. 433.

Observations on some Points in the Chemistry of the Urine.
By J. W. GRIFFITH, M.D.

1. It has usually been considered that the amorphous deposit ordinarily occurring in the urine is the lithate of ammonia, mixed with variable portions of urate of soda and lime, and sometimes magnesia. The cause of the deposit assuming the amorphous form has always been, and still remains, in our opinion, a difficulty, and we think receives no explanation from the mere fact of the lithate of ammonia being mixed with lithate of soda and lime. If so, why does it ever assume the crystalline form when mixed with the soda? and the spheres of lithate not uncommonly occurring in urine are decided crystals, and possess the optical characters of such. We think it a question whether the crystalline salt obtained by M. Heintz [*], and containing from 12·73 to 14·79 per cent. of soda, is the same as the amorphous urinary compound, the inorganic constituents of

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[*] Page 449 of the present volume.

which are exceedingly variable in quantity and amount (2·98–8·02 per cent.).

2. We differ from those who with Liebig consider that soda has anything to do with the solubility of uric acid in urine. The fact of urate of ammonia being deposited from the urine, either by exposure to cold or the air-pump, is sufficient to show that it exists therein in combination with ammonia, and not soda; and how can this occur from a mixture of phosphate of soda, uric acid and hippuric acid (Liebig's artificial urine)? In our opinion, uric acid most probably exists in the blood in combination with soda; and although under ordinary circumstances, as in the case with urea, we cannot detect it, (being probably excreted as rapidly as it is formed), still in certain morbid conditions, where it apparently formed in excess, it is secreted from the blood in this form, as we see in and around the joints of gouty patients: here the compound is not exposed to the salts capable of decomposing it, as in the urine. At the moment of its secretion from the kidney it is probably decomposed by muriate of ammonia. If a deficiency of this is formed, a quantity of the urate of soda will escape decomposition and appear in the urine. Whether tribasic phosphate preexists in the urine is very problematical, as we know of no process by which either the soda or its carbonate, or such compounds as yield this on incineration, can be removed from the alkaline phosphate prior to the combustion of the ash; and supposing with Löwig that the phosphate is the ordinary one, the atom of water it contains could be replaced by an atom of soda, as long since shown by Graham.

3. Regarding the presence of ammonia in urine, the chloride of platinum test applied previously to evaporation (and of course it cannot be applied after) is entirely fallacious. Admitting that the lithic acid exists as bi-lithate of ammonia, 1000 grs. of urine contain on an average 1 gr. of lithic acid; this would combine with 0·1892 gr. ammonia, which would form 2·341 grs. of ammonio-chloride of platinum. Since 1 part of ammonio-chloride of platinum dissolves in 150 parts of cold water, 1000 grs. of urine (admitting urine to be as good a solvent as water) might contain more than twice as much ammonia, and yet the chloride of platinum would yield no precipitate.

On a crystalline Combination of Iodide of Potassium with Iodide of Lead.

On precipitating iodide of lead from iodide of potassium and neutral acetate of lead, the precipitate obtained always amounts to about one-twelfth less than it ought according to calculation; because a soluble double salt of iodide of potassium and iodide of lead is formed, which may also be obtained when biniodide of lead is mixed at a high temperature with an equal weight of acetate of potash. This double salt crystallizes in beautiful sulphur-coloured silky needles.—Buchn. *Rept.*, xxxviii. p. 390.

Occurrence of Malic Acid in the Fruit of the Pyrus Cydonia.

By Dr. RIECKHER.

In a quantity of 4 quarts of quince juice, to which some lime had been added in order to remove the acid taste, there was deposited in the course of 4 months a large quantity of a crystalline salt. It was pretty soluble in water, and gave the reactions of malate of lime. The quantitative examination of the salt, purified by recrystallization, yielded—

Malic acid	..	..	1	1461·39	56·10
Lime	13·25	13·74	1	356·02	13·64
Water	..	..	7	787·36	30·23

This salt corresponds therefore to the acid malate of lime examined by Hagen. About 3 oz. of the salt were obtained from the 4 quarts of quince juice; and if we consider the proportion of the *Succus Cydoniorum* to the other ingredients as 2 : 5, the amount of malic acid contained in the quince juice would be from 3 to $3\frac{1}{2}$ per cent. Herberger found only 1·02 per cent. malic acid in it.—*Jahrb. für Prakt. Pharm.*, x. p. 238.

Examination of Gratiola officinalis. *By* EUG. MARCHAND.

The *Herb. Gratiolæ* is known as a violent purgative, and is considered in France as one of the most injurious of the wild plants; very little however is yet known of its chemical constituents. In 1809 Vauquelin published an examination of it; he found it to contain a bitter resinous substance, animal matter, brown gum, a vegetable acid (acetic or malic acid), combined with potash, soda and lime; further, phosphate of lime and iron, oxalate of lime, chloride of sodium, silicic acid and vegetable fibre. From the author's investigation, it results that the bitter resinous substance which Vauquelin considered to be the active principle of the *Gratiola* is not a simple chemical body, but consists of several substances, of which only a portion produce the energetic effect of the plant. One substance which Vauquelin overlooked is the tannic acid, which occurs in the resinous body in combination with several substances, of which one at least must be placed near digitaline. If the resinous body be treated with alcohol, a solution of persulphate of iron then added, and the free acid saturated with lime, diluted with some water, digested with charcoal and filtered, a white substance of an excessively bitter taste is obtained on evaporation of the liquid *in vacuo*. This is treated with some water, in which it dissolves with difficulty, in order to remove the saline admixtures. The residuary substance is a white powder, which swells in æther and partially dissolves, while a purple substance remains undissolved. If this liquid be separated from the supernatant æther and alcohol added to it, it is not rendered turbid. On evaporating the alcoholic solution, small crystals grouped in warts are obtained, for which the author proposes the name *Gratioline*.

This substance is very sparingly soluble in water, to which it however imparts a very bitter taste; readily in alcohol, from which it is partially precipitated by water; it is very sparingly soluble in æther. Boiled in water, it becomes soft, and floats in the form of oily drops on the liquid. Heated in a platinum spoon, it puffs up, melts, burns with a smoky flame, and leaves a black cinder, which it is very difficult to burn entirely, and leaves a slight residue of white ash. Sulphuric acid is first coloured yellow by gratioline, subsequently purplish-red; the solution, on the addition of water, does not become green, but only somewhat turbid, and after a time perfectly colourless. It dissolves in nitric acid without any change of colour, in hydrochloric acid with a yellow colour. Caustic potash imparts to gratioline a dirty green colour, which subsequently becomes yellowish-green, and finally white. Caustic ammonia colours it at first blue, then white, without however dissolving it. Tincture of galls precipitates gratioline from its alcoholic solution; but if this is very acid or strongly alkaline, the reaction does not occur.

The above-mentioned æthereal solution leaves on evaporation a non-crystalline substance, which has a faintly bitter taste, is insoluble in water, but soluble in alcohol and æther. On being heated, it behaves like gratioline; in sulphuric acid, which dissolves it with difficulty, it assumes a pale yellow colour, having a reddish tint.—*Journ. de Chim. Méd.*, 1845, p. 518.

On Tropæolum majus. *By* Fr. J. Bernays.

The seed of this plant yields on distillation an essential oil of a yellow colour, which sinks in water, possesses an acrid taste and contains sulphur. This may readily be proved by adding to some of the distilled water zinc and sulphuric acid, and conveying the evolved gas into basic acetate of lead. Braconnot states that he also found phosphorus in the Indian cress; the author however could not succeed in detecting it.—Buchn. *Repert.*, xxxviii. p. 387.

On a new Method of effecting the Quantitative Determination of Urea. By F. Rabsky, M.D.

Two methods have hitherto been used for quantitatively determining the urea in urine, viz. its separation as nitrate and calculating its proportion, or as oxalate, this being subsequently decomposed by carbonate of lime and the urea weighed in its pure state. The solubility of the nitrate and oxalate of urea preventing their perfect precipitation and thorough washing, are serious objections to these processes. The author proposes the following method, in which the products of the decomposition of the urea are used for this purpose:—

Concentrated sulphuric acid, in the quantity of half that of the urine used, is added to the latter, and the mixture kept in a moderate state of ebullition; much water is thus vaporized, and the fluid becomes black. The temperature continues to rise until at about 392°*

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* The mixture is heated in a sand-bath. The temperature must not exceed 572°, otherwise ammonia will be lost.

carbonic acid gas is evolved in small bubbles; the cessation of this disengagement of gas indicates that the urea is completely decomposed. The black residue is then thoroughly exhausted with water and the solution filtered; the clear yellow filtrate is then evaporated in the water-bath, and the generated sulphate of ammonia treated with alcohol and chloride of platinum. Since urine contains salts of potash and ammonia, which will likewise be precipitated upon the addition of the chloride of platinum, their exact proportion must be determined from a separate weighed portion by precipitation with chloride of platinum; and the corresponding amount must be subtracted from the first quantity.

The author decomposed some pure urea, which had been dried at 212° by this method, and found that 0·2612 grm. of urea yielded 1·9323 grm. of ammonio-chloride of platinum, corresponding to 0·2598 grm. of urea; 0·3139 gave 2·3175 of ammonio-chloride, corresponding to 0·3116 of urea and 0·2761 : 2·0400 : 0·2743. No indication of the presence of ammonia was obtained by treating the extractives of urine in a similar manner; nor was the accuracy of the result interfered with by mixing sugar with the urea previously to analysis. In applying this method, of course all those substances which are likely to interfere with the process, as uric acid, hippuric acid, albumen, &c., must be previously removed. In many instances it might be advisable to separate the urea previously by oxalic acid, and to decompose the oxalate subsequently with sulphuric acid. In calculating the amount of urea, 1 part of ammonio-chloride of platinum corresponds to 0·134498 of urea.—*Lancet*, Dec. 6, 1845.

Preparation of Digitaline. By O. HENRY.

To obtain this body, the author extracts the finely-divided leaves with alcohol, and treats the residue, evaporated to the consistency of a syrup, with 1 part acetic acid and 3 parts water; agitates the solution with animal charcoal, neutralizes with ammonia, and precipitates the digitaline with tannic acid. The precipitate is treated with oxide of lead and digested with alcohol. The solution, decolorized by animal charcoal, yields on evaporation a residue, from which æther removes some foreign matters, leaving the pure digitaline undissolved.—*Journ. de Chim. et de Pharm.*, 4 ann. p. 460.

Preparation of Cyanogen. By B. KOLB.

Hitherto cyanogen has been generally prepared from the cyanide of mercury, but it may also be easily obtained by heating 1 equiv. ferrocyanide of potassium, 1 equiv. peroxide of manganese and 2 equiv. bisulphate of potash: in order that the water which is formed at the commencement may not cause the glass to break, it is first heated gently, and then gradually to redness. The product is tolerably abundant, but it is remarkable that the gas, on being passed into a solution of protosulphate of iron, occasions a brown precipitate, which becomes blue on the addition of hydrochloric acid.—*Jahrb. für Prakt. Pharm.*, x. p. 312.

Observations on Lac. By LARUE DE BARRY.

Lac is a resinous substance, which occurs in discoid cakes of various sizes, but never more than 50 millimetres long and 15 thick. Its surface is warty, shining, and of a dark brownish-red colour. The taste is astringent, at first somewhat bitter; the odour is aromatic. Lac can be reduced to powder, and grates between the teeth. The fracture is shining, and exhibits a large number of irregular cells, which inclose small dried larvæ and fragments of the insects, but very rarely the entire insects. When powdered lac is treated with water, it takes an amaranth-red colour, and has a faint acid reaction; but the author could not ascertain the nature of the acid. It melts on being heated, giving off white vapours, which have an agreeable smell and an acid reaction, and burn with a white flame. The colouring principle can be entirely extracted by means of boiling water. Its taste is more bitter and less astringent than that of the lac; it also dissolves entirely in water, and has no action upon litmus-paper. It is insoluble in æther; alcohol acquires a saffron-yellow colour, and produces a brown precipitate. Acetate of lead yields a yellowish one.—*Journ. de Chim. Méd.*, 1845.

On the Property of removing the Odour of Essential Oils, &c. in Substances containing Prussic Acid. By M. MAHIER.

The observation of Fauré, that the odour not merely of musk, but likewise of essential oils, is destroyed by syrup of almonds, led the author to make use of this property for cleansing vessels which had contained essential oils, &c. A mortar which smelt strongly of assafœtida immediately lost this odour on triturating in the vessel some bitter almond paste. In the same manner, vessels in which essential oils, powerfully smelling tinctures, &c. had been preserved, were freed from the tenaciously-adherent odours by being rubbed with fresh bitter almond paste, leaves of the cherry-laurel, of the wild cherry, and other substances containing prussic acid. With oils, however, it is previously necessary to remove the fat by caustic potash, and with tinctures to get rid of the resin by means of alcohol. The author thinks that probably the substances containing prussic acid might also be used for the disinfection of rooms in which sick people are confined, anatomical theatres (!) &c.—*Journ. de Chim. Méd.*, 1845, p. 535.

Improvement in the Manufacture of Stearic Acid.

M. Cambacères proposes to render the manufacture of stearic acid less expensive, by obtaining, instead of the useless sulphate of lime, a salt of alumina as accessory product. But as it is impossible to saponify with alumina, the tallow must be converted into soap with potash, the soap decomposed by a solution of alumina in caustic potash, and from the gelatinous aluminous soap the fatty acids separated by acetic or sulphuric acid, when acetate or sulphate of alumina is obtained. The ley remaining after separation of the aluminous soap is caustic potash-ley, and may be employed for fresh operations. Not more than a tenth of the potash is lost in each operation, which certainly does not amount to more than the additional expenditure of sulphuric acid required by the excess of lime in the old method.—*Polytechn. Central Bl.*, 1845, No. 9.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Nov. 17*th*, 1845. (John Thomas Cooper, Esq., Vice-President, in the Chair.)

"On the Resin of the *Xanthorœa hastilis*," by Dr. John Stenhouse.

This resin, known in commerce under the name of the Botany Bay resin, exudes from the above-mentioned tree, which grows freely in the neighbourhood of Sydney. It forms brittle yellowish masses, or coarse powder, having an agreeable balsamic odour and slightly astringent taste. When heated, it melts, takes fire and burns with smoky flame, exhaling an odour like that of balsam of Tolu. When distilled with a solution of carbonate of soda, it yields a small quantity of fragrant volatile oil. Alcohol and æther dissolve the resin freely; the solution refuses to crystallize. Caustic alkalies dissolve it also with brown colour; from this solution the resin is precipitated in a modified state by an acid. The mother-liquor on concentration yields crystals of impure cinnamic acid mixed with a little benzoic acid; the quantity is but small, however, and the purification of the acid from colouring matter is very difficult.

Nitric acid acts with great energy on the Botany Bay resin; the chief products are picric, oxalic and nitro-benzoic acids The proportion of picric acid is so considerable that the author suggests the use of the resin for the purpose of obtaining that substance. By destructive distillation the Botany Bay resin yielded a large quantity of heavy acid oil, mixed with a little light fragrant oil, easily separated from the former by its insolubility in alkalies. When the resin had previously been digested with caustic alkali, the heavy oil alone was obtained on distillation. The light oil was apparently benzide or cinnamine, derived from the acids of the resin: the heavy acid oil was hydrate of phenyle (Runge's carbolic acid).

Dec. 1*st*, 1845. (The President in the Chair.)

"Account of various Substances found in the Guano Deposits and in their vicinity," by E. F. Teschemacher, Esq.

In the course of researches on the coast of Africa for saltpetre, in the neighbourhood of the deposits of guano, various other substances were discovered, which Mr. Teschemacher has described and analysed.

The first substance examined, found at present only in small quantities, and described, was the phosphate of ammonia in a crystallized state. The next substance was the bicarbonate of ammonia, also found crystallized, of which the analysis is given. The third substance described was a new mineral body well-known in the laboratory as an artificial compound, viz. the ammonio-magnesian phosphate; this however was found in patches in the guano beds in crystals of a considerable size. The primary form is the right rhombic prism, of which Mr. Teschemacher has given the measurements taken by the reflecting goniometer; the analysis follows; and then the importance of this compound is pointed out as an ingredient in manure, as containing ammonia and phosphoric acid in a state insoluble in water. The last substance described was composed of carbonate of lime and magnesia and phosphate of lime, and found imbedded in guano: it consists of concentric laminæ slightly adhering together, and had the appearance of an organic structure: it was supposed to be derived from remains of bones and shells partially decomposed.

"On some Chemical Effects produced by Platinum," by Dr. C. F. Schœnbein.

The oxidizing action of divided platinum on hydrogen and æther-vapour mixed with air, led the author to the expectation that it might be found capable of rendering blue the resin of guaiacum, a change known to be produced by the action of oxidizing bodies in general. Free oxygen, even by the aid of solar light, acts but slowly on paper washed with an alcoholic solution of the resin. If platinum sponge, however, or better, platinum-black, be spread upon the moistened paper, it is speedily rendered blue at those points where the metal touched its surface.

Iodide of potassium is decomposed by moist spongy platinum with evolution of a brown substance, thought to be a compound of periodide of platinum with iodide of potassium. Platinum-black decomposes hydriodic acid in the same manner, liberating iodine.

Dr. Schœnbein next discusses at length the explanations usually given of the well-known chemical effects of the finely-divided metal. He rejects the idea that the platinum exists in the state of an oxide, and inclines much more to the view of Faraday and Dœbereiner, that the gas is condensed upon its surface or into its pores. He suggests, however, another explanation, viz. that the real agent may be no other than ozone, the isomer of Thenard's peroxide of hydrogen, generated by the action of oxygen upon the watery vapour, present in minute quantity even after apparently careful desiccation of the gas. The author suggests also that the electric spark which so easily explodes a mixture of combustible gas and oxygen, and generates nitric acid in moist air, may act not immediately, but by the intervention of ozone, which is first formed and then decomposed, yielding up its oxygen. He is not yet however in possession of any experimental evidence bearing upon the point.

"On the Wax of the *Chamærops*," by J. E. Teschemacher.

Mr. Teschemacher describes this wax as the produce of the *Chamærops humilis*, which grows in Cuba and other parts of the West Indies, and is imported into the United States in large quantities for the purpose of manufacturing into hats. When the leaves are split the wax falls off in the state of a white powder, is collected and burnt or thrown away; the weight of this substance this destroyed is probably about 100,000 lbs. annually. Mr. Teschemacher points out the quantity of myricine and cerine which may be obtained from this wax, and compares it with bees' wax as to its composition, and finally recommends its collection and its employment for many of the purposes to which bees' wax is applied.

PATENT.

Patent granted to Charles Robert Roper, Hackney, *for Improvements in the Manufacture of Gelatine.*

This invention consists in manufacturing a concentrated preparation of gelatine from bones, combined with sugar and the essence of lemon or almonds, or with other essences or essential oils, to be used for making jellies and *blanc-mange.*

The gelatine is prepared from bones or ivory in the following manner:—The cylinder of a digester is charged with bones (sheep-bones being preferred), broken into small pieces or reduced to dust, and 6 gallons of water are added to each hundred-weight of bones; the digester is then closed, and steam admitted from a boiler at a pressure of 20 lbs. per square inch; after the expiration of an hour the pressure is gradually raised to 32 lbs., which is continued for 3½ hours, and the charge of gelatine is then drawn off; if the dust of bones or ivory has been used, gelatine is pressed out of the charge after its withdrawal from the digester; but this is not requisite when the bones have been only broken into pieces, and placed in a strong woollen fabric. The gelatine is run into shallow tins or pans, and afterwards dried on nets, in the usual way; it is then well-washed, and melted with an equal weight of sugar, flavoured with essence of lemon when for jellies, and with essence of almonds when for *blanc-mange*; and these matters are melted in a digester by steam. When essence of lemon is used, it is in the proportion of 2 drms. to every 3 lbs. of gelatine; it is first mixed with the sugar, which is added to the gelatine after the latter has been melted with lemon-juice, in the proportion of 18 oz. of lemon-juice to 3 lbs. of gelatine. Essence of almonds is used in the same proportion as the essence of lemon, but water is substituted for the lemon-juice. Other essences or essential oils may be used in a similar manner.

The gelatine, prepared as above, is placed in jars for sale. Jellies may be quickly made therefrom by the use of boiling water, containing the white and shell (?) of an egg, adding wine according to taste. To make a *blanc-mange* only boiling milk is required.—Sealed April 22, 1845.

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