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PROCEEDINGS

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VOL. XXIV.

PAPERS READ BEFORE THE ACADEMY.

I.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF SODIUM MALONIC ESTER ON TRIBROMDINITROBENZOL.

By C. Loring Jackson and W. S. Robinson.

Presented June 13, 1888.

In an earlier paper from this laboratory,* the preparation of tribromtrinitrobenzol and its action with ammonia and aniline were described, and the announcement was made that the study of the behavior of this very reactive body would be continued. G. D. Moore and one of us accordingly have taken up the action of sodium malonic ester upon it, in the hope of substituting for each of the bromine atoms the radical of malonic ester, $CH(COOC_2H_5)_2$, and obtaining in this way a substance which might have yielded interesting derivatives. As, however, an entirely different product was the result of the reaction, it seemed wiser to study it with the much more accessible tribromdinitrobenzol, which acted in the same way, and to confine the work on the trinitro compound, which at best can be obtained only with difficulty, to those points in which the two substances showed a different behavior. In this paper, therefore, we give the results obtained up to the present time from the action of sodium malonic ester on

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* These Proceedings, Vol. XXIII. p. 138.

tribromdinitrobenzol, which we are obliged to publish now, although in some respects the work is not so finished as we could wish, because the departure of one of us from Cambridge will prevent us from continuing the investigation together.

The most important of these results can be summarized briefly as follows. Sodium malonic ester under the conditions used by us removes from tribromdinitrobenzol only two atoms of bromine, one of which is replaced by the radical of malonic ester, the other by hydrogen, so that the formula of the product is

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2.$$

This substance shows marked acid properties, and, although of a pale yellow color itself, forms salts most of which are dark blood-red; of these the sodium salt was analyzed, and its formula proved to be

$$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2.$$

The yellow copper salt was also analyzed, but proved to be a somewhat complex basic salt. The bromine contained in the substance is easily removed by treatment with aniline, the product being

$$C_6H_2C_6H_5NH(NO_2)_2CH(COOC_2H_5)_2,$$

which also gives a blood-red sodium salt with a formula similar to that of the salt derived from the original substance, but the acid properties of the anilido compound are much less pronounced. When heated with strong hydrochloric acid the bromdinitrophenylmalonic ester gives ethylchloride and a new substance melting at 170°, the analysis of which led to the formula $C_6H_2Br(NO_2)_2C_3H_3O_2$, but the determination of its constitution must be postponed till a later paper.

Action of Sodium Malonic Ester on Tribromdinitrobenzol.

If an alcoholic solution of sodium malonic ester is added to tribromdinitrobenzol (melting point 192°) dissolved in ether, the first drop imparts to the ethereal solution a blood-red color, which increases in intensity as more of the solution of sodium malonic ester is added, and the liquid contains the sodium salt of a new substance, which we prepared in the following way. To an ethereal solution of a weighed quantity of tribromdinitrobenzol we added an alcoholic solution of sodium malonic ester in the proportion of three molecules of the ester to one of the tribromdinitrobenzol. The following were found to be convenient proportions: 20 grm. of tribromdinitrobenzol, 16 grm. of malonic ester dissolved in 100 to 150 c.c. of absolute alcohol and treated with 2.4 grm. of sodium as sodic ethylate. It was not necessary to add the ester gradually, and there was no perceptible evolution of heat during the reaction. The mixture was allowed to stand in a corked flask at ordinary temperatures for three or more hours, and the dark blood-red liquid thus obtained filtered from the precipitate of sodic bromide, which had been deposited, acidified with dilute sulphuric acid, which changed the dark red color to pale yellow, and filtered once more to remove the sodic sulphate formed. The filtrate was then distilled on the water bath until most of the ether had passed over, when the residue in the flask deposited, as it cooled, crystals of the new substance mixed with a large quantity of unaltered tribromdinitrobenzol. The mother liquor from these crystals was allowed to evaporate spontaneously, and left a red or yellow oil mixed with a small additional quantity of the crystals, which were separated from it, and the oil allowed to stand in an open dish for some weeks, when it deposited an additional quantity of the crystals. The crystals, whether obtained by cooling the hot alcoholic solution, or from the oil by long standing in the cold, were purified by dissolving them in a little hot alcohol, and adding a moderately strong aqueous solution of sodic hydrate (the common laboratory solution diluted with its own volume of water), which converted the new substance into its soluble sodium salt, but left the tribromdinitrobenzol unaltered, the red solution was then poured into a large quantity of water, and the tribromdinitrobenzol removed by filtration. If the solid crystals were treated directly with the aqueous solution of sodic hydrate, the tribromdinitrobenzol was left in a form which clogged the filter very badly, whereas when an alcoholic solution was used, as directed above, no difficulty was encountered in the filtration. The red filtrate was acidified with dilute sulphuric acid, and the precipitate purified by crystallization from hot alcohol until it showed the constant melting point 75°–76°. After being dried *in vacuo*, its composition was determined by the following analyses.

I. 0.2061 grm. of the substance gave on combustion* 0.2910 grm. of carbonic dioxide and 0.0602 grm. of water.

II. 0.2013 grm. gave 0.2827 grm. of carbonic dioxide and 0.0511 grm. of water.

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* Care must be taken to heat the substance very gradually, as it shows a tendency to explode in the combustion tube.

III. 0.1975 grm. gave 0.2780 grm. of carbonic dioxide.*

IV. 0.1926 grm. of substance gave 12.4 c.c. of nitrogen at a temperature of 20° and a pressure of 740 mm.

V. 0.2214 grm. of substance gave by the method of Carius 0.1036 grm. of argentic bromide.

VI. 0.2005 grm. gave 0.0937 grm. of argentic bromide.

	Found					
	I.	II.	III	IV.	V.	VI.
Carbon	38.51	38.30	38.38			
Hydrogen	3.24	2.83				
Nitrogen				7.17		
Bromine					19.91	19.88

These results agree about equally well with the numbers calculated from two different formulas, as appears by the following comparison.

	Calculated for $C_6HBr(NO_2)_2C(CO_2C_2H_5)_2$.	Found Mean.	Calculated for $C_6H_2Br(NO_2)_2CH(CO_2C_2H_5)_2$.
Carbon	38.71	38.40	38.51
Hydrogen	2.72	3.03	3.21
Nitrogen	6.94	7.17	6.91
Bromine	19.85	19.89	19.75

The first of these formulas, in which the two atoms of bromine removed from the tribromdinitrobenzol have been replaced by the bivalent radical $=C(CO_2C_2H_5)_2$, seems at first sight the most probable, especially since W. H. Perkin, Jr. and others have observed the strong tendency of sodium malonic ester to react in this way; but although this is the only formula we have been able to find which explains easily the removal of two atoms of bromine in this reaction, we are inclined to reject it in favor of the second one, in which one atom of bromine has been replaced by the univalent radical $-CH(CO_2C_2H_5)_2$, and the other by hydrogen, for the following reasons: —

First, the formation of a sodium salt is hard to reconcile with the first formula, unless, indeed, sodic hydrate was added to it,† giving

$$C_6HBr(NO_2)_2OHCNa(CO_2C_2H_5)_2;$$

but our analyses of the sodium salt, given later in this paper, prove that it contains no hydroxyl, and to make this proof more convincing we prepared the salt for one of our analyses from sodic ethylate, as

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* The water was lost in this analysis.

† Wislicenus, Ann. Chem., ccxlii. 23.

the radical C_2H_5O-, which in this case would be added instead of hydroxyl, would make a very great difference in the percentage composition of the salt; but this preparation, like the others, gave on analysis numbers corresponding to the formula

$$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2.$$

Secondly, the ease with which the sodium salt is formed, and with which it is decomposed by an acid giving the original substance, militates against the first formula, as we can hardly suppose that a ring of carbon atoms, such as must be assumed in this formula, would break, when treated with an alkali, and reunite under the influence of an acid in dilute solutions. Finally, we may add that the meta position of the bromine atoms replaced deprives the first formula of any support from analogy.* The principal objection to the formula

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2,$$

which we adopt, is that we cannot account as yet for the formation of such a substance by the reaction of sodium malonic ester on tribromdinitrobenzol. We hope, however, that a careful study of the quantitative conditions of the reaction, and of the oil which is the secondary product, will throw light on this part of the subject; but owing to the departure of one of us from Cambridge, its further investigation must be postponed till next autumn.

The yield was far from satisfactory, 14 grm. of tribromdinitrobenzol after treatment with 12 grm. of malonic ester and 1.7 grm. of sodium, as described above, giving only 4.3 grm. of the bromdinitrophenylmalonic ester instead of the 14 grm. required, if the whole of the tribromdinitrobenzol was converted into the new substance, that is, 30.7 per cent of the theoretical yield. A large amount of the tribromdinitrobenzol was recovered, however, amounting to 5.5 grm., or 39.3 per cent. This leaves 30 per cent unaccounted for, which probably remains dissolved in the oil deposited by the alcoholic mother liquors; but that the dissolved substance is bromdinitrophenylmalonic ester admits of great doubt, as we have not succeeded in obtaining any considerable quantity of this substance from the oil by treatment with aqueous sodic hydrate. This point will be investigated more thoroughly hereafter. We have tried several modifications of the process, in hopes of improving the yield, but none of them have given satisfactory results; if, for instance, the proportion of sodium malonic ester is

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* Compare J. Stanley Kipping, Ber. d. ch. G. 1888, p. 32.

increased in order to bring more of the tribromdinitrobenzol into the reaction, any gain from this cause is more than compensated by the larger amount of the product taken up by the greater quantity of oil, which is only in part deposited on long standing. Nor was the yield increased by longer standing, or by boiling the materials with a reverse condenser; in this latter case the product came down in an oily form, and with, if anything, rather a smaller yield was much harder to purify.

Properties of the Bromdinitrophenylmalonic Ester, $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$.

The substance crystallizes in pale yellow flattened needles, or long plates terminated by a single plane, which forms with the sides angles not very far from 90°, but distinctly obtuse and acute. It melts between 75° and 76°, and shows a tendency to explode at high temperatures, so that the heat must be applied carefully when making a combustion of the substance. It is not very soluble in cold alcohol, but freely in hot, more soluble in methyl than in ethyl alcohol, freely soluble in ether, benzol, or glacial acetic acid, even more so in chloroform, moderately soluble in acetone or carbonic disulphide, nearly insoluble in ligroine or water. Strong sulphuric acid in the cold has little action on it, although perhaps a small quantity dissolves; on warming the mixture, complete solution takes place, and addition of water precipitates a solid, which seems to consist principally of unaltered bromdinitrophenylmalonic ester mixed with a small amount of a substance with a higher melting point, probably the compound formed by the action of concentrated hydrochloric acid in sealed tubes (see page 11). Nitric acid, either strong or fuming, dissolves the bromdinitrophenylmalonic ester in the cold, but does not produce any change of color. In this respect, it differs markedly from the corresponding trinitro compound. If the acid solution is warmed, decomposition seems to take place.

The bromdinitrophenylmalonic ester possesses well-marked acid properties, as was to be expected, since it contains a hydrogen atom standing between the two carboxyls of the malonic ester and a phenyl, which, as Victor Meyer* has shown, frequently exercises a negative influence, much heightened in this case by the presence of the two nitro groups. Sodic hydrate in either aqueous or alcoholic solution at once converts it into a soluble red sodium salt, and the same salt is

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* Ber. d. ch G. 1887, p. 534, 1888, p. 1291 *et seq.*

formed by an alcoholic solution of sodium malonic ester, by sodic carbonate dissolved in water, or by acid sodic carbonate mixed with very dilute alcohol. The aqueous solution of the salt is, however, entirely decomposed by carbonic dioxide, the original substance being precipitated. An aqueous solution of the sodium salt prepared by treating an excess of the original substance with a solution of sodic hydrate gave precipitates with salts of all the common metals except those of the alkalis. Most of these precipitates were red, and among them the following were especially characteristic: —

Baric, strontic, or calcic chloride, dark brick-red.

Magnesic sulphate, rust color.

Zincic acetate, dark chrome-orange.

Basic plumbic acetate, very dark brick-red.

The neutral plumbic acetate gave a yellow precipitate, which turned white when in contact with an excess of lead salt.

Cupric sulphate, dark golden yellow.

Ammonic hydrate also dissolved the substance with a red color, but the salt was decomposed on trying to evaporate off the excess of ammonia on the water-bath, leaving a whitish residue, which seemed to consist principally of the original substance, with a small amount of decomposition product. The substance is in fact easily decomposed by either ammonic or sodic hydrate, and our rather unsatisfactory observations on these reactions will be found on page 11. The sodium salt boiled under a reverse condenser with ethylbromide in alcoholic solution, passed from red through purple, bluish green, green, and brown to reddish yellow; sodic bromide was formed, and the other product was an oily substance, which solidified after some time. It will be studied later. The bromine atom in the bromdinitrophenylmalonic ester seems to be removed with comparative ease. Up to this time, we have studied its behavior in this direction only with aniline (see page 9).

The Sodium Salt $C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2$.

This substance was prepared by dissolving some of the bromdinitrophenylmalonic ester in alcohol and adding a little sodic hydrate, care being taken that the hydrate was not in excess; a little ether was then added, and the mixture evaporated rapidly in a small beaker sunk throughout its whole length in the water-bath. The ether vapor kept the air from coming in contact with the liquid, while the alcohol was being heated to its boiling point. The residue, after all the alcohol had evaporated, was extracted with benzol to remove the excess of the ester, and then dried by gentle warming, and standing *in vacuo* over paraffine and sulphuric acid. These precautions were adopted to avoid the contamination of the substance with the carbonic dioxide of the air. The same substance was obtained when sodic ethylate was used instead of sodic hydrate, and Analysis III. was made with a sample prepared in this way.

I. 0.1950 grm. of the substance ignited with sulphuric acid gave 0.0324 grm. of sodic sulphate.

II. 0.1354 grm. gave 0.0216 grm. of sodic sulphate.

III. 0.1943 grm. gave by the method of Carius 0.0838 grm. of argentic bromide and the filtrate gave 0.0330 grm. of sodic sulphate.

IV. 0.2148 grm. gave 14.3 c.c. nitrogen at a temperature of 25° and a pressure of 759.6 mm.

	Calculated for $C_6H_2Br(NO_2)_2CNa(CO_2C_2H_5)_2$.	Found.			
		I.	II.	III.	IV.
Sodium	5.39	5.38	5.16	5.50	
Bromine	18.74			18.35	
Nitrogen	6.55				7.42

The results of these analyses show that the substance is the normal salt, containing but one atom of sodium, and the important bearing of this point on the determination of the formula of the bromdinitrophenylmalonic ester has been discussed already. (See page 4.)

Properties. — The salt forms a dark blood-red powder, easily soluble in water, alcohol, or ether. From a solution containing much sodic hydrate, the salt can be extracted with ether; but pure water, on the other hand, extracts the salt from its ethereal solution. Its aqueous solution is decolorized by carbonic dioxide bromdinitrophenylmalonic ester being precipitated.

The *copper salt* seemed from its appearance to promise excellent results on investigation, and was accordingly prepared as follows. An alcoholic solution of the bromdinitrophenylmalonic ester was treated with a small quantity of sodic hydrate taking care that the ester was in large excess, and then poured into a volume of water sufficient to precipitate all the unaltered ester; after filtering, an alcoholic solution of cupric chloride was added, and the precipitate washed first with 50 per cent alcohol, then with water, and finally once with hot alcohol; it was then dried *in vacuo*. It is not necessary to protect the salt from contact with the air during its preparation, as it is not perceptibly affected by carbonic dioxide. It gave the following results on analysis.

I. 0.2052 grm. of the salt was treated according to the method of Carius and gave 0.0844 grm. of argentic bromide. The filtrate was freed from argentic nitrate, and the copper precipitated by electricity from a sulphuric of nitric acid solution giving 0.0197 grm. of copper.

II. 0.2073 grm. treated in the same way gave 0.0864 grm. of argentic bromide and 0.0198 grm. of copper.

III. 0.1455 grm. gave 0.0138 grm. of copper.

	Calculated for $HOCu_2[C_6H_2Br(NO_2)_2C(CO_2C_2H_5)_2]_3$.	Found.		
		I.	II.	III.
Copper	9.36	9.60	9.55	9.48
Bromine	17.70	17.50	17.74	

From these results it would appear that the substance is a basic salt, or, at least, that it is not the normal salt, and in spite of its very promising appearance is not fitted to throw light on the nature of the original substance. We have not thought it worth while, therefore, to examine it more carefully. We may add, that the salt changes color from a lighter to a darker yellow soon after it is prepared, which we are inclined to ascribe to the conversion of

$$ClCu_2[C_6H_2Br(NO_2)_2C(CO_2C_2H_5)_2]_3$$

into the corresponding hydroxyl compound by the action of the water in which it is suspended.

Properties. — The copper salt forms an obscurely crystalline precipitate of a golden yellow color, with a very slight greenish tinge. It is essentially insoluble in water, alcohol, or ether, and is a comparatively stable substance, as it seems to be unaltered by exposure to the air, or by heating to 100°. Strong nitric acid, even in excess, decomposes it, setting free the bromdinitrophenylmalonic ester.

Anilidodinitrophenylmalonic Ester,

$C_6H_5NHC_6H_2(NO_2)_2CH(COOC_2H_5)_2$.

This substance was made by mixing the bromdinitrophenylmalonic ester with aniline in the proportion of one molecule of the ester to two of the base. The solid becomes yellow almost immediately, and the action has come essentially to an end after the mixture has stood for a few minutes in the cold. As a measure of precaution, however, we always heated it gently for a few minutes to make certain that all the bromine had been removed. The product was purified by cystallization from alcohol, until it showed the constant melting point 118°, dried at 100°, and analyzed.

I. 0.2104 grm. of the substance gave on combustion 0.4262 grm. of carbonic dioxide and 0.0903 grm. of water.

II. 0.1886 grm. of the substance gave 16.9 c.c. of nitrogen at a temperature of 22° and a pressure of 766.6 mm.

	Calculated for $C_6H_2(NHC_6H_5)(NO_2)_2CH(CO_2C_2H_5)_2$.	Found.	
		I.	II.
Carbon	54.68	55.24	
Hydrogen	4.56	4.77	
Nitrogen	10.07		10.24

Properties. — The anilidodinitrophenylmalonic ester forms flattened needles terminated by one or two planes, which form much more oblique angles with the sides than those which appear in the bromdinitrophenylmalonic ester. It is also found occasionally in star-shaped groups of needles, has a bright yellow color, and melts at 118°. It is only slightly soluble in cold alcohol, much more soluble in hot, but not freely even in this. More soluble in methyl than in ethyl alcohol; soluble in ether, or in carbonic disulphide; freely soluble in benzol, glacial acetic acid, or acetone, very freely in chloroform; essentially insoluble in water or ligroine. The best solvent for it is alcohol. Concentrated hydrochloric acid does not dissolve, or act on it in open vessels, either hot or cold. An aqueous solution of sodic hydrate acts on it in the cold only very slowly and imperfectly, but gives a red solution when boiled with it. In alcoholic solution sodic hydrate converts it into a red soluble salt; the anilido compound therefore still possesses acid properties, but these are much less marked than in the corresponding bromine compound; the negative influence of the dinitrophenyl therefore has been partly neutralized by the introduction of the basic aniline radical C_6H_5NH.

The Sodium Salt $C_6H_2(C_6H_5NH)(NO_2)_2CNa(COOC_2H_5)_2$.

This substance was formed in the same way as the sodium salt of the bromdinitrophenylmalonic ester; that is, by treating an alcoholic solution of the substance with alcoholic sodic hydrate not in excess, evaporating to dryness with a little ether on the water-bath, and extracting the excess of the ester with benzol. It was dried at 100°, and analyzed.

0.1180 grm. of substance gave 0.0194 grm. of sodic sulphate.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2CNa(CO_2C_2H_5)_2$.	Found.
Sodium	5.24	5.32

Properties. — It resembles the sodium salt of the bromdinitrophenylmalonic ester closely in appearance and solubility, but is of a somewhat lighter red. Its solution is decomposed, when treated with carbonic dioxide.

Experiments on the Saponification of Bromdinitrophenylmalonic Ester.

In taking up this subject we considered it necessary to study the action of alkalis on the ester, although, owing to the ease with which the nitro groups are attacked, we had little expectation of reaching satisfactory results. In this we were not deceived, but we think it best to give a brief account of these experiments before describing our more successful work with strong hydrochloric acid in sealed tubes.

A solution of sodic hydrate in water, if boiled with the brom- or anilidodinitromalonic ester, gave a brownish red solution, from which acids precipitated nothing; but after acidification, and extraction with ether, an unpromising oil was obtained in very small quantity. Cold alcoholic sodic hydrate with the anilido compound gave a somewhat more promising result, but in this case also most of the substance seemed to be decomposed. The bromine compound after standing for two weeks with ammonic hydrate at ordinary temperatures was converted into a similar brown solution, which on acidification gave a resinous brown precipitate and a yellow filtrate, from which ether extracted a substance melting above 200°, ammonic bromide being formed during the process. This is the only one of these products which seems worth further investigation.

Action of Hydrochloric Acid.[*]

When the bromdinitrophenylmalonic ester was heated with strong hydrochloric acid in a sealed tube to 140°–145°, it was decomposed, and upon opening the tube a gas was given off in tolerable quantity, which burnt with a green-bordered flame, and was without doubt ethylchloride. About one gram of the substance and 20 c.c. of common strong hydrochloric acid were used in each tube, and the temperature should not be allowed to go above 150°, as in this case an impure product was the result. If proper care was used in the heating, the tube contained crystals, or a clear liquid, from which crystals were deposited after the pressure was relieved; these were

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[*] All our work on this part of the subject must be regarded as preliminary.

filtered out and the filtrate thrown away, as it gave almost no residue on evaporation, and no extract when shaken with ether.

The crystals were purified by crystallization from dilute alcohol (three parts of water to one part of alcohol). If the temperature was kept below 150°, the product was nearly pure, as it came from the tube; but if it had risen above this point, a small quantity of a lower melting substance was formed, which it was almost impossible to remove with dilute alcohol. In this case the best plan was to dissolve the substance in chloroform, when the impurity separated at first as a pasty mass, leaving the principal product in solution, which after one crystallization from dilute alcohol showed the constant melting point 170°. It was dried at 100°, and analyzed with the following results.

I. 0.1307 grm. of substance gave on combustion 0.1634 grm. of carbonic dioxide and 0.0278 grm. of water.
II. 0.2162 grm. of substance gave 0.2688 grm. of carbonic dioxide and 0.0495 grm. of water.
III. 0.2136 grm. of substance gave 18.3 c.c. of nitrogen at a temperature of 22° and a pressure of 760 mm.
IV. 0.1197 grm. gave 10.2 c.c. of nitrogen at a temperature of 28° and a pressure of 762.9 mm.
V. 0.2212 grm. of substance gave by the method of Carius 0.1365 grm. of argentic bromide.
VI. 0.2120 grm. gave 0.1275 grm. of argentic bromide.

	Found.					
	I.	II.	III.	IV.	V.	VI.
Carbon	34.10	33.91				
Hydrogen	2.37	2.54				
Nitrogen			9.48	9.39		
Bromine					26.29	25.59

These numbers agree tolerably well with those required for the formula $C_6H_2Br(NO_2)_2C_3H_5O_2$.

	Calculated.
Carbon	33.86
Hydrogen	2.19
Nitrogen	8.77
Bromine	25.08

But the formula cannot be considered definitely established, until we have supported our analytical results by a careful study of the derivatives of the substance.

Properties. — The substance crystallizes from dilute alcohol in yellowish white narrow plates, sometimes half a centimeter in length, which are made up of needles attached to another needle acting as a midrib at very acute angles, giving an exact imitation of a feather or more commonly of one side of a feather; this form is very characteristic, and, when not so well developed, the substance can be recognized by the formation of narrow plates, usually smooth on one side and rather irregularly serrated on the other, or upon the ends. The plates often occur in radiating groups, the members of which form very acute angles with each other. From methyl alcohol or ether it crystallizes in very slender needles, much branched at very sharp angles, often forming circular groups resembling certain seaweeds. It melts at 170°, is not very soluble in cold alcohol, freely in hot, more soluble in methyl than in ethyl alcohol, freely soluble in glacial acetic acid or acetone, tolerably soluble in ether, slightly soluble in benzol either cold or hot, or in carbonic disulphide, slightly soluble in cold chloroform, more soluble but not freely in hot, nearly insoluble but not quite so in cold water, more soluble but still very slightly in hot, essentially insoluble in ligroine. The best solvent for it is chloroform, or a mixture of alcohol and water. Its behavior with alkalis is very characteristic. If a drop of an aqueous solution of sodic hydrate is added to the substance dissolved in alcohol, the solution takes on a dark but brilliant Prussian green color. This solution becomes colorless on addition of hydrochloric acid, but turns green again on addition of sodic hydrate. The green alcoholic solution, if allowed to evaporate spontaneously, leaves a brownish yellow residue, and a solution of the same brownish yellow color is obtained if an *excess* of sodic hydrate is added to the original substance. If the yellow solution, in whichever way prepared, is acidified with hydrochloric acid, it loses its color, and oil-drops are precipitated, which solidify in time. These dissolve in sodic hydrate with a brownish claret * or pale magenta color, which is unaltered by dilution with water, but turns green on addition of alcohol. The substance melting at 170° is not affected by an aqueous solution of sodic carbonate. The further study of these interesting reactions has been broken off by the summer vacation, but will be continued in this laboratory in the autumn.

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* A somewhat similar change of color was observed during the action of ethylbromide on the sodium salt of the bromdinitrophenylmalonic ester.

II.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON SODIC ZINCATES.

BY ARTHUR M. COMEY AND C. LORING JACKSON.

Presented June 13, 1888.

ALTHOUGH the solubility of zincic hydrate in alkalis is one of the most familiar facts in chemistry, very few attempts, so far as we can find, have been made to determine what compounds exist in such a solution. The reason for this is not far to seek, as the results obtained by the few who have studied this subject are so decidedly unsatisfactory, that they are not likely to induce others to take up this line of work.

The first important papers in this field appeared in the *Annalen der Chemie und Pharmacie* in 1834, having been brought out by a prize offered from the Hagen-Bucholz foundation for work on zincic oxide. Of the various competitors Laux,* who was most successful in his work on this part of the subject, found that a solution of zincic oxide in caustic alkali, if covered with a layer of alcohol, gradually deposited little shining crystals, which were easily soluble in water, and, he states, contained equal molecules of zincic oxide and the alkaline oxide (ZnO_2K_2). These crystals were decomposed by heat, giving a white powder, which contained one molecule of alkaline oxide to two of zincic oxide, but no analyses of either of these substances are given.

Two other competitors for this Hagen-Bucholz prize, Bonnet † and Sander,‡ also touch on this subject, but their results are of less importance. Sander, in fact, comes to the conclusion that no definite compound is formed when zincic oxide is dissolved in a caustic alkali.

The next paper on the subject was published in 1842, by Fremy, §

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* Ann. Chem. Pharm., ix. 183.

† Ibid., ix. 177.

‡ Ibid., ix. 181

§ Comptes Rendus, xv. 1106.

who states that the compounds formed by zincic oxide and an alkali were in general deliquescent and amorphous, but by using a potassic hydrate solution of zincic oxide, and adding to it a small quantity of alcohol, long needles were obtained, which he considered a "bi-zincate of potassa." It was immediately decomposed by water into zincic oxide and potassic hydrate. A few years later, in his article in the *Annales de Chimie et de Physique*,* Fremy states that he has met with great difficulties in obtaining the crystals, and hopes to return to the subject when he has determined the conditions under which they are formed. Neither of his papers contains analyses, and he has never published anything more on the subject, the reason for which we can well understand after our unsuccessful attempts to prepare potassic zincates.

The work on the ammonic zincates has led to about the same unsatisfactory results, no analyses of laboratory products having been published; but Malaguti † gives an analysis of an incrustation found upon a brick in the vault of a privy, which had the composition $3ZnO \cdot 4NH_3 \cdot 12H_2O$.

The only other research which has approached this subject is one by Prescott,‡ published in 1880, on the solubility of zincic oxide in caustic alkalis. He found that more alkali is needed for complete solution of the zincic oxide than would be required by the following reaction,

$$ZnSO_4 + 4\,KOH = Zn(OK)_2 + K_2SO_4 + 2\,H_2O,$$

but this excess was smaller in the case of sodic or ammonic hydrate than with potassic hydrate; also that the excess of alkali could be neutralized in such a solution without precipitating zincic hydrate, until the amount was reached indicated by the reaction given above. Addition of a large quantity of water precipitated the zincic hydrate from the solution, even when it contained the excess of alkali. The effect of dilution and temperature on the solubility were also studied, but the determination of the composition of the substances formed did not come within the scheme of his work.

As, therefore, we could find in the chemical literature no analyses of a zincate, with the exception of Malaguti's ammonic zincate, we decided to take up the subject, and fortunately began our work with the sodic zincate, since this proved to be the one of them all which can be most easily prepared.

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* Ann. Chim. Phys., Ser. 3, xii.

† Comptes Rendus, lxii. 413.

‡ Chem. News, xlii. 30.

The principal results which we have obtained can be briefly summarized as follows. From a solution of zincic oxide in aqueous sodic hydrate two crystalline sodic zincates can be separated by the action of alcohol; the principal product, which fuses below 100°, has the formula $Zn_3O_6Na_4H_2 . 17 H_2O$, the other, which does not fuse at 300°, is $(ZnO_2NaH)_2 . 7 H_2O$. Both substances are decomposed into zincic oxide and sodic hydrate by water or alcohol. We had hoped at first to extend our work to other zincates, but, after a number of experiments, have abandoned this intention, as with potassic hydrate no crystalline or definite compound could be obtained, and, although ammonic hydrate gave a product crystallizing in needles, it was obtained with difficulty, and proved to be of varying composition. We give, however, at the end of this paper, a brief account of the negative results of these experiments, and of some others in similar directions.

Preparation of the Sodic Zincates.

The sodic zincates can be prepared by the action of sodic hydrate on either metallic zinc, zincic oxide, or zincic hydrate, and the product seemed to be the same in every case. It is most convenient, therefore, to prepare them from zincic oxide, as the metallic zinc dissolves very slowly, long boiling with aqueous sodic hydrate being necessary to prepare a sufficiently strong solution. On the other hand, we have not succeeded in preparing the sodic zincates from sodic carbonate, as a mixture of this substance with zincic oxide showed no loss of weight even when kept at a white heat for some time. The method adopted by us consisted in dissolving zincic oxide in a strong aqueous solution of sodic hydrate,* with the aid of heat, in a flask, which was usually closed with a cork fitted with a set of potash bulbs, to prevent the absorption of carbonic dioxide by the alkaline liquid, but this precaution was not absolutely necessary. The solution, after it had cooled, was treated with twice or three times its volume of alcohol, and the mixture, after being thoroughly shaken, allowed to stand securely corked for about twenty-four hours. During this standing two layers were formed, a heavy aqueous solution, and a lighter alcoholic liquid. These were separated, the aqueous solution treated again with alcohol in the same way, and this extraction with alcohol repeated until the heavier portion solidified shortly after it had been removed from the alcohol, which happened usually after the third or fourth extraction. The crystalline mass thus obtained we have called fusible sodic zinc-

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* The sodic hydrate used by us had been purified by alcohol.

ate, because it melts below 100°. The second sodic zincate was obtained from the alcoholic washings, which were mixed, and allowed to stand in a corked flask, when after some time, which varied from a few hours to several days, white crystals were deposited on the sides of the flask, which gradually increased in quantity. The formation of these crystals did not occur invariably, but they could often be made to appear by adding more alcohol to the washings. This compound deposited from the alcoholic washings does not fuse even at 300°, and we shall call it infusible sodic zincate.

Analysis of the Fusible Sodic Zincate, $Zn_3O_6Na_4H_2 \,.\, 17\, H_2O$.

This substance is the principal product of the reaction, forming, as nearly as we could estimate, over 90 per cent of the total product. Since both water and alcohol decompose it, a further purification seemed impossible, and we were obliged to analyze it as it was obtained by the precipitation with alcohol, simply drying it by pressure between filter paper under heavy weights.

The method of analysis, which we adopted after trying several others, consisted in dissolving the substance in dilute sulphuric acid, and precipitating the zinc by means of a measured quantity of a standard solution of sodic carbonate. The zinc was weighed as oxide. The filtrate was acidified with sulphuric acid, evaporated to dryness, weighed, and then the amount of sodium calculated after subtracting from the total weight of the sodic sulphate the weight of sodic sulphate corresponding to the sodic carbonate added.

I. 0.4720 grm. of the substance gave 0.1744 grm. of zincic oxide and 0.2080 grm. of sodic sulphate.

II. 0.6420 grm. of the substance gave 0.2302 grm. of zincic oxide and 0.2718 grm. of sodic sulphate. 0.8802 grm. of substance from the same preparation lost at 240° 0.3920 grm. of water, and the dried product gave on heating with chromic oxide in a stream of dry oxygen 0.0342 grm. of water.

III. 0.9682 grm. of the substance gave 0.3370 grm. of zincic oxide and 0.3992 grm. of sodic sulphate. 0.8770 grm. of substance from the same preparation lost at 240° 0.4021 grm. of water.

	I.	II.	III
Zinc	29.66	28.78	27.93
Sodium	14.28	13.72	13.36
Water		44.54	45.83
Constitutional Water		3.88	

Each of these three analyses was made with a sample from an entirely separate preparation, in order to determine whether the substance had a definite composition, and when it is remembered that it could not be purified by crystallization, and was dried only imperfectly by pressing with filter paper, the agreement is as close as could be expected; but it is obvious that in a case like this the atomic ratios are of much more importance than the percentages, and we have accordingly calculated them as follows.

Atomic Ratio of Zinc to Sodium in Fusible Sodic Zincate.

	Zinc	:	Sodium.
I.	1.	:	1.36
II.	1.	:	1.35
III.	1.	:	1.35

The agreement between these numbers proves conclusively that the substance is a definite compound, and that the proportion of zinc to sodium is as three to four. In trying to calculate a formula for it, we have felt much doubt in regard to the amount of water of crystallization for the reasons given above; but the one finally adopted by us gives percentages which agree so well with those found, that it cannot be far from the truth, especially as the amounts of water found are about as much higher than those calculated as was to be expected. The constitutional water, on the other hand, comes very high, but we do not have much faith in this determination.

	Calculated for		Found.	
	$Zn_3O_6Na_4H_2$ 17 H_2O.	I.	II.	III.
Zinc	28.28	29.66	28.78	27.93
Sodium	13.30	14.28	13.72	13.36
Water	44.24		44.54	45.83
Constitutional Water	2.60		3.88	

To prove that the substance contained water, and not alcohol of crystallization, a combustion of it was made in the usual manner, but only a mere trace of carbonic dioxide was obtained.

The formula of this substance, $Zn_3O_6Na_4H_2 . 17 H_2O$, agrees, except in water of crystallization, with that of the substance analyzed by Malaguti (see page 15), which, written in the same way, becomes $Zn_3O_6(NH_4)_4H_2 . 9 H_2O$. This, as has been mentioned already, is the only zincate of which an analysis has been published.

We have made only one analysis of another preparation of this substance, which is comparable to those given above; this gave about the same percentage of zinc, 29.45, but a much larger amount of sodium, 19.56, which was undoubtedly due to a small quantity of sodic hydrate left adhering to the crystals, as this was the first preparation we made, and therefore was not pressed out so thoroughly as the later ones, after we had become more familiar with the manipulation.

Properties of the Fusible Sodic Zincate.

The substance as precipitated by alcohol from its solution in aqueous sodic hydrate forms a white mass, made up of radiating crystals, often of considerable size. It fuses at about 70°, but, owing to the difficulty of drying it, no attempts were made to determine the melting point accurately. Water decomposes it rapidly and completely. converting it into a white insoluble powder, which gave on analysis the following result.

0.1990 grm. of the substance gave 0.1910 grm. of zincic oxide and no sodic sulphate.

	Calculated for		Found.
	ZnO_2H_2.	ZnO.	
Zinc	65.72	80.28	77.03

The substance therefore seems to be principally zincic oxide mixed with a slight impurity of the hydrate. Alcohol decomposes it in a similar way, but more slowly, as is shown by the following percentages obtained from the analyses of two preparations (IV., V.), which we had attempted to purify by washing with alcohol.

	III.	IV.	V.
Zinc	27.93	29.96	33.36
Sodium	13.36	12.27	10.48

III. is one of the analyses already given. The substance for this analysis was only pressed with filter paper. IV. was a sample which had been washed three times with common alcohol, while the substance which had the composition given under V. had been washed four times with absolute alcohol. These numbers show that the action of the alcohol consists in gradually removing the sodium as sodic hydrate, and this point is brought out even more sharply by a comparison of the atomic ratios.

	Zinc	:	Sodium.
III.	1.		1.35
IV.	1.		1.16
V.	1.		0.89

It follows from what has been said on this subject, that care must be taken not to continue longer than is absolutely necessary the treatment with alcohol during the preparation of the sodic zincate. Although the substance is decomposed by both alcohol and water, it seems to exist during the process of manufacture dissolved in a mixture of these solvents in presence of an excess of sodic hydrate, an observation which is confirmed by that of Prescott (see page 15). It is insoluble in ether, and absorbs carbonic dioxide rapidly from the air. At 100° it loses only 12 molecules of its water of crystallization, as is shown by the following analysis.

0.4720 grm. of the substance analyzed under I., when heated to 100° in a stream of pure dry air, lost 0.1510 grm. of water.

	Calculated for a loss of $12H_2O$.	Found.
Water	31.23	32.00

Analyses and Properties of the Infusible Sodic Zincate, $(ZnO_2NaH)_2 . 7\ H_2O$.

This substance, which crystallizes from the alcoholic washings obtained in the preparation of the fusible compound just described, is formed in comparatively small quantities. As nearly as we could estimate, only a few per cent of the total product consisted of it. As, like the fusible compound, it is decomposed by both water and alcohol, no attempt was made to purify it further, but it was analyzed after drying at ordinary temperatures by the method already described (see page 17).

I. 0.7470 grm. of the substance gave 0.3424 grm. of zincic oxide and 0.2913 grm. of sodic sulphate; 0.4762 grm. of substance from the same preparation lost at 220° 0.1637 grm. of water.

II. 0.6044 grm. of the substance lost at 300° 0.2066 grm. of water, and gave 0.2700 grm. of zincic oxide and 0.2355 grm. of sodic sulphate.

	Calculated for $(ZnO_2NaH)_27H_2O$.	Found. I.	Found. II.
Zinc	35.32	36.78	35.86
Sodium	12.50	12.62	12.62
Water	34.24	34.37	34.19

The considerable difference between the percentages of zinc is not greater than was to be expected, when the impossibility of purifying the substance is remembered. Each of these analyses was made with a sample from a separate preparation, and we add the following analysis, made early in the work simply to determine the ratio between the zinc and sodium, no care having been taken to dry the substance.

III. 0.7025 grm. of slightly moist substance gave 0.2260 grm. of zincic oxide and 0.1951 grm. of sodic sulphate.

The percentages derived from this analysis are of course of no value, but it gives an atomic ratio which agrees with those from the preceding analyses so closely that there can be no doubt that this substance possesses a definite composition.

Atomic Ratio of Zinc to Sodium in the Infusible Sodic Zincate.

	Zinc	:	Sodium.
I.	1.03		1.
II.	1.03		1.
III.	1.02		1.

A combustion of the substance showed that it contained no alcohol.

This substance undoubtedly corresponds to the crystalline body obtained by Fremy (see page 15), who assigned to it the same ratio between the zinc and potassium. Laux (see page 14), on the other hand, ascribed to his crystals, which were soluble in water, the formula ZnO_2K_2, but stated that upon heating these crystals he obtained an amorphous powder, which showed the ratio of 1 : 1 between zinc and potassium; that is, the same obtained in the crystals by Fremy and us. We have met with no substance corresponding to the soluble crystals of Laux.

Properties. — The infusible sodic zincate crystallizes from a solution in dilute alcohol containing an excess of sodic hydrate in white needles, sometimes over a centimeter long, forming loose radiating groups usually of a conical shape, but occasionally circular or spherical. It does not melt even at 300°, and is decomposed by alcohol, or water, if these solvents are free from sodic hydrate, absorbs carbonic dioxide from the air, but much less rapidly than the fusible compound, and does not lose the whole of its water of crystallization until heated above 200°.

We have not succeeded in finding any other definite compound among the products of the action of sodic hydrate on zincic oxide, and, if any other exists, it can be only in very small quantity.

After we had settled the composition of the sodic zincates, we turned our attention to the study of other zincates, and also tried some experiments with magnesic oxide. The results of all this work were negative, but nevertheless we think it best to give a brief statement of what we have done.

In all our attempts to prepare potassic zincate we encountered the difficulties already mentioned by Fremy; in fact, we have not succeeded in obtaining in any experiment the crystals described by him, although we have modified the process employed in a number of different ways; but the solution of zincic oxide in potassic hydrate, when treated with alcohol according to the method which had yielded such good results with sodic zincate, gave only amorphous precipitates, which looked like zincic oxide, but were not wholly free from potassium; as the absence of crystalline form left us no means by which we could judge of the purity of this substance, we did not think it worth analysis.

With ammonic hydrate the results looked more promising at first, as the solution of zincic hydrate in ammonic hydrate occasionally gave a small quantity of crystals, after it had been mixed with alcohol and allowed to stand; but in this case there was no separation of the liquid into two layers. These crystals looked very much like the infusible sodic zincate described above, but the analyses of four preparations showed that they had no constant composition, the following percentages being obtained.

	I.	II.	III.	IV.
Zinc	48.66	45.90		59.96
Ammonia	7.35	4.58	3.67	5.28

In view of these results, it did not seem worth while to continue the investigation.

In beginning this research we had hoped, by acting on the sodic zincate with a cobaltous salt, to obtain Rinman's green, and in this way throw some light on the composition of this pigment. These hopes have not been fulfilled, as the zincates were decomposed by alcohol or water, as already stated, and therefore the action could not be carried on in solution, and the melted fusible zincate, when treated with cobaltous chloride, gave only a blackish precipitate with no shade of green. The same result was obtained when an ethereal or absolute alcohol solution of cobaltous chloride was allowed to act on the zincate. We have also made many attempts to purify Rinman's green, prepared according to the usual method, in order to fit it for analysis, but none of these have succeeded, the substance being decomposed by solutions of alkalis or acids, in fact even by a solution of carbonic dioxide under pressure, which dissolved both zincic and cobaltous carbonates, and finally left a blackish gray residue.

Although magnesic hydrate does not dissolve in sodic hydrate under ordinary conditions, we thought that possibly a very strong solution of sodic hydrate might have some solvent action at its boiling point, and, upon trying the experiment, obtained long prismatic crystals, which, however, we found contained only a mere trace of magnesium (0.39 per cent), and consisted of the crystallized sodic hydrate recently obtained by Cripps,* as shown by the following analytical results.

I. 0.5620 grm. of the substance lost 0.2150 grm. of water.
II. 0.4115 grm. of the substance gave 0.4585 grm. of sodic sulphate.

	Calculated for $(NaOH)_3\,4H_2O$	Found. I.	II.
Water	37.50	38.26	
Sodium	35.93		36.11

The curious point about this observation, which alone makes it worth recording, is that the solution of sodic hydrate used could not be made to crystallize before it was treated with magnesic oxide, but after such treatment crystallized so rapidly that it was impossible to filter it. The experiment was repeated several times, each time with the same result. What the cause of this difference in behavior may be we have been unable to determine, but think that possibly a small quantity of sodic carbonate in our solution of sodic hydrate may have prevented the crystallization, which took place as soon as this was converted into hydrate by the magnesic oxide.

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* Pharm. Jour. Trans , Ser. 3, xiv. 833 (1884).

III.

STUDIES FROM THE NEWPORT MARINE LABORATORY.

XXI. — A PRELIMINARY ACCOUNT OF THE DEVELOPMENT AND HISTOLOGY OF THE EYES IN THE LOBSTER.

By G. H. Parker.

Presented by Alexander Agassiz, October 10, 1888.

The following is a brief statement of the results obtained from studying the development and histology of the eyes in lobsters. The method in which the optic nerve appears to terminate is so exceptional, that, before making a final publication on this subject, it seems desirable to seek confirmation in the structure of the eyes in other Crustacea. As this will delay the appearance of the paper, and since in other directions definite conclusions have been reached, it seems advisable to publish now an account of my present conclusions.

The first indication of the optic apparatus in the young lobster is a pair of ectodermic thickenings on either side, and slightly in front of where the mouth is to appear. The superficial part of each of these thickenings gives rise to the retina, and the deep part to the optic ganglion. The ganglionic portion is cut off from the retinal portion by the ingrowth of the basement membrane. In certain regions, however, the basement membrane does not cut the connection between the retina and ganglion. These primitive connections persist in the adult as optic nerve fibres.

In the eye of an adult lobster each ommatidium consists of at least sixteen cells. Directly under each corneal facet are found two flat lentigenous cells (corneal hypodermis). Under these are four retinophoræ, one for each angle of the corneal facet. The retinophoræ are extremely elongated, and extend from the deep face of the corneal hypodermis to the basement membrane. From the corneal hypodermis to the spindle the four retinophoræ are closely applied to one another. At the distal end of the spindle they separate, passing around that structure as fibres. As they approach the basement membrane they converge slightly, and terminate on the retinal surface of that membrane. Under the centre of each ommatidium the basement membrane is considerably thickened, and it is on this thickening that the four retinophoræ terminate.

Each ommatidium has ten pigment cells, — two distal and eight proximal. The distal cells surround the retinophoræ in the region of the crystalline cones, and from this region they are continued inward as fibres till they pass through the basement membrane. The eight proximal pigment cells are closely applied to the spindle, the fibres of the four retinophoræ passing between them. Seven of these are deeply pigmented; one is without pigment. The eight cells extend only a short distance in front of the spindle; the seven pigment cells proper are continued inward as large fibres *through the basement membrane.* In addition to the sixteen cells just described, each ommatidium has two or three irregular cells filled with a pigment, brownish by transmitted, white by reflected light. These cells envelop the proximal half of the spindle, and extend to the basement membrane. The spindles themselves do not reach the basement membrane.

The sixteen cells already described are ectodermic in origin. The two or three additional cells may be from either an ectodermic or mesodermic source, but the evidence thus far gathered points decidedly to their ectodermic origin.

The basement membrane, as was previously mentioned, has a thickening in it under each ommatidium. Around a given thickening there are four openings through the membrane. Each opening, however, is placed between two thickenings, so that in reality only half of each cluster of four openings belongs to a given thickening. There are two classes of openings, one with a single small and four large fibres, and another with one small and three large fibres, passing through. Each thickening has two of each class accompanying it. Of the fourteen large and four small fibres passing through the four openings, only one half, or seven large and two small fibres, belong to a given ommatidium. These represent the seven deep and two superficial pigment cells. After passing through the basement membrane, these fibrous ends of the pigment cells thicken considerably, and, having grouped themselves in bundles, pass inward, constantly diminishing in calibre, till they reach the optic ganglion. The optic nerve between the retina and first optic ganglion is composed of these fibres bound together by a small amount of connective tissue. All attempts at isolating any other form of fibres have failed, and it would therefore seem that the fibres of the optic nerve terminate in these nine pigment cells.

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IV.

ATMOSPHERIC ECONOMY OF SOLAR RADIATION.

By Arthur Searle.

Presented October 10, 1888.

The terrestrial atmosphere acquires energy from the solar radiation by direct absorption, by the absorption of terrestrial radiation, and by conduction from terrestrial solids and liquids. It loses energy in three corresponding ways; by radiation into space, by downward radiation, and by conduction.

As some time must elapse between the acquisition and the loss of any given amount of energy, the air always contains a certain accumulated store of activity resulting from the solar radiation, and manifested in warmth, expansion, and movement. It is a general and apparently well founded belief, the reasons for which need not here be repeated, that terrestrial temperatures are maintained to a great extent by the aid of this atmospheric accumulation of energy; so that a far lower temperature would prevail in the absence of the air. The hypothesis which has been current until recently with regard to this protective action of the atmosphere depended upon a supposed effect of selective absorption, which has now been largely, if not entirely, disproved by Langley's experiments. The supposition, indeed, was always somewhat difficult to reconcile with the familiar fact that celestial bodies appear redder at a small than at a great altitude; since, so far as the visible spectrum is concerned, this proved that among the constituents of the atmosphere there were some, abounding in its lower strata, which absorbed radiations of small wave-length more readily than the others. Hence it did not seem probable that the radiation from terrestrial substances the temperature of which was far below red heat would be absorbed by the air with peculiar readiness, and thus prevented from escaping into space. This reasoning, however, could not be conclusive, and actual experiment was required to overthrow the assumption that the air was much more transparent to solar than to terrestrial radiation.

As we are now obliged to abandon this assumption, it is natural to inquire whether the known phenomena of conduction will suggest a better explanation of the protective action of the atmosphere than can be afforded by the observed laws of absorption and radiation. By conduction, fluids acquire heat most readily when hot bodies are applied to their lower surfaces, in consequence of the convection currents thus established. On the other hand, the application of cold bodies to their lower surfaces, as it does not originate such currents, withdraws their heat only by the much slower process of conduction through their own substance.

Hence, an undisturbed atmosphere will acquire heat more readily by contact with warm ground than it loses heat by contact with cold ground. Part of the heat thus acquired might have been conducted to adjacent portions of the ground in the absence of the atmosphere, but another portion would have been directly radiated into space. It now becomes a question whether the atmosphere thus heated will discharge its recently acquired energy by radiation into space as readily as the ground would have done in the absence of an atmosphere.

Without undertaking to decide this question, it will here be assumed that the heat acquired by the atmosphere from warm ground will not be radiated as readily as it would have been radiated by the ground itself. Since it will not be readily lost by conduction, in the absence of violent agitation of the air, for the reason already given, the hypothesis seems admissible that it tends to accumulate, and to increase the stock of energy contained in the atmosphere much more efficiently than can be done by the processes of absorption and radiation.

If we admit the existence of this tendency, we have next to consider what natural provision can be suggested for checking its effects when they have attained a certain magnitude; for it is obvious that they do not increase indefinitely. If we suppose atmospheric energy to be manifested only as heat, its accumulation would ultimately be checked by an increasing radiation from terrestrial solids and liquids; if manifested only by expansion, it is perhaps possible that portions of the atmosphere would be driven off into space, carrying away the energy mechanically; but a more immediate check is afforded by that portion of the accumulated energy which displays itself as atmospheric movement. When the winds have attained a certain degree of violence, they disturb the portions of the air which would otherwise remain stagnant over the colder parts of the ground, and the process of heating the atmosphere from beneath gradually ceases to retain sufficient advantage over that of cooling it from beneath to permit a further accumulation of energy.

If a permanent increase should take place in the amount of solar radiation, it is clear, upon the present hypothesis, that some time would elapse before the increasing agitation of the atmosphere put an end to the increase of its energy. The stock of atmospheric energy in general, and that part of it manifested as heat, would thus be permanently increased. The terrestrial temperature would be raised, tempests would be more frequent and severe, and the entire atmosphere would probably occupy more space.

On the other hand, a permanent diminution in solar radiation would tend to diminish the agitation of the air, and, although the terrestrial temperature would decline, this loss of temperature would not be so great as that which would have occurred if the winds had maintained their previous force. The atmosphere, accordingly, acts as a check upon extreme variations of heat and cold; when little heat is received, it will be better economized than when the supply of heat is excessive, although particular regions may have, in the former case, a very severe climate.

The observed association of extreme cold with still air, and the greater violence of tempests in the heated portions of the world, on the whole, are among the facts tending to support the hypothesis above explained.

In the present discussion, the consequences resulting from the compressibility of the atmosphere have thus far been neglected, and what has been said above would be equally applicable to an atmosphere wholly incompressible. But in such an atmosphere the distribution of heat would materially differ from that actually observed. As a convection current rises, the air composing it expands, from the removal of pressure, and its energy largely ceases to exhibit itself as heat. Under these circumstances, the solid and liquid particles carried up with it are reduced in temperature, and made less capable of radiation into space than before. It may likewise be supposed, indeed, that the expanded air itself will have its previously small capacity for the discharge of its energy into space still further diminished. The additional tendency to retain energy, thus suggested, would demand more consideration if the discharge were effected by any process of the nature of conduction; that is, if the outer surface of the atmosphere were chiefly instrumental in the process. In this case, the expansion of the ascending air would be a highly important means of delaying the escape of energy received by conduction from warm ground; and an incompressible atmosphere might not in any considerable degree protect the planet which it surrounded.

However slightly the expansion of ascending currents may check the escape of energy, it is certain that the subsequent descent of the air composing them must exhibit more and more of its remaining energy in the form of heat. This phenomenon is generally recognized by recent writers upon meteorology, and there can be little doubt that it powerfully affects the relative climates of places at different altitudes. The climate of an elevated region is colder than that of the sea level, because a smaller part of the atmospheric energy appears there as heat, and a larger part as expansion. Whether this is a sufficient explanation of the observed difference of climate can scarcely be determined until we have more knowledge with regard to the actual extent and velocity of the convection currents of the atmosphere.

The considerations above set forth indicate the conclusion, that the effect of conduction, aided by convection currents, is probably an important means of maintaining the present terrestrial temperature, as well as the present distribution of warmth in different latitudes and at different elevations. If this conclusion should hereafter find a more satisfactory basis in observation and experiment, it would have some interesting applications to the climate of the larger planets. Their extensive atmospheres, subjected to a powerful force of gravitation, may perhaps enable them to economize very efficiently the comparatively small quantity of solar radiation which they receive. Another branch of inquiry connected with the same general subject relates to the conditions of temperature in different parts of the ocean. The atmospheric and oceanic currents prevailing in former times are also frequently discussed by geologists. If the atmospheric convection currents have the effects here attributed to them, they may help to account for some of the unexplained phenomena of prehistoric climates, the evidences of which have remained to the present day.

V.

THE CRYSTALLINE STRUCTURE OF THE COAHUILA IRONS.

By Oliver W. Huntington.

Presented October 10, 1888.

In a previous paper on the crystalline structure of iron meteorites,* the author described two cleavage crystals broken from a specimen of the Butcher meteorite (Coahuila), but, from the compact nature and softness of the iron, no further examples of cleavage were at that time obtained. Recently, however, on examining a large number of small sawed slabs of the same iron in the Harvard Collection, one slab was found to be intersected by an angular crack, as shown of actual size in Fig. 1. On taking the slab in the hand, it was found that the two portions could be readily separated by a slight pressure, and the surfaces, though considerably oxidized, showed sharply defined crystal faces extending through the entire thickness of the plate (about six millimeters) and forming angles of about 132° and 90°.

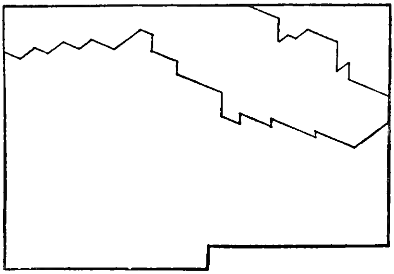

Fig. 1.

As this cleavage was so very striking, an attempt was made to break another slab artificially. It was mounted in a vice for the purpose, and the projecting portion struck with repeated blows of the

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* American Journal of Science, 3d series, vol. xxxii. pp. 284–303.

hammer. The slab broke readily along the jaws of the vice, exhibiting a superb crystalline cleavage, the faces of the crystals having a most brilliant lustre, almost like antimony, and, though the iron was soft enough to cut with a knife, yet some of the single cleavage faces were nine or ten millimeters in extent. These crystal faces usually formed angles of about 132°, or else right angles, though in some parts there were sharp projecting points, formed by the meeting of two rectangular planes with a third set obliquely. Furthermore, all the faces were most beautifully striated by numerous sets of fine parallel lines, easily distinguished by the eye, generally making angles with each other of 127°, 90°, and 53° respectively, a few of the lines appearing to be parallel to the intersections of the faces.

Fig. 2 shows enlarged one set of crystal faces as they appeared on the surface of fracture. The planes were absolutely perfect, and large enough to be readily measured with an application goniometer. Thus

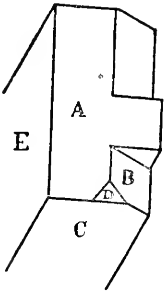

FIG. 2.

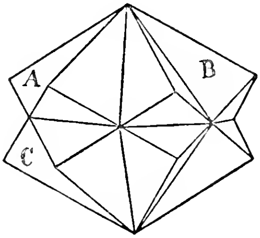

FIG. 3.

it was found that the plane B made with C a right angle, B and A an angle of about 132°, A and C an angle of about 109°; and the small plane D, set obliquely on the solid angle thus formed, made an angle of about 125° with B and C, and 164° with A. The plane E and the one parallel to it were the sawed faces of the slab. All the other planes forming the surface of fracture were parallel to the ones shown in the figure, and they could all be referred to faces of the twin cube, as shown in Fig. 3, where the corresponding faces are lettered the same and placed in a parallel position. The striations already mentioned appeared most markedly on the face A, that being the largest, and therefore the one most easily examined.

Fig. 4 shows, on a large scale, this plane referred to the face of a cube, only the most prominent of the striations being represented, in order to preserve clearness in the figure. It will be seen by the diagram, that all the lines follow the intersections of the different members of an ordinary cube twinned on all of the trigonal axes, and

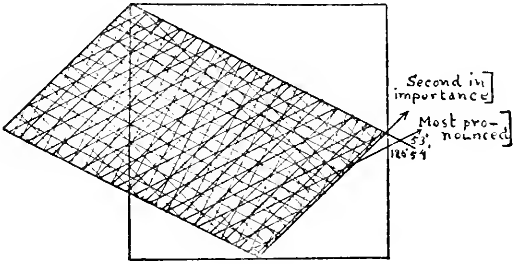

FIG. 4.

there were no markings on the face which could not be thus referred. However, on examining the triangular face D of Fig. 2, it appeared in marked contrast to the face just described, as all the markings were parallel to the octahedral edges, thus forming simple triangles.

A large number of specimens of the Butcher iron were afterwards examined, and they all exhibited the same crystalline cleavage on a fresh fracture. Moreover, it made no difference in what direction the slab was broken, the planes always showed a prevalence of the 132° angle (theoretical angle 131° 48′ 37″), with here and there the sharp projecting points already referred to, but, contrary to expectation, the simple cube angles seldom appeared, though in some parts they were evident.

It now appeared important to examine the cleavage of the Sancha Estate or Saltillo iron (Santa Rosa), which has been considered part of the same meteorite as the Butcher specimens. For this purpose Mr. S. C. H. Bailey sent us a wedge-shaped slab which had been sawed to a thin edge and then broken, giving a surface of fracture about seventy millimeters long and two millimeters wide in the thickest part, diminishing towards the two ends. The crystal faces over this surface were very small, and appeared to have a grayer color than those of the other irons. When this surface was examined under a low power microscope, the crystals were found to be all simple cubes, looking exactly like a specimen of galena, and, instead of the faces being striated as in the Butcher irons, they exhibited the little crystalline projections and depressions which are so characteristic of some alloys. However, on the face of the slab there was the suggestion of two cracks crossing at angles of about 132° and 53°, and an attempt was made to break the specimen parallel to one of these cracks, with the expectation of getting the planes already described in the previous iron.

When the slab was mounted in the vice and struck with the hammer, there at once appeared on the surface numerous very fine cracks parallel to the two directions just mentioned, and at once suggesting the two sets of fine parallel lines which are first brought out on an etched surface of this iron but are obliterated by the continued action of the acid. Finally, the slab broke, but exhibited only a single plane through the entire extent of the fracture (33 mm. in length by 6 mm. in breadth), and, instead of being striated, there was developed a very striking flaky surface as if little thin layers had resisted the cleavage, parting at last with irregular edges more or less separated from the main surface. An attempt was next made to break the slab at right angles to the first direction, in order to get other crystal faces; but, instead of breaking along the edge of the vice, as a Butcher specimen readily would have done, the Saltillo iron broke again with the same single cleavage plane, at right angles to the desired direction and running directly down into the jaws of the vice, entirely regardless of the way it had been clamped and the blows of the hammer applied.

Every attempt to break the slab gave the same result. It would only break in the two directions indicated by the first fine cracks, and corresponding to the angle that a cube face makes with the adjacent face of a twin cube, and always broke along a single plane exhibiting the flaky surface already mentioned. The only way of getting a different fracture was to saw the specimen to a thin edge, and so *force* it to break in the desired direction, and then it would present a surface of fine cubes wholly different in character from the large striated faces of the Butcher irons.

Just at this time we received from Ward and Howell a large slab of a new meteorite found in Allen County, Kentucky, and the whole character of this iron, including the etched surface, so closely resembled the Coahuila specimens that we were interested to see whether it would show any striking cleavage. Ward and Howell kindly furnished us with some small slabs, and, on breaking them in the way already described, they showed exactly the same characters as the Saltillo iron. The fine parallel cracks appeared under the first blows of the hammer, and then the slab broke regardless of the way it was clamped in only the two directions at angles of about 132° and 53°, presenting a single cleavage plane with the marked flaky appearance characteristic of the Saltillo iron.

Exactly the same result was obtained in breaking slabs of the Maverick County* iron, and also the iron from Chattooga County, Georgia,† both of which were described as independent falls, although closely resembling the Coahuila specimens.

Now it will be borne in mind that the Coahuila irons form a group by themselves, their etched surfaces appearing so markedly different from any other known meteorite, and for this reason, together with a resemblance in composition, they have commonly all been considered to belong to one fall. But, after examining the structure of the Butcher irons and that of the Saltillo or Sancha Estate as exhibited by the cleavage, it is impossible to class them as portions of a single original mass. And, on the other hand, when we compare in the same way the Saltillo iron with those of the Allen County, Chattooga County, and Maverick County meteorites, it seems equally impossible to believe that they did not at one time form a single meteorite, especially when they also resemble each other in composition as shown in the following analyses, though to be sure it is hard to tell how far such analyses can be depended upon as a means for comparison or distinction of irons.

	‡ Allen Co.	§ Santa Rosa.	‖ Maverick Co.	¶ Chattooga Co.
Iron	94.32	95.82	94.90	94.60
Nickel	5.01	3.18	By diff. 4.87	4.97
Cobalt	trace	.35		.21
Sulphur	.31	....	....	....
Phosphorus	.16	.24	....	.21
Carbon	.12	....	.23	....
	99.95	99.59	100.00	99.99

That these masses were found in places so remote from each other does not seem to preclude their having belonged to one individual, since the Rochester meteorite was seen to pass over the States of Kansas, Missouri, Illinois, Indiana, Ohio, and is supposed to have passed over Pennsylvania and New York, and thence out to sea, dropping fragments in its course. It therefore is possible that at some remote period an enormous iron meteorite may have passed over the

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* Amer. Jour. Sci., 3d series, vol. xxxii. p. 304, October, 1886.

† Ibid., vol. xxxiv. p. 471, December, 1887.

‡ Ibid., vol. xxxiii. p. 500, 1887.

§ Ibid., 2d series, vol. xix. pp. 160, 161, May, 1855.

‖ Ibid., 3d series, vol. xxxii. p. 304, October, 1886.

¶ Ibid., vol. xxxiv p. 472, December, 1887.

entire breadth of the United States, the main mass reaching Mexico, but large fragments breaking off and falling during its passage across the country.

Two irons commonly classed under the general head of "Coahuila" have not been included in the above consideration. They are labelled in the Harvard College collection, "Hacienda de Concepcion," * and "San Gregorio Iron, Chihuahua, Mexico," † both bearing the signature of Dr. H. B. Butcher. The specimen of the Hacienda de Concepcion was small, and had been hammered, so that its structure could not be conclusively studied, but it appeared to be markedly different from any of the other Mexican irons.

The San Gregorio iron, of which there were numerous specimens, appeared to be made up of very striking octahedral plates, and therefore must be placed among a very different class of irons from the Coahuila group, which it has been the purpose of this paper to describe.

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* Amer. Jour. Sci., 2d series, vol. xix. p. 163, 1855.

† Ibid., 3d series, vol. ii. p. 336, 1871.

VI.

CONTRIBUTIONS TO AMERICAN BOTANY.

By Sereno Watson.

Presented October 10, 1888.

1. *Upon a Collection of Plants made by Dr. E. Palmer, in 1887, about Guaymas, Mexico, at Muleje and Los Angeles Bay in Lower California, and on the Island of San Pedro Martin in the Gulf of California.*

The peninsula of Lower California and that portion of the Mexican mainland which borders the intervening Gulf, though reputed a sterile land, have always wherever they have been explored yielded a rich harvest of novelties to the botanical collector. Much therefore was expected from so keen and careful a collector as Dr. Palmer, when he undertook to spend a season at Guaymas, and from that point to explore such other places as might be accessible to him. Though the season of 1887 proved very unfavorable on account of its dryness, the result has nevertheless been very satisfactory. Of the 415 native species collected, 89 species, or more than one fifth, are wholly new, and many others are of great interest in various respects.

The larger part of the collection was made about Guaymas itself, which town lies on the eastern side of the Gulf of California, in the State of Sonora, in lat. 28° N., and 250 miles south of the United States boundary. It is hemmed in closely by very rocky hills and low mountains (of 1200 to 1500 feet altitude), intersected by narrow valleys. The artificially watered gardens, with their irrigating ditches and brush fences, protecting and favoring the growth of numerous native plants, the rocky islands in the harbor, and the valleys and mountains around, were all alike searched. Dr. Palmer remained here from the middle of June to the middle of November, during which time there were only occasional slight showers, which commenced in August. The species obtained here numbered 283, of which 40 were also found in other localities.* Muleje, upon the western side of the Gulf, 90 miles from Guaymas, is described as in a dry, barren, and mountainous region, where except in the very short rainy season the only green vegetation to be seen is along the banks of a small creek. This place was visited early in June, and again late in December. Of the 49 species collected here, 24 occurred elsewhere, mostly at Guaymas. Los Angeles Bay, also on the peninsula, about 200 miles northwest from Guaymas, was visited at an unusually favorable time, after a rain which was the first that had fallen in twenty-two months, and when vegetation was in full bloom. The surrounding country is very mountainous, some of the ridges having an altitude of 2,000 to 3,000 feet. About a month was spent here (from November 22 to December 20) and 112 species were collected, of which 23 had been found previously. The remaining station was the island of San Pedro Martin, lying about 80 miles northwest from Guaymas. This island has a circumference of about 4½ miles and an altitude of 1,200 feet, and is exceedingly rough and rocky, intersected by cañons and largely covered with guano. A very few small fig trees were found, but the only useful wood is furnished by the *Cereus Pringlei*, which forms almost a forest over the summit. During an eight days' stay (October 24 to November 5) only 19 species were collected, of which seven were not peculiar to the island.

The characteristics of the flora of the region bordering the Gulf of California, so far as shown by this collection, are for the most part those common to the flora of the whole arid region of the interior, from southeastern California, Arizona, and New Mexico southward into Mexico, distinct in a great measure from that of California proper on the one side, and that of the Gulf States on the other. Nearly or quite two thirds of the species range northward beyond the Mexican boundary. In the mountains about Guaymas we find a considerable number that are identical with or allied to species that have recently been collected by Pringle and Palmer in the mountains of Chihuahua. We have here also probably the northern limit on the Pacific coast of the tropical or subtropical genera *Rhizophora*, *Hæmatoxylon*, *Portlandia*, *Citharexylum*, *Pedilanthus*, *Ficus*, etc. The pro

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* Cultivated and introduced plants are not included in the numbers above given. Sixteen species of the collection are considered of this character, viz *Oligomeris glaucescens*, *Portulaca oleracea*, *Gossypium herbaceum*, *Triphasia trifoliata*, *Melilotus parviflorus*, *Tamarindus Indicus*, *Capsicum cordiforme*, *C. annuum*, *Crescentia alata*, *Beta vulgaris*, *Panicum sanguinale*, *Sorghum Halepense*, *Eleusine Ægyptiaca*, *E. Indica*, *Eragrostis major*, and *Lolium perenne*.

portion in which the several orders are represented in the collection is somewhat remarkable. Of the 415 species, one fourth are equally divided between the *Gramineæ* (50) and the *Compositæ* (50). Another fourth includes only the four orders *Leguminosæ* (44), *Euphorbiaceæ* (32), *Malvaceæ* (17), and *Solanaceæ* (15). These are followed by the *Nyctaginaceæ* (15), *Convolvulaceæ* (13), *Asclepiadaceæ* (10), and 53 other orders with still fewer species. The important orders *Ranunculaceæ*, *Rosaceæ*, *Saxifragaceæ*, *Umbelliferæ*, *Ericaceæ*, *Cupuliferæ*, *Coniferæ*, and *Orchidaceæ* are wholly unrepresented. Excluding the *Cyperaceæ* and *Gramineæ*, there are only five endogenous species in the entire collection.

For the determination of the species the *Cyperaceæ* were referred to Dr. N. L. BRITTON, Curator of the Torrey Herbarium, the *Gramineæ* to Dr. GEORGE VASEY, Botanist of the Agricultural Department at Washington, and the *Filices* to Prof. DANIEL C. EATON. Special acknowledgment is also due to Prof. DANIEL OLIVER, of the Kew Herbarium, for suggestions respecting the relations of a few of the more difficult species in other orders.

COCCULUS DIVERSIFOLIUS, DC. Guaymas. (60.)

ARGEMONE ALBIFLORA, Hornem. Differing from *A. Mexicana* in the narrower, less distinctly mottled, and less deeply sinuate leaves, more naked peduncles, white flowers, narrower buds and capsules, the capsules narrowed upward from near the base, and the much smaller seeds. "Cardo"; the dried juice used as a remedy for inflamed eyes. Mulejo. (7.)

ARGEMONE MEXICANA, var. (?), with obovate-spatulate petals, few stamens, narrow buds, narrow capsule attenuate to a distinct style, and irregularly pitted seeds much smaller than usual. About Guaymas. (105.)

ESCHSCHOLTZIA CÆSPITOSA, Benth., var., with more coarsely divided leaves. Rocky ridges, Los Angeles Bay. (590.)

CARDAMINE PALMERI. Annual, erect, smooth and somewhat glaucous, branching above, 1 or 2 feet high: leaves simple, thin, round-ovate, cordate at base, obtuse, usually rather deeply sinuate-toothed or -lobed, the larger 2 inches long; petioles a little shorter: flowers purplish, 3 or 4 lines long: pods slender, 1 to 1½ inches long by ⅔ of a line wide, beaked with a slender style, ascending on petioles 3 or 4 lines long: seeds small. — Resembling *C. cordifolia* of the Rocky Mountains. Under bushes near salt water, Mulejo. (421.)

Cardamine angelorum. Annual, glabrous and glaucous, suberect, branching above, leafy to the base of the short raceme: leaves pinnately divided, the straight divaricate lobes (5 or 6 pairs) linear, obtuse, entire or rarely with a lateral lobe at base, 9 lines long or less: flowers purplish, 2 lines long: pods slender, 1¾ inches long by ⅔ of a line wide, ascending; style short: seeds small. — On stony ridges near Los Angeles Bay. (594.)

Nasturtium (?) laxum. Annual, glabrous, slender, ascending, the elongated branches very lax: leaves pinnately divided, the narrowly linear straight divaricate segments (2 or 3 pairs) entire, acute, 8 lines long or less: raceme lax, elongated, the soon distant flowers small (1½ lines), purplish; on slender spreading pedicels: immature pods reflexed, narrow, 3 to 6 lines long, about equalling the pedicels, the cells about 6-seeded; style stout. — The purplish flowers and immature pods leave the genus somewhat doubtful. It may be a *Thelypodium*, though differing in habit from other species of that genus. On sandy plains near Los Angeles Bay. (598.)

Sisymbrium canescens, Nutt. Mountains, Los Angeles Bay. (579.)

Lepidium Palmeri. Annual, decumbent or procumbent, branching from the base, hispid throughout: leaves pinnately divided, the narrow lobes with usually a single tooth on the upper margin: racemes sessile, short, rather dense; pedicels short, broad and flat: flowers minute, apetalous: stamens 2: pods thinly pubescent, round-ovate with short blunt wings, 1½ to nearly 2 lines long, on spreading or somewhat recurved pedicels; stigma sessile. — At Los Angeles Bay, in the shade of rocks and bushes. (560.)

Lyrocarpa Coulteri, Hook. & Arn. The typical form. At Los Angeles Bay, among rocks and under bushes. (510.)

Cleome tenuis. Annual, erect, slender, branching, 1 to 3 feet high or more, glabrous or the petioles pubescent: leaves 5-foliolate, the leaflets narrowly to linear-oblanceolate, obtuse, ½ to 1 inch long, equalling the petioles: racemes loose, few-flowered; flowers yellow, 2 lines long, on slender pedicels: pods sessile, narrow, spreading, 1 to 1½ inches long, including the style: seeds transversely rugose. — At Guaymas, on hillsides. (214.)

Wislizenia Palmeri, Gray. Three to five feet high; leaves mostly 3-foliolate. At Guaymas. (74.)

Atamisquea emarginata, Miers. A stiff brittle shrub, about 6 feet high, with white flowers. Muleje. (28.)

Oligomeris glaucescens, Camb. At Los Angeles Bay, in saline soil. (547.)

IONIDIUM POLYGALÆFOLIUM, Vent. Among rocks in dried creek-beds; Guaymas. (253.)

AMOREUXIA PALMATIFIDA, DC. "Sayas": the roots have the taste of the parsnip and carrot, and are eaten by the Yaqui Indians, and made into a preserve by the Mexicans. Guaymas. (176.)

KRAMERIA CANESCENS, Gray, var.; slightly pubescent, and leaves small and distant. Guaymas and Los Angeles Bay. (151, 565.)

KRAMERIA PARVIFOLIA, Benth. The typical form. At Guaymas. (248.)

FRANKENIA PALMERI, Watson. A compact shrub, 1 to 3 feet high. At Los Angeles Bay. (541.)

DRYMARIA CRASSIFOLIA, Benth. At Los Angeles Bay. (570.)

PORTULACA OLERACEA, Linn. "Verdulaga; common all over the country." Guaymas. (116.)

ANODA PENTASCHISTA, Gray. Guaymas. (661.)

HORSFORDIA NEWBERRYI, Gray. Flowers orange. On rocky hills at Guaymas. (314.)

HORSFORDIA ROTUNDIFOLIA. Annual, erect, slender, 2 feet high or more, finely and softly pubescent; branches short: leaves round-cordate, obtuse or retuse, crenate, an inch broad or usually much less, white-velutinous beneath, greener above: inflorescence elongated and paniculate, nearly naked; peduncles slender, 4 to 9 lines long, jointed above the middle: flowers orange to sulphur-yellow, 9 lines broad; calyx 2 lines long, the lobes acute or short-acuminate: carpels 6 to 8, 4 lines long, 2-ovuled, 1-seeded, the thin sides of the cell strongly reticulate and becoming clathrate, the erect wings lanceolate: seed pubescent. — On an island in the harbor of Guaymas. (351.)

HORSFORDIA PALMERI. Erect, 3 to 6 feet high, stout and branching, densely stellate-pubescent throughout: leaves lanceolate, obtusish, cordate at base, entire or subcrenate, 3 inches long or less: flowers axillary, solitary or clustered, on slender peduncles 6 or 8 lines long and jointed above the middle: calyx 3 lines broad; corolla "light pink," turning blue, an inch broad: carpels 10 to 12, 4 lines long, 1-seeded, the basal portion strongly reticulated, the wing obliquely deltoid: seed puberulent. — On broken stony ground near Los Angeles Bay. (558.)

SIDA CARPINIFOLIA, Linn. Guaymas. (316.)

ABUTILON CRISPUM, Don. Guaymas. (95.)

ABUTILON INCANUM, Don. (*A. Texense*, Gray.) Guaymas. (104, 288.)

ABUTILON PALMERI, Gray. Guaymas. (239.)

ABUTILON AURANTIACUM, Watson. San Pedro Martin Island. (401.)

ABUTILON SCABRUM. Erect, 3 feet high, scabrous throughout with very fine stellate pubescence, scarcely at all canescent: leaves thin, cordate to cordate-lanceolate, acuminate, rather coarsely and unequally toothed, 3 inches long or less, on slender petioles: flowers bright orange, an inch broad, axillary, solitary, on slender peduncles exceeding the petioles and jointed near the top; calyx as long as the petals, the ovate acute lobes apparently cordate, enlarged in fruit: carpels 8, shortly acuminate, very finely pubescent, 5 lines long. — Near *A. Jacquini* and *A. Berlandieri*, which are softly pubescent and not at all scabrous. Among bushes in ravines and by garden fences near Guaymas. (97, 662.)

SPHÆRALCEA AMBIGUA, Gray. In mountain cañons near Los Angeles Bay (537), and a small-flowered form from S. Pedro Martin Island (405). Also what is probably a form of this species from garden fences at Guaymas. (90.)

SPHÆRALCEA AXILLARIS. Stellate-pubescent: stems long and slender: leaves ovate to lanceolate, acutish, subcuneate at base, finely crenate, 2½ inches long or less, the petioles half as long: flowers yellowish, an inch broad, in short axillary solitary or clustered racemes or panicles; calyx 3 lines long, the lobes acuminate: carpels about 15, 1-seeded, 1½ lines long, obtuse, the base very strongly reticulated, the broader empty cell thin and scarious. — Muleje; common in shady places. (17.)

SPHÆRALCEA (?), sp. Imperfect specimens from S. Pedro Martin Island. (404.)

KOSTELETZKYA COULTERI, Gray? A rather stout branching plant, 3 feet high, with deeply 5–7-lobed leaves, and "white" flowers drying to greenish yellow. Coulter's original specimens are much reduced, with only the upper leaves deeply lobed, the flowers apparently yellow, and the anthers few. The present plant is probably the fully developed form. In waste places about Guaymas. (236.)

HIBISCUS DENUDATUS, Benth. Los Angeles Bay. (523.)

HIBISCUS COULTERI, Gray. River-bed, Guaymas. (668, 669.)

GOSSYPIUM HERBACEUM, Linn. In garden fences at Guaymas; the plants 8 feet high and said to be forty years old. (110.)

GOSSYPIUM DAVIDSONI, Kell. A loose shrub 3 to 5 feet high, the larger leaves 3-lobed; bractlets ample, deeply laciniate, persistent about the ovate capsule, which is half an inch long and 3- or rarely 4-celled; seeds 6 or 8 in each cell, in two rows, not at all lanate or the testa showing only a rudimentary lanate condition. The flowers are sulphur-yellow with a brown spot at the base of each petal. This appears to be a true *Gossypium*, notwithstanding the naked seeds. In mountain ravines near Guaymas. (244.)

HERMANNIA PAUCIFLORA, Watson. Among rocks in the mountains near Guaymas. (227.)

MELOCHIA TOMENTOSA, Linn. In fences about Guaymas. (148.)

MELOCHIA SPECIOSA. Closely resembling *M. pyramidata* in foliage and fruit, but more shrubby and branching, less virgate, and finely stellate-pubescent throughout: flowers in loose axillary and terminal cymes, large, rose-color turning purple; sepals 3 lines long; petals 8 lines long, spreading: capsule finely pubescent, shortly stipitate, resembling that of *M. pyramidata*, but the margins of the cells rounded (not acuminate). — In mountain cañons about Guaymas. (650.)

WALTHERIA DETONSA, Gray. Guaymas. (251.)

AYENIA BERLANDIERI, Watson, var.? Less pubescent, etc.; the same as 83 Palmer (1885) from Batopilas. In ravines near Guaymas. (243.)

AYENIA FILIFORMIS. Annual, erect, the slender stems finely pubescent: leaves thin and glabrous or nearly so, from narrowly ovate and obtuse to narrowly lanceolate and acute, 2½ inches long or less, on slender petioles, subtruncate at base, coarsely toothed: pedicels clustered or solitary in the axils: sepals narrow, a line long; petals purple, the blade rhombic, attenuate to the filiform claw, with a deep sinus at the apex embracing the filament, and a filiform dorsal appendage: fruit 2 lines in diameter, beset with numerous slender green processes: seeds surrounded by 2 or 3 stout irregular rugæ, the intervals more or less pitted. — Resembling and probably including some western forms that have been referred to *A. pusilla*, but certainly distinct from the typical form of that species as it is found in the West Indies and Brazil. In the shade of rocks high in the mountains about Guaymas. (292.)

BUNCHOSIA PARVIFOLIA. A shrub 3 or 4 feet high, intricately much branched: leaves sparsely appressed-hairy, round-ovate to ovate-oblong, acute, mostly obtuse at base, glandless, 15 lines long or less, on very short petioles: racemes few-flowered, pubescent: calyx 10-glandular; petals pink, 2 lines long: ovary glabrous; styles nearly distinct: drupe red, 5 to 6 lines in diameter. — On a high rocky peak near Guaymas. (336.)

GALPHIMIA ANGUSTIFOLIA, Benth., var. OBLONGIFOLIA, Gray. Mountains about Guaymas. (217.)

ECHINOPTERYS LAPPULA, Juss. A shrub 3 to 5 feet high, with an abundance of golden yellow flowers. The plant differs from Jussieu's description only in the acute or acutish instead of acuminate leaves, and perhaps in the indumentum of the ovary. The cocci of the mature fruit, which was not known by him, are 2 lines long, ovate, acute, densely pubescent, carinate with a row of stout subspinulose pubescent bristles, and the whole dorsal surface covered more or less densely with similar bristles. The seed is oblong-ovate, with a thin membranous testa, the cotyledons curved and somewhat unequal, and the radicle short and straight. Rocky mesas near Guaymas. (181.)

HIRÆA MACROPTERA, DC. "Matanene"; the leaves used in poultices for bruises and sores. Muleje. (19.)

JANUSIA CALIFORNICA, Benth. In mountain ravines about Guaymas. (263.)

TRIBULUS GRANDIFLORUS, Benth. & Hook. "Mal de ojos"; the pollen is said to be injurious to the eyes. Common about Guaymas. (177, 225.)

TRIBULUS CALIFORNICUS, Watson. Guaymas. (651.)

TRIBULUS MAXIMUS, Linn., var.? Scarcely or not at all hispid, the pubescence short and mostly appressed: flowers smaller; calyx (1⅓ lines long) usually deciduous: fruit smaller; nutlets about 8, more strongly tuberculate. — About Guaymas. (107.)

FAGONIA CALIFORNICA, Benth. Los Angeles Bay. (546.)

GUAIACUM COULTERI, Gray, — at least as to Thurber's specimens from Sonora. It is probably also the *G. parvifolium* of Planchon (Gray, Pl. Wright. 1. 29; *G. Planchoni*, Gray, Proc. Am. Acad. 22. 306, where this name is proposed on account of a supposed earlier "G. parvifolium, Engelm.," by which *G. angustifolium*, Engelm., must have been meant), of which there is a fragment in Herb. Gray. A shrub or small tree, 10 to 15 feet high and 15 inches in diameter, on hills and mesas about Guaymas, where it is known as "guayacan." The flowers are dark purplish blue and very fragrant; filaments naked. (113.)

VISCAINOA GENICULATA, Greene. A weak shrub, 5 to 8 feet high: flowers white. The genus is nearly allied to *Chitonia*. Muleje and Guaymas. (27.)

ERODIUM TEXANUM, Gray. Los Angeles Bay. (566.)

TRIPHASIA TRIFOLIATA, DC. Cultivated at Guaymas. (649.)

BURSERA MICROPHYLLA, Gray. "Torote blanco": 6 to 12 feet high; the bark used for tanning. Common on the mesas about Guaymas. (163.)

BURSERA HINDSIANA, Benth. & Hook. A scrubby bush, 8 feet high, the leaves simple or 3-foliolate upon the same plant: seed black at base, covered above with a hard salmon-colored arillus. The bark is much used for tanning, giving a reddish brown color. Los Angeles Bay. (572.)

BURSERA LAXIFLORA. A small tree with a trunk from 6 inches to a foot in diameter: leaves pinnate, sparingly pubescent, the pubescence short and mostly spreading: rhachis narrowly winged; leaflets 2 to 4 pairs, thin, ovate to oblong, mostly obtuse, entire or usually with 1 to 4 (rarely 6) blunt teeth, 3 to 9 lines long: peduncles axillary, solitary, very slender, 1 to 4 inches long, 1–3-flowered, and often with 1 to 3 simple foliaceous bracts; pedicels about 6 lines long: sepals narrow, nearly a line long: fruit obovate, narrowed at base, somewhat compressed, 2-valved, 4 lines long. — "Copal"; in ravines about Guaymas. (280.)

BURSERA PUBESCENS. A tree 10 to 15 feet high, with stout trunk and branches: leaves finely pubescent, pinnate, the rhachis not winged, 1 or 2 inches long: leaflets 4 or 5 pairs, rather thick, oblong-elliptic and entire, 2 to 4 lines long, obtuse, the terminal one cuneate-obovate and crenately toothed or lobed: flowers and fruit unknown. — Evidently a *Bursera*, but unlike any known species in its foliage. Wood brittle and bark deciduous in broad thin flakes. Plains and stony ridges about Los Angeles Bay. The bark is exported to Europe for tanning. (585.)

MAYTENUS PHYLLANTHOIDES, Benth. A low bush or small tree in sandy and alkaline soils. Muleje and Guaymas. (30.)

ZIZYPHUS LYCIOIDES, Gray, var. CANESCENS, Gray. A small tree, 10 feet high. In sandy bottoms about Muleje and Guaymas. (29.)

ZIZYPHUS SONORENSIS. A small tree with a trunk 5 to 8 feet high and 6 to 10 inches in diameter, with smooth grayish bark and a compact top, the short rigid branches very thorny: leaves nearly glabrous, thin, ovate to ovate-elliptical, obtuse or retuse, subcuneate to slightly cordate at base, entire or slightly toothed, 1 or 2 inches long with petioles 2 lines long: panicles short, finely pubescent, axillary and terminal: fruit subglobose and reddish brown when ripe, about 5 lines long, edible, the pedicel 2 lines long: putamen oblong-obovate, 2-celled, 2-seeded, 4 lines long. — Common about Guaymas, near brackish water. (124, 659.)

COLUBRINA GLABRA. A compact shrub, 5 or 6 feet high, unarmed, glabrous or very nearly so: stipules subulate, rigid, deciduous; leaves mostly fascicled, oblong-ovate to elliptical or obovate, obtuse or retuse, subcuneate at base upon a short slender petiole, 2 to 10 lines long: pedicels very slender, 2 to 4 (or in fruit 6 to 8) lines long: petals linear, equalling the filaments: fruit depressed-globose, 2 or 3 lines broad. — Ravines about Guaymas. (200.)

SERJANIA (PHACOCOCCUS) PALMERI. A stout climber, pubescent throughout with short soft spreading hairs: leaves twice pinnate, the lowest pinnæ 5-foliolate, the next 3-foliolate, and the upper of a simple leaflet; leaflets entire or rarely toothed, mostly oblong, acute or acutish, cuneate at base, 2 to 6 or sometimes 12 lines long: peduncles solitary, equalling or exceeding the leaves, the narrow panicles much longer: sepals finely pubescent, a line long: filaments pubescent: fruit 7 to 11 lines long, finely pubescent, the cells subglobose, 2 lines or more broad, faintly reticulate, thin and crustaceous, narrowly crested on the back, the wing broadly dilated to a rounded base (3 or 4 lines broad); dissepiment narrow: seed attached below the middle, globose and filling the cavity. — In foliage and pubescence closely resembling *S. sphenocarpa*, as described, but the fruit is very different; flowers very fragrant. Common about Guaymas. (61.)

CARDIOSPERMUM HALICACABUM, Linn. Guaymas. (126.)

PAULLINIA SONORENSIS. A compact shrub 2 or 3 feet high, with flexuous branches, very finely tomentose when young: leaves glabrous, pinnately 5-foliolate, the rhachis narrowly winged above: leaflets ovate to oblong-ovate, 3–5-toothed or -lobed, the lower often ternate, cuneate at base or shortly winged-petiolate, 6 to 8 lines long: peduncles about equalling the leaves (2 inches long or less), few-flowered: sepals oblong, obtuse, a line long or more: capsule depressed-globose, abruptly stipitate, finely tomentose, 3 lines long, on a pedicel 1 or 2 lines long. — On rocks in the mountains about Guaymas. (238.)

DODONÆA VISCOSA, Linn. Guaymas. (290.)

LUPINUS ARIZONICUS, Watson. Sandy bottoms at Los Angeles Bay. (595.)

LUPINUS, sp. near *L. concinnus*, Ag. Mountains near Los Angeles Bay. (586.)

MELILOTUS PARVIFLORUS, Desv. Muleje. (12.)

HOSACKIA RIGIDA, Benth. Mountains; Los Angeles Bay. (532.)

HOSACKIA STRIGOSA, Nutt. A broad-leaved and small-flowered form. Rocky ridges at Los Angeles Bay. (602.)

DALEA MEGACARPA, Watson. Leaflets often glabrous on the upper surface; 2 or 3 feet high, with very fragrant yellow flowers. Rocky ravines near Los Angeles Bay. (522.)

DALEA PRINGLEI, Gray. Guaymas. (667.)

Dalea mollis, Benth. Guaymas and Los Angeles Bay. (333, 512, and 550.)

Dalea Parryi, Gray. Guaymas and Los Angeles Bay. (315, 666.)

Dalea Emoryi, Gray. Leaves mostly oblong-obovate, occasionally obtusely toothed. A rough bush, 2 to 5 feet high; used as a yellow dye by the Indians. Los Angeles Bay. (542.)

Indigofera Anil, Linn. Used by the Indians for dyeing palm leaves. Guaymas. (102.)

Indigofera mucronata, Spreng. Mountains about Guaymas, in the shade. (296.)

Tephrosia tenella, Gray. Mountains about Guaymas. (249.)

Tephrosia Palmeri. A tall slender much branched perennial, very finely appressed-pubescent throughout: stipules narrow, 1 or 2 lines long; leaflets 3 to 6 pairs, linear to linear-oblong, 8 to 20 lines long, obtuse or acutish, the rhachis 1½ to 3 inches long: peduncles and racemes elongated: flowers scattered on short pedicels, light yellow, 9 lines long; calyx 3 lines long, the teeth as long as the broad tube; banner pubescent: pod narrow, nearly straight, 1½ to 2½ inches long or more, pubescent, spreading. — In the mountains near Guaymas. (246.)

Tephrosia constricta. Annual, slender, erect, glabrous or nearly so, a foot high: stipules linear-subulate; leaves 1-foliolate, the leaflet nearly sessile, linear, 1 to 2½ inches long by a line wide or less; flowers solitary, opposite or lateral to the axil; calyx-lobes acuminate, exceeding the campanulate tube; corolla reddish and white, 3 lines long: pod glabrous, linear, an inch long, spreading or reflexed upon the short pedicel, 6–10-seeded, with a thin septum between the seeds and usually a partial one at the stricture: seeds quadrate-oblong, sharply constricted in the middle. — In habit much resembling *T. tenuis* of India. The seed is very peculiar. In ravines in the mountains about Guaymas, sometimes very abundant. (222, 261.)

Diphysa sennoides, Benth. On stony mesas; Guaymas. (198.)

Cracca Edwardsii, Gray. Mountain slopes; Guaymas. (218.)

Sesbania macrocarpa, Muhl., var. picta. Wings orange; banner strongly marked with dark brown. "Bequilla"; the older roots were formerly used for tinder by the Yaqui Indians. Guaymas. (286.)

Astragalus Nuttallianus, Gray. Los Angeles Bay. (571.)

Nissolia Schottii, Gray. Guaymas. (170.)

Desmodium (Heteroloma) scopulorum. Annual, erect, branched, 2 feet high, the stem seabrous with very short stiff uncinate hairs; leaves 3-foliolate, the stipules and stipels setaceous; petioles $\frac{1}{2}$ to 1 inch long; leaflets thin, linear-lanceolate, 1 to $2\frac{1}{2}$ inches long by 1 to 5 lines broad, acutish, pubescent on the margin and nerves: racemes terminal and axillary, very slender, loosely flowered: flowers whitish, minute (scarcely $1\frac{1}{2}$ lines long), on spreading pedicels, solitary or in pairs: fruit 4-lobed, only the terminal lobe usually fertile; lobes 4 or 5 lines long, nearly semicircular, the ventral side straight, finely uncinate-bristly on the margin, the sides nearly glabrous. — On rocky ledges in the mountains about Guaymas. (258.)

Phaseolus filiformis, Benth. Mountains about Guaymas. (250.)

Phaseolus atropurpureus, DC., var. **sericeus**, Gray. Muleje and Guaymas. (8.)

Rhynchosia phaseoloides, DC. Seeds wholly red. Muleje. (1.)

Cæsalpinia gracilis, Benth. A shrub 3 to 6 feet high, with bijugate leaves, 10 stamens, and pods (1 to $1\frac{1}{4}$ inches long by 9 lines broad) mostly 1-seeded: seeds 5 lines in diameter. — Hills and mountains about Guaymas. (147, $147\frac{1}{2}$.)

Cæsalpinia (Pomaria) Palmeri. An unarmed glabrous shrub 8 to 10 feet high: jugæ 1 to 4 pairs and an odd one, on a slender rhachis from $\frac{1}{4}$ to 3 inches long; leaflets 2 or 3 pairs, oblong-elliptical, obtuse, 1 to 3 lines long: racemes terminal or axillary, sessile, short, few-flowered, glabrous or subpubescent: calyx-tube oblique; lobes nearly equal, obtuse, 3 lines long; petals brownish orange, covered more or less thickly on the back and claw with white substipitate glands: filaments and ovary pubescent: pod sessile, thin-coriaceous, glandular-dotted, falcate, $1\frac{1}{2}$ inches long by nearly $\frac{1}{2}$ broad, attenuate downward, usually 2-seeded: seeds 3 lines broad. — Guaymas. (70.)

Hæmatoxylon boreale, Watson. "Brazil"; used as a dye, and the young wood as a remedy for jaundice. Hillsides and stony ravines about Guaymas. (125.)

Hoffmanseggia microphylla, Torr., and var. **glabra**. On stony ridges at Los Angeles Bay. (513.)

Cassia Covesii, Gray. "Ojacen"; used in infusion for colds and fevers. Guaymas and Los Angeles Bay. (313, 575.)

Cassia nictitans, Linn. About Guaymas. (212)

Tamarindus Indica, Linn. From three small trees in abandoned gardens at Guaymas, said to have been planted many years ago by Chinamen from Manilla. (56.)

Prosopis (?) heterophylla, Benth. Without flowers or fruit, but the peculiar foliage leaves the species unmistakable. A slender tree 10 to 15 feet high, with two or three drooping branches and thinly laminated bark, which cleaves off in large pieces. Guaymas. (628.)

Prosopis (Algarobia) articulata. An upright shrub 8 to 12 feet high, somewhat finely pubescent, armed with straight stipular spines ½ inch long or less: pinnæ a single pair on a rhachis 2 or 3 lines long; leaflets 6 to 15 pairs, narrowly oblong, somewhat reticulated, 1½ to 3 lines long: flowers greenish yellow, pedicellate in loose short-pedunculate spikes an inch or two long: petals distinct, villous at the apex, nearly 1½ lines long: anthers glanduliferous: ovary stipitate, pubescent; pod glabrous, thin-coriaceous, compressed, moniliform, 5–12-jointed, the joints about 2½ lines broad. — On stony mesas and foot-hills about Guaymas. (197.)

Prosopis (Algarobia) Palmeri. A loosely branching shrub 4 feet high, finely pubescent, armed with straight stipular spines an inch long or less: pinnæ a single pair on a very short rhachis; leaflets 3 to 6 pairs, oblong-elliptic, 2 lines long or less: flowers minutely silky, sessile in a loose short-pedunculate spike an inch long; corolla tubular and somewhat angled, deeply 5-toothed, not villous within, 2 lines long: style and filaments twice longer, yellow, the anthers bearing a large deciduous gland: ovary tomentose, stipitate, straight, many-ovuled. — Without fruit, but there can be little doubt as to the genus, though the petals are connate to near the top and without villosity. The flowers are said to be of a bright golden yellow and very fragrant. Muleje. (2.)

Desmanthus virgatus, Benth. Shrubby, about 4 feet high. Guaymas. (86.)

Desmanthus Jamesii, Torr. & Gray, var. Glabrous; the pods 3 to nearly 5 inches long; said to be a shrub. Common at Guaymas. (641, 642.)

Mimosa laxiflora, Benth. A shrub 5 to 8 feet high; flowers rose-color turning to white. About Guaymas. (149, 169.)

Acacia Wrightii, Benth. A compact shrub 5 or 6 feet high, armed with stout recurved spines. This is occasionally the case in more eastern specimens, though usually they are wholly unarmed. In a deep cañon, Los Angeles Bay. (534.)

Acacia flexicaulis, Benth. A rigid shrub, 5 feet high. Deep cañons at Los Angeles Bay. (548.)

Acacia filicina, Willd. Guaymas, in mountain ravines. (254.)

Acacia cochliacantha, Humb. & Bonpl. A small tree, 10 feet high and 2 inches thick, with fragrant flowers, and straight or curved spines 3 to 5 inches long. A decoction of the thorns is used as a remedy for vesical inflammation, etc. On mesas and hillsides at Guaymas. (101.)

Acacia Farnesiana, Willd. "Binorama"; the pods are used for dyeing black and for making ink, and an ointment is made of the flowers for the cure of headache. About Guaymas. (305.)

Lysiloma microphylla, Benth. A rather stiff shrub, 6 feet high. In mountain cañons at Guaymas. (640.)

Calliandra Coulteri, Watson. A loose shrub, 5 feet high. Mountains about Guaymas. (297.)

Calliandra eriophylla, Benth. A stiff shrub, in high mountain ravines. Guaymas. (293.)

Pithecolobium (Ortholobium) Sonoræ. A shrub or small tree (15 or 20 feet high), armed with short stout recurved stipular spines, the foliage, inflorescence, and younger branches canescent with very short spreading pubescence: pinnæ 1 or 2 pairs on a short (1 or 2 lines) or very short rhachis; leaflets 10 to 15 pairs, oblong-elliptical, about a line long: peduncles mostly solitary (1 to 3) in the axils, 6 lines long or less; heads loose: flowers white, fragrant, finely pubescent, nearly 2 lines long: pods rather thin, short-stipitate, flat, straight, dehiscent, puberulent, 2 to 4 inches long by 6 to 9 lines wide, 3–6-seeded. — "Uña de gato"; wood very hard and taking a fine polish. Common at Guaymas, and at Loreto and Muleje. (58.)

Rhizophora Mangle, Linn. On a low island in Guaymas harbor. (342.)

Jussiæa octonervis, Lam. Guaymas. (257.)

Œnothera cæspitosa, Nutt. On stony ridges near Los Angeles Bay. (582.)

Œnothera (Sphærostigma) angelorum. Annual, from nearly acaulescent to a foot high or more; stems slender, glabrous: leaves more or less finely pubescent, narrow, pinnatifid nearly to the midnerve, the linear divaricate lobes mostly entire: flowers axillary, bright yellow, about 9 lines broad: capsule very slender (1 to 1½ inches long or more, by half a line wide), becoming more or less curved. — Of the *Œ. bistorta* group. Abundant in sandy valleys and on ridges near Los Angeles Bay. (519.)

Œnothera cardiophylla, Torr. A form with very small flowers. S. Pedro Martin Island and Los Angeles Bay. (103, 520.)

Gaura parviflora, Dougl. At Muleje. (11.)

Petalonyx linearis, Greene. On S. Pedro Martin Island and at Los Angeles Bay. (411.)

Sympetaleia rupestris, Gray. (*Loasella rupestris*, Baill.) With the habit of *Eucnide:* leaves round-cordate, sinuately toothed and rather obscurely 5–7-lobed, 3 inches broad or less: corolla cylindrical, 4 to 6 lines long, yellow below, dark green above, the erect lobes broadly oblong, the tube appendaged within near the base by a dense ring of hairs; calyx-lobes narrowly oblong, shorter than the tube of the corolla: stamens very numerous, covering the upper half of the tube, the uppermost filaments stout, green and erect, the lower shorter and slender: capsule subglobose, truncate, 3 lines long, opening by 5 valves at the summit: seeds minute, linear-oblong. — Doubtless the species from Guaymas described by Baillon. The corolla-lobes are imbricate and the anthers 1-celled as in *S. aurea,* which differs especially in its yellow corolla with narrow tube and the lobes of the spreading limb rounded. In the shade of rocks near the shore on islands in Guaymas harbor, "and at Los Angeles Bay." (325.)

Eucnide cordata, Kell. Described as 5 feet high, reclining upon rocks, with white flowers. Mountains about Guaymas and Los Angeles Bay. (341.)

Mentzelia multiflora, Nutt. Los Angeles Bay. (591.)

Mentzelia adhaerens, Benth. Summit of S. Pedro Martin Island and at Los Angeles Bay. "Commonly called *pega-pega;* it sticks to everything." (402.)

Passiflora fœtida, Linn. Fruit edible. Guaymas. (91.)

Cucurbita cordata. Root long and large: pubescent throughout with a dense rigid strigose pubescence, mostly reflexed except on the leaves: leaves broadly cordate in outline, 2 to 4 inches wide, 3–5-lobed nearly to the middle with narrow sinuses, the lobes coarsely and obtusely toothed; tendrils short, glandular-tipped: flowers solitary, on peduncles 1½ inches long, the corolla 2 inches long: ovary pubescent, subglobose: fruit globose, 3 inches in diameter, smooth, green with about 10 whitish longitudinal lines: seeds white, 4 or 5 lines long. — The fruit resembles that of *C. palmata.* Sandy plains near Los Angeles Bay. (584.)

Apodanthera (?) Palmeri. Stems prostrate, from large long white roots, glabrous or slightly scabrous on the angles: leaves thin, rather thinly strigose-scabrous on both sides, round-cordate in outline, 1½ to 2½ inches broad, 5-lobed to the middle or deeper, with open sinuses, the lobes acutely toothed; tendrils mostly bifid: male flowers racemose on long slender pedicels; calyx-lobes linear, 3 lines long, equalling the tube; petals 15 lines long; anthers much curved: fertile flowers on slender peduncles 1 to 1½ inches long: ovary oblong, thinly pubescent; fruit 1½ inches long, broadly ellipsoidal, abruptly attenuate at base, very shortly beaked, smooth, with green markings; rind thin; placentas 4 (or sometimes 5?), distinct, pulpy, many-seeded: seeds brown with whitish margin, 3 lines long. — Apparently diœcious; differing from the genus in the number and distinctness of the placentas. Fruit edible, with the taste nearly of muskmelon, ripening in September. Plains about Guaymas. (282.)

MAXIMOWICZIA SONORÆ. Climbing, glabrous throughout, the large root projecting above ground: leaves 4 inches broad or less, twice 3-cleft nearly to the base, with broad sinuses, the lobes coarsely sinuate-toothed: male flowers racemose, short-pedicellate, the calyx-tube cylindrical, 3 lines long; petals pubescent, villous within, bifid: fertile flowers on peduncles 2 or 3 lines long: ovary ovate, long-attenuate above; fruit ovate, abruptly stout-beaked, "amber-colored," 1¼ to 1½ inches long, smooth with a thick fleshy rind; placentas many-(about 14-) seeded: seeds "covered with a red pulp," compressed, rough-coated excepting the smooth margin, obovate or oblong-obovate with a broad base, 3 lines long or more. — This species much resembles *M. Lindheimeri*, but the leaves are more dissected and the ovary and fruit more attenuate above, and the seeds though decidedly turgid in the young fruit become compressed and are peculiar in their generally very rugose-tuberculate surface. The green fruit is described as having about 10 longitudinal rows of white dots. A decoction of the root is used as a cathartic. About Guaymas, and known as "guarequi." (283.)

ECHINOPEPON INSULARIS. Annual, finely and rather softly pubescent, or glabrate: petioles not pilose: leaves broadly cordate, 1½ to 3 inches broad, 5-lobed nearly to the middle, the short triangular lobes acute, finely and acutely toothed, the sinuses acute: male flowers in narrow panicles mostly exceeding the leaves; corolla 5-cleft, 1½ to 2 lines broad; anthers sigmoid, horizontal; pistillate flowers solitary in the same axils, on slender peduncles 3 or 4 lines long: ovary obliquely oblong-ovate, subpubescent, echinate, attenuate and naked above: fruit subglobose after the falling of the beak, about 4 lines in diameter, covered with stiff straight spines ½ line long, firm and spongy within, 1-celled, 1-seeded: seed ascending, smooth, oblong-obovate, subcompressed with a broad flat base, 2 lines long, dark. — The ovary appears to have an upper cell with an abortive ovule. Common on S. Pedro Martin Island. (409.)

Echinopepon Palmeri. Annual; stems glabrous: petioles not pilose; leaves thin, very minutely scabrous above, nearly glabrous beneath, broadly cordate, 1 to 2 inches broad, 5-lobed to beyond the middle with rounded sinuses, the subrhombic lobes acute and somewhat setosely apiculate, sparingly denticulate: male flowers in narrow panicles mostly exceeding the leaves; corolla 5-lobed to below the middle, 1½ to 2 lines broad; anthers sigmoid; pistillate flowers solitary in the same axils, on filiform peduncles 3 or 4 lines long; ovary very oblique, glabrous, the naked slender beak longer than the echinate base: fruit without the beak about 2½ lines long, covered with stout straight spines ¾ line long, 1-celled, 1-seeded: seed ascending, compressed, 2 lines long. — In the shade of overhanging rocks in the mountains about Guaymas. (304.) This and the preceding species, with *E. Bigelovii*, *E. parviflora*, and *E. minima*, form a well marked group in Naudin's genus *Echinopepon*, which genus should in my opinion be restored.

Cereus Pringlei, Watson. "Cardon"; forming a forest on the summit of S. Pedro Martin Island. The dead wood is much used for fuel and other purposes, and the seedy fruit is an article of food. It attains an average height of 25 feet (sometimes reaching 35 feet), with a circumference below the branches of 6 or 7 feet. (418.)

Opuntia ——? Of the *O. prolifera* group, but the specimens are without flowers or fruit. About 4 feet high, much branched and very spiny, the joints of the specimens 1 to 1½ inches long, with the areolæ of the tubercles terminated above by a dense tuft of spiny bristles 2 lines long; spines 3 to 7, vaginate, the longer 9 to 12 lines long. — "Choyer"; common on S. Pedro Martin Island. (419.)

Trianthema monogyna, Linn. Glabrous and stems red: sepals very shortly cuspidate: stamens 10: crest of the capsule 2-parted. — Common in some gardens at Guaymas. (155.)

Trianthema monogyna, Linn., var. (?) Glabrous and green throughout or pubescent: sepals long-cuspidate: stamens usually 5: concave crest of the capsule entire. — Apparently distinct from the last, but the species as represented in the Gray herbarium is very variable. Very common in gardens at Guaymas. (153, 156.)

Mollugo verticillata, Linn. In the mountains about Guaymas. (255.)

Mollugo Cerviana, Ser. Common in sand and on high gravelly mesas, Guaymas. (184.)

Portlandia pterosperma. A shrub or small tree. 2 to 10 feet high: leaves thin, rhombic-ovate to oblong, acute or subacuminate, cuneate at base, glabrous or usually pubescent on the margin and rather short slender petiole, 2 or 3 inches long; stipules broadly triangular: peduncles solitary in the axils, bracteolate, 6 to 9 lines long: calyx-lobes very narrow, 6 to 9 lines long; corolla white, funnel-form, 2½ inches long, the tube pubescent within, the limb nearly two inches broad; filaments 6, pilose only near the base, the anthers (8 lines long) equalling the corolla: capsule oblong, angled, 9 lines long: seeds ascending, very thin and broadly winged, 4 lines long. — Peculiar in the thin leaves and very broadly winged seeds: flowers large and handsome, abundant, pendent, and very fragrant. The capsule is tardily dehiscent septicidally, as in other species. In deep cañons near Guaymas. (298.)

Randia Thurberi. An upright shrub, 6 or 8 feet high, armed with slender spines, the young branches canescent with fine spreading pubescence: leaves obovate, attenuate to a short winged petiole, obtuse or retuse, 6 to 15 lines long, finely pubescent or glabrate: calyx less than a line long: fruit globose or ellipsoidal, axillary, sessile or nearly so, 8 or 9 lines long, the pericarp thin-crustaceous: seeds numerous (about 20) in black pulp. — "Papachi"; the fruit eaten by the Indians. In ravines about Guaymas; first collected by Thurber on the hills between Rayon and Ures, Oct., 1851. (229.)

Randia obcordata. An upright bush, 6 or 8 feet high, armed with stout spines and very leafy: leaves obovate or mostly obcordate, attenuate to a very short petiole, finely puberulent or glabrate, 9 lines long or less, much exceeding the internodes: calyx deciduous: fruit sessile in the axils, globose, 3 or 4 lines in diameter, black, 2–4-seeded. — On high gravelly mesas near Guaymas. (618.)

Genipa echinocarpa, Gray. A thorny shrub, 8 feet high; flowers "orange-yellow," fragrant. About Guaymas. (106.)

Galium stellatum, Kell. Mountain-sides, Los Angeles Bay. (525, pistillate: 526. staminate.)

Hofmeisteria crassifolia. Suffruticose (?) with brittle branches, glabrous: leaves alternate, very fleshy, linear, once or twice pinnatifid with 1 to 3 pairs of linear divisions, 1 or 2 inches long: peduncles long, naked, mostly solitary; involucre broadly campanulate, of very numerous linear acuminate bracts; receptacle broad, strongly convex, naked: flowers very numerous; corolla white, very narrow, 1½ lines long: style-branches elongated, much exserted: pappus of 5 scabrous setæ nearly equalling the corolla and 3 or 4 intermediate on each side, short, unequal, and rigid. — In crevices of rocks in the high mountains about Guaymas; flowers very fragrant. (309.)

HOFMEISTERIA PUBESCENS. Herbaceous, rather fleshy, pubescent with short spreading somewhat scurfy hairs, the stout branches opposite or in threes: leaves alternate, broadly ovate in outline, 3-parted with segments deeply lobed or toothed, 6 or 8 lines long or less, the stout petiole much longer: peduncles solitary, elongated (6 to 10 inches long), bracteate with several scattered very narrowly linear bracts; heads campanulate, very many-flowered, ½ inch high, with numerous linear setaceously acuminate bracts and a convex naked receptacle: corolla white, very narrow, the cylindrical throat as long as and little broader than the tube: pappus of 2 hispidulous setæ longer than the corolla and 2 broad irregularly fimbriate paleæ. — At Muleje, in rounded masses on hillsides and stony ridges. (422.)

MALPERIA* TENUIS. Slender, a foot high with ascending branches, slightly scabrous: leaves narrowly linear, entire or occasionally with a few teeth, subacuminate, 1 or 2 inches long or less: heads ½ inch high, narrowed at base, the short outer bracts descending upon the peduncle: corolla (apparently white) very slender, rather contracted at the throat: the short stigmas scarcely at all exserted: achenes slightly hispid on the angles. — Abundant on stony ridges near Los Angeles Bay. (567.)

EUPATORIUM SAGITTATUM, Gray. Growing 8 feet high, over bushes and hedges; flowers lilac. Guaymas. (87.)

BRICKELLIA COULTERI, Gray. Guaymas, by garden fences. (62.)

BRICKELLIA FLORIBUNDA, Gray, var., with the inflorescence reduced to a terminal sessile compound cyme, and the achenes more pubescent. Shrubby, 3 to 5 feet high, under overhanging rocks on an island in Guaymas harbor. (322; 323, with entire leaves.)

GUTIERREZIA EUTHAMIÆ, Torr. & Gray. Los Angeles Bay. (533.)

APLOPAPPUS SPINULOSUS, DC. Foothills; Los Angeles Bay. (539.)

BIGELOVIA DIFFUSA, Gray. Compact, 3 feet high. In saline localities near the beach at Guaymas. (212, 212½.)

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* MALPERIA, a new genus of *Ageratеæ*. Head several-flowered. Involucre narrowly turbinate, of several rows of very unequal thin narrow nerved bracts. Receptacle naked, flat. Corolla narrow, the throat not dilated, the short lobes erect. Anthers with ovate obtuse appendages. Style-branches short, filiform, truncate, included. Achenes pentagonal, slender. Pappus of 3 hispidulous setæ as long as the corolla, wing-margined at base, and 3 or 4 broad truncate erose paleæ. — An erect annual, with narrow sessile and mostly entire leaves, and the heads solitary or subcorymbose on short peduncles. Near *Hofmeisteria*, but very different in habit.

Bigelovia veneta, Gray, var. (?), with small heads and the leaves mostly entire, somewhat pubescent. On an island in Guaymas harbor. (334.)

Psilactis Coulteri, Gray. In waste places at Guaymas. (99.)

Aster frutescens. Shrubby "with very compact rounded top," with gray stem and branches, the herbaceous portion glandular-scabrous: leaves oblong-obovate to oblanceolate, an inch long or less, the lower attenuate to a narrow base, the upper sessile by a broader or somewhat clasping or even subcordate base, coarsely spinulose-dentate, rather rigid and conspicuously reticulate, sparingly glandular-scabrous: heads solitary and terminal on the leafy branchlets, large (5 or 6 lines high); bracts of the involucre loosely imbricated, linear, narrowly acuminate, the green tips somewhat spreading; rays "lilac," about 20, rather short; achenes canescent with subappressed hairs, nerved, subcompressed; pappus whitish. — A species of peculiar habit, most nearly related to the section *Megalastrum*, but the heads smaller and not naked-pedunculate. On a stony ridge near Los Angeles Bay. (513.)

Baccharis sarothroides, Gray. "Yerba del pasmo"; the twigs are used as a remedy for toothache. Rarely over 2 feet high. San Pedro Martin Island. (414, 415.)

Pelucha* **trifida.** A much branched and leafy shrub, about 3 feet high, canescent with a thin fine close tomentum: leaves linear with a broader obtusely 3-toothed or usually 3-cleft summit, 6 to 9 lines long: heads about 2 lines high, mostly 10–15-flowered: achene hispid. — On San Pedro Martin Island, in crevices of rocks near the sea. (407.)

Lagascea decipiens, Hemsl. A compact shrub, 4 feet high. Mountain ravines above Guaymas. (256.)

Franseria ambrosioides, Cav. At Muleje and Guaymas. (21.)

Franseria ilicifolia, Gray. Stems herbaceous, 1½ feet high. Ravines near Los Angeles Bay. (578.)

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* PELUCHA, a new genus of *Plucheineæ*. Heads discoid, rather few-flowered, homogamous, the flowers all perfect or some sterile. Involucre of two rows of nearly equal linear herbaceous bracts. Receptacle naked. Corolla slender, slightly dilated upward, very shortly toothed. Anthers very narrowly sagittate at base. Style-branches narrow, or the style sometimes undivided. Achene small; pappus rigid, scabrous. — Shrubby, very heavy scented, tomentulose, with alternate 3-fid leaves and small heads in terminal cymes. Closely allied to *Blumea* and *Pluchea*. The specimens are not in very good condition, but a careful study of the material leaves little doubt of the distinctness and tribal position of the genus.

FRANSERIA DUMOSA, Nutt. Common on foothills about Los Angeles Bay, growing 1½ to 2 feet high. (559, 564.)

FRANSERIA TENUIFOLIA, Gray. "Istafiate"; a remedy for liver complaints, used by filling the shoes with its leaves. Muleje. (10.)

ECLIPTA ALBA, Hassk. High in the mountains above Guaymas. (220.)

VIGUIERA LACINIATA, Gray. Compact, suffrutescent. 2 feet high. Abundant on the mountains about Los Angeles Bay. (529.)

VIGUIERA PARISHII, Greene, — which may be a variety of *V. deltoidea*. A form with more numerous heads. About 3 feet high, forming large bunches in the cañons above Los Angeles Bay. (530.)

HELIANTHUS ANNUUS. Muleje. (6.)

ENCELIA FARINOSA, Gray. The stems exude a resin which is used as incense in the churches. Ravines about Guaymas. (111.)

VERBESINA (PTEROPHYTON) PALMERI. Suffruticose, forming large bunches 3 or 4 feet high, scabrous throughout; stems not winged: leaves opposite, the upper alternate, triangular or rhombic-ovate, more or less abruptly contracted to a broadly winged auriculately clasping petiole, acute, repandly few-toothed or entire, 3 inches long or less: heads loosely panicled, on slender peduncles, about ½ inch high; inner bracts thin, erect, linear, acute or acuminate, the outer herbaceous, spatulate-oblong, obtuse, somewhat spreading: rays about 10, neutral, 4 or 5 lines long: achenes obovate, pubescent or some only glandular-scabrous, the thin wing ciliate; awns 2, erect or spreading, equalling the corolla. — In cañons above Los Angeles Bay. (528.)

LEPTOSYNE PARTHENIOIDES, Gray. With the foliage of *Coreocarpus parthenioides*, Benth., as figured in Bot. Sulphur, but the achenes mostly narrow and nearly wingless, the lobed margin only rarely distinctly developed. *L. heterocarpa* is with little doubt a form of this species with the lobed margin of the achene in most cases prominently developed. Near a waterfall high in the mountains above Guaymas. (299.)

LEPTOSYNE PARTHENIOIDES, var. DISSECTA. (*L. dissecta*, Gray; *Acoma dissecta*, Benth. in Bot. Sulphur, t. 17.) With the more dissected foliage of Bentham's figure, the achenes rather broader than in the last, the margin either entire or lobed. It would seem that the three species that have been described should probably be considered as forms of one, with very polymorphous achenes. — Shady mountain-sides near Los Angeles Bay. (660.)

Laphamia (?), sp. Foliage only of a shrubby composite, 2 feet high, much resembling *L. insularis*, but the pubescence different. Common over the summit of San Pedro Martin Island. (406.)

Perityle Californica, Benth. Abundant about Los Angeles Bay and around the old French fort at Guaymas. (562.)

Perityle deltoidea. Annual, low and slender, minutely pubescent: leaves ovate-deltoid, coarsely and somewhat irregularly toothed, an inch long or less, exceeding the petioles: peduncles an inch long or less; heads 2 or 3 lines high, the bracts linear, acuminate: flowers yellow; ligule linear-oblong, 2 lines long: style-appendages linear, flattened, obtuse, not hispidulous: achenes a line long, shortly ciliate, the crown of very short bristles; awn solitary, as long as the disk-corolla, strongly hispidulous. — With the habit of *P. microglossa*. Common in the shade on mountains and hillsides about Los Angeles Bay. (568.)

Perityle Palmeri. Of the *P. leptoglossa* group; a low perennial (?) with herbaceous succulent brittle stems, glandular-villous when young, becoming finely pubescent or subglabrate below: leaves thin, broadly ovate, acute, subcordate at base, very acutely lobed and toothed, the petiole equalling or exceeding the blade (1 or 2 inches long): peduncles 1½ to 3 inches long; heads 4 or 5 lines long, the bracts very narrow, acuminate: flowers golden yellow; ray 4 lines long: achenes strongly ciliate, a line long, the prominent crown deeply fimbriate, the hispidulous awn equalling the disk-corolla. — In crevices of bare but shaded rocks; Guaymas. (308.)

Riddellia Cooperi, Gray. Mountains about Los Angeles Bay. (538.)

Palafoxia linearis, Lag. Sandy plains; Los Angeles Bay. (581.)

Porophyllum gracile, Benth. Hillsides near Los Angeles Bay. (555.)

Porophyllum Seemanni, Schultz Bip., var., with larger heads of white flowers. "Mara villa"; used for headache. Crevices of exposed rocks high in the mountains about Guaymas. (279.)

Porophyllum crassifolium. Suffruticose, much branched and compact: leaves somewhat fleshy, linear, attenuate at base, gland-tipped and often setosely apiculate, ½ to 1 inch long or often less: heads terminal on the short stout branchlets; bracts broad, obtuse, 3 or 4 lines long, the yellowish flowers nearly twice longer: achenes 1½ lines long. — Apparently near *P. tridentatum*, Benth., from Magdalena Bay, but the leaves are wholly entire and the flowers are much longer than the involucre. Muleje, on rocky hills and on sandy beaches near salt water; also collected by Dr. Palmer in 1870 on Carmen Island. (423.)

NICOLLETIA EDWARDSII, Gray. Annual; ray white with a reddish stripe on the outer side. Common on sandy plains and stony ridges at Los Angeles Bay. (469.)

DYSODIA POROPHYLLOIDES, Gray. Mountain-sides, Los Angeles Bay. (531.)

PECTIS PROSTRATA, Cav. In gardens at Guaymas. (145.)

PECTIS ANGUSTIFOLIA, Torr. The awnless form. Ravines near the beach; Los Angeles Bay. (657.)

PECTIS (PECTOTHRIX) PALMERI. Closely resembling *P. papposa*, but the solitary setæ at the base of the leaves more slender, the peduncles longer (1 or 2 inches), the longer hairs upon the achenes straight and slightly thickened upward (not at all uncinate or capitate), and the pappus merely scabrous (not barbellate). — Hillsides near Guaymas. (652, 653.) What may perhaps be a form of this with the pappus reduced to an irregular subfimbriate margin was collected on a rocky island in Guaymas harbor. (655.)

PECTIS COULTERI, Gray. Low and diffuse, somewhat viscid-pubescent, with leaves an inch long or less. — In gardens at Guaymas and on islands in the harbor. (143, 654.)

PECTIS PUNCTATA, Jacq. In sandy ravines and high upon the mountains about Guaymas. (224. 656.)

TRICHOPTILIUM INCISUM, Gray. Stony ridges at Los Angeles Bay. (563.)

BEBBIA JUNCEA, Greene. Flowers yellow, very fragrant. Sandy ravines at Muleje and Guaymas. (22.)

PEUCEPHYLLUM SCHOTTII, Gray. A shrub, 3 or 4 feet high. Stony ridges at Los Angeles Bay. (587.)

SENECIO LEMMONI, Gray. Mountain-sides near Los Angeles Bay. (577.)

PEREZIA PALMERI. Tall and branching, green and minutely glandular-pubescent throughout: leaves thin, oblong-lanceolate, acuminate, sessile and cordate at base, very acutely dentate and denticulate, 6 inches long by 2 wide or smaller: heads few on the branchlets, pedunculate, ½ inch long, many-flowered; involucre campanulate with thin acute bracts, the lower ovate and subacuminate: flowers "lilac": achenes glandular-puberulent. — To be grouped with *P. patens* and *P. carpholepis*. On mountain-sides near Los Angeles Bay; rare. (527.)

Trixis angustifolia, DC., var. latiuscula, Gray. A very compact shrub, 2 or 3 feet high, common upon the summit of S. Pedro Martin Island. (408.)

Lobelia splendens, Willd. Near a waterfall in the mountains above Guaymas. (301.)

Jacquinia pungens, Gray. "San Juanico"; a small evergreen tree, 12 to 15 feet high, the wood useless even for fuel. The globose fruit is 8 or 9 lines in diameter, the seeds several, oblong-peltate, imbedded or enclosed in the resinous-waxy placenta. The flowers are used by the Indians to give a durable yellow color to the palm-leaves used in making baskets, etc., and they are also strung like beads and worn for ornament. About Guaymas. (69.)

Sideroxylon leucophyllum. A small tree, 5 to 8 feet high and sometimes a foot in diameter: leaves finely white-tomentose on both sides, oblong-elliptic or -lanceolate, obtuse or acutish, subcuneate at base, short-petiolate, 2 inches long or less: flowers rather crowded in the axils on short pedicels, 5-merous; calyx tomentose, campanulate; corolla greenish yellow, 2½ lines long: staminodia petaloid, entire, broadly lanceolate, equalling the corolla: ovary densely villous. — The fruit was not collected. The wood is hard, burning with much smoke. In deep cañons near Los Angeles Bay. (516.)

Vallesia dichotoma, Ruiz & Pavon. A large evergreen bush with white fruit, which is eaten by children, and its juice is used for inflammation of the eyes. This specific name is adopted as the oldest in the genus, in preference to the later *V. glabra* of Link. The species so named that is found in Florida and the West Indies appears to have longer pedicels, a larger calyx, a longer corolla with longer narrowly oblong lobes, and the leaves oblong rather than lanceolate. — In garden hedges and sandy ravines about Guaymas and Muleje. (32.)

Haplophyton cimicidum, A. DC. High in the mountains about Guaymas. (228.)

Philibertia linearis, Gray, var. heterophylla, Gray. Flowers creamy white; fruit 3 inches long. At Muleje and Guaymas. (5.)

Philibertia Pavoni, Hemsl. Climbing, 5 to 6 feet high; leaves very white-tomentose beneath; flowers white. The same as 340 Palmer, 1886. In ravines at Guaymas. (195.)

Asclepias subulata, Decaisne. "Yumete"; the juice an active emetic. Common in dry arroyos about Guaymas. (57.)

Asclepias albicans. Erect, 4 feet high, white-puberulent: leaves verticillate in threes, very narrowly linear, mostly deciduous: umbels short-pedunculate, many-flowered, pubescent, the pedicels half an inch long: lobes of the greenish corolla tinged with brown, narrowly oblong, acute, nearly 3 lines long; column short; hoods yellowish, shorter than the anthers, somewhat thickened dorsally and bluntly beaked, the sides subquadrate and the nearly straight subulate spur scarcely exserted: follicle erect on the erect pedicel, 4 inches long, smooth. — In rocky ravines near Los Angeles Bay. (588.)

METASTELMA PRINGLEI, Gray, var. (?), with longer and acuter calyx-lobes and the filiform lobes of the crown somewhat shorter; flowers yellow. — Hillsides near Guaymas. (626.)

METASTELMA ALBIFLORA. Glabrous or nearly so; stems twining, 4 feet long: leaves petiolate, narrowly oblong to linear, short-acuminate, 6 to 10 lines long: flowers white, in sessile fascicles, the pedicels very short: calyx-lobes narrowly linear, acuminate; corolla a half longer (nearly 2 lines), densely villous within, the lobes narrowly lanceolate; crown of 5 very narrow and attenuate scales attached to the very short column and equalling the distinct corneous cuneate-obcordate anthers; appendage of the anthers oblong. — Exposed cliffs near Guaymas. (223.)

PATTALIAS* PALMERI. Stems slender, several from a rather thick branching rootstalk, slightly puberulent or glabrate, a foot long or more: leaves very narrow, 2 inches long or less, sessile, acute: flowers (2 to 6) yellow, on pedicels 1 or 2 lines long or less: corolla 2 lines long, twice longer than the calyx: lobes of corona ovate, attached to the column at the base of the anthers, lanceolate, acute, half the length of the stout conical beak: follicle 4 inches long by 3 lines broad, narrowed at base and long-attenuate above. — Near a sandy beach at Muleje. (424). — A second species of this genus is *P. angustifolius*, a Sonora plant doubtfully referred by Dr. Torrey in the Mexican Boundary Report to *Metastelma*, and more recently by Dr. Gray to the extra-tropical South American genus *Melinia*. It is of similar habit, but has petiolate leaves, a longer calyx, the crown at the base of the column, the anther-tips much more conspicuous, and the beak of the stigma narrow and columnar.

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* PATTALIAS, a new genus of the *Asclepiadaceæ*, of the *Metastelma* group. Calyx 5-parted, the lobes narrow, acuminate, eglandular. Corolla becoming open-campanulate, 5-parted, narrowly convolute in the bud, naked, the lobes lanceolate. Crown of 5 distinct fleshy entire lobes inserted upon the short column, exceeding the short anthers. Stigma surmounted by a prominent conical or columnar entire beak, exceeding the membranous erect tips of the anthers. Follicles smooth, slender. — Low twining herbaceous perennials, with narrowly linear opposite leaves, and small flowers shortly pedicellate in an axillary nearly sessile umbel.

Rothrockia cordifolia, Gray. In shady ravines, etc., about Guaymas. (213.)

Himantostemma Pringlei, Gray. In an orange grove at Guaymas. (318.)

Marsdenia edulis. Stem frutescent, with corky bark when old, climbing: leaves rather thick, undulate, ovate-lanceolate, acuminate, rounded at base, glabrous, 1 to 4 inches long, petiolate: flowers in a nearly sessile simple or compound umbel, the calyx and short pedicels pubescent: calyx-lobes ovate, acutish; corolla cream-color, rather fleshy, 2½ lines long, cleft to the middle, the throat very villous: lobes of the crown subulate-acuminate, a little shorter than the tall conical bifid summit of the stigma: fruit ovate, obtuse, smooth, 3 inches long; seeds suborbicular, 3 lines long. — "Talajote"; the green fruit is eaten. On sandy saline mesas near salt water, Guaymas. (150, 658).

Gilia (Eugilia) Palmeri. Annual, erect and branched, somewhat pubescent with floccose tomentum especially in the axils, a foot high: leaves alternate, very narrowly linear, entire, pungent, 1½ inches long or less: pedicels scattered, about an inch long: corolla "violet," 5-parted, the spreading lobes oblanceolate, acute and denticulate, 5 lines long, the calyx half as long: filaments very slender and anthers small: capsule oblong, equalling the calyx; cells several-seeded. — Near *G. rigidula*. On stony ridges near Los Angeles Bay. (593.)

Ellisia chrysanthemifolia, Benth. Shady mountain-sides near Los Angeles Bay. (580.)

Phacelia crenulata, Torr. A small-flowered form. Stony ridges at Los Angeles Bay. (592.)

Phacelia (Eutoca) pauciflora. Annual, setosely hispid, lax and very slender, a foot high or more: leaves (except the uppermost) pinnately divided, the oblong segments pinnatifid: flowers few, shortly pedicellate in a short loose simple or geminate raceme: calyx-lobes setosely hispid, linear-oblanceolate, 2 becoming 4 lines long, equalling the corolla (scarcely 3 lines long); appendages narrow and united at base over the filament: stamens and style included, the style cleft to the middle: capsule ellipsoidal, obtuse, 2 lines long, 8-seeded. — Technically of the *Eutoca* section, but closely related to *P. hispida*. On mountains near Los Angeles Bay. (583.)

Cordia Greggii, Torr., var. (?) Palmeri. Leaves somewhat larger (5 to 9 lines long), ovate-oblong, acute to obtuse, more abruptly cuneate at base on a slender petiole 2 to 4 lines long, and with more numerous serratures: corolla more broadly funnel-form, the limb 12 to 15 lines broad; calyx-teeth slender, nearly equalling the tube. — A shrub, 5 to 8 feet high, in gravelly ravines about Guaymas. (112.)

CORDIA (MYXA § SPICIFORMES) PALMERI. A shrub, 4 or 5 feet high, the young branches and lower side of the leaves finely pubescent: leaves oblong-lanceolate, attenuate at base, very shortly petiolate, acutish, rather coarsely toothed, scabrous above, 1 to $2\frac{1}{2}$ inches long by 3 to 6 lines broad: spikes pedunculate, loose, tomentulose, 1 to $1\frac{1}{2}$ inches long: corolla 3 lines long, twice longer than the calyx: fruit red, exserted, nearly 3 lines long. — "Yerba del pasmo." In ravines in the high mountains above Guaymas. (281.)

BOURRERIA SONORÆ. A shrub, about 10 feet high, with stout very leafy branches: leaves very roughly papillose-scabrous above, soft-pubescent beneath, obovate to oblong-spatulate, obtuse or retuse, attenuate to a very short petiole, entire, $1\frac{1}{2}$ inches long or less: flowers few on slender pubescent pedicels 2 to 5 lines long: calyx cleft to the middle, the deltoid lobes acute, half the length of the corolla-tube; corolla greenish yellow, puberulent, 5 lines long, the lobes oblong, acute; filaments glabrous, exserted: fruit black, depressed-globose, $2\frac{1}{2}$ lines broad. — Near a waterfall in the mountains above Guaymas. (289.)

COLDENIA[*] ANGELICA. Annual, prostrate, wide-spreading, somewhat hispid: leaves ovate to rhombic, acute, strigose-hispid on the margin and finely appressed-pubescent, entire or the margin sinuate, irregularly 2–3-nerved each side of the midvein: calyx nearly 2 lines long, the narrowly acuminate hispid lobes nearly twice longer than the tube; corolla "mauve," 3 lines long; filaments slender, adnate nearly to the middle, with a short obtuse prominent appendage at

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[*] Two other species of this genus may be defined as follows: —

C. BREVICALYX. White with a close fine pubescence and scarcely at all hispid: leaves very like those of *C. angelica* in form and veining: calyx very short (1 line), the broadish acute lobes shorter than the tube; corolla 2 lines long; filaments slender, slightly dilated below the insertion: nutlet subglobose, much smaller; embryo similar. — Confused with the true *C. Palmeri* as to characters of flower and fruit. On the lower Colorado (Palmer, 1869; *C. Palmeri*, Gray, Proc. Am. Acad. 7. 292, and Syn. Fl., in part); San Bernardino (147 W. G. Wright, 1880).

C. PALMERI, Gray. Limiting the species to the one of Palmer's original specimens which has the leaves "plicate-lineate by about 6 pairs of straight and strong veins," it may be otherwise distinguished by the 5-parted calyx ($1\frac{1}{2}$ lines long), the lobes linear and acute. The corolla is $2\frac{1}{2}$ lines long, with the rather stout filament somewhat dilated below the insertion. The fruit is unknown.

base: nutlet globose, nearly ½ line broad: cotyledons thick, orbicular. — Very common on sandy bottoms near Los Angeles Bay. (517.) A flowering specimen collected by M. E. Jones at San Quentin is probably the same, but is more woody and apparently perennial.

Heliotropium Curassavicum, Linn. Muleje. (15.)

Heliotropium phyllostachyum, Torr. On rocky mesas at Guaymas. (232.)

Krynitzkia angustifolia, Gray. The root was formerly used as a purple dye by the Indians. On stony ridges at Los Angeles Bay. (606.)

Krynitzkia ramosissima, Greene. Stony ridges, Los Angeles Bay. (551.)

Ipomœa coccinea, Linn. Mountain ravines near Guaymas. (310.)

Ipomœa hederacea, Jacq. In ravines near Guaymas. (295.)

Ipomœa leptotoma, Torr. Very common about Guaymas. (231.)

Ipomœa Bona-nox, Linn. River-banks at Muleje. (33.)

Ipomœa triloba, Linn., var., with glabrous calyx. Collected also by Pringle in 1884 in Santa Cruz Valley, Arizona, and by Palmer (213) in 1885 in Chihuahua. In hedges and ravines about Guaymas. (306.)

Ipomœa Palmeri. A vigorous climber, glabrous: leaves digitately divided, on slender petioles, the 5 segments linear-lanceolate, attenuate to each end, obtusish, 1 to 4 inches long: peduncles 1-flowered, 2 to 4 inches long: calyx glabrous, becoming 1½ inches long, the sepals oblong, obtuse, chartaceous in fruit; corolla white, 2 inches long, with broad tube and rather narrow limb: anthers much twisted, a little exserted: stigma biglobose: capsule globose, ½ inch broad, 4-valved, 4-seeded; seeds very finely pubescent. — "Flowers with the odor of Stramonium." Margin of a dry creek-bed near Guaymas. (75.)

Jacquemontia Pringlei, Gray, var. glabrescens, Gray. Flowers "pale blue with white lines." Hills near Guaymas. (291.)

Jacquemontia Palmeri. An erect slender annual, or at length somewhat climbing, simple or branched, a foot high or more, sparingly soft-pubescent: leaves ovate, usually cordate at base, acute, punctate, 15 lines long or much less, rather shortly petiolate: flowers few (1 to 5), scattered on slender peduncles: calyx-lobes ovate-lanceolate, 2 to 2½ lines long; corolla blue, 3 or 4 lines long: capsule globose, equalling the calyx, the four valves splitting equally to the base: seeds somewhat roughened. — In shade in the mountains about Guaymas. (221.)

Evolvulus linifolius, Linn. Mountains about Guaymas. (291.)

CRESSA CRETICA, Linn. Guaymas, near salt water. (303.)

CUSCUTA UMBELLATA, HBK. About Guaymas, upon species of *Boerhaavia*. (173.)

CUSCUTA AMERICANA, Linn. With small flowers and entire scales, as in *C. congesta*, Benth., from Acapulco, which is referred to this species. About Guaymas. (331.)

CUSCUTA (EUGRAMMICA) PALMERI. Very slender: umbels solitary or in loose fascicles, few-flowered, the pedicels about equalling the flowers: calyx subcampanulate, acutely lobed, about half as long as the corolla-tube; corolla white, persistent, 1½ lines long, the lobes equalling the tube, lanceolate, subacuminate, becoming reflexed: stamens half as long, the filaments rather stout; scales very short, deltoid, fimbriate: styles slender, the longer equalling the stamens: capsule globose, small (½ line broad), breaking away at base. — At Los Angeles Bay, very common, covering prostrate Euphorbias, etc., and forming sheets several yards in extent. (544.)

SOLANUM NIGRUM, Linn., var. NODIFLORUM, Gray. "Yerba mora"; the young leaves and tops are much used by the Indians in cooking. At Muleje and Guaymas. (9.)

SOLANUM HINDSIANUM, Benth. Erect, very thorny, 3 to 6 feet high; flowers light to dark purple. "Perhaps distinct from *S. elæagnifolium*" (Gray). Guaymas. (109.)

PHYSALIS PUBESCENS, Linn. Muleje and Guaymas. (14.)

PHYSALIS ANGULATA, Linn.? Flowers yellow with brown base; fruit edible. About gardens at Guaymas. (622.)

PHYSALIS ANGULATA, Linn., var. LINKIANA, Gray. Stem succulent, 3 feet high; flowers "white with green centre"; fruit fleshy and edible. At Guaymas. (175.)

PHYSALIS ——? Resembling an entire-leaved *P. pubescens*, but the pedicels elongated; fruit tinged with purple when ripe, sometimes eaten and used in cooking. Rocky ridges, in shade, at Los Angeles Bay. (561.)

PHYSALIS ——? Prostrate, very finely pubescent, the upper side of the small ovate to rhombic-lanceolate irregularly blunt-toothed leaves nearly glabrous: calyx-teeth deltoid; corolla 6 lines broad, yellow with dark brown centre: anthers yellow: fruiting calyx puberulent, subglobose with open orifice, 6 to 8 lines long, equalling the pedicel. — Guaymas. (94.)

PHYSALIS ——? Flowers in the dried specimens purplish blue, but described as "drab with wood-colored centre." Under shaded cliffs in the mountains about Guaymas. (621.)

CAPSICUM BACCATUM, Linn. A perennial, 5 feet high, with small red fruit which is sent to San Francisco as "chiltepin peppers." Guaymas. (136.)

CAPSICUM CORDIFORME, Mill., var. GLOBOSUM, Dun.? A cultivated perennial, 6 feet high, with globose orange-colored fruit. Guaymas. (135.)

CAPSICUM ANNUUM, Linn. Various cultivated forms. Guaymas. (137–140.)

LYCIUM RICHII, Torr. Unarmed, 6 to 8 feet high; flowers lilac; fruit edible. Like the type of *L. Palmeri*, Gray. At Muleje. (4.)

LYCIUM RICHII, Torr., var. A very thorny shrub, sometimes 15 feet high; pedicels shorter; flowers "violet"; fruit edible. In alkaline bottoms about Guaymas. (71.)

LYCIUM ANDERSONI, Gray, var. PUBESCENS. A shrub, 4 or 5 feet high, resembling var. *Wrightii*, but finely pubescent, the calyx half a line and the corolla 3 lines long with a very narrow tube; flowers "lavender," tetramerous, the filaments glabrous: berries red. — In stony ravines near Los Angeles Bay. (559.)

LYCIUM BARBINODUM, Miers? A loose shrub, 5 feet high, with black wood, small white flowers, and scarlet fruit. Hillsides and ravines at Guaymas. (230.)

LYCIUM CARINATUM. A thorny glabrous shrub, 1 or 2 feet high: leaves narrowly spatulate, 3 lines long or less, glaucous: pedicels clavate, compressed, 2 or 3 lines long: calyx bifid, the broad acutish lobes carinate; corolla 4-lobed, white, 2 lines long, the tube very short and the throat scarcely as long as the lobes: stamens 4, villous-tufted at the point of insertion, equalling the corolla: fruit said to be red. — "Sal sieso." In large patches near Guaymas. (178.)

LYCIUM? A shrub, 4 feet high, with woolly nodes, very broadly spatulate leaves, and "white flowers." The specimens are without flowers or fruit, and the reference to this genus is only a conjecture. Guaymas. (337.)

NICOTIANA TRIGONOPHYLLA, Dun. At Muleje and on San Pedro Martin Island. (18. 410.)

NICOTIANA CLEVELANDI, Gray. Common at Los Angeles Bay, and used for smoking by the Indians. (556.)

MOHAVEA VISCIDA, Gray. Flowers lemon-color with brown dots, the lower stamens wholly wanting in the flower examined. On stony ridges at Los Angeles Bay. (597.)

ANTIRRHINUM CYATHIFERUM, Benth. (*A. chytrospermum*, Gray.) In gardens at Guaymas. (152.)

ANTIRRHINUM KINGII, Watson, var., with longer pedicels. Collected also in Sonora by Pringle in 1884. Among rocks near Los Angeles Bay. (589.)

STEMODIA DURANTIFOLIA, Sw. Flowers white. Muleje. (25.)

CONOBEA INTERMEDIA, Gray. In dried rocky river-bottoms in the mountains about Guaymas. (241.)

MIMULUS MOSCHATUS, Dougl. On wet rocks near Guaymas. (664.)

CRESCENTIA ALATA, HBK. The gourd-like fruit is subglobose, about 4 inches in diameter, 1-celled (as also the ovary), filled by the pulpy parietal placentæ and numerous flattened obcordate seeds (4 lines long). The species appears to be in every respect a *Crescentia*. It is cultivated at Guaymas, under the name of "ayal," for shade and for the medical properties of the fruit, which is filled with water and the liquid afterwards taken as a remedy for contusions and "internal bruises." (85.)

MARTYNIA ALTHEÆFOLIA, Benth. Flowers yellow, lined with orange and dotted below with brown. Guaymas. (114.)

MARTYNIA FRAGRANS, Lindl. Flowers honey-scented. In low moist places at Guaymas. (326.)

MARTYNIA PALMERI. Stems herbaceous, prostrate, from a large yellow fusiform root: leaves opposite (the upper alternate), long-petiolate, ovate-cordate, obtuse, the margin sinuate, 1½ inches long or less: inflorescence floccose-pubescent and viscid; pedicels 2 or 3 inches long; bracts at base of calyx ovate, short, becoming thickened and spongy: calyx campanulate, 5-toothed, 4 to 6 lines long, the throat oblique; corolla 1½ inches long, buff with orange and red stripes and the throat dotted with red: stamens 4: seeds irregularly oblong, angled and more or less prominently tuberculate, 3 lines long. — Root resembling a carrot and often weighing 3 or 4 pounds; flowers carnation-scented. The green fruit and the seeds are used for food by the Yaqui Indians. Sandy places at Los Angeles Bay. (599.)

ELYTRARIA TRIDENTATA, Vahl. "Cordoncillo"; used as a remedy for fevers, venereal diseases, etc. In shaded places at Guaymas. (285.)

RUELLIA TUBEROSA, Linn. Under hedges at Guaymas. (98.)

RUELLIA ——? A shrub, 4 feet high, with glandular-pubescent narrowly ovate leaves (6 to 10 lines long), and 1 to 3 flowers in the axils upon a very short peduncle; bracts very small: calyx-lobes linear, acuminate, 5 or 6 lines long; corolla light purple, 2 inches long, the tube equalling the calyx and the dilated throat longer than the lobes: stamens unequal: capsule 6 to 9 lines long, acute, 8-seeded. — In moist shaded places on the mesas and in ravines about Guaymas. (196.)

BELOPERONE CALIFORNICA, Benth. Shaded spots in the mountains, at Muleje and Guaymas. (16.)

DIANTHERA SONORÆ. Perennial (?), the herbaceous stems very finely roughish-puberulent, about a foot high: leaves ovate to lanceolate, shortly petiolate, acutish, sparsely pubescent on the margin and veins beneath, 1 or 2 inches long; spikes dense, terminal, sessile, solitary, 1½ inches long or less; bracts imbricated, oblanceolate, acute and mucronate, strongly 3-nerved and ciliate, 4 to 6 lines long: calyx 4-parted, the very narrow attenuate ciliate segments 2 lines long; corolla cream-color, 8 lines long, the straight narrow tube somewhat longer than the limb: anther-cells parallel, nearly equal, separated by a rather narrow connective. — Near a creek in the mountains about Guaymas. (240.)

JACOBINIA OVATA, Gray, var. SUBGLABRA. Branches glabrous and leaves nearly so; flowers in short spikes; otherwise apparently identical with the original of the species. Shrubby, 4 to 6 feet high, the flowers bright scarlet. Mountain ravines near Guaymas. (264.)

LANTANA CAMARA, Linn. A nearly glabrous form. "Confiturea"; used as a preventive of hydrophobia. Plains about Guaymas. (284.)

LIPPIA (ZAPANIA) PALMERI. Near *L. graveolens*; shrubby, 3 to 5 feet high: leaves ovate to elliptical, the blade decurrent upon the short petiole, obtuse or acutish, rugose, subcrenately toothed, finely substrigose-pubescent, an inch long or often much less: peduncles solitary or in pairs in the axils, very short; heads often few-flowered, 2 to 6 lines long; bracts decussate, the lower united to the middle, the upper distinct: calyx thin, not carinate; corolla salverform. — "Origano"; with a strong sage-like odor and used as a potherb. In arroyos about Guaymas. Flowers white or cream-color (277, 644), or rose-color (643).

CITHAREXYLUM (CACOCALYX) FLABELLIFOLIUM. A tall shrub, the younger portions more or less pubescent with short spreading hairs: leaves thin, flabelliform, truncate or rounded above and crenately few-toothed, abruptly contracted to a short petiole, ½ inch long or less: racemes terminal or sometimes axillary, sessile, loosely flowered; pedicels very short: calyx 5-nerved and -angled, acutely toothed, 3 lines long, becoming thin and dilated and loosely enclosing the fruit; corolla dark violet, 6 lines long, the yellowish tube shorter than the calyx, tomentose within, the broadly expanded limb with nearly equal rounded lobes: fifth stamen antherous: fruit black, 2 or 3 lines long. — Differing from *Citharexylum* in foliage, in the large violet flowers, and in the calyx enveloping the fruit. The juice of the fruit stains a persistent black. Mountain ravines about Guaymas. (237.)

BOUCHEA DISSECTA. Annual, slender, erect, branched, very finely puberulent or glabrate, 2 feet high: leaves thin, petiolate, ovate in outline, pinnately cleft nearly to the rhachis, the narrow segments entire or 1–3-toothed: spikes slender, elongated, nearly sessile, the appressed flowers about equalling the internodes; bracts very small, subulate: fruiting calyx 3 or 4 lines long, narrowly and acutely toothed; corolla white, scarcely exserted: fruit linear, 6 lines long, conspicuously long-beaked.— Peculiar in its dissected leaves. On rocky ridges about Guaymas. (259.)

VITEX MOLLIS, HBK. "Uvalama"; a small tree with fragrant violet-colored flowers and black edible fruit. At Muleje. (3.)

HYPTIS EMORYI, Torr., var., with leaves less tomentose. A shrub, 3 to 6 feet high, known as "salvia" and used for seasoning. Sandy bottoms near the beach at Los Angeles Bay. (573.)

HYPTIS PALMERI. Shrubby, 6 to 8 feet high, more or less hoary-puberulent throughout: leaves petiolate, lanceolate, rounded or cuneate at base, acute, crenately denticulate or the larger more coarsely toothed, 1 or 2 inches long: flowers in loose umbel-like very shortly pedunculate axillary cymes, the upper nearly naked; pedicels slender, 1 or 2 lines long: calyx narrowly turbinate-cylindrical, white furfuraceous-puberulent (like the pedicel), the slender teeth more than half the length of the tube; corolla lilac. — "Salvia"; used for rheumatism. Common in arroyos about Guaymas. (278.)

SALVIA PRIVOIDES, Benth. At Guaymas. (320.)

STACHYS COCCINEA, Jacq. Near a waterfall in the mountains above Guaymas. (300.)

PLANTAGO PATAGONICA, Jacq. On stony ridges at Los Angeles Bay. (524.)

MIRABILIS TENUILOBA, Watson. A foot high or more, with fleshy leaves and white flowers; fruit globose, 2 lines in diameter. Mountains near Los Angeles Bay. (600.)

MIRABILIS CALIFORNICA, Gray. Flowers purple. Mountains, Los Angeles Bay. (601.)

ALLIONIA INCARNATA, Linn. Guaymas. (100.)

BOERHAAVIA PANICULATA, Rich. Rocky ledges at Guaymas. (663.)

BOERHAAVIA ——? A doubtful species, not in good fruit, between the last and *B. hirsuta.* Common in gardens at Guaymas, widely procumbent (172) or smaller and upright (172½).

BOERHAAVIA ERECTA, Linn. Bloom white, becoming pink. High mesas at Guaymas. (182.)

BOERHAAVIA ERECTA, Linn., var., with narrow leaves; a common western form. Guaymas. (678–680, 684–687.) Also what is probably an abnormal form of the same. (682.)

BOERHAAVIA ALATA. Apparently erect, 2 feet high, much branched, puberulent, reddish: leaves narrowly oblong to linear, or the lower broader, 1½ inches long or less: inflorescence loosely paniculate, the slender pedicels (1 to 3 lines long) solitary or subumbellate: perianth pink, 2 lines long: stamens (5) and style included: fruit nearly 2 lines long, truncate, more or less broadly 5-winged, the wings often broader than the body, narrower below. — On a small rocky island in Guaymas harbor. (332.)

BOERHAAVIA TRIQUETRA. Similar to the last, puberulent and viscid, procumbent: leaves lanceolate, acute or obtusish: pedicels very short (about ½ line): perianth pink, a line long: stamens (2) and style included: fruit a line long, truncate, broadly obpyramidal, very acutely 3–4-angled, the sides rugose. — Allied to *B. pterocarpa*, which has still smaller flowers (½ line long) with 2 or 3 stamens, and a broader-bodied wing-angled fruit attenuate to a stipe-like base. Sandy plains and stony ridges near Los Angeles Bay. (521.)

BOERHAAVIA WRIGHTII, Gray. (*B. bracteosa*, Watson.) Flowers "waxy white": distinguished from the following triandrous spicate species by the usually conspicuous thin bracts and the broader fruit, which is obtuse and acutely angled. Los Angeles Bay. (603.)

BOERHAAVIA XANTI. Annual; stems sparingly branched, somewhat floccose-pubescent and puberulent, or glabrous above, occasionally with viscid spots, 2 feet high or less: leaves ovate to oblong-ovate or the upper narrowly lanceolate, sinuate, obtuse or acute: flowers large, in a rather loose raceme an inch long or less; bracts lanceolate and bractlets linear, acuminate: perianth "white," spreading, 1½ lines long: stamens (4) and style long-exserted: fruit oblong-obovate, obtuse, a line long, rather acutely 5- (4–6-) angled, rugose in the intervals. First collected by Xantus (n. 93) at Cape Saint Lucas. Sandy mesas; Guaymas. (681.)

BOERHAAVIA PALMERI. Resembling the last; stems procumbent or ascending, glandular-pubescent nearly throughout: spike-like raceme short and dense in flower, 4 lines long or less, about 6 lines long in fruit; bracts obovate and bractlets lanceolate, acuminate, ciliate: perianth "white," $\frac{3}{4}$ line long: stamens (3) and style included: fruit a line long, clavate, obtuse and obtusely-angled, the rather shallow intervals transversely rugose. — Dry sandy soil near Guaymas. (683.) It is also n. 209 of Palmer's collection in 1885, from Hacienda San Miguel near Batopilas, Chihuahua. — B. COULTERI (*Senkenbergia Coulteri*, Hook.) is a similar species, but less glutinous and the loose slender spikes more elongated; bracts and bractlets very narrow; perianth a line long; fruit clavate, 1 to $1\frac{1}{2}$ lines long, truncate, the angles acutish and the channels extending to the very apex. Coulter's specimen (n. 1425) is labelled as from "Mexico." Arizona specimens of Palmer's early collections, 378 Rothrock from Camp Grant, and specimens of Pringle's collection in 1881 from the foothills of the Santa Catalina Mountains appear to be the same.

BOERHAAVIA SPICATA, Choisy, var. (?) PALMERI. Similar to the preceding group; stems procumbent or ascending, finely pubescent: leaves thin, nearly glabrous: flowering racemes open and very slender, becoming 1 or 2 inches long; bracts lanceolate or linear, acuminate; bractlets none: perianth pink, $\frac{1}{2}$ line long: stamens (2) and style included: fruit clavate-oblong, a line long, obtuse and mostly obtusely angled, the channel very narrow and sinuate. — Sandy mesas about Guaymas. (141.) — Typical B. SPICATA, as shown by a flowering and fruiting spike from Pavon's original specimen in Herb. Boissier, which was very kindly loaned me for comparison by M. Barbey, is peculiar in the ovate or ovate-lanceolate acute dark-colored bracts (with a pair of very narrow bractlets at the base of the young fruit), and in the conspicuous brown nerves of the nearly truncate perianth ($\frac{1}{2}$ line long). The fruit in the specimen is still young. The stamens are described as solitary, and but one was detected in the first flower examined, though there were two in the second one. I have seen no specimens that correspond to the type. The form of Texas, New Mexico, and Arizona that has been referred to this species is usually more glandular than the var. *Palmeri*, the leaves thickish and scabrous, and the perianth about a line long. It may be distinguished as var. (?) *Torreyana*.

BOERHAAVIA SCANDENS, Linn. An "evergreen, its many weak stems hanging upon bushes and fences, with greenish yellow flowers, and the fruits adherent to everything they touch." Near Guaymas. (146.)

ABRONIA UMBELLATA, Lam. Sandy plains near Los Angeles Bay. (604.)

CRYPTOCARPUS (?) CAPITATUS. A scraggy shrub, 10–15 feet high, with rigid divaricate branches and branchlets, the younger portions finely pubescent throughout: leaves alternate, entire, mostly broadly obovate, obtuse or acutish, cuneate at base, 1 or 2 inches long including the slender petiole (3 to 6 lines long): peduncles solitary, axillary, naked, becoming 6 to 9 lines long, bearing a globose head (4 to 6 lines broad) of cymosely clustered flowers on very short minutely bracteate pedicels; involucre none: perianth cream-colored, turbinate-campanulate, very shortly and obtusely 5-toothed, a line long: stamens 5, distinct, the slender filaments exserted; anthers rounded: ovary obliquely linear-oblong, acute, shorter than the slender included style, attenuate to the base; ovule solitary, sessile, erect; fruit unknown. — A single head of flowers was collected in August, but it appears to be a winter bloomer, as the January specimens show an abundance of imperfectly developed flowers. In most of its characters, so far as known, the plant is certainly closely allied to *Cryptocarpus*. The fruit and fuller flowering specimens may, however, modify the reference. Near Guaymas. (647.)

ACHYRONYCHIA COOPERI, Torr. & Gray. Los Angeles Bay. (545.)

AMARANTUS FIMBRIATUS, Benth. Sandy plains near Los Angeles Bay (515), and in gardens at Guaymas (154, in part).

AMARANTUS VENULOSUS, Watson. Gardens at Guaymas. (154, in part.)

AMARANTUS PALMERI, Watson. Varying in habit from procumbent or ascending to erect and 5 or 6 feet high, and in the more or less slender or compact spikes, which are often much elongated. It is one of the commonest plants in Sonora and Lower California after the setting in of the rains, in gardens and cultivated fields and in all bottom lands. It is valuable as a forage plant, and the seeds are largely gathered and sold in the markets for making bread and "attole." The collection includes numerous forms. (76–78, 127–134, 312, 675, 676, 688.)

AMARANTUS PALMERI, Watson, var. (?), with very thin-scarious broad perianth-segments, the midvein scarcely reaching to the apex; seeds rather smaller. — On an island in Guaymas harbor, near salt water, prostrate. (311½.)

CLADOTHRIX LANUGINOSA, Nutt. Gardens at Guaymas. (157.)

GOMPHRENA SONORÆ, Torr. Rocky mountain-sides above Guaymas. (252.)

FRŒLICHIA ALATA, Watson. By irrigating ditches near Guaymas. (245.)

IRESINE ALTERNIFOLIA. A shrub, 6 feet high, the young branches finely white-tomentose: leaves often or mostly alternate, thin, ovate or sometimes oblong-ovate, obtuse or acute, truncate or cuneate at base, tomentulose beneath, nearly glabrous or glabrate above, an inch long or less: flowers diœcious, in mostly broad rather open and nearly sessile panicles 2 to 4 inches long, scattered or subapproximate along the ultimate branches, $\frac{2}{3}$ line long, the staminate pubescent, with very short bracts, the pistillate with smooth and shining bracts. — In the mountains about Guaymas. (276.)

CHENOPODIUM ALBUM, Linn. Guaymas. (72, 73.)

CHENOPODIUM AMBROSIOIDES, Linn. "Hipasote"; Guaymas. (171.)

BETA VULGARIS, Linn. "Acelga"; Guaymas, in old gardens. (115.)

ATRIPLEX ELEGANS, Dietr. Upright, 3 feet high. Guaymas. (117, 122.)

ATRIPLEX BARCLAYI, Dietr. Though varying somewhat in habit, as well as in fruit, the specimens are apparently all to be referred to one species, which is very probably the same as the little known *A. Barclayi* from Magdalena Bay on the Pacific side of the peninsula. The specimens from about the gardens at Guaymas are noted as growing 2 or 3 feet high. Those from the beach and islands of the harbor are low, and evidently sometimes perennial. (118, 119, 670, 677, pistillate; 123, 673, 674, staminate.)

ATRIPLEX LINEARIS. Diœcious, woody at base, 1 to 8 feet high, much branched, the branches slender: leaves canescent, narrowly linear, $\frac{1}{2}$ to 2 inches long, attenuate to the base: staminate flowers in mostly small globose clusters in slender spikes bracteate below; pistillate flowers in similar spikes, sessile or shortly pedicellate, solitary or somewhat clustered, the bracts 2 or 3 lines long in fruit, lanceolate with broad free and more or less spreading tips, the sides irregularly tuberculate and developing 4 broad wings, which are more or less deeply toothed or lacerate. — Near forms of *A. canescens*, which is very variable in its fruit but appears never to have the tips of the bracts so large and conspicuous. In alkaline soil about Guaymas. (120, 121, 235.)

SUÆDA TORREYANA, Watson. Very common on sea-beaches and in alkaline soil, in large bunches 2 to 6 feet high. The ashes are used in soap-making. Muleje and Guaymas. (13, 329.)

SPIROSTACHYS OCCIDENTALIS, Watson. Sea-beach at Guaymas. (330.)

Phaulothamnus spinescens, Gray. A thorny shrub, 10 feet high; fruit a drupe with white fleshy pericarp, the embryo surrounding copious mealy albumen. About Guaymas. (68.)

Stegnosperma halimifolium, Benth. An upright evergreen, 5 or 6 feet high, with fleshy leaves, white flowers, and red pulpy fruit. At Muleje, on the island of San Pedro Martin, and at Guaymas. (31, 400.)

Eriogonum inflatum, Torr. "Tivinagua"; much used as a remedy for fevers. Muleje and Los Angeles Bay. (24, 574.)

Eriogonum fasciculatum, Benth. Los Angeles Bay, abundant; 1 or 2 feet high. (549.)

Eriogonum insigne, Watson, var., with the small leaves round-ovate instead of reniform, and the sepals broader. On mountains near Los Angeles Bay. (535.)

Polygonum Persicaria, Linn. High mountains above Guaymas. (211.)

Antigonon leptopus, Hook. & Arn. "San Miguelito"; its long black wiry roots develop large tubers at intervals, which have a pleasant nutty flavor and are an article of food with the Yaqui Indians. About Guaymas. (59.)

Aristolochia brevipes, Benth., var. acuminata, Watson. "Yerba del Indio"; the root used for aches and pains. About Guaymas. (174.)

Loranthus Spirostylis, DC.? Leaves narrower than described (2 to 3½ inches long by 2 to 5 lines broad), and sessile or subsessile. Flowers white and very fragrant; fruit ovoid, 3 lines long, said to be red. About Guaymas, growing on fig, lime, mesquite, and other trees, the stems elongated, rooting or hanging in long tangled masses. (199.)

Loranthus (Psittacanthus) Sonoræ. Glaucous and glabrous, the slender stems 3 or 4 inches long: leaves alternate, very narrowly linear or terete, 1 or 2 inches long and less than a line broad: flowers solitary or in pairs, terminating the branchlets, on pedicels 3 lines long or less; ovary a line long, subtended by a very shallow cupule and a short lateral bractlet; perianth scarlet, an inch long, the petals distinct: fruit unknown.— Hillsides and edges of ravines about Guaymas, growing upon *Bursera microphylla*. (287.)

Phoradendron flavescens, Nutt. Guaymas, on *Maytenus phyllanthoides*. (88.)

Phoradendron Californicum, Nutt. About Guaymas, in large bunches, chiefly upon the thorny mimosas and acacias. (665.)

PEDILANTHUS MACROCARPUS, Benth. Growing in large masses, the flowers and fruit bright crimson. A decoction of the plant is used as an active cathartic. Mountains and hills about Los Angeles Bay. (605.)

EUPHORBIA CAPITELLATA, Engelm., var. LAXIFLORA. Differing from the type of the species in the looser cymes, the mostly smaller gland-appendages, the glabrous capsules, and more sparingly toothed leaves. In gardens (83, 142) and high in the mountains (210) about Guaymas. Specimens from a sandy spit in the harbor (317) vary also in having the narrow and narrowly acuminate leaves nearly all entire, the involucres few in the cymes, and the stipules of the floral leaves shorter and less dissected. Pringle's n. 699 of his 1885 collection in Chihuahua, referred doubtfully to *E. pycnanthemum*, belongs rather to this variety of *E. capitellata*.

EUPHORBIA BRASILIENSIS, Lam. At Guaymas. (81, 82.)

EUPHORBIA ALBOMARGINATA, Torr. & Gray. At Guaymas. (93.)

EUPHORBIA (CHAMÆSYCEÆ) INTERMIXTA. Annual, prostrate, glabrous: stipules broadly triangular, entire; leaves more or less broadly oblong or oblong-ovate, obtuse or acutish, obliquely truncate or subcuneate at base, 3 lines long or less, several times shorter than the internodes: involucres solitary in the forks and axils, pedunculate, turbinate-campanulate, ½ line long; glands dark brown, reniform, with a usually conspicuous white or pinkish appendage: capsule glabrous, rather acutely lobed: seeds (immature) pinkish, oblong, angled, smooth. — Near *E. cordifolia* among the *Leiospermæ*. Guaymas. (187, in part; distributed with *E. glyptosperma*.)

EUPHORBIA TRACHYSPERMA, Engelm. High mesas about Guaymas. (183, 319.)

EUPHORBIA MAGDALENÆ, Benth.? A low glabrous shrub (the branches finely tomentulose), with slender elongated virgate branches: leaves opposite, very shortly petiolate, oblong (2 to 4 lines long), obtuse at both ends, shorter than the internodes (upon the short spurs shorter, broadly elliptical, and exceeding the internodes): involucres solitary, terminal on the spurs. ½ line long, the broad subreniform glands and appendages entire: styles long, 2-parted: fruit unknown. With little doubt the same as Bentham's species from Magdalena Bay, though not fully agreeing with the description. At Muleje, in dry ravines. (26.) Found also by Palmer in 1870 on Carmen Island.

EUPHORBIA TOMENTULOSA, Watson. With white glands and appendages and green capsules, or pinkish, or dark purple; 1½ to 3 feet high. Mountains; Los Angeles Bay and Guaymas. (216, 536.)

EUPHORBIA SERPYLLIFOLIA, Pers. On gravelly ridges near Guaymas. (187.)

EUPHORBIA SETILOBA, Engelm. Near the beach, Los Angeles Bay. (629.) — About Guaymas. (185, 185½, 634.) The latter a more open form with longer internodes and larger leaves, and the appendages less deeply 3–4-lobed.

EUPHORBIA PETRINA. Near *E. setiloba*; annual, prostrate, much branched and slender, more or less densely pubescent throughout with short spreading hairs: leaves very shortly petiolate, entire, obliquely ovate or oblong-ovate, obtuse, somewhat cordate at base, 3 lines long or usually much less: involucres solitary in the axils, shortly pedunculate, minute, turbinate-campanulate; glands greenish, reniform, unappendaged: capsule (and pedicel) pubescent, ⅓ line long: seeds oblong-ovate, quadrangular, strongly and irregularly 3–4-rugose or -pitted. — Common among rocks at summit of San Pedro Martin Island. (412.)

EUPHORBIA PORTULANA. Of the same group; annual, prostrate, much branched and slender, the minute and sparse pubescence spreading: leaves oblong to broadly elliptical, obtuse at both ends, entire, petiolate, 4 lines long or less: involucres oblong, ¾ line long, nearly glabrous, somewhat contracted above; lobes subulate, slightly ciliate; glands dark purple, the appendages variable in form, often unequal (1 or 2 larger), entire or nearly so, white or pinkish: stamens very few: ovary villous; styles bifid nearly to the middle: capsule subacutely lobed, nearly a line long: seed oblong, tetragonal, very strongly 4–5-rugose. — Island in Guaymas harbor. (321.)

EUPHORBIA GLYPTOSPERMA, Engelm. High gravelly ridges at Guaymas. (187, in part.)

EUPHORBIA POLYCARPA, Benth. Several forms, belonging chiefly to the variety with scarcely appendiculate glands (*E. micromera*, Boiss.). By garden fences at Guaymas and on islands in the harbor (96, 324, 335), and at Los Angeles Bay on sandy bottoms, sometimes covering many yards of surface (632, 633). — Also var. HIRTELLA, Boiss., in like localities at Los Angeles Bay. (630.)

EUPHORBIA FLORIDA, Engelm. In rocky places high in the mountains above Guaymas. (209.)

EUPHORBIA MACULATA, Linn., or near it: the glands unappendaged and capsules glabrous. Abundant in low sandy places about Guaymas. (186.)

EUPHORBIA PEDICULIFERA, Engelm. Stony ridges near Los Angeles Bay. (631.)

EUPHORBIA PEDICULIFERA, Engelm., var. LINEARIFOLIA. Closely resembling the ordinary form in the characters of the inflorescence and fruit, but erect and branching above the base, the stem and leaves mostly glabrous; leaves thin, glaucous beneath, linear, acutish at both ends, an inch long or less. In both forms the appendages are unequal, the upper pair larger and oblique. — Hills and mountains about Guaymas. (215, 627.)

EUPHORBIA CALIFORNICA, Benth.? Probably not only this species but also *E. Hindsiana*, Benth. A shrub 3 or 4 feet high, with slender branches; leaves round-obovate, 3 to 6 lines long, obtuse or retuse, on very slender petioles longer than the blade: peduncles terminal, mostly solitary: appendages lobed or merely crenate even in the same involucre: lobes of the capsule (2 lines long) scarcely carinate. — High mountain ravines above Guaymas. (260.)

EUPHORBIA MISERA, Benth. A shrub 3 to 5 feet high. On stony mountain-sides above Los Angeles Bay. (514.)

EUPHORBIA ERIANTHA, Benth. Rocky ridges about Guaymas and Los Angeles Bay. (84, 518.)

SIMMONDSIA CALIFORNICA, Nutt. Common about Guaymas. (343, 344.)

JATROPHA CANESCENS, Müll. "Sangre en grado." A shrub, 3 to 8 feet high, with rose-colored flowers, and thick clustered roots. A decoction of the plant is used as a mordant in dyeing, and the juice as a remedy for warts, diseased gums, sore throats, etc. Common on the mesas about Guaymas. (103.)

JATROPHA SPATHULATA, Müll., var. SESSILIFLORA, Müll. "Tocote prieto." A shrub, 5 to 15 feet high, common about Guaymas and Los Angeles Bay. The fruit of this variety appears to be always 1-coccous. The bark is used as a mordant and for tanning, and is exported for these purposes. It is also a dye, giving a reddish brown color, but is injurious to cloth. (164, 576.)

JATROPHA PALMERI. A shrub, the branches softly pubescent: leaves round-ovate, coarsely and very acutely sinuate-dentate (the teeth glandular-tipped), densely and subtomentosely pubescent on both sides, 1½ inches long by 2 wide or smaller: panicles shorter than the leaves; flowers apetalous, the white cylindrical pubescent calyx 4 or 5 lines long, with round-ovate lobes: stamens of male flowers 10, in two unequal ranks, the filaments connate and disk densely tomentose: ovary densely pubescent (becoming 3 or 4 lines long), the styles twice bifid. — Apparently referable to Müller's subsection *Calyptrosolen*, but it is more shrubby in habit and the calyx is less deeply lobed. Only a single plant found at a high elevation in the mountains above Guaymas. (302.)

Croton Pringlei, Watson. With a minty odor. Ravines and mesas about Guaymas. (180.)

Argythamnia sericophylla, Gray. In gravelly waste places about Guaymas. (108.)

Argythamnia Neo-Mexicana, Müll. Several forms, all of which appear to belong to this species. Plains and mountain-sides about Guaymas. (80, 624, 625.)

Argythamnia Palmeri. Stems numerous, erect, 1½ to 2 feet high, rather sparsely appressed-villous except on the young branches: leaves oblong to lanceolate, acute, more or less attenuate to a very short petiole, entire, 1½ or 2 inches long or smaller: flowers apparently diœcious, the pistillate solitary or in pairs in the axils, on recurved pedicels 1 or 2 lines long; sepals 2 lines long, becoming 4 lines in fruit; petals pilose, ovate-lanceolate, shortly acuminate: styles bifid, the stout branches dilated upward and hispid on the inner side: seeds ovate-globose, over a line long, coarsely reticulate-pitted. — High in the mountains above Guaymas. (247.)

Manihot angustiloba, Müll. Growing 2 or 3 feet high. In the shade on high mountains above Guaymas. (233.)

Acalypha Pringlei, Watson, var., with the pubescence scarcely or not at all glandular, and the teeth of the bracts more numerous (often 13). Mountains above Guaymas. (219, 262.)

Tragia nepetæfolia, Cav. Hedges about Guaymas. (63.) — Also var. **amblyodonta**, Müll. (623.)

Sebastiania (?) bilocularis, Watson. A shrub or small tree, sometimes 15 feet high. "Yerba fleche"; the juice is an exceedingly active and violent cathartic, and the fresh bark is used by the Indians to stupefy fish. Common on the shores and in the hills and mountains about Guaymas. (234.)

Celtis pallida, Torr. A thorny shrub, 6 feet high or more, with orange-colored fruit. Guaymas. (89.)

Ficus (Urostigma) Palmeri. A tree 8 to 12 feet high, branching near the ground; young branchlets white-villous-pubescent: leaves at first densely white-tomentose beneath, becoming nearly equally green on both sides and finely pubescent or subglabrous above, rather thick, ovate, with a somewhat cordate or rounded base, acute, 3 inches long by 2 or 2½ broad, on petioles an inch long: fruit in pairs in the axils, on stout peduncles 6 lines long, globose, thick and fleshy, 6 lines in diameter, subtended by an irregular disk-like involucre 3 lines broad: fertile flowers sessile, the perianth of three distinct sepals exceeding the compressed ovary, the lateral ovate and somewhat concave, the other carinate; abortive pistillate flowers very similar, but upon a short stout pedicel and the lateral sepals narrower; staminate flowers also short-pedicellate, the perianth of three large oblong-obovate sepals; anther sessile, broad, obtuse. — Fruit edible. On San Pedro Martin Island; rare. (413.)

Ficus (Urostigma) fasciculata. A tree with a large trunk (8 feet high) bearing a widely spreading top, the lower limbs horizontal, sending down and supported by aerial roots; foliage and rather slender branchlets wholly glabrous: leaves somewhat crowded at the ends of the branchlets, thin, oblong-lanceolate, short-acuminate or acute, 3-nerved at the rounded or acutish base, puncticulate above, finely reticulated beneath, 1½–2½ inches long, on petioles ½ inch long: fruit solitary in the axils, on slender peduncles 2 lines long, subtended by a 4-lobed involucre, depressed-globose with a sunken orifice, 5 lines in diameter (immature); flowers all on short stout pedicels, somewhat oblique, the perianth short, gamophyllous, unequally and irregularly 2–3-lobed, the lobes short and obtuse; style of some of the pistillate flowers filiform and entire, of others bifid; anther sessile, ovate, acute, the cells rather long-apiculate. — Cultivated at Guaymas, but said to be native to the region. (646.)

Ficus (Urostigma) Sonoræ. A tree 15 to 40 feet high, without aerial roots, glabrous throughout: leaves as in the last, but more scattered on the branchlets and more cuneate at base, the larger nearly 4 inches long: fruit solitary, on slender peduncles 4 or 5 lines long, subtended by an irregular disk-like involucre, globose, 5 lines in diameter: fertile flowers sessile, the perianth cleft to the middle with broad acutish lobes, shorter than the globose nutlet, which develops much mucilage when wetted; abortive pistillate flowers with a stipitate oblong-obovate empty ovary (not mucilaginous) surrounded by a tubular-funnelform 3-cleft perianth; staminate perianth similar, but shorter and somewhat broader, the anther ovate, acute. — Fruit black, edible, and known as "Nacapuli." Cultivated at Guaymas (92), and also found wild in the ravines of the mountains (645). In its foliage it closely resembles *F. turbinata*.

Brodiæa Palmeri. Stem 1½ to 2 feet high, bearing numerous bulblets at and below the surface; leaves linear, a little shorter than the scape, 8 lines broad or less: pedicels numerous, ½ to 1 inch long or more: corolla purple, 6 to 8 lines long, funnel-form from a narrow base, cleft to the middle, the throat coronate with a row of very short thin laminæ between the principal veins: filaments 6, naked, scabrous, free from near the top of the tube and nearly equalling the corolla; anthers basifixed, linear, 1½ lines long: capsule equalling the perianth, ovate, narrowed to a short stipe, the cells 2-seeded. — Of the *Seubertia* section, though with the basifixed anthers of *Eubrodiæa*. Abundant in low places on the sandy plains about Los Angeles Bay. (596.)

WASHINGTONIA SONORÆ. A tree reaching 25 feet in height and a foot in diameter: leaves 3 or 4 feet in diameter, somewhat glaucous, very filiferous, upon rather slender petioles which are armed with stout curved spines: spadix slender, 5 or 6 feet long: fruit about 3 lines long, the flattened-globose seed 2 to 2½ lines in the longest diameter. — Apparently distinct from *W. filifera* and *W. robusta* in its more slender petioles, more glaucous leaves, and smaller fruit. The seeds are used for food by the Indians. It may here be noted that in the "Genera Plantarum" the genus *Washingtonia* is placed in the group having basilar styles, though it is correctly described as having the style terminal. In secluded cañons in the mountains about Guaymas. (311.)

POTAMOGETON PECTINATUS, Linn. "Grama"; used in decoction "to purify the blood." In a small lake near Muleje. (23.)

NAIAS MAJOR, All. "Saragossa." Abundant in a shallow lake near Muleje. (20.)

JUNCUS* ROBUSTUS, Watson. In brackish water. Muleje. (34.)

CYPERUS SPECIOSUS, Vahl. Margin of a fresh-water lake near Muleje (36), and high in the mountains above Guaymas (640). — C. LÆVIGATUS, Linn. Near Muleje and at Los Angeles Bay. (39, 509.) — C. ARISTATUS, Rottb. At Guaymas, near the harbor and also high in the mountains (193, 637), and on the summit of San Pedro Martin Island (417). — C. ESCULENTUS, Linn. At Guaymas. (203.) — C. ARTICULATUS, Linn. High in the mountains above Guaymas. (636.) — C. FERAX, Rich. At the same locality. (639.)

ELEOCHARIS CAPITATA, R. Br. Same locality. (635, 635½.)

FIMBRISTYLIS LAXA. With pale glumes. Same locality. (638.)

SCIRPUS OLNEYI, Gray. At Muleje. (37.)

PASPALUM DISTICHUM, Linn. High in the mountains above Guaymas. (693.) — P. PUBIFLORUM, Rupprecht. At Muleje and Guaymas. (45, 79.)

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* The following *Juncaceæ* and *Cyperaceæ* were determined by Dr. N. L. BRITTON, and the *Gramineæ* by Dr. GEORGE VASEY.

ERIOCHLOA PUNCTATA, Desv. At Muleje (44), and at Guaymas.

PANICUM SANGUINALE, Linn. At Muleje (48), and the var. CILIARE near Guaymas (269, 695). — P. HALLII, Vasey. About Guaymas. (206.) — P. DISSITIFLORUM, Vasey, *n. sp.* In deep ravines and by irrigating ditches about Guaymas. (159, 190.) — P. FASCICULATUM, Sw. Plains and foothills about Guaymas. (207.) Also var. MAJUS, by ditches. (158.) — P. PASPALOIDES, Pers. Near Guaymas. (690.) — P. COLONUM, Linn. At Muleje (46), and about Guaymas. (51, 202.) — P. LACHNANTHUM, Torr. Not eaten even by goats. About Guaymas. (54, 348.) — P. CAPILLARE, Linn., var. At Guaymas. (208.)

SETARIA COMPOSITA, HBK. About Guaymas. (53.) — S. CAUDATA, R. & S. At Guaymas and upon a small sandy island in the harbor. (340.) Also var. PAUCIFLORA. At Guaymas. (191.)

CENCHRUS ECHINATUS, Linn. At Guaymas. (168.) — C. MYOSUROIDES, HBK. Near salt water on an island in Guaymas harbor. (327.) — C. TRIBULOIDES, Linn. On the ruins of the old French fort at Guaymas. (349.) — C. PALMERI, Vasey, *n. sp.* Near Guaymas and at Los Angeles Bay. (271, 689.)

HILARIA CENCHROIDES, HBK., var. LONGIFOLIA. Islands in Guaymas harbor. (347.)

CATHESTICUM ERECTUM, Vasey & Hack., and var. Abundant on mesas and hillsides and in gardens about Guaymas, and on islands in the harbor. (161, 345.)

HETEROPOGON CONTORTUS, R. & S. Hillsides and mountains about Guaymas. (267.)

SORGHUM HALEPENSE, Pers. Gardens and fields about Guaymas. (64.)

ARISTIDA DISPERSA, Trin. Gardens and fields about Guaymas. (66.) — A. BROMOIDES, HBK., and var. On rocky ridges at Los Angeles Bay. (503, 504.) —A. SCHIEDEANA, Trin. & Rupr. Hedges and rocky ledges about Guaymas. (55, 268.) — A. FUGITIVA, Vasey, *n. sp.* On sandy beaches at Los Angeles Bay. (501.)

STIPA CALIFORNICA, Vasey, *n: sp.* In mountain cañons about Los Angeles Bay. (505.)

MUHLENBERGIA SPICIFORMIS, Trin. Rocky hills near Guaymas. (272.) — M. TENELLA, Trin. Island of San Pedro Martin, common among rocks; the only grass. (416.) — M. DEBILIS, Trin. Plains and mountains about Los Angeles Bay. (510.)

SPOROBOLUS CRYPTANDRUS, Gray. Abundant about Guaymas. (65.) — S. HUMIFUSUS, Kunth. Abundant about Guaymas in the rainy season. (188.) — S. Virginicus, Kunth. On islands in Guaymas harbor. (338.) — S. Domingensis, Kunth, and vars. Common about Guaymas. (160, 165, 696.)

Agrostis verticillata, Vill. At Muleje. (41.)

Chloris elegans, Kunth. Near Los Angeles Bay. (506.)

Bouteloua aristidoides, Thurb. About Guaymas (162, 191), and at Los Angeles Bay (507). — B. Rothrockii, Vasey. Gardens and fields at Guaymas. (166.) — B. arenosa, Vasey, *n. sp.* Plains and ridges about Guaymas. (189.) — B. bromoides, Lag. Mountains and ledges about Guaymas. (201.) — B. polystachya, Torr. Sandy bottoms near the sea at Los Angeles Bay. (346 ?, 508.) Also var. major. Common about Guaymas. (204, 205.)

Eleusine Indica, Gaertn. Common at Muleje. (35.) — E. Ægyptiaca, Pers. About Guaymas. (275, 328.)

Leptochloa mucronata, Kunth, and var. Common about Guaymas. (50, 192, 694.)

Pappophorum apertum, Munro. On the old fort at Guaymas and on rocky mountain-sides. (274, 350.) — P. Wrightii, Watson. Rocky ridges near Bay of Los Angeles. (511.)

Cottea pappophoroides, Kunth. Rocky island in Guaymas harbor. (339.)

Triodia pulchella, HBK. On a high rocky point above Los Angeles Bay. (500.)

Diplachne imbricata, Vasey. Common at Muleje (47), and at Guaymas. — D. dubia, Benth. High in the mountains above Guaymas. (270, 273.) — D. Tracyi, Vasey. Same locality. (691.) — D. viscida, Scribner. Same locality. (692.)

Phragmites communis, Trin. At Muleje. (38.)

Eragrostis major, Host; forms. At Muleje (10, 40½), and about Guaymas. — E. Purshii, Schrad. At Muleje. (42, 49.) Also var. diffusa. Common about Guaymas. (167.)

Distichlis maritima, Raf. At Muleje, common. (43.)

Lolium perenne, Linn. In a garden at Guaymas. (52.)

Notholæna* Lemmoni, Eaton. In high mountains near Guaymas. (266.) — N. cretacea, Liebm. (*N. Californica*, Eaton.) Rocky mountain-sides above Los Angeles Bay. (552.)

Cheilanthes Pringlei, Davenport. Rocky mountain ledges near Guaymas. (265.) — C. myriophylla, Desv. Mountains at Los Angeles Bay. (553.)

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* The Ferns were determined by Prof. D. C. Eaton.

Pellæa Seemanni, Hook. Shaded rocky ledges in the mountains about Guaymas. (226.) — P. Wrightiana, Hook. The form with numerous pinnules (*P. longimucronata*, Hook.). Los Angeles Bay. (554.)

Indeterminable Species.

179. Flowering specimens from a tree growing on sandy plains about Guaymas, described as 12 to 15 feet high and 1 to 5 feet in diameter, with very green bark and a dense symmetrical top. Its wood is said to be useless even for fuel. The young branches are finely pubescent, and the leaves are alternate, coriaceous, entire, linear with a cordate base, obtuse, glabrous and veiny above, very strongly reticulate-veined beneath, with a stout midnerve and the margins revolute, about 3 inches long by 2 lines broad, the very short petiole (a line long) jointed upon the stem; stipules none. The flowers as collected are in loose simple naked racemes 2 inches long, the scattered spreading pedicels 2 or 3 lines long. They are probably diœcious, as all those collected have only an imperfectly or scarcely at all developed ovary. The calyx is very small, 6–8-parted, apparently valvate; petals none; stamens about 20 (18–22) upon a prominent lobed hypogynous disk (nearly equalling the calyx), the filaments distinct, slender, 3 lines long, and the anthers short, basifixed, 2-celled, and longitudinally dehiscent. The most fully developed ovaries are smooth, oblong, somewhat obcompressed, 2-celled, with a nearly sessile thick 2-lobed stigma, and apparently one or more (?) pairs of collateral rudimentary ovules upon the axis. The relations of this remarkable species are very obscure, and must await fuller material for their determination. It will probably be found to belong to the *Tiliaceæ*.

307. "Yerba del ayre"; foliage only of an unrecognized shrub, found in ravines about Guaymas. A decoction of the leaves is used as a remedy for paralysis.

2. *Descriptions of some New Species of Plants, chiefly Californian, with miscellaneous Notes.*

Silene Bernardina. Finely glandular-pubescent throughout; stems slender from slender rootstocks, a foot high, few-flowered: leaves very narrowly linear-oblanceolate, 1 or 2 inches long: peduncles slender, 1–3-flowered: calyx cylindrical, ½ inch long, with oblong-ovate teeth; petals greenish, 8 lines long, the blade cleft to below the middle into four equal narrow lobes; coronal appendages nearly half the length of the blade, thin, 2-parted, the outer segment linear, entire, the inner oblong and lacerate; claw naked, broadly auriculate: stamens included, unequal: capsule oblong, shortly stipitate. — Of the *S. Lemmoni* and *S. occidentalis* group. On shady slopes in Long Meadow, Tulare Co., California; Dr. E. Palmer, June, 1888 (n. 185).

ERIGERON SANCTARUM. Perennial and dwarfish, the branches of the rootstock very slender and naked, bearing one to several erect or subdecumbent 1-flowered stems, leafy except toward the top, a span high or less, rough-pubescent: leaves entire, narrowly oblanceolate, becoming linear above, the lower an inch long (or sometimes longer and with a slender petiole): heads medium-sized; involucre of numerous very narrow acuminate bracts in two series, the outer hispid, densely so at base: rays many, purple or fading to white; pappus simple. — Not closely allied to any other of the *Euerigeron* section. Collected by Mr. T. S. Brandegee in the Santa Inez Mountains, California, also near Santa Barbara, and on the island of Santa Rosa, 1888.

BÆRIA (EUBÆRIA) PARISHII. Low and slender, much branched, pubescent with loose woolly hairs: leaves narrowly linear, acute, mostly pinnately cleft with one to several pairs of lobes: heads small, 2 lines high or rarely more; involucral bracts 10 to 12, thin and lax, the midvein not prominent: ligules short: style-tips truncate, with an oblique apiculation on the inner side: achenes slender, without pappus. — Resembling epappose small-headed forms of *B. gracilis*, differing in the pubescence and cleft leaves and in the apiculate style-tips, and approaching the *B. platycarpha* group. On the foothills of the San Bernardino Mountains, at 1500 feet altitude; collected by Mr. S. B. Parish, in May, 1888.

BAHIA PALMERI. Low and slender (not 6 inches high), somewhat soft-pubescent and resinous-atomiferous: leaves mostly alternate, entire, very narrowly linear, an inch long or less: heads sessile and somewhat clustered, narrowly turbinate, 2–6-flowered: involucral bracts 3 or 4, narrowly oblanceolate, acutish, wholly green and herbaceous: rays none; corolla-lobes 5, more or less unequal: achenes rather broad, obtusely quadrangular, finely striate and glandular-puberulent; pappus of 8 to 10 thin obtuse oblong-spatulate denticulate chaff, narrowed and thickened toward the base, half the length of the corolla-tube. — An anomalous species, intermediate between *Schkuhria* and *Bahia* as defined by Dr. Gray, and tending to invalidate the distinction drawn by him between the genera. It is placed in *Bahia* as nearer to the section *Achyropappus* of that genus than to *Schkuhria* § *Hopkirkia*, especially in the characters of the involucre and achene. Found by Dr. E. Palmer (n. 168) on low slopes and ridges in Long Meadow, Tulare Co., California, June, 1888.

CACALIA TUSSILAGINOIDES, HBK. In the notes made by Dr. Gray (as given in these Proceedings, vol xxii. p. 432) upon the specimens collected by Dr. Palmer in Jalisco (n. 168, of 1886), which he referred with some uncertainty to this species, the words "ex char." should have been erased in the proof-reading. These were in his notes as sent from the Kew Herbarium, where he had found only the Coulter specimen to which he alludes. Later, he examined at Paris Humboldt's original specimens upon which the species was based, with the result that he directed the retention of the reference, though leaving it still questionable.

MICROSERIS ANOMALA, Watson, in Proc. Amer. Acad., 22. 474. This species was described under a misapprehension of the character of the pappus. It is without a doubt a form of *M. macrochæta*, Gray. The mature fruit of this species is still unknown.

COLLINSIA WRIGHTII. Low and divaricately branching (3 or 4 inches high), glandular-pubescent and viscid: leaves opposite, linear-oblong or -lanceolate, entire, about an inch long: flowers pedicellate, 1 or 2 in the axils, the uppermost in a naked umbel; calyx 2 lines long, the narrow lobes obtusish; corolla but little longer, the tube and throat shorter than the broad obtuse lobes of the limb, the lower lip blue, the upper yellowish: capsule equalling or a little shorter than the calyx, 2-seeded: seeds oblong, nearly terete, with a deep ventral sulcus. — Near *C. Torreyi*, with the habit and flowers of *C. parviflora*. On the Greenhorn Mountains, Kern County, California, at 6,000 to 7,000 feet altitude; collected by Mr. W. G. Wright and Dr. E. Palmer in June, 1888.

MIMULUS (EUMIMULUS) DEFLEXUS. A dwarf slender annual, 2 or 3 inches high, sparingly viscid-puberulent: leaves linear to linear-oblong, entire, less than ½ inch long: pedicels exceeding the leaves, soon widely spreading or usually reflexed: calyx glabrous, narrow, not strongly nerved or angled, nearly equally and obtusely toothed, 2 to 2½ lines long; corolla 6 or 7 lines long, the narrow tube nearly twice the length of the calyx, the broad limb deeply bilabiate; upper lip deep purple, with emarginate lobes, the lower deep yellow with bifid lobes, somewhat hairy and spotted below: capsule 1½ lines long: seeds brownish, irregularly ovate to oblong-ovate, somewhat rugulose longitudinally. — A very pretty little species, of the same group with *M. bicolor*, *montioides*, and *rubellus*. The placenta splits at the apex. Collected by Dr. E. Palmer (n. 176) in June, 1888, on the drier edges of low wet places in Long Meadow, Tulare Co., California.

LOUTERIDIUM DONNELL-SMITHII, Watson, Proc. Amer. Acad. 23. 283. In the description of this curious Guatemalan genus the calyx is inadvertently described as inverted. It is of course the three upper sepals that are united into one, the two lower remaining distinct. The same plant has since been detected in my own collection made in Guatemala in March, 1885, — found in flower at the plantation on the Chocon River and noted as growing from 3 to 9 feet high.

ERIOGONUM (GANYSMA) ESMERALDENSE. Leaves all radical, hispid, especially on the margins, round-obovate, cuneate at base, small (an inch long including the petiole), the rest of the plant wholly glabrous and glaucous: stem slender, repeatedly dichotomous above; bracts small, deltoid to oblong; pedicels very slender, 2 or 3 lines long, mostly strongly reflexed: involucres narrowly turbinate, ½ line long, cleft to the middle: flowers glabrous, white or pinkish, the oblong to oblong-spatulate segments nearly equal, retuse or obtuse, ½ line long. — Near *E. glandulosum*, but wholly destitute of glands. Found by Mr. W. H. Shockley, July, 1888, in Esmeralda Co., Nevada, at Candelaria, and on Miller Mountain at 7,000 feet altitude.

ERIOGONUM (OREGONIUM) GRACILIPES. A dwarf cespitose perennial, with compactly branched caudex and crowded oblanceolate tomentose leaves, ½ inch long or less: peduncles slender, ½ to 2 inches long, glandular-puberulent: involucres few in the small solitary head, turbinate, tomentose: flower glabrous, more or less deep rose-color, exserted. — Of the *E. Kennedyi* group, distinguished most conspicuously by the glandular-puberulent peduncle. On the White Mountains, Mono Co., California, at 13,000 feet altitude; W. H. Shockley, August, 1888.

NEMASTYLIS PRINGLEI. Stem a span high, terete, usually simple, 1-leaved near or above the middle: radical leaves shorter than the stem, 1 or 2 lines broad, 2–3-nerved (the nerves somewhat winged alternately on the two sides); spathe-bracts unequal, the larger nearly equalling the solitary pedicel, 1½ inches long: flowers very fragrant, of a delicate pale blue, the segments oblong-oblanceolate, obtusish, the outer 15 lines and the inner 13 lines long, minutely apiculate: stamineal column nearly 2 lines long, half the length of the linear yellow anthers: divergent stigma-lobes 1½ lines long: capsule oblong, 5 to 10 lines long. — Collected by Mr. C. G. Pringle in 1887 (n. 1378) in the mountains of Chihuahua in fruit, and described from plants in flower at the Cambridge Botanic Garden in July, 1888.

NEMASTYLIS DUGESII. The plant described by myself as a *Tigridia* in Proc. Am. Acad. 20. 375, based upon drawings by Prof. Dugès, should doubtless have been referred rather to *Nemastylis*, as the style-branches are plainly represented to be alternate with the anthers.

CALATHEA CROTALIFERA. Low; leaves oval, abruptly acute at each end, 1½ to 2 feet long by 10 or 12 inches broad, yellowish green, the midvein with a narrow whitish margin, paler beneath; petiole 2 or 3 feet long, at base sheathing the one or two peduncles, which are 8 or 10 inches high: spike erect, distichous, 6 to 10 inches long, the bracts (20 to 40) closely imbricated, duplicate-reniform, subtruncate, 1¼ inches long or less, yellowish green tinged with red; bractlets doubly winged on the back: flowers mostly included, yellowish; sepals scarious, 4 to 6 lines long, about half the length of the petals. — In wet shaded places at the base of the El Mico Mountains near Yzabal, Guatemala, April, 1885; also received in flower from Messrs. Reasoner Brothers, of Manatee, Florida, cultivated from Guatemala roots. The resemblance of the spike to the rattle of a *Crotalus* suggests the name.

SISYRINCHIUM ANCEPS, Cav. Having had occasion to investigate the nomenclature and synonymy, as well as validity, of the species of *Sisyrinchium* found within the limits of Gray's Manual, I would again propose the restoration of the above name for one of our forms. The error made by Linnæus in uniting the Tournefortian *Bermudiana* from Bermuda with the species that had come into cultivation in Europe from this country was recognized by the botanists generally of that day, and the two species were kept distinct afterward, as they had been before. Miller (1768) was the first to give a definite binomial name to the American plant, calling it *S. angustifolium*, and the form intended by him is easily recognized from his description, and from the figure given by Dillenius, which represent a plant with a simple stem bearing a single spathe. In 1783, Lamarck published the name *S. gramineum* for what as described by him and afterward, figured by Redouté would appear to be the same thing. In 1788, Cavanilles gave the name *S. anceps* to what might also be considered the same, except that his figure shows a plant with a branching stem. Michaux afterwards in his Flora described two species (*S. Bermudiana* and *S. mucronatum*) as found by him in the Atlantic States. Of these, *S. mucronatum* is the old species, i. e. *S. angustifolium* of Miller. His *S. Bermudiana* is distinguished as having a broadly winged branching stem and equally bracted spathes, and he cites *S. anceps*, Cav., as probably a variety. Nuttall in his "Genera" simply mentions three species, *S. anceps, S. mucronatum*, and *S. Bermudiana*, and Sweet is cited ("Brit. Fl. Gard., 2 ed., 498") as having given to the last the name *S. Nuttallii*. Later American botanists have endeavored to distinguish two species, *S. anceps* and *S. mucronatum*, by the characters of the perianth, spathes, and stems, but with so little satisfaction that more recently Dr. Torrey and Dr. Gray have united them as varieties under the Bermudan species *S. Bermudiana*. A comparison of such fruiting specimens as have come in my way have shown an evident difference in the seeds of our common species, some being globose, quite strongly pitted, and less than $\frac{1}{2}$ a line in diameter, others more angled, rather less pitted, and about twice larger (rather more than $\frac{1}{2}$ line broad). This difference of seed appears always to accompany a difference of habit, the larger seed belonging to the simple stemmed form (*S. angustifolium*), while the plant with smaller seeds is always branching, bearing several spathes. This seems to justify the retention of the two species of our early botanists, and, restoring Miller's name for one, there seems to me no good objection to keeping up Cavanilles's name for the other. Both species are very commonly distributed through the eastern United States, from Canada to the Gulf. The species of the Gulf region still need investigation.

Allium hyalinum, Curran in herb. Bulb-coats gray, the areolæ of the peculiar reticulation narrowly linear and much contorted: leaves several, very narrow: scape slender, a foot high or less; spathe bifid, unilateral; pedicels rather few, an inch long or less: perianth white to purplish, broad, 3 to 4$\frac{1}{2}$ lines long, the acute segments broadly lanceolate to ovate, the inner somewhat narrower: stamens a third shorter, the filaments dilated at base: ovary not crested. — First collected at Salmon Falls in Eldorado Co., California, by Mrs. M. K. Curran, June, 1881; also recently found by Mr. T. S. Brandegee on Santa Cruz Island. The flowers much resemble those of *A. campanulatum*, which is a stouter plant with broader leaves, the reticulation in the bulb-coats minute and extremely sinuous, the filaments more slender, and the ovary crested.

VII.

THE DETERMINATION OF CHROMIUM IN CHROME IRON ORE.

By Leonard P. Kinnicutt and George W. Patterson.

Presented January 9, 1889.

The complete decomposition of chrome iron ore, and the determination of the amount of chromium, is one of the difficult problems of quantitative analysis. Of the very many methods that have from time to time been published, one given last year by Donath,[*] using barium dioxide as the oxidizing and fusing agent, seemed the most expeditious and simple.

The method as given by him was as follows. One part of the very finely divided mineral was mixed with five times its weight of barium dioxide, and heated for one half-hour in a porcelain crucible over one Bunsen lamp. The semifused yellowish green mass thus obtained was treated with dilute hydrochloric acid. After a few hours, all the chromium was found in solution as the chromate of barium. The barium was precipitated with sulphuric acid, and the filtrate from the barium sulphate neutralized with sodium carbonate, and a few drops of an alkaline solution of permanganate of potassium added to oxidize any chromium that might have been reduced. The excess of permanganate was then removed by the very careful addition of ferrous sulphate, and the amount of chromium determined volumetrically.

Donath, however, did not publish any results to show the accuracy of the method, and it was on this account that we were led to repeat his work.

A few experiments were sufficient to satisfy us that the perfect decomposition of chrome iron ore from Pennsylvania could not be accomplished in the manner described by Donath. A number of fusions of the very finely powdered and sifted mineral with five or even ten times its weight of barium dioxide were made, and in every case the residue contained a greater or less amount of the black undecomposed mineral. Also we were unable to obtain any porcelain crucibles in which more than one fusion could be safely accomplished; while if the fusion was made in platinum crucibles, we obtained, as

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[*] Dingler's Polytechnisches Journal, vol. cclxiii. p. 245.

was also noticed by Donath, a comparatively large amount of the sesquioxide of chromium.

Another serious difficulty was met with later in the process; namely, in determining the exact point where sufficient ferrous sulphate had been added to reduce the excess of permanganate of potassium, used in oxidizing the small amount of reduced chromic acid. The change of color of the solution being so slight as to be almost useless as an indicator.

We were therefore unable, with the most careful manipulation, to obtain satisfactory results with the above process. In our study of the process we made a great many experiments with different fusing mixtures, and also tried various ways of oxidizing the small amount of sesquioxide of chromium we always found present in the solution. The result of these experiments have enabled us to formulate a very quick and simple process, which, as can be seen by the results given below, is also, as regards accuracy, very satisfactory.

About three tenths of the very finely divided mineral is mixed with twenty times its weight of a mixture containing equal parts of dry sodium carbonate and barium dioxide, and heated in a platinum crucible with the full flame of one Bunsen lamp for one half-hour. At the end of this time a quiet fusion is obtained and the decomposition is completed. The crucible is then placed in a beaker, covered with water, and hydrochloric acid added, a little at a time, till the mass is completely disintegrated. The crucible is then removed, the solution made strongly alkaline with caustic potash, and five or six cubic centimeters of a five per cent solution of hydrogen dioxide added to oxidize the small amount of reduced chromic acid that may be present. The solution is now boiled for twenty minutes to remove any excess of hydrogen dioxide, made acid with hydrochloric acid, and the amount of chromic acid determined by the aid of a standardized solution of ferrous chloride.

Six analyses of a sample of chrome iron gave the following per cents of chromium sesquioxide.

1.	2.	3.	4.	5.	6.
49.87	49.97	49.84	49.85	49.88	49.87

The solution of ferrous chloride used was kept under oil and titrated before each analysis. One cubic centimeter equalled about 0.015 gram of chromium sesquioxide.

Salisbury Laboratories,
Worcester Polytechnic Institute.

VIII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXXI. — THE STRENGTH OF THE MICROPHONE CURRENT AS INFLUENCED BY VARIATIONS IN NORMAL PRESSURE AND MASS OF THE ELECTRODES.

By Annie W. Sabine.

Presented by Charles R. Cross, November 14, 1888.

The experiments described in the present paper, undertaken at the suggestion of Professor Cross, constitute a study of the variation of the current in the secondary circuit of a microphone transmitter, as related to variations in the normal pressure and in the mass of the electrodes of the microphone. They form a continuation of work of a similar character which has been prosecuted in the Rogers Laboratory during the past few years, and a portion of which has already been presented to the Academy.*

The instruments used were similar to those previously employed by Messrs. Patterson and Tucker, and described in the latter of the two articles just referred to. The electrodynamometer was calibrated by means of a Hartmann galvanometer, using reversals in the ordinary manner so as by four readings to eliminate the effect of the earth's magnetism on the suspended coil.

The microphone contact was set into vibration by the sound of a stopped organ-pipe (C_4 of 512 vibrations) kept as constant as possible by means of an air-blast furnished with a regulating air-chamber. Weights were gradually added to the upper (anvil) electrode, so that the mass of this and its pressure on the lower electrode were thereby increased by measured amounts. The weights added were usually in the form of thin copper washers weighing $\frac{8}{10}$ of a gram each, though fractions of this weight were used in some cases. One chromic acid cell was used as a battery.

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* See Proc. Am. Acad., Vol. XXI. p. 248; Ibid., Vol. XXIII. p. 228.

The character of the results obtained will be seen by an inspection of Figure 1, which gives the curve showing the relation between the normal pressure and the resulting current, with electrodes of the materials employed in the Blake transmitter, viz. a platinum hammer and a hard carbon anvil electrode. The abscissas represent the normal pressures, i. e. the added weights, and the ordinates the currents produced in the secondary. The data from which this curve is constructed will be found in the following table. The load is given in terms of the arbitrary unit employed; the currents are given in milliampères.

TABLE.

Load.	Current.	Remarks.
0	0	
.5	.18	
1.0	.46	Loud, good quality, fluttering.
1.5	.48	“ “ “ “
2.5	.56	“ “ “ “
3.0	.49	
3.5	.45	Faint, good quality.
4.0	.33	“ “ “
4.5	.21	
5.0	.19	

The curve shows a rapid rise at first, as the mass of the anvil electrode, and with it the pressure between the electrodes, is increased, which rise soon reaches a maximum, the curve then falling off rapidly at first, more slowly afterwards.

The nature of the curve is interesting, and requires explanation. In his article already referred to, Mr. G. W. Patterson, who obtained similar results to my own, considers the curve to be composed of two separate branches, the rising portion of the curve corresponding to a motion of the electrodes sufficient to break the circuit, and the falling portion to the case when the pressure is too great to allow this to occur. The curve (these Proceedings, Vol. XXIII. p. 235, Fig. 1) constructed upon this hypothesis greatly resembles one of the experimental curves shown in Fig. 3 of the same paper. There is less resemblance, however, to the lower curve in Fig. 3, and but little to the curve shown in Fig. 1 of this article, which was obtained under exceptional conditions of quietness of the piers upon which the apparatus was placed. The sound in a receiving telephone placed in the secondary circuit is so harsh for this portion of the curve, that one might well infer that actual breaks occurred; but this is very doubtful, and such breaking is certainly not essential to the production of the

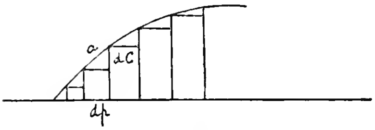

FIG. 2.

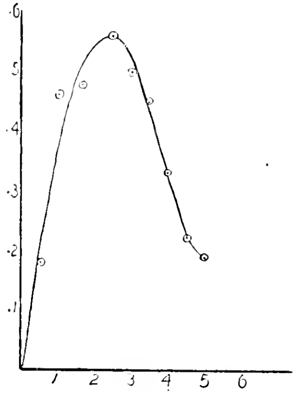

FIG. 1.

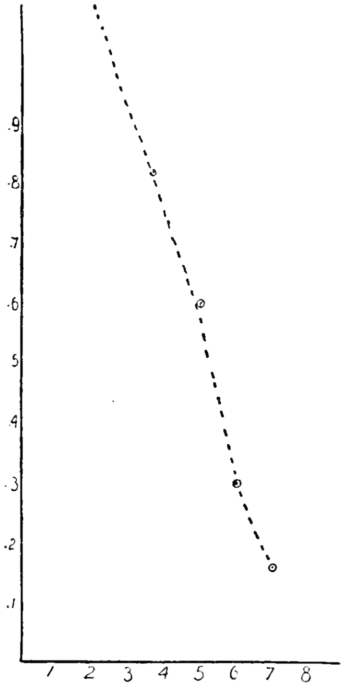

FIG. 3.

results which are obtained. In fact, the article referred to assumes that the varying pressure on the contact due to the action of the given sound-waves will always have the same maximum value, ± δ. This would be approximately true were the normal pressure between the two electrodes alone to be varied, but the effect of the addition of weights, as in the method of experiment adopted, is to increase the mass at the same time that the normal pressure is increased, and under these circumstances the effect of a sound-wave of given intensity will necessarily be to give to the corresponding pressure-variation a variable value, increasing with the added mass, and hence, with the form of apparatus used, as the normal pressure is greater. The effect of this will be to cause at first a gradual increase of current in the secondary, which increase is succeeded by a diminution of current when the mass is still further increased. This will be apparent from an inspection of the curve shown in Figure 2, which illustrates in a general manner the relation of the pressure between the electrodes to the current in the primary circuit.

In this the momentary changes in pressure, Δp, $\Delta p'$, $\Delta p''$, etc., due to the sound-waves, and corresponding to loads and normal pressures p, p', p'', etc., have increasing values within certain working limits, owing to the increasing mass of the anvil electrode. The currents in the primary also increase, though at a gradually diminishing rate, as the pressure between the electrodes is increased, so that the increments of current, Δc, $\Delta c'$, $\Delta c''$, corresponding to the pressure-changes Δp, $\Delta p'$, $\Delta p''$, have increasing values up to some point, as a, after which they decrease. This being the case, it is evident that the current in the secondary will at first increase to a maximum, and afterwards diminish, since the currents in the secondary corresponding to pressures p, p', p'', etc. will be proportioned to Δc, $\Delta c'$, $\Delta c''$, etc., and this is precisely the curve which is obtained in the experiments. The explanation just offered seems therefore to be the true one.

The matter was still further tested by carrying out a set of experiments similar to those already described, except that the variations in normal pressure were brought about by means of a spring instead of by adding weights. In such a case the successive values of Δp in the curve (Fig. 2) would be of the same magnitude, while Δc would continually diminish. The current in the secondary should therefore have its maximum value when the initial normal pressure is least, and continually diminish as that pressure becomes greater.

The experimental results verified this conclusion, as will be seen by reference to Figure 3, in which the normal pressures are represented by abscissas, and the currents in the secondary by ordinates, as before. The curve is approximately a straight line. It is possible that the deviations from this are due to instrumental imperfections, as the apparatus used did not allow of more than an approximate determination of the pressure applied by the spring.

Rogers Laboratory of Physics,
June, 1888.

IX.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXXII. — RESEARCHES ON MICROPHONE CURRENTS.

By Charles R. Cross and Annie W. Sabine.

Presented November 14, 1888.

In continuation of studies described in former papers from the Rogers Laboratory, the authors have observed the variations in the secondary current which occur under different circumstances as to mass and normal pressure when the material of the electrodes of a microphone is varied. The methods and apparatus employed were identical with those described in the immediately preceding paper in these Proceedings (page 89).

In the first series of experiments both electrodes were made of the same material, the hammer electrode being a very small button, and the anvil electrode a large one, as in the Blake transmitter. As the mass and pressure upon the anvil electrode were varied, the currents in the secondary at first increased up to a maximum, and afterwards diminished, as shown in the article just referred to, as well as in the curves given with the present paper. Tables I. to XVI. give the numerical results obtained, and Figures 1 to 14 are curves showing the relations between the variables, the loads being abscissas, and the corresponding currents in milliampères the ordinates. The unit of weight adopted was $\frac{8}{10}$ of a gram. The remarks in the third column of the tables indicate the nature of the sound heard in a receiving telephone placed in the secondary circuit. The current was in all cases zero when the load was zero.

TABLE I.

Electrodes. — *Iron, Iron.*

Load.	Current.	Remarks.
1	.19	Sound rough and unsteady.
2	.24	Shrill, clear, metallic, unsteady.
3	.16	" " " "

TABLE II.

Electrodes. — *Platinum, Platinum.*

Load.	Current.	Remarks.
1	.43	
2	.62	Quality good ; fluttering.
3	.73	“ “ metallic.
4	.23	“ “ “
5	.10	“ “ fluttering.

TABLE III.

Electrodes. — *Carbon, Carbon.*

Load.	Current.	Remarks.
1	.44	Harsh ; loud.
2	.63	“ “
3	.71	Quality good ; fluttering.
4	.67	“ “ slight fluttering.
5	.27	“ “ faint fluttering.
6	.18	“ “ “ “
7	.12	“ “ “ “

TABLE IV.

Electrodes. — *Platinum, Carbon.*

Load.	Current.	Remarks.
1	.43	Harsh and loud.
2	.59	“ “
3	.67	Quality good and clear, some fluttering.
4	.59	“ “ “ “ “
5	.12	Faint, fluttering.
6	.09	“ “

TABLE V.

Electrodes. — *Carbon, Platinum.*

Load	Current.	Remarks.
1	.445	Harsh and loud.
2	.61	Clear : good quality.
3	.66	Clear ; some fluttering.
4	.63	Faint ; good quality ; some fluttering
5	.29	“ “ “ “ “
6	.20	“ “ “ “ “

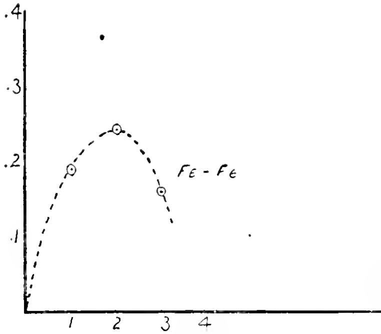

FIG. 1.

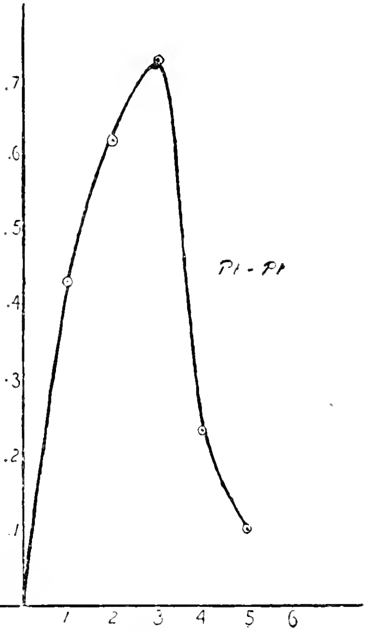

FIG. 2.

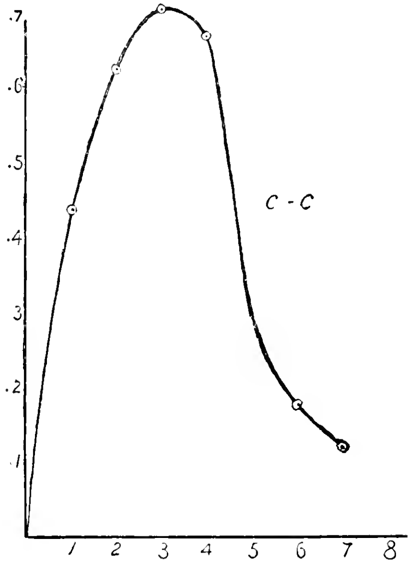

FIG. 3.

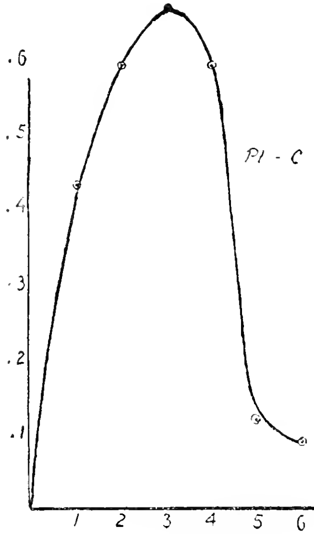

Fig. 4.

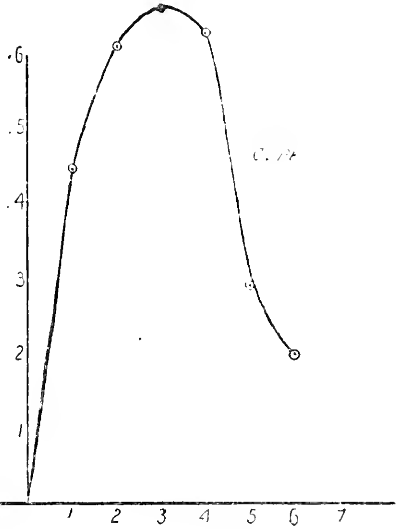

Fig. 5.

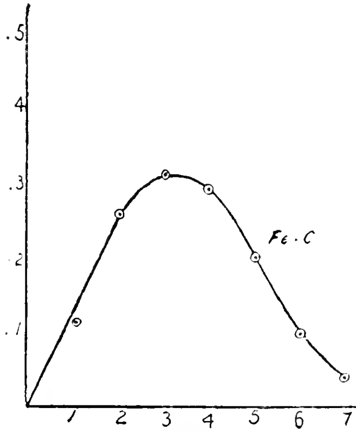

Fig. 6.

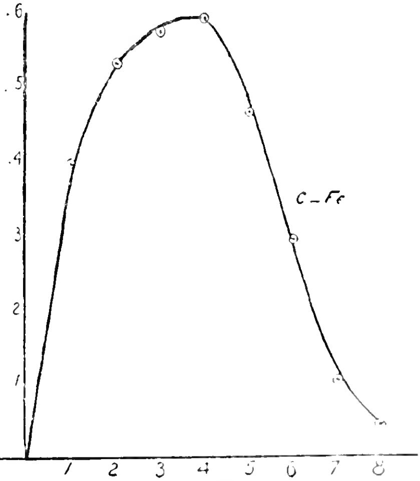

Fig. 7.

TABLE VI.

Electrodes. — *Iron, Carbon.*

Load.	Current.	Remarks.
1	.115	Harsh, irregular noise.
2	.260	" " "
3	.310	" " "
4	.290	Clear, good quality; faint.
5	.200	Faint; slight fluttering.
6	.095	Faint.
7	.040	"

TABLE VII.

Electrodes. — *Carbon, Iron.*

Load.	Current.	Remarks.
1	.395	Harsh and loud.
2	.530	Clear, shrill, good quality.
3	.570	Clear; fluttering.
4	.590	Quality good; slightly harsh.
5	.460	" " " "
6	.290	" " " "
7	.100	Very faint.
8	.040	"

TABLE VIII.

Electrodes. — *Platinum, Platinum.*

Load.	Current.	Remarks.
1	.450	Harsh and loud.
2	.560	" "
3	.670	Uncertain; sometimes good quality.
4	.230	Harsh; fluttering.

TABLE IX.

Electrodes. — *Carbon, Carbon.*

Load.	Current.	Remarks.
1	.360	Harsh and loud.
2	.560	Somewhat shrill; good quality.
3	.620	Good quality, somewhat rough.
4	.545	" " fluttering.
4.5	.225	Faint and rough.
5	.140	Faint.
5.5	.050	"

TABLE X.

Electrodes. — *Iron, Iron.*

Load.	Current.	Remarks.
1	.140	
2	.310	Quality good.
3	.270	
4	.180	

TABLE XI.

Electrodes. — *Platinum, Carbon.*

Load.	Current.	Remarks.
1	.210	Rough.
2	.420	“
3	.540	Quality good ; loud.
4	.630	“ “ slight fluttering.
5	.120	“ “ faint fluttering.
6	.070	“ “ “ “

TABLE XII.

Electrodes. — *Carbon, Platinum.*

Load.	Current.	Remarks.
1	.260	
2	.440	Shrill and loud.
3	.530	Clear, loud, good quality.
4	.620	“ “ “ “
5	.555	Fainter and rougher.

TABLE XIII.

Electrodes — *Iron, Carbon.*

Load	Current.	Remarks.
1	.240	Sound uncertain.
2	.300	
3	.310	Clear ; good quality.
4	.290	“ “ “
5	.180	“ “ “ faint.
6	.099	“ “ “ “

TABLE XIV.

Electrodes. — *Carbon, Iron.*

Load.	Current.	Remarks
1	.345	Rough, steady.
2	.515	
3	.615	Good quality.
4	.560	“ “
5	.235	Faint, rough.
6	.140	Faint ; clear

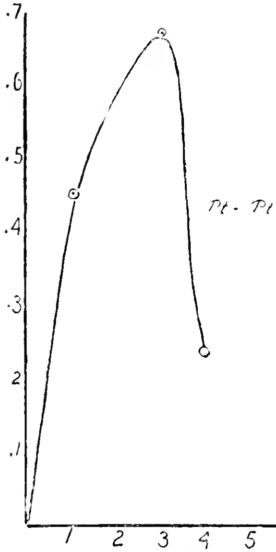

FIG. 8.

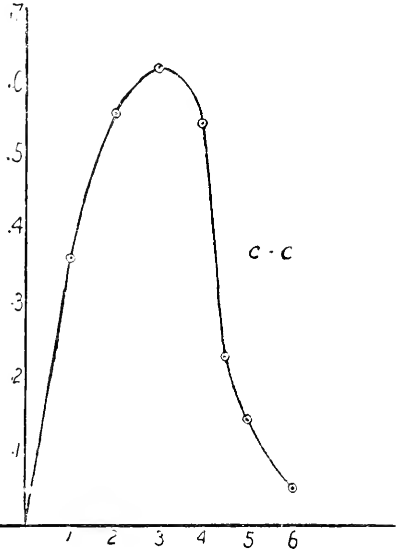

FIG. 9.

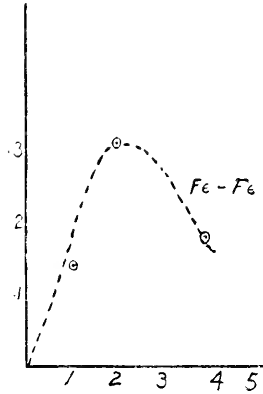

FIG. 10.

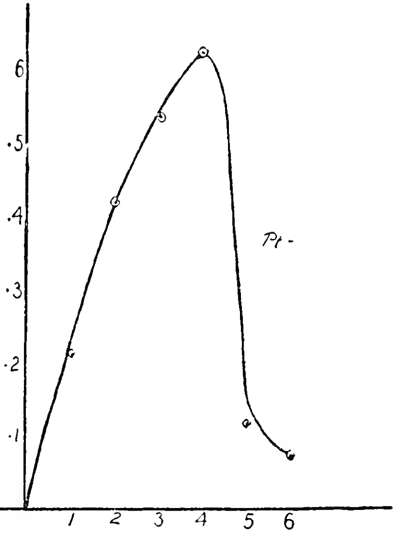

FIG. 11.

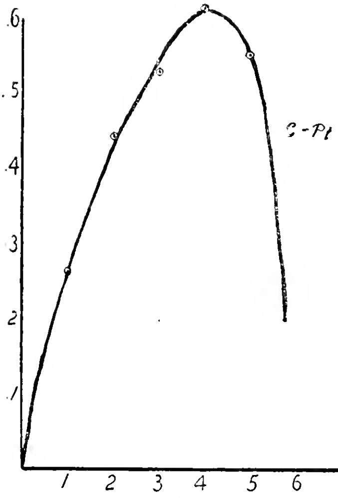

FIG. 12.

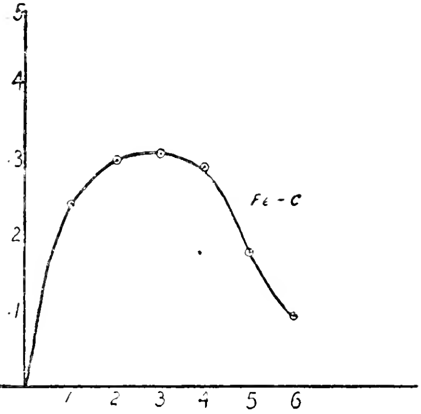

FIG. 13.

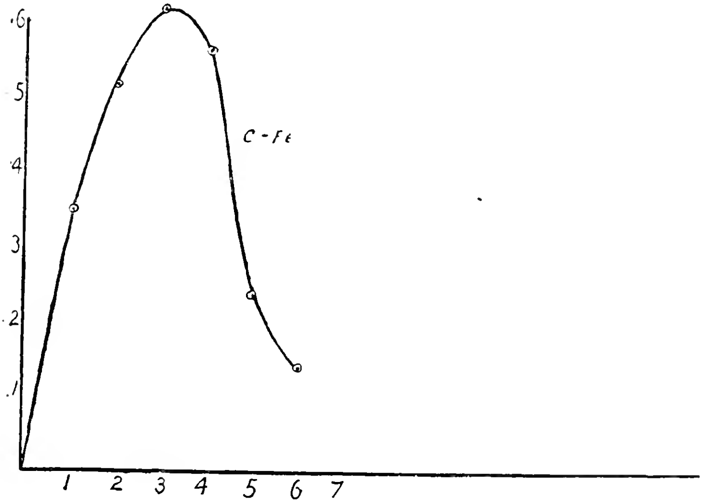

FIG. 14.

TABLE XV.

ELECTRODES. — *Copper, Carbon.*

Load.	Current.	Remarks.
1	.390	Rough and loud.
1.5	.490	" "
2	.590	" "
2.5	.550	" "
3	.250	" "
3.5	.130	" "

TABLE XVI.

ELECTRODES. — *Carbon, Copper.*

Load.	Current.	Remarks.
1	.240	Good quality; fluttering.
2	.520	" " "
3	.600	" " "
4	.660	" " "
5	.240	" " "
6	.090	" " "

Figures 1 to 3 show very well the characteristics of the substances iron, platinum, carbon. Comparing the curves for carbon and platinum (Figs. 2, 3), it will be seen that the maximum current obtained under the conditions of the experiment was about the same in both cases. But the current falls off far more rapidly with platinum as the pressure is further increased, thus giving to carbon a greater working range of pressure-variation within which it can be practically used in a microphone transmitter, a fact long since recognized in practice. Iron (Fig. 1) has a considerable range, but the current produced is not great.

Tables IV. to VIII., and Figures 4 to 8, illustrate the results obtained when the electrodes were of different materials, the substance of which the anvil electrode is made being the first mentioned. In the experiments now particularly referred to, the two electrodes were made of the customary size, the hammer small and the anvil large.

An inspection of the curves shows that the character of the result obtained under these circumstances was determined chiefly by the material of the anvil rather than of the hammer electrode. This is particularly well illustrated in the case of iron and carbon, as shown in Figures 6 and 7.

This difference persisted even when the hammer and anvil electrodes were made of the same size and shape, as will be seen by an inspection of Tables IX. to XVI. and Figures 9 to 14. We have still to determine whether the same peculiarity would be observed with other modes of mounting the electrodes.

Besides the foregoing results, we have made a determination of the actual strength of the working currents employed on telephone lines. The values previously obtained in the Laboratory had been ascertained from experiments on very short experimental circuits. But through the courtesy of the Long Distance Telephone Company, we were able to put our measuring apparatus in circuit both with the city telephone lines and with one of the long lines to New York.

Several interesting results were thus reached, as shown in Table XVII. The first column gives the name of the transmitter employed, the second the nature of the sound transmitted, the third the location of the transmitter, the fourth the strength of the telephone current in milliampères. The length of the line from 95 Milk Street to the Institute was about two miles; that of the line to New York was two hundred and sixty miles.

TABLE XVII.

Transmitter	Sound.	Locality of Transmitter.	Current.
Blake	Talking	95 Milk Street	.185
"	Singing	"	.52
Hunnings	Talking	"	.28
"	Singing	"	.78
"	Talking	New York	.02
"	Counting	"	.02−
"	Organ Pipe	"	.01+
"	Counting	Rogers Laboratory	2.05
"	Talking	"	2.20
"	Organ Pipe	"	1.24

The speakers were Dr. W. W. Jacques of Boston and Mr. F. A. Pickernell of New York, who kindly aided us in our work. They are both experts in the use of the telephone, and accustomed to work with each other. The pitch, as well as the loudness of the sounds used, was kept as nearly as possible the same. The vocal sounds transmitted were spoken in a very loud tone, and close to the transmitter.

The figures obtained with the long line to New York are very instructive, as they give some knowledge of the loss of current which is sustained in long distance telephony. When the transmitter was at the Institute, near to the dynamometer, the full current produced by the former passed through the latter instrument, while, when the transmitter in New York was the one used, it is clear that only what was left after all leakage, etc. passed through the measuring instrument. Assuming the sounds as produced at the two stations to be of approximately the same pitch and loudness, it appears that only about one one-hundredth of the original current produced at the transmitting station is finally utilized at the receiving station. It further appears from these figures that about 13 per cent of the current produced at the transmitting station was utilized in ordinary telephonic transmission over the local lines from 95 Milk Street to the Laboratory.

ROGERS LABORATORY OF PHYSICS,
June, 1888.

X.

ON PENTAMIDOBENZOL.

By A. W. Palmer and C. Loring Jackson.

Presented February 13, 1889.

Nearly two years ago, in a paper upon Tribromtrinitrobenzol,* one of us in conjunction with J. F. Wing described some attempts to reduce triamidotrinitrobenzol, and announced that the work would be continued. Before doing this, however, it seemed advisable to try similar experiments with the triamidodinitrobenzol, as this substance can be obtained much more easily, and the experience gained in this way would be useful when we returned to the much less accessible trinitro compound. Accordingly, we have undertaken together the work on the dinitro compound, which has led, as we had hoped, to the preparation of the chloride of pentamidobenzol; but, shortly after we had sent to the *Berichte der deutschen chemischen Gesellschaft* a preliminary notice† of this substance, a number of the same journal reached us containing a paper by Andrew Barr‡ in which the chloride of pentamidobenzol was also described, and, as this paper, although it came into our hands after our preliminary notice had been sent, was presented to the German Chemical Society a fortnight before ours was written, we have dropped this line of work in order to avoid interfering with Barr, or Merz, in whose laboratory the research of Barr was carried on, and publish in this paper the results which had been already obtained by us when we received Barr's paper.§ The method of making pentamidobenzol used by us is different from that of Barr, who pre-

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* These Proceedings, Vol. XXIII. p. 138.

† Ber. d. ch. G., 1888, p. 1706.

‡ Ber. d. ch. G., 1888, p. 1541.

§ The publication of this paper has been delayed until the present time, because the change of residence of one of us prevented us from finishing more promptly the study of trianilidodinitrobenzol, a substance which does not come into Barr's field of work.

pared the diamidotrinitrobenzol from the ethylether of trinitroresorcine and alcoholic ammonia, and then reduced this product with tin and hydrochloric acid, whereas we submitted to a similar reduction the triamidodinitrobenzol made by the action of alcoholic ammonia on tribromdinitrobenzol. Both this triamido and the corresponding trianilido compound are new, and an account of them is therefore included in this paper.

Triamidodinitrobenzol, $C_6H(NH_2)_3(NO_2)_2$.

This substance was prepared by treating tribromdinitrobenzol,* melting point 192°, with alcoholic ammonia; but this action takes place much less easily than in the case of the corresponding trinitro compound, for whereas that was attacked by alcoholic ammonia in the cold, and the reaction was rendered complete by short boiling in a flask with a return condenser, the dinitro compound gave no action with alcoholic ammonia in open vessels, but it was necessary to heat the two substances under pressure in the water bath to bring about the reaction.

As we had no digester fit for this purpose, we were obliged to heat the mixture in soda-water bottles, which were kept in a boiling water bath for about eight hours. The contents of the bottles at the end of this time consisted principally of a mixture of dark reddish yellow needles with nearly black amorphous masses. There was also a colored alcoholic solution, which on evaporation left a red amorphous substance with a comparatively low melting point; but this was formed in such small quantities that we did not attempt to study it beyond ascertaining the fact that it is not altered by further heating with alcoholic ammonia. The tribromtrinitrobenzol, when treated with alcoholic ammonia, forms a similar by-product,† soluble in alcohol, which is now under investigation. The two products of the reaction which were not dissolved in the alcohol were separated mechanically, washed thoroughly with various solvents, and analyzed without further purification, as they both showed such a slight solubility in all the common

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* The tribrombenzol used in making this substance must be purified by crystallization from alcohol after it has been distilled, as, if this crystallization is omitted, a substance melting in the neighborhood of 95° remains mixed with the tribrombenzol, and gives rise to very impure products after the treatment with nitric acid. The nature of this impurity will be considered in another paper.

† These Proceedings, Vol. XXIII. p. 145.

solvents that a crystallization of them in any quantity was a matter of very great difficulty. In spite of the great difference in their appearance they both had the same composition, that of the expected triamidodinitrobenzol, as is shown by the following analytical data, in which Analyses I. and II. were made with the reddish yellow needles, Analysis III. with the black amorphous body.

I. 0.3000 grm. of the substance crystallized in yellow needles gave on combustion 0.3710 grm. of carbonic dioxide and 0.1085 grm. of water.

II. 0.1510 grm. of the crystalline substance like that used in I. gave 42.4 c.c. of nitrogen at a temperature of 8°.6 and a pressure of 748.5 mm.

III. 0.3028 grm. of the substance deposited in black amorphous masses gave on combustion 0.3778 grm. of carbonic dioxide and 0.0925 grm. of water.

	Calculated for		Found.	
	$C_6H(NH_2)_3(NO_2)_2$.	I.	II.	III.
Carbon	33.80	33.73		34.02
Hydrogen	3.28	4.02		3.39
Nitrogen	32.87		33.31	

Properties. — The triamidodinitrobenzol, as deposited by the action of alcoholic ammonia on tribromdinitrobenzol, forms either reddish yellow needles, or nearly black amorphous masses. When the substance is crystallized from a mixture of chloroform and alcohol, which can be done only with great difficulty on account of its slight solubility, it forms microscopic yellow plates, or broad flattened prisms, and, if the treatment with the mixed solvents is carried on in a continuous extracter, these crystals collect into characteristic yellow masses shaped like an S or U. It does not melt even above 300°, but is decomposed if heated more intensely. It is very slightly soluble in alcohol or chloroform, although it imparts a perceptible yellow color to these solvents, more soluble in nitrobenzol, but cannot be obtained in crystals easily from this solution, so that a mixture of alcohol and chloroform is the best solvent for it. In the other common solvents it is either entirely insoluble or very slightly soluble. In this respect it resembles the corresponding trinitro compound, but it is, if there is any difference, slightly more soluble than that. The substance does not form definite salts, although it dissolves easily in concentrated hydrochloric acid forming a dark red liquid. It shows therefore a greater tendency to form salts than the triamidotrinitrobenzol, which is insoluble in strong hydrochloric acid.

Trichloride of Pentamidobenzol, $C_6H(NH_2)_2(NH_3Cl)_3$.

To prepare this substance, some of the triamidodinitrobenzol (either the crystalline or amorphous) was heated on the water bath in a flask with strong hydrochloric acid, a very strong solution of stannous chloride, granulated tin, and some pieces of platinum foil. After some hours the very deep red solution had lost most of its color, but still showed a dirty brownish yellow tint; it was then allowed to cool, when crystals were deposited, which increased in quantity, if the liquid was saturated with hydrochloric acid gas. The crystals were filtered out, and washed with concentrated hydrochloric acid, then, as we did not succeed in removing the salts of tin completely by precipitation from an aqueous solution with hydrochloric acid gas,* the substance was dissolved in very little water and the solution saturated with sulphuretted hydrogen, the stannic sulphide formed was filtered out, and the filtrate, after freeing it from sulphuretted hydrogen with a stream of air, once more saturated with hydrochloric acid gas, which threw down the substance in an essentially pure state and nearly white. In all this work care must be taken to avoid heating the solutions, as the chloride of pentamidobenzol, after the reducing agents have been removed, is easily decomposed by heat into a black tar; the solutions, therefore, should never be concentrated by evaporation on the water bath. We obtained a less pure substance also, if the solution in water and precipitation with hydrochloric acid gas was repeated more than once. The crystals were dried at first in a desiccator over calcic oxide, calcic chloride, and potassic hydrate, and finally heated to 70°–80° for about five hours in an air bath. On analysis they gave the following results.

I. 0.2372 grm. of the substance gave on combustion 0.2445 grm. of carbonic dioxide and 0.1157 grm. of water.

II. 0.1827 grm. of the substance gave 0.1880 grm. of carbonic dioxide and 0.0880 grm. of water.

III. 0.1533 grm. of the substance gave 35.8 c.c. of nitrogen at a tempernature of 14°.2 and a pressure of 750 mm.

IV. 0.1457 grm. of the substance gave according to the method of Carius 0.2377 grm. of argentic chloride.

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* Barr succeeded in removing all the tin from his preparation in this way.

	Calculated for $C_6H(NH_2)_2(NH_3Cl)_3$.	Found I.	II.	III.	IV.
Carbon	27.43	28.11	28.06		
Hydrogen	5.33	5.42	5.35		
Nitrogen	26.67			27.08	
Chlorine	40.58				40.33

Considering the ease with which the substance is decomposed, the agreement between these results and those calculated from the formula is as close as can be expected. The method of purification described above, however, does not always give such satisfactory results. Samples from two other preparations gave numbers which differed by about one per cent from those corresponding to the formula, the chlorine being too low and the other constituents too high by this amount; but we ascribe this to partial decomposition of the substance during the purification, as both of these specimens were much darker in color than that which gave the more satisfactory analyses. The objection which might be founded on these results, that our substance was not a definite compound, but a mixture of ammonic chloride with some organic body less rich in nitrogen than the chloride of pentamidobenzol, is removed by the microscopic examination of the substance, which showed that it consisted of well developed rhombic crystals without any admixture whatever, to which may be added the fact that chlorplatinic acid gave no precipitate with a solution of the substance.

Properties. — The trichloride of pentamidobenzol, as precipitated by hydrochloric acid from its aqueous solution, is seen under the microscope to consist of rather thick well developed transparent rhombic plates, with the sharper angles truncated by a single plane. It is colorless when first prepared, but soon turns pink or gray, and on long standing passes through dark brown to black, a change which is much accelerated by heat; yet even after it has become nearly black, if examined with the microscope, it is found to retain unaltered its crystalline form, and the individual crystals are still transparent, although very much darkened, so that this change in color seems to have taken place only superficially. It is very easily soluble in water, but only slightly soluble in strong hydrochloric acid, a property which is useful in the purification of the substance. The aqueous solution decomposes quickly when heated, a black tar being formed, and a similar change takes place more slowly at ordinary temperatures, the solution becoming at first clear pink, and then darkening through shades of red to black. The action of more violent oxidizing agents is described below, and resembles that of the air. The salt when dry or moistened with strong hydrochloric acid is much more stable than a solution, or the wet salt. The substance is sparingly soluble in alcohol and essentially insoluble in ether, benzol, or chloroform.

If ammonic hydrate is added with caution to a concentrated solution of the salt, a black jelly is precipitated; if the solution is dilute, no precipitate is formed, but the liquid takes on a pink color, which in a few minutes passes through purple and violet blue to a yellowish green; from this solution hydrochloric acid precipitates black flocks, which redissolve in an excess of the acid, or on the addition of ammonic hydrate. Sodic hydrate acts on the chloride in the same way. The free base seems to be insoluble in ether; at any rate, nothing was extracted by this solvent from an aqueous solution of the salt, to which an excess of sodic hydrate had been added. It is evident from the observations just described, that the isolation of the free base would be a matter of great difficulty.

The foregoing results correspond to those of Barr in every respect except the crystalline form of the chloride, which he describes as white needles as fine as hairs. He also made the pentacetyl compound $C_6H(NHC_2H_3O)_5$.

Chlorplatinic acid with a solution of the trichloride of pentamidobenzol gives no precipitate at first, but after some time a slimy brown substance is deposited on the sides of the test-tube, evidently a product of oxidation. We are inclined to think, however, that the oxidizing agent is the oxygen of the air rather than the chlorplatinic acid, as a similar result was obtained by the action of picric acid. Benzaldehyd added to a solution of the salt also gave a tarry product.

When the trichloride of pentamidobenzol is treated with nitric acid and ferric chloride, a deep purple solution* is formed looking very much like potassic permanganate, and when an excess of the ferric chloride has been added, a brown flocculent precipitate is deposited, which when dried forms a hard mass of a brown color without crystalline form, since under the microscope it appears to be made up of sandy granules. It is slightly soluble in water, imparting to it a dark brown color. Preliminary analyses gave the following results.

0.1600 grm. of the substance on combustion gave 0.2592 grm. of carbonic dioxide and 0.0650 grm. of water.

0.1685 grm. of the substance gave according to the method of Carius 0.0797 grm. of argentic chloride.

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* Compare this with the action of air on a solution of the salt or of the free base described earlier in this paper.

	Found.
Carbon	44.18
Hydrogen	4.51
Chlorine	11.69

We were engaged on the study of this substance when we received Barr's paper, and accordingly stopped our work on this subject, and we publish these analyses only because they may be of use to any one who may continue the investigation of this substance, as it would be idle to try to derive a formula from them until they have been supported by further work. Barr also observed the formation of this substance, but did not attempt to study it carefully, or analyze it.

It seems probable that the pentamidobenzol, in addition to the trichloride, can form a *pentachloride*, as one of our first preparations, in which the reduction was carried on at a lower temperature than usual, yielded a substance which, dried at first in a desiccator over calcic chloride without any alkaline absorbent, and finally for a short time in an air bath at 90°, gave the following result on analysis.

0.1738 grm. of the substance gave 30.9 c.c. of nitrogen at a temperature of 6° and a pressure of 750 mm.

	Calculated for $C_6H(NH_3Cl)_5$.	Found
Nitrogen	20.86	21.37

The appearance of Barr's paper has prevented us from making another attempt to prepare this substance. If it is a definite compound, it is a very unstable one, as it gave off a distinct smell of hydrochloric acid.

Trianilidodinitrobenzol, $C_6H(C_6H_5NH)_3(NO_2)_2$.

This substance can be made by heating for a short time aniline with tribromdinitrobenzol in the proportion of six molecules of the base to one of the bromine compound. It seems that the two substances do not act on each other in the cold, or, if there is any action, it is a very slow one, and in this respect the dinitro compound differs from the tribromtrinitrobenzol, which acts on aniline quickly at ordinary temperatures. The product was purified by crystallizing it from alcohol till it showed the melting point 179°, dried at 100°, and analyzed with the following results.

I. 0.1820 grm. of the substance gave on combustion 0.4347 grm. of carbonic dioxide and 0.0760 grm. of water.

II. 0.1906 grm. of the substance gave 26 c.c. of nitrogen at a temperature of 12° and a pressure of 762 mm.

III. 0.1815 gr. of the substance gave 26 c.c. of nitrogen at a temperature of 17° and a pressure of 743 mm.

	Calculated for $C_6H(NHC_6H_5)_3(NO_2)_2$.	Found. I.	II.	III.
Carbon	65.31	65.13		
Hydrogen	4.30	4.64		
Nitrogen	15.88		16.24	16.24

Properties. — The trianilidodinitrobenzol, when crystallized from alcohol, forms vivid orange-red needles, which under the microscope appear as long prisms terminated by a single plane at angles not very far from right angles to the sides, occasionally groups of radiating needles are observed also. When crystallized from ether, it forms irregularly spherical crowded groups of short stout radiating prisms with blunt ends made up of several planes, a form which is decidedly characteristic. It melts at 179°, and is essentially insoluble in either cold or boiling water, or in ligroine; slightly soluble in cold alcohol, freely in hot; moderately soluble in ether, carbonic disulphide, glacial acetic acid, or acetone; freely soluble in benzol, or chloroform, but the substance is deposited from the two solvents last mentioned in an amorphous form, so that hot alcohol is the best solvent for it. Strong hydrochloric acid, either hot or cold, has no perceptible action on it. Strong nitric acid dissolves a very little, with a pale yellow color; strong sulphuric acid dissolves rather more of the substance, with a stronger yellow color. Upon heating it with either of these last two acids it is charred. It is therefore, as was to be expected, less basic in its properties than the triamidodinitrobenzol.

XI.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXXIII. — THE STRENGTH OF THE INDUCED CURRENT WITH A MAGNETO TELEPHONE TRANSMITTER AS INFLUENCED BY THE STRENGTH OF THE MAGNET.

By Charles R. Cross and Arthur S. Williams.

Presented November 14, 1888.

It is a well-known fact in practice, as well as an evident consequence of theoretical considerations, that the effectiveness of a magneto telephone when used either as a transmitter or as a receiver varies with the strength of the magnetism of the core. But the relation of the one to the other has never been studied, so far as we are aware.

Our investigations include a study of the changes in strength of the current produced by a magneto transmitter under varying conditions of magnetization, and of the magnitude of the momentary changes in the magnetic condition of the core of the receiving telephone when subjected to the action of undulatory or other brief currents, as influenced by the strength of the primitive permanent magnetization of the core. The present paper contains only the results of a series of experiments relating to the first of these, that is, to the effect of varying strength in the magnet of the transmitter, the study of the allied problem of the receiver being still in progress.

The apparatus employed consisted of a cylindrical bar of soft iron about $4\frac{1}{2}$ inches in length and $\frac{1}{4}$ of an inch in diameter, around one end of which was placed a coil of fine wire similar to that used in ordinary telephonic practice. The resistance of this coil was 100 ohms. It was placed in circuit with a ballistic mirror galvanometer, from whose deflection the momentary current produced in the coil by any variation in the strength of the core could be determined. The diaphragm, which was in all cases $2\frac{5}{16}$ inches in diameter, was in its usual place opposite the end of the magnet about which the wire coil was wound, and about $\frac{3}{100}$ of an inch from that end. By means of a rod carrying a cam moved by a weight, a rapid inward push of definite amount was given to the diaphragm, thereby inducing a current in the coil already referred to, and so deflecting the needle of the ballistic galvanometer. The soft iron bar was also surrounded by a second helix, through which was passed a current from a storage battery, serving to magnetize the core. A tangent galvanometer inserted in this circuit gave the strength of the magnetizing current. A magnetometer placed in the prolongation of the axis of the core, which last occupied an east and west position, made known the relative strengths of the field produced by the core under different conditions of magnetization.

Corresponding observations of the magnetometer reading, and of the current induced when the diaphragm was moved by the cam, were made throughout a widely varying range of strength of field, and the results were represented graphically by constructing a series of curves in which ordinates represent the relative strength of field, and abscissas the current due to a given predetermined throw of the diaphragm (about $\frac{1}{100}$ of an inch), as ascertained from the readings of the ballistic galvanometer.

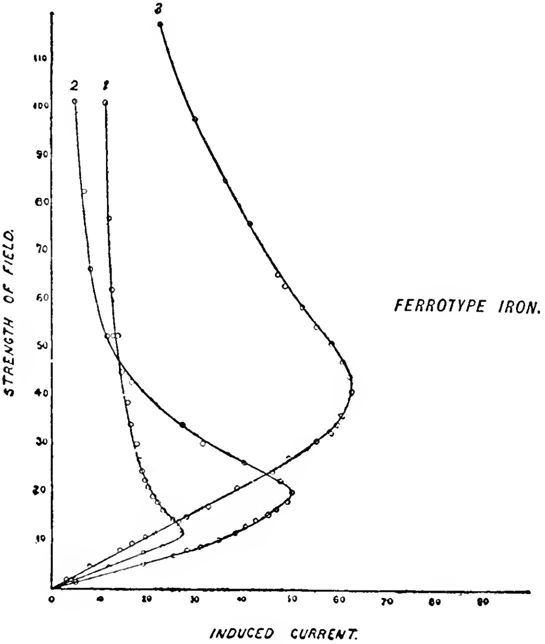

Fig. 1.

One of these curves is shown at 1, Figure 1, the core in this case being a cylindrical bar of Norway iron $4\frac{1}{2}$ inches long and $\frac{1}{4}$ of an inch in diameter, and the diaphragm an ordinary disk of ferrotype iron $2\frac{7}{16}$ inches in diameter and $\frac{1}{100}$ of an inch thick (No. 31 B. W. G.).

Table I. gives the data from which Figure 1 was constructed. The strength of field is given in terms of the tangents of the angles of deflection of the magnetometer needle. The induced current is given in arbitrary units, as only relative values are needed. A determination of the value of the deflections was made by observing the excursion due to the discharge of a condenser through the ballistic galvanometer, and it was found that the abscissa 100 on the curves corresponds to a sudden discharge of approximately 0.00000097 of a coulomb through the coils of the galvanometer.

TABLE I.

Core, Norway Iron. — Diaphragm, Disk of Ferrotype Iron, No. 31.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
. . .	0.7	.211	20.5
.016	3.3	.229	19.8
.044	12.0	.248	19.2
.058	19.3	.270	18.7
.089	23.3	.302	18.0
.118	27.0	.342	16.9
.141	26.8	.390	16.1
.132	26.6	.454	14.7
.146	25.3	.530	13.3
.164	23.8	.625	12.7
.182	22.5	.773	12.0
.196	21.6	1.014	11.5

Cores of Bessemer steel and of untempered soft steel were also used, with results given in Tables II. and III.

TABLE II.

Core, Bessemer Steel. — Diaphragm, Disk of Ferrotype Iron, No. 31.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.005	2.0	.279	17.8
.030	7.7	.333	16.7
.082	20.7	.396	15.0
.137	26.7	.507	13.5
.160	24.8	.625	11.7
.191	21.2	.748	10.8
.213	19.3	.907	9.7
.248	18.6	1.099	8.7

TABLE III.

CORE, UNTEMPERED SOFT STEEL. — DIAPHRAGM, DISK OF FERROTYPE IRON, No. 31.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.031	8.2	.275	18.0
.049	12.0	.321	16.5
.089	22.0	.388	15.2
.137	25.9	.473	13.8
.157	24.9	.618	12.7
.171	22.9	.776	11.0
.194	21.1	1.011	9.5
.216	19.7		

An examination of Figure 1, as well as of the various curves following it, will show that the effect of increasing the strength of the magnet of the transmitter is in all cases to cause at first a rather rapid increase of the strength of the induced current, which later increases less rapidly, rising soon to a maximum value, from which it falls off, at first rapidly, and afterwards more and more slowly as the strength of the field is further increased. We proceed to consider the explanation of these results.

It is evident that three distinct sources of variation exist to affect the current furnished by a magneto transmitter as the strength of the magnet is increased. First, the direct effect of the increased strength of field in which the diaphragm moves is to increase proportionally the strength of the induced current, since it increases correspondingly the rate of change in the number of lines of force enclosed by the coil of the instrument; second, an approach toward saturation of the magnet, so far as it alone is concerned, will tend to diminish the induced current, on account of the smaller variation in the strength of the pole due to a given motion of the diaphragm; and, third, the nearer approach toward saturation of the diaphragm will have the same tendency.

The rapid rise in the induced current at the beginning is of course due to the predominating influence of the increasing strength of the field in which the diaphragm moves, as both core and diaphragm are then but slightly magnetized. The subsequent changes in the current must be explained by a consideration of the increasing magnetization of either the core or the diaphragm, or both.

It will be seen by comparing Tables I., II., and III., that the value of the maximum induced current for a given excursion of the diaphragm is approximately the same with all the three cores used, and that the same is true as to the strength of field corresponding to this maximum current. Moreover, saturation curves constructed for the several cores showed that in all cases the magnet was still very far removed even from half-saturation when the maximum induced current was obtained. From these facts it appears that the degree of saturation of the magnet is practically unimportant, so far as the general results shown in Figure 1 are concerned.

It remains to observe the part played by the increasing magnetization of the diaphragm. Other things remaining the same, as this approaches more and more closely towards saturation the increase in the number of lines of force passing between it and the magnet on the approach of the diaphragm to the magnet must become smaller and smaller, and this change will tend to oppose the effect of the increased absolute strength of the magnetizing force. The small mass of the diaphragm will evidently cause it to show the effect of an approach to saturation while the core is far below that condition. And such an action will clearly explain the observed changes in the current strength.

In order to test this matter still further, the experiment was tried of varying the mass and material of the diaphragm.

The results are shown by the curves in Figures 1, 2, and 3, which are constructed from the data given in Tables I. to X.; further results of the same character are given in Tables XI. and XII.

TABLE IV.

Core, Norway Iron. — Diaphragm, Two superposed Disks of Ferrotype Iron, No. 31.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.016	5.0	.184	49.3
.054	19.3	.205	50.2
.070	25.7	.229	48.0
.081	28.5	.266	40.3
.089	30.2	.306	31.8
.103	35.0	.342	27.7
.119	38.5	.433	16.7
.133	40.7	.530	11.9
.144	42.7	.667	8.3
.155	45.7	.830	7.0
.169	47.0	1.018	5.0

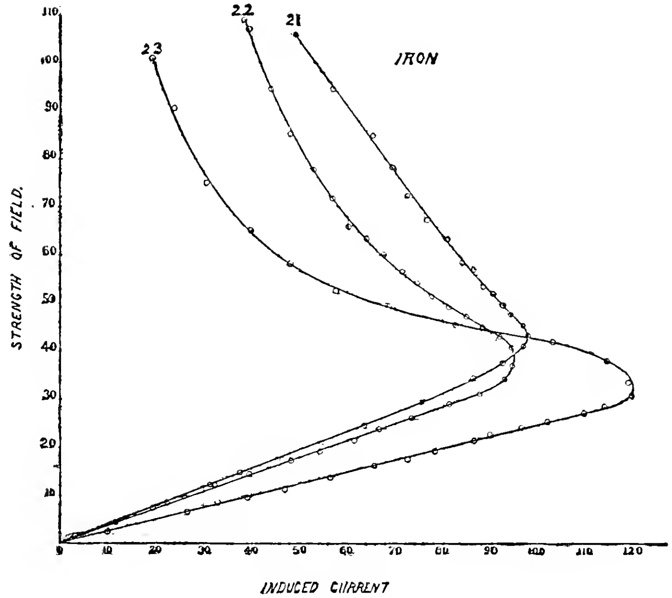
110
100
90
80
70
60
50
40
30
20
10
STRENGTH OF FIELD.
23
22
21
IRON
0
10
20
30
40
50
60
70
80
90
100
110
120
INDUCED CURRENT

Fig. 2.

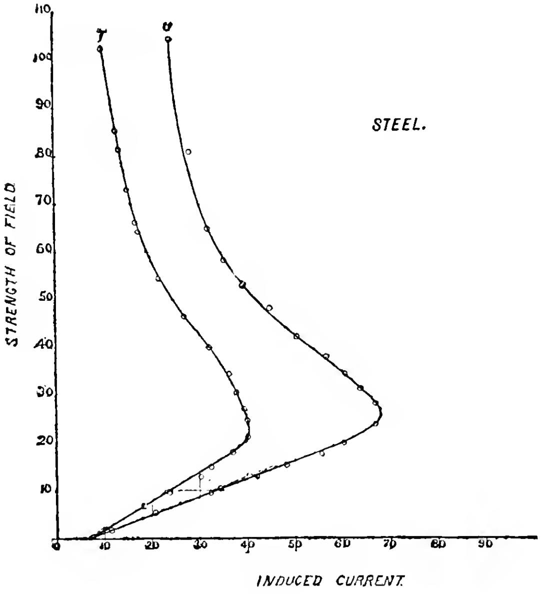
110
100
90
80
70
60
50
40
30
20
10
STRENGTH OF FIELD
7
8
STEEL.
0
10
20
30
40
50
60
70
80
90
INDUCED CURRENT

Fig. 3.

TABLE V.

CORE, NORWAY IRON. — DIAPHRAGM, THREE SUPERPOSED DISKS OF FERROTYPE IRON, No. 31.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.000	0.5	.346	59.7
.018	3.2	.366	60.7
.047	8.0	.390	61.3
.079	14.2	.416	63.0
.084	14.7	.445	62.3
.096	17.0	.479	61.0
.110	19.7	.514	58.5
.118	21.8	.550	55.7
.135	25.5	.591	52.4
.151	28.3	.637	48.7
.175	33.0	.659	47.3
.213	39.0	.765	41.7
.249	46.3	.854	36.7
.277	49.8	.983	30.0
.313	55.3	1.180	22.8
.329	58.7		

TABLE VI.

CORE, NORWAY IRON. — DIAPHRAGM, SHEET IRON, No. 21.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
. . .	0.3	.456	96.7
.016	3.1	.477	94.0
.058	13.7	.499	92.5
.082	20.3	.521	90.5
.102	25.2	.536	88.3
.125	31.2	.573	86.7
.150	37.8	.584	84.0
.178	45.5	.637	81.0
.213	54.7	.675	76.7
.249	63.8	.724	72.3
.296	75.5	.784	69.3
.348	86.2	.851	65.6
.378	92.3	.949	57.3
.416	96.7	1.061	49.1
.437	97.8		

TABLE VII.

Core, Norway Iron. — Diaphragm, Sheet Iron, No. 22.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
...	1.7	.410	94 2
.018	4.7	.431	92.0
.047	11.7	.452	88.3
.075	19.7	.473	85.0
.088	22.3	.494	81.2
.100	26.0	.516	77.5
.123	32.5	.541	74.7
.146	39.5	.566	71.3
.171	48.2	.601	67.7
.194	54.2	.635	64.0
.218	61.3	.659	60.0
.240	66.9	.719	56.7
.262	73.2	.779	53.0
.292	81.3	.851	48.0
.313	87.7	.946	44.0
.342	92.7	1.072	39.3
.372	94.3	1.091	38.3

TABLE VIII.

Core, Norway Iron. — Diaphragm, Sheet Iron, No. 23.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
...	1.7	.272	109.3
.026	10.0	.289	113.8
.068	26.8	.310	119.3
.086	33.0	.339	118.6
.096	39.0	.382	114.1
.116	47.0	.420	102.9
.139	56.3	.458	82.2
.162	65.8	.499	68.7
.176	72.3	.529	57.6
.194	78.3	.582	48.0
.216	86.4	.652	39.9
.229	90.0	.751	30.8
.242	96.3	904	23.7
.255	101.8	1.011	19.0

TABLE IX.

Core, Norway Iron. — Diaphragm, Steel, No. 26, Untempered.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.004	7.7	.281	66.7
.019	11.5	.313	63.8
.054	20.5	.342	60.4
.095	32.2	.380	56.3
.105	34.5	.422	50.5
.128	42.0	.483	44.7
.153	48.3	.530	39.0
.178	55.7	.584	35.3
.200	60.3	.652	32.0
.227	64.3	.810	28.2
.236	67.0	1.043	24.3

TABLE X.

Core, Norway Iron. — Diaphragm, Steel, No. 26, Tempered.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.002	7.8	.344	36.3
.019	10.4	.400	32.0
.068	18.5	.466	26.9
.096	23.8	.545	21.7
.128	30.3	.642	17.7
.151	32.4	.662	17.3
.180	37.0	.732	15.2
.214	40.2	.816	13.8
.246	40.0	.854	13.0
.272	39.5	1.025	10.0
.304	37.9		

TABLE XI.

Core, Norway Iron. — Diaphragm, Steel, No. 22, Untempered.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.007	6.2	.272	36.7
.023	8.0	.302	34.8
.070	17.3	.340	33.0
.103	23.0	.392	29.7
.121	26.4	.458	26.3
.139	30.1	.538	23.2
.157	32.8	.566	23.0
.176	35.0	.647	21.7
.202	37.1	.773	19.8
.224	34.9	1.046	17.6
.246	37.0		

TABLE XII.

Core, Norway Iron. — Diaphragm Steel, No. 30, Tempered.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.007	6.2	.272	36.7
.023	8.0	.302	34.8
.070	17.3	.340	33.0
.103	23.0	.392	29.7
.121	26.4	.458	26.3
.139	30.1	.538	23.2
.157	32.8	.566	23.0
.176	35.0	.647	21.7
.202	37.1	.773	19.8
.224	...	1.046	17.6
.246	37.0		

TABLE XIII.

Core, Norway Iron. — Diaphragm, Steel, No. 30, Untempered.

Strength of Field.	Induced Current.	Strength of Field.	Induced Current.
.005	5.2	.331	31.2
.031	11.7	.376	28.9
.082	24.2	.437	26.0
.103	29.7	.512	23.3
.130	37.7	.632	20.4
.160	41.9	.735	19.7
.200	38.3	.819	18.0
.231	36.2	.956	16.3
.272	35.2		

Curve 2, Figure 1, represents the results when two of the ordinary ferrotype diaphragms were superposed, forming a diaphragm of double thickness, and Curve 3 of the same figure shows the results when three such diaphragms were superposed. Each diaphragm was 0.01 of an inch thick. The curves of Figure 2, marked 21, 22, 23, respectively, show the results of similar experiments with diaphragms of sheet iron whose thickness was 0.030, 0.027, 0.024 of an inch, respectively (Nos. 21, 22, 23, B. W. G.). Figure 3 shows the results when a steel diaphragm 0.017 of an inch thick (No. 26) was used, the curve *U* being that for untempered steel, and *T* that for tempered steel. Steel diaphragms respectively 0.026 and 0.012 of an inch thick (Nos. 22 and 30) gave similar results, as will be seen from Tables XI., XII., and XIII.

An inspection of these curves shows immediately that the greater the strength of the field required to saturate the diaphragm, the greater is the strength of the field at which the maximum current occurs. Thus in Figure 1 the maximum current with Curve 1 corresponds to a strength of field of about 12 units of the scale used, while with Curves 2 and 3 the corresponding strengths of field are 20 and 43 units respectively. Also in Figure 2 the maximum currents will be seen to correspond to greater strengths of field in proportion to the thickness of the diaphragm, and in Figure 3 similar though less marked results hold for tempered as compared with untempered steel of the same thickness.

It would also be expected that the value of the maximum current would be greater with a thick than with a thin diaphragm. This was usually the case in our experiments. Thus the Curves 1, 2, 3, of Figure 1 give maximum currents of 27.5, 50.2, and 62.6 units respectively. Results of a similar nature are shown by Figure 3, the maximum current with the untempered diaphragm being far greater than with the tempered one. Curve No. 23 of Figure 2 is apparently an exception. It is probable, however, that this is in appearance only, and that the three curves of that figure are not strictly comparable with one another. The rigidity of the diaphragms here used, especially of the thicker ones, is considerable, and any slight yielding of the supports of the rod which carried the cam would prevent the actual throw of the diaphragm from being as great when this had considerable thickness, and would greatly diminish the strength of the current produced.

The peculiarity of Curve 2, as compared with 1 and 3, is probably caused by the want of both magnetic and mechanical continuity in the material of the multiple plate formed by the several diaphragms used.

In those cases where steel diaphragms were employed, there was always a notable induced current, even when the reading of the magnetometer was zero. This was probably due to a slight residual magnetization of the diaphragms.

The results stated in this paper may serve to explain a phenomenon which has seemed somewhat obscure. Frequent attempts have been made to increase the efficiency of a magneto transmitter by polarizing the diaphragm as well as the magnet, a common way of doing this being to employ a horseshoe magnet one leg of which is in contact with the edge of the diaphragm, while the other, about which the coil is wound, is placed in its usual position opposite the centre. But as a general rule little or no gain has seemed to result therefrom, so far as can be judged by the performance of such instruments in actual practice. It is quite probable in this case that the increased approach to saturation of the diaphragm may have so great an effect as entirely to prevent the expected improvement.

It will also be seen from our results, that an increase in the thickness of the diaphragm of a magneto transmitter tends to allow of the use of a stronger magnet, and for a given amplitude of vibration to produce a stronger current. But it must be remembered, on the other hand, that the greater rigidity of the thick diaphragm will diminish this range of vibration under the action of the voice, a difficulty which may to a certain extent be remedied by using a diaphragm of large diameter.

Rogers Laboratory of Physics,
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XII.

AN ACCOUNT OF A NEW THERMOGRAPH, AND OF SOME MEASURES IN LUNAR RADIATION.

BY C. C. HUTCHINS, ASSISTED BY DANIEL EDWARD OWEN.

Presented by Professor Trowbridge, March 13, 1889.

DURING the winter of 1886–87 the writer carried out at Cambridge a series of experiments with the bolometer and other sensitive heat-measuring devices, the intention being, if the apparatus could be made to perform satisfactorily, to attempt the solution of some problem in radiation. One in particular in mind was that of the radiation from rocks, as important from a geological standpoint. It was also thought possible that the work might be made a valuable supplement to Langley's investigations in lunar radiation.

After two or three months of preliminary experimentation the matter was abandoned, and the further pursuit of the subject was not undertaken until October, 1887. In designing a working apparatus for use in the research thus resumed, some modification of the thermopile suggested itself, and a contrivance was finally adopted constructed upon the principle embodied in that familiar instrument. This new device possesses the sensitiveness necessary for accurate and delicate work, and at the same time is very simple in operation. This last is an important feature, for in all instruments intended for measuring small quantities of heat the matter of simplicity is a very grave one. It hardly needs saying, that the number of the parts in the instrument should be limited to as few as possible, and that the whole should be as simple as it can be made. Multiplication of parts leads to inaccuracy in performance with almost absolute certainty. It is the element of simplicity that has, until recently, rendered the ordinary thermopile the most successful instrument possible to be employed in dealing with small quantities of heat. The failings of the thermopile, however, are so numerous and so fatal that it becomes an instrument of precision in the hands of a very few, who must serve a long apprenticeship in its use.

Impressed with the number of the difficulties which beset the use of the thermopile, the writer set about a systematic study of the conditions necessary to their removal. It was soon observed that a great advantage could be gained by employing a single thermal junction, instead of many, and by condensing the heat rays upon this one by means of a concave mirror. All of the advantages of the thermopile are thus retained, while its most serious failing — the slowness with which the large mass of metal presenting the sensitive surface parts with its heat — is obviated altogether. The condensing mirror fulfils the function of multiplied junctions, while the single union of bars employed in the new instrument rapidly attains thermal equilibrium under any series of conditions.

This preliminary proposition having been laid down, — that a single junction of two metals, suitably supplemented by a concave mirror, can be made as effective as a larger number of junctions without the mirror, — various experiments were next undertaken with a view to ascertaining the best form for the single junction, as well as the most suitable materials to enter into it. With these ends in view a great number of unions were made, including some very delicate combinations into which tellurium was introduced. The bars of metal used in these experiments were made very thin, and in attempting to form certain junctions great difficulty was experienced; for when very thin bars of easily fusible metals are to be soldered together, it is sometimes almost impossible to perform the act properly, without melting the bars. In such cases the electro-deposition of silver or copper in the junction succeeds admirably.

As the outcome of these experiments it was learned that the best results could be obtained from a junction formed by two of the stronger metals, worked into very thin strips, the opposite ends of the metal ribbon thus formed being attached to copper rods — the terminals — with the point of junction midway between. The reasons for such a construction and the advantages especially to be derived from it are briefly these. It is plain that a thin strip of metal will not only take up and part with its heat in a much shorter period of time than will a thick bar, but that it will also, in a given interval, be raised to a much higher temperature than the thick bar. The strong metals are employed for the obvious reason that the brittle metals cannot be made into very thin leaves and at the same time remain self-sustaining. Further, thin strips of even such metals as iron and copper, the thermoelectric force of which is comparatively feeble, brought into conjunction, give a greater electric current when excited by a feeble radiation than is obtained from a junction of bars of antimony and bismuth under similar circumstances. Finally, to employ a condensing mirror having the junction at its focus is simpler than to multiply the number of junctions, and, moreover, it adds nothing to the resistance of the circuit.

INSTRUMENTS.

The Thermograph.

There will now be described, in detail, the instrument which was the outgrowth of the principles touched upon above. It is not beyond the power of one possessed of very ordinary mechanical skill, and who may be perforce his own instrument-maker in matters like the present. The measures will be given in inches, since most workmen still employ that unit.

A cylinder is turned from vulcanite, or some hard wood, 3 in. long and 1 in. in diameter. For $\frac{3}{4}$ in. at one end this cylinder is made of less diameter by $\frac{1}{16}$ in., in order that it may receive and hold firmly a piece of brass tubing 3 in. long, 1 in. in external diameter, and $\frac{1}{32}$ in. thick. The end of the cylinder carrying the tube will be designated in what follows as the "front end." The cylinder is next pierced, in the direction of its length, with two $\frac{1}{8}$ in. holes lying upon the same diameter and $\frac{7}{16}$ in. apart. Through these holes copper rods are firmly driven, being left to project $\frac{1}{2}$ in. above the front end of the cylinder. They are allowed to project $\frac{3}{4}$ in. from the back end of the cylinder, and are afterwards bent apart somewhat to facilitate the attachment of screw cups. The front ends of the rods are made somewhat smaller than the other portion by filing.

The thermal junction is made as follows. Some bits of rather wide watch-spring are procured, together with some rolled sheet nickel. A strip of the same width as that of the watch-spring is cut from the nickel, and, the ends of the spring and of the piece of nickel having been scarfed with a file, the two are united by means of the strongest hard solder obtainable. For convenience in handling, it is well to leave the piece of watch-spring long. The compound strip can now be made straight upon the edges, and worked thin with a fine file. Trial is occasionally made with a screw caliper, and when the thickness has been reduced to .02 mm. it is best to discontinue. The solder junction must be very perfect, or it will be pulled apart in the filing. With great care and patience the thickness of the strip of metal can be reduced to .01 mm., but there is no compensating advantage for the labor expended. When finished, the wide strip can be cut with scissors into several narrow bands, and preserved in a dry bottle.

To complete the thermograph, a strip is selected from the stock, laid across the rods at the front of the cylinder, and secured in place with a little soft wax. The wax permits the strip to be shifted, until it is proved by measurement that the junction is exactly midway between the rods, when the strip is permanently fixed by soldering it to the rods. A small concave mirror of glass, silvered upon the first surface, is now fixed to the front end of the cylinder, between the copper rods, with glue or varnish. The mirror should be $\frac{1}{2}$ in. in diameter and of $\frac{2}{5}$ in. focus. When in place, the junction in the metal strip should be exactly at its focus.

The brass tube is carefully blackened within, and is provided with diaphragms, the openings in which are determined by the character of the work for which the instrument is intended. The front end of the brass tube is also furnished with a suitably perforated end-piece of the same material as the cylinder. For some purposes the tube of the instrument requires to be made longer than that of the sample described above, and for other purposes it may be dispensed with. For linear measurements, as in spectrum work, it is only necessary to replace one or more of the diaphragms by slits at right angles to the direction of the strip. The apparatus is particularly successful in dealing with small quantities of heat at a point. When employed for this purpose, the condensing mirror is not used, the junction being merely placed behind a small hole in a triple screen, formed by two plates of metal separated by a thick plate of cork or other non-conducting substance.

If for any particular purpose it should be desired to make use of a strip thinner than can be produced by the methods given above, it can be prepared after the following manner. A flat plate of copper is rubbed with graphite and nickel-plated over one half its surface. It is then dried, rubbed with graphite a second time, and the nickel-coated end dipped in melted paraffine nearly to the junction of the nickel and copper. The remaining half of the copper surface can now be plated with iron from a solution of the citrate, the nickel already deposited being protected by its paraffine coating. When the entire thin film is afterward stripped from the copper backing, one half of it will be nickel, the other half iron, and it can be cut into narrow strips as before. The writer has to learn that there is any advantage to be gained from employing strips made in this manner, and they are certainly difficult of manufacture. In general, thin films of electrically deposited metals are hard to manipulate, for they possess the elasticity and brittleness of highly tempered steel, and usually require careful annealing.

The Galvanometer.

The galvanometer intended to accompany the heat-measuring device should receive as careful attention as the device itself. The writer had had some previous experience in the construction of sensitive galvanometers before attempting the research of which the present article is an account; nevertheless, several different forms were tried before one was found exactly adapted to the thermograph. The requirements to be met were, in brief, first, considerable sensitiveness, and secondly, rapidity of working, — qualities which are to some extent incompatible, but which have, as far as possible, been combined in the instrument in use. It would have been possible to produce an instrument much more sensitive than the one actually employed, had the rate of working been left out of account; but nothing is more annoying than to be obliged, when time is precious and opportunities for observation are perhaps few, to wait for a galvanometer needle to come to rest; consequently the element of time has had the first consideration.

The galvanometer adopted for use with the thermograph has four coils, each containing about four feet of wire 0.063 in. in diameter. The wire was twice shellacked and baked before being wound. The coils are contained between brass plates, which constitute the body of the instrument, the inner faces of the two plates, which are in contact, being grooved for the passage of the staff of the needle and its supporting silk fibre. The needle thus swings in an entirely closed space but little larger than itself, and needs no damping vanes to bring it quickly to rest. Two minute scales of mica are attached to the needle to prevent it from being turned completely round. The astatic system has the magnets fixed upon a very slender aluminum staff two inches in length. The magnets are from $\frac{1}{4}$ in. to $\frac{3}{8}$ in. in length, and very slender. The mirror is flat, and $\frac{3}{8}$ in. in diameter. Much of the success of the instrument depends upon the perfection of the mirror. It is difficult to obtain perfectly plane mirrors, and, moreover, those to be had in the market are too heavy. They can be made, of great perfection, by selecting a perfectly flat piece of thin plate glass, cementing it to a thicker piece of glass for a support, and then grinding it down to the thickness of stout letter paper. A very thin sheet of glass is thus obtained, from which circles of the required size can be cut with a diamond. The glass being now silvered upon the surface, the polish of which was not destroyed by the grinding, we have a first surface reflector which will bear a high magnifying power if the mirror be not strained in mounting.

The scale is read in a novel manner. The cell in which the mirror swings is closed by a bit cut from the centre of an ordinary spectacle lens of from 36 to 48 inches' focus. The scale is located as in the ordinary arrangement of telescope and scale, but instead of the telescope we have the following device. A tin or paper tube is provided, and in it, at a distance of five inches from one end, is placed a lens, three inches in diameter, and of six inches' focus. The end of the large tube has a draw-tube, which is closed by a metal plate provided with a peep-hole at its centre. The peep-hole may be made to occupy the focus of the lens by sliding the draw-tube backward or forward as required. A horse-hair or very fine wire is stretched across the tube in the focus of the lens opposite the draw-tube, so that it may be clearly seen by the eye applied to the peep-hole. This arrangement is to be mounted in the place occupied by the ordinary telescope, which it far surpasses both in definition and in the breadth of the field of view. The whole apparatus when in position opposite to the galvanometer constitutes a telescope, of which the lens in the galvanometer is the object-glass, the large lens in the tube the eye-piece, and the scale the object viewed. The definition is quite remarkable, the fibre of the paper upon which the scale is ruled showing clearly, as though seen through a magnifying-glass.

The details of construction of the entire apparatus having thus been outlined, it remains to speak of the action of the whole. As an example of the accuracy that may be expected in the performance of the instrument, the following test may be taken.

October 23d, 1888, the sun was taken as a source of heat, the rays being reduced by passage through a small opening. The following galvanometer deflections were obtained: —

	Divisions.		Divisions.
First	162	Sixth	164
Second	162	Seventh	162
Third	161	Eighth	161
Fourth	162	Ninth	161
Fifth	162	Tenth	162

The observations were taken rapidly, occupying less than ten minutes in all.

No great effort has been made to secure superior sensitiveness, yet the heat from the face of a person at a distance of fifty feet is measurable. A comparison was made between the thermograph and a thermopile of forty-eight couples. Using the same galvanometer for each, the thermograph proved about twelve times as sensitive as the other instrument. The limit of sensitiveness could be very much extended, if it were desired, by the use of a more delicate galvanometer. As actually adjusted, the galvanometer employed gives a deflection of one scale division for 0.00000007 Ampère, the period being ten seconds. The constant of Langley's galvanometer was 0.0000000013 Ampère, or fifty times less.

Radiation from Rocks.

As experiments upon the radiating power of rocks and minerals were the first in which the new instrument was employed, they will be first discussed.

The want of a standard of radiation which should be more satisfactory than a lamp-black-coated surface was seriously felt in these experiments. Lamp-black is a hygroscopic substance, and radiates differently when in different states, unless it be applied with sufficient varnish to make it water proof. But if it be mixed with the smallest possible amount of varnish, and applied to a surface, then the radiating power is different from that of the same surface coated by camphor smoke. Also, it appears to radiate differently when applied in the same manner to different substances. The writer has always found ordinary white pumice-stone a better radiator than the same blackened. There is no other instance in which so variable and imperfect a *standard* is tolerated. The writer has employed as a working standard in these experiments a piece of pure quartz finely ground with emery but unpolished. Such a standard seems to possess many advantages. Quartz is readily obtainable in a pure state. It is imperishable and unalterable at any ordinary temperature. It has the great merit of perfect definiteness of composition.

The measures of radiation from the rocks were made as follows. Each specimen had a wooden handle adapted to it, for convenience in handling when hot. The rocks were heated in an oven intended for drying chemical precipitates. The oven was of heavy iron, and was heated from beneath by numerous small gas jets. It was found that, after the gas had been lighted about an hour, the temperature of the oven became constant, and remained so for any length of time. The rock under experiment and the quartz standard were placed in the oven together, side by side, and after the lapse of an hour they were removed, first the quartz and then the rock being quickly taken from the oven, presented before the opening in the thermograph, and the deflection noted. The specimens were then returned to the oven, and some time allowed to elapse before the experiment was repeated. In this way as many measures were obtained from each specimen as could be made in the course of a day, i. e. from ten to thirty. The method seems far from perfect, but it was the best of several that were tried.

To reduce the results to the lamp-black standard, a very careful comparison was made between the radiating powers of blackened and unblackened faces of the quartz. The temperature at which the measures were made was near 100°. The results are given in the following table, the radiation from a blackened surface of quartz being taken as 100.

Name.	Locality.	Character.		Radiating Power.
Lava	Hawaii	Imperfectly fused.	Black	91.2
Lava	Vesuvius	Dense.	Gray	90 4
Lava	D'Auvergne	Basaltic.	Dark	81.8
Lava	D'Auvergne	Scoria.	Light red	86.5
Lava	Hawaii	Well fused.	Red	91.9
Pumice	. . . . .	Common.	White	71.3
Lava	Vesuvius	Vesicular.	Black	86.3
Scoria	Vesuvius	Very light and porous.	Black	91.6
Pumice	Vesuvius		Red	89.1
Trap	Nova Scotia		Dark	83.2
Trap	Mt. Kineo		Light gray	94
Obsidian	. . . . .		Black	88.5
New Red Sandstone	Pembroke	. . . .		89.3
Flexible Sandstone	Georgia		Red	85.9
Slate	Pennsylvania	From coal beds, with pyrite.		89.8
Slate	Georgia		Red	84 1
Feldspar	Topsham, Me.		Pure white	88.5
Gypsum	. . . . .		Pure white	86
Iceland Spar	. . . . .		Pure	85
Mica	Hebron, Me.	. . . .		76.3
Serpentine	. . . . .	Common.	Green	89 1
Quartz	. . . . .	Pure.	Transparent	90 8
Amphibole	New York	Common.	Green	91.4
Tremaolite	. . . . .		Pure white	85.5
Pyrite	. . . . .	. . . .		76.4
White Marble	. . . . .	. . . .		86.7
Mica Schist	. . . . .	. . . .		80.8
Granite	. . . . .	Fine-grained.		93.5

An inspection of the table shows a remarkable uniformity in radiating power for materials so diverse in character. The large number of volcanic rocks was selected, because it seems probable, from its physical features, that the rocks of which the surface of the moon is made up are of volcanic character.

Lunar Radiation.

While the light received from the moon has been frequently measured by many different observers, the more important problem of its dynamic radiation has been solved by but a single person. Observers previous to Langley can pretend to so little accuracy in their results, that our knowledge of lunar radiation may be said to rest upon his authority alone. This condition does not arise from any lack of interest in the subject, — on the contrary the problem has always been a fascinating one, — but is due to the fact, that, previous to the invention of the bolometer, no instrument existed capable of dealing accurately with so small an amount of heat as the moon affords. Great interest, therefore, cannot fail to attend the results of careful observation, made with competent instruments, and tending to increase our knowledge of the subject.

The first trial of the new thermograph on the moon was made on January 27, 1888. The apparatus, tested at that time, has been regularly employed since, and has performed so satisfactorily that it has scarcely been altered from its original form. The arrangement of the thermograph for the measurement of lunar radiation is this. An oblong box of pine wood carries at one end a silvered glass mirror, 0.196 metre in diameter, and of one metre focus. This mirror is adjustable by screws passing through the end of the box and bearing upon its back. Near the other end of the box is fixed a grooved block, upon which the thermograph may be placed and secured. The block is also provided with adjusting screws, so that the thermograph may be made to point exactly at the centre of the mirror. The mirror is inclined, so that the moon's image is thrown into the opening of the thermograph, and brought to a focus upon the strip. The whole arrangement is that of a Herschel's telescope with the thermograph in place of an eye-piece.

To secure accuracy in pointing, the opening in the thermograph is made of such a size as just to receive the cone of rays from the large mirror, and, a rim of white paper being glued about the opening, the slightest departure from a central position of the cone of rays is announced by the appearance of light upon this paper. A window of plate glass has its place in the side of the box, just in front of the position occupied by the thermograph, and a person looking through this can readily direct the image of the moon into the orifice of the thermograph. A telescope, with cross wires, is also attached to the box, and may be used to direct it, but the former method is much the more satisfactory.

The entire apparatus is mounted upon a massive telescope tripod. The mounting has tangent screw motions, and is provided with a vertical circle for reading the altitudes. An hour or two before it is intended to observe, the apparatus is mounted in the open air, in order that it may have time to acquire the external temperature. Two strands of heavy electric light wire pass from the thermograph to the laboratory, where they are attached to the galvanometer, which is mounted upon a firm pier.

For some reasons the effect of phase should precede all other considerations as a subject of investigation, but it has been postponed until later. The subjects that have engaged our attention, up to the present time, may be for the most part classed under two heads: 1. The comparative intensity of radiation of the full moon and of the sun. 2. The absorptive effect of the earth's atmosphere upon the radiation of the moon. These two topics will be considered in turn.

It is obviously impossible to confine the observations to the time of full moon without giving undue time to the investigation; hence the effect of phase demands to be considered. To avoid the introduction of errors from this source the following precautions have been taken: 1. To confine the observations to the three days nearest full moon. 2. To measure always the radiation from a constant area of the moon's surface. To fulfil the conditions of the second precaution, there is placed, close to the strip of the thermograph, a diaphragm, the opening in which is much smaller than the moon's image which falls upon it. Thus there may be a large change of phase, and the opening still remain full of the moon's image. This arrangement would completely remove the difficulty, provided that the moon reflects like a flat disk, as Zölner thinks, — which is not at all certain. It is believed, however, that, when taken in connection with the first precaution, the outstanding error cannot be large. The method has the disadvantage of reducing the available heat by about one half; but, as it is, the heat is sufficient to drive the needle off the scale with the galvanometer in its most sensitive condition. The controlling magnet is set so that a deflection of between one and two hundred scale divisions is obtained, corresponding to a period of between five and ten seconds' vibration of the needle.

One observer being stationed at the galvanometer, and a second at the instrument out of doors, at a signal from the first, the latter brings the image of the moon into the opening of the thermograph, and the deflection occasioned is noted and recorded by the observer at the galvanometer. In this manner a set of ten readings is taken, and, the altitude of the moon being measured at the beginning and the end of the set, the mean of the ten deflections is taken as the deflection corresponding to the mean altitude. About six minutes are required to make a set of the readings.

The following series, selected at random from the observation-book, will serve as an example of the results obtained.

DATE. — FEBRUARY 24, 1888.

Mean Altitude.	Mean Time.	Deflection.	Mean Deflection.
52° 40′	7 h. 34 m.	....	....
....	....	171.5	....
....	....	172	....
....	....	168.5	....
....	....	166	....
....	....	171	....
....	....	174	....
....	....	172	....
....	....	175	....
....	....	173.2	....
....	....	175	....
....	....	....	171.8

The probable error of a single observation, when the moon is the source of heat, is considerably greater than is the case with an artificial source, or even with the sun. The cause is, in part, due to invisible clouds of vapor floating in the atmosphere, as Langley thinks. It has been observed that immediately after rain this effect is particularly noticeable, even when the sky appears perfectly clear to the eye. There is another cause, which doubtless exerts a large influence; that is, the irregular radiation of different portions of the moon's surface. It has been found* that, photographically, the mean brightness of the dark region is to that of the bright region in the ratio of 55 to 100. We might be prepared to expect large differences in the radiant energy of the respective regions, and the average radiation may therefore be more closely attained from a series in which the individual readings vary considerably, than from a more perfectly concordant set.

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* Annals of Harvard College Observatory, Vol. XVIII. No. IV.

Having obtained a sufficient number of sets, as perfect as may be, we have next to effect a comparison between the deflections produced by the moon, and the deflections brought about by the sun under similar circumstances of observation, — such as altitude, height of barometer, etc. The heat of the sun's rays must be reduced in some manner in order to bring them within the range of the same instrument employed in measuring the feeble radiation of the moon. Both Lord Rosse and Langley accomplished the reduction by passing the sun's rays through a small opening, and placing the heat-measuring appliance in the diverging beam.

The enormous differences that appear in the results of observers who have measured the light of the moon, and compared it with sunlight, put us upon our guard against sources of error, and impressed upon us the necessity of going over the ground by independent methods. Let us consider the probable sources of error in the above mentioned method of comparison: —

1. Errors of observation. These are small, and can be reduced to any extent by repeating the observations.

2. Absorption by the mirror, used in condensing the lunar rays. The mirror is always kept perfect by frequent silvering, and a flat mirror, silvered by the same process, is employed in reflecting the sun's rays to the small opening.

3. The plate of metal in which is the perforation becomes a source of heat when the sun's rays are thrown upon it, and would increase the heat indication. This effect is avoided by placing the thermograph so far from the metal plate as to render its influence practically imperceptible.

4. Effect of diffraction at the opening. Unknown.

As an example of the results obtained by this method, let us take the observations of April 25 and 26, 1888.

On the night of April 25, the deflection produced by the moon at an altitude of 42° was 184.8 scale divisions.

We have also:

Semidiameter of condensing mirror	. .	95 mm.
Focus " "	. .	1000 mm.
Semidiameter of moon, augmented	. .	17′.

Hence we have, for the concentration of the moon's rays,

$$\frac{\overline{95}^2}{(1000 \times \sin 17')^2} = 369.1.$$

Had the moon's rays, uncondensed, acted upon the thermograph, the deflection would have been:

$$\frac{184.8}{369.1} = 0.5008 \text{ scale divisions.}$$

On the following morning, the altitude of the sun being 42°, its rays were reflected through a small opening, and being received by the thermograph, placed at a distance, a deflection of 147.16 scale divisions was found to be the mean of 30 readings. The opening through which the sun's rays were reflected was a carefully reamed hole in a metal plate. Its diameter, being measured under the microscope, with the aid of a stage micrometer which purported to be divided into tenths and hundredths of a millimeter, was found to be 1.67 mm. A paper screen received the spot of light, formed by the rays from this opening. The diameter of the spot was 40.6 mm. The thermograph was thrust through an opening in the screen until its strip lay in the plane of the paper. The spot of light could then be thrown into it by turning one of the screws of the heliostat.

We have for the reduction of the sun's rays:

$$\frac{\overline{40.6}^2}{\overline{1.67}^2} = 615.3.$$

Had the thermograph received the undiminished sunbeam, the deflection would have been:

$$615.3 \times 147.16 = 90596.$$

The ratio of the sun's radiation to that of the moon is, therefore,

$$\frac{90596}{0.5008} = 180,900.$$

Second Method.

In the second method, the sunbeam is employed without diminution, but its effect is reduced by interposing a resistance in the galvanometer circuit. This method is free from all objections, as far as can be seen, for its accuracy depends upon the measurement of a resistance. an operation which can be accomplished with great accuracy. Moreover, it removes any effect due to minor disturbing causes, such as the heating of the metal plate in the first method, since, when a large resistance is interposed, the apparatus becomes insensible to such influences.

The resistance of the thermograph, galvanometer, and the connecting wires, is 0.2095 ohm. On October 21, 1888, the sun's altitude being 31°, 100 ohms were added to the resistance of the circuit, and when the sun's rays were thrown directly into the thermograph a deflection of 114.6 scale divisions was obtained. Without the 100 ohms of additional resistance, the deflection would have been:

$$\frac{100 \times 114.6}{0.2095} = 54700 \text{ scale divisions.}$$

That same evening the moon was observed at an altitude of 30° 15′, the deflection being 124.59 scale divisions. From its augmented semi-diameter, 14′ 52″.7, and the same constants as in the previous example, we find the deflection for the uncondensed moonbeam to be 0.2945 of a scale division.

The ratio of 54700 to 0.2945 is 186,300. The results obtained by the two methods are here tabulated.

Ratio of Sun Radiation to Moon Radiation.

FIRST METHOD.		SECOND METHOD.	
March 30, 1888 . . .	181,000	October 18, 1888 . . .	187,200
April 25, 1888	180,900	October 21, 1888 . . .	186,300
October 18, 1888 . . .	167,400		

Mean of the five results 184,560

The results given by the two methods do not show the wide disagreement so noticeable in the comparative light of the two bodies, as found by different methods. This fact is strong evidence in favor of the accuracy of the mean result. In reality, the problem of the total comparative radiation of the sun and moon is in many respects simpler than the problem of the comparative light intensity of the two bodies. In the former case, there is freedom from all personal bias; the measurements are all given by the indications of the instruments directly, and, in general, the chances for error seem to be fewer.

Lord Rosse found the ratio of solar to lunar radiation to be 80,000 to 1. Langley obtained the ratio 96,509 to 1. Provided the moon were a flat disk, reflecting perfectly all of the sun's rays that fall upon it, we could not receive more than one 97,000th part of the solar heat from such a disk, as Zölner has shown. The close agreement of his result with this number Langley considers to be largely a matter of chance, or, rather, of constant errors, tending in an unknown degree to increase the observed values.

It would be *a priori* quite improbable that we should, under the circumstances of reflection from the lunar surface and subsequent passage of the reflected rays to the surface of our planet, receive anything like the maximum possible radiation. Our atmosphere cuts off a considerable portion of the lunar rays. It has been observed that aqueous vapor is particularly efficacious in stopping them. It may not be uninstructive, as illustrating the minuteness of the quantity of heat that we receive from the moon, to express it in terms of melting ice. It will not be far from the truth if we say that the sun's rays will thaw through an inch of ice in 100 minutes, whence it follows, from our determination, that the rays of the moon will melt the same thickness of ice in 18,456,000 minutes, or 35 years.

That portion of the solar rays not reflected from the lunar surface is absorbed by it, and radiated at different wave lengths. At what wave lengths we do not know, and whether or not those rays are capable of passing our atmosphere we cannot tell. An idea of the general character of the lunar rays may be gained from experiments with absorbing media. For example, on April 25, 1888, the percentage of lunar rays transmitted by a plate of quartz was determined. The quartz plate was 5 mm. thick, cut perpendicularly to the axis of the crystal. It was arranged to be drawn before the thermograph by a thread, so that the observations could be made in pairs, alternately with and without the quartz. The results were as follows: —

Moon's Altitude.	Deflection through Quartz.	Deflection without Quartz.	Per Cent transmitted.
13°	38.4	137.2	34.6
19°	54 4	157.0	27.9
24° 30′	51.3	163.2	31.4

Mean of the whole (60 readings) . . . 31.3%

An attempt was then made to find some artificial source of heat whose radiations would be transmitted by the plate of quartz to the extent, approximately, of 31%. It was discovered that a coil of platinum wire, in a Bunsen lamp, turned as low as possible, very nearly fulfilled the requirement. We may say, then, that in general character the rays from the moon resemble those from an incandescent platinum wire. The plate of quartz used in the above experiments transmits 93.3% of the sun's rays.

A study of the reflection of the sun's rays from rocks may serve, to some extent, to aid in the lunar problem, and to this end a few experiments have been made, after the following manner.

The thermograph is mounted upon a strip of board, which can be turned about a pin passing through it and into the table below. The rock under experiment is held in a clamp a short distance in front of the instrument. The board bearing the thermograph is moved about the pin by drawing upon a cord, and is brought back to place by an opposed spiral spring. Should it not be desired that the thermograph remain continuously exposed to the radiation from the rock, it may be turned away from it by a pull upon the cord. When a reading is to be made, the cord being released, the spiral spring draws back the board, which is stopped at the proper position by a pin fixed in the table. The rock under examination is given a flat surface by grinding it upon a sheet of glass with emery. The sun's rays are directed upon it by a heliostat, the diameter of the solar beam being limited to 26 mm. by a circular diaphragm.

On November 4, 1888, a slab of white marble was made the subject of experiment. The distance from the slab to the thermograph strip was 217 mm. The mean deflection obtained was 82.5 scale divisions. Had the marble slab reflected perfectly in every direction the solar rays that fell upon it, the ratio of the radiation received at the thermograph strip to the solar radiation would have equalled the ratio of the area of the cross section of the solar beam employed to the area of the hemisphere of which the distance from the marble to the thermograph strip is the radius; or,

$$\frac{82.5}{\text{Solar Radiation}} = \frac{\pi\,\overline{13}^2}{2\,\pi\,\overline{217}^2}.$$

From which we find, Solar Radiation = 45980 scale divisions, upon the supposition of perfect reflection by the marble.

The thermograph was next placed in the direct solar beam, with a resistance in the galvanometer circuit, and the true solar radiation was found to be measured by 84170 scale divisions of deflection. Hence, of the solar rays falling upon it, the marble slab reflected $\frac{45980}{84170}$ part, or 54.6%. In the same manner, it is found that a surface of black slate reflects 38% of the solar rays.

We learn, then, that of the solar rays falling upon rocks a large portion is absorbed and conducted through the mass of the rock, the remaining portion being reflected. In both of the cases given, the sunlight was flashed upon the rock when the reading was to be made, the rock remaining, practically, at the temperature of the room. It appears, therefore, that the solar rays are about equally divided into two portions, one of which is reflected directly, the other absorbed, conducted through the mass of the rock, and radiated in long waves. If the rocks were in large masses, and continuously acted upon by the solar rays, their temperature would be considerably raised by the absorbed heat. The radiation of a body like the moon must consist, in considerable part, of emanations from such a heated surface; and it becomes important to inquire whether our atmosphere is permeable by such rays.

Lord Rosse found, at the time of total lunar eclipse, that with the disappearance of the last ray of light from the vanishing moon radiation, to which his thermopile was sensitive, vanished also. On the night of January 28, 1888, the first systematic observations were made by the writer and his assistants with the previously described apparatus. The moon rose eclipsed. A reduction of the observations shows that

19 minutes before totality the deflection was 11.2 divisions.
8 “ “ “ “ “ “ 7.3 “
During first minute of totality “ “ 3.2 “

Mean of 30 readings taken during total phase 2.09 “

After the total phase had passed, but while the moon was still in the penumbra, 254.4 was obtained as the mean of 20 readings.

No attempt was made to observe continuously. The evening was so intensely cold, that one could not stand quietly in the open air for any length of time without freezing. The inference to be drawn from these observations is, that all but a minute portion of the rays from the lunar soil and rock are cut off by our atmosphere, for it is impossible to conceive that a surface like that of the moon, upon which the sun has been shining continuously for many days, should suddenly cease to radiate upon withdrawal from the sunshine. It is very questionable, then, if at any time we receive any considerable portion of the radiation from the lunar rocks.

The results given above are in substantial agreement with those obtained by Dr. Boedicker during the same eclipse. He employed a thermopile, and condensed the lunar rays with the three-foot speculum of Lord Rosse. He says,* that, twenty minutes before totality commenced, the heat was reduced to less than five per cent of what it was before first contact with the penumbra. He also observes, that the heat radiated by the moon commences to diminish long before first contact; and that the heat, after last contact with the penumbra, did not mount immediately to what it had been before first contact with penumbra.

It was intended, upon the occasion of the total lunar eclipse of July,

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* Nature, March 8, 1888.

1888, to make as complete an investigation as possible of these and allied matters. With this purpose in view, two complete sets of apparatus were prepared, and two parties of observers were in the field. Upon the night of the eclipse, however, it rained, and observation was consequently impossible.

If we are to conclude that our atmosphere is opaque to radiations from the lunar rocks, we must endeavor to explain the observed behavior of the lunar rays, with reference to absorbing media, upon the hypothesis of selective reflection. We have found that 31% of the lunar rays will pass through quartz; and if it is observed that ordinary rocks absorb and reflect selectively, taking up the short waves, and reflecting the long, the absorption of the lunar rays may be as effectively explained as upon the supposition that we receive radiations from the lunar rocks.

We have arranged to reflect the solar rays from rocks, and, by placing in the path of the reflected ray the same quartz plate that was used in the lunar observations, have ascertained the amount of absorption. The results are shown in tabular form below.

Material.	Mean Deflection without Quartz.	Mean Deflection through Quartz.	Per Cent transmitted.
Red Lava, Porous	153	112	73
Quartz	131	116	88
Black Lava	82	65	80
White Marble	180	147	82
Slate	103	77.8	79
Direct rays of sun transmitted		....	93

The results show that selective absorption takes place, but to an extent quite limited, and altogether insufficient to explain the great absorption of the lunar rays. When we consider the great differences in character of the specimens of rocks experimented upon, as compared with the very inconsiderable differences in the transmitted rays, it seems useless to undertake to find a material that shall absorb so large a proportion of the short solar waves that only one third of the reflected rays will pass through the quartz plate.

The question is how to reconcile the results here obtained with the eclipse observations, showing that our atmosphere is nearly opaque to radiations from the lunar rocks. The materials for the solution of this problem do not seem to be at hand. It is, of course, possible that the materials of the moon's surface may absorb selectively to a much greater extent than those that we have examined. On the other hand, if the lunar surface were of very light and porous materials, like our volcanic pumice rocks, a withdrawal of the solar rays might be attended by so sudden a fall of temperature as to explain the eclipse observations. Somewhere between the two the explanation probably lies: but at present we can do little better than conjecture.

Atmospheric Transmission Curve.

An attempt has been made to construct a curve which would show the transmission of the atmosphere for lunar rays at every altitude of the moon. Observations for this purpose have been made, at every opportunity, for nearly a year, and already amount to some thousands in number. It has been customary to begin the observations at moonrise, or, if the moon were already in the sky, as soon as the evening temperature had become sufficiently stationary, and to continue them until culmination.

The working of the apparatus is attended with considerable fatigue, and it is not possible for one person to operate it uninterruptedly. The readings, therefore, are made in sets of ten or twenty with a short rest between the sets. Sometimes a third person has measured the altitudes with a portable transit, while two gave their attention to making the readings; but usually the same person has directed the thermograph-box and taken altitudes at the beginning and the end of each set, the mean reading of each set being regarded as the deflection corresponding to the mean altitude.

Below is given the work of the night of February 28, 1888. Considerable difficulty has been experienced in obtaining the deflections for the high altitudes, as it very frequently happens that, late in the evening, clouds arise from the ocean near at hand and obscure the sky. On this particular evening the sky was very serene and beautiful until 10 h. 40 m., when the clouds arose. Because of this unusual serenity, this series of observations shows more than ordinary regularity, although less than the customary number of observations was made to a set.

February 28, 1888.

Barometer 30.35. *Thermometer* — 13° C.

Altitude.	Time P. M.	Deflection.	Altitude.	Time P. M.	Deflection.
° ′	h. m.		° ′	h. m.	
3 10	7 24	67.2	20 0	9 5	174.3
7 30	7 51	128.6	20 30	9 8	177.5
8 0	7 53	129.4	23 10	9 24	183.1
8 30	7 56	134.5	23 30	9 27	185.3
11 0	8 13	146.6	24 0	9 31	187.1
11 30	8 15	147.5	24 30	9 33	184.1
12 0	8 19	149.0	25 0	9 36	188.1
12 30	8 22	152.2	25 30	9 40	188.3
15 0	8 34	158.3	26 0	9 44	189.0
15 30	8 37	160.3	28 10	9 56	191.0
16 0	8 41	161.6	28 30	9 58	192.0
16 30	8 44	165.1	29 0	10 2	193.4
19 0	8 59	168.1	33 40	10 31	202.1
19 30	9 2	172.3			

To illustrate the effect of the weather upon such observations as these, we may compare with the above the following table, made up from the results of October 21, 1888. On the former occasion the air was very calm, and from its low temperature (—13° C.), must have been quite dry. The evening of the latter date was fine, after many days of fog and rain, and, although clear to the eye save for the merest visible milkiness, the drifting clouds of vapor were made manifest by the irregular transmission of the lunar rays.

October 21, 1888.

Altitudes	Deflections.	Altitudes.	Deflections.
° ′		° ′	
6 45	105.1	20 15	182.7
11 45	146.1	21 0	175.7
12 15	149.1	22 45	178.7
15 45	163.3	29 45	187.8
17 0	159.1	31 0	191.8

Following Langley,[*] we may find the approximate transmission coefficient for a column of air capable of supporting one decimeter of mercury, by employing the formula

$$t = (M_2\beta_2 - M_1\beta_1)\sqrt{\frac{d_2}{d_1}}.$$

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[*] American Journal of Science, vol. cxxv p. 176.

The dates upon which this has been determined, together with the principal quantities entering into the computation, are here given in tabular form.

TABLE OF TRANSMISSION COEFFICIENTS.

Date. 1888.	Altitude (1).	Altitude (2).	d_2.	d_1.	β_2.	β_1.	$M_2\beta_2 - M_1\beta_1$.	t.
	° ′	° ′						
Feb. 28	12 0	33 40	149.0	202.1	7.696	7.676	22.47	0.9866
" 28	15 0	29 0	158.3	193.4	7.696	7.696	13.52	0.9852
March 29	14 54	30 25	112.2	143.4	7.645	7.640	14.42	0.9832
Oct. 18	22 30	41 0	174.5	222.3	7.670	7.670	7.82	0.9708

The mean of the values of t is 0.9852, and t 7.6, the amount of lunar radiation transmitted by the entire atmosphere at the ordinary pressure, is 0.8925.

SUMMARY.

I. We have shown how an instrument may be constructed, capable of measuring very minute radiations.

II. We have measured the radiations of several rocks at near 100°, and presented the results in a table.

III. We have found that the heat which our planet receives from the moon is to that from the sun as 1 to 184,560.

IV. We have compared the lunar rays with solar rays reflected from rocks, with reference to the absorption of each by quartz.

V. We have constructed a curve, representing the change of transmission of lunar rays by our atmosphere with changes in altitude of the moon.

VI. We have found that our atmosphere, at the ordinary pressure, transmits 89.25% of the vertical lunar beam.

XIII.

ON THE CHARGING OF CONDENSERS BY GALVANIC BATTERIES.

By B. O. Peirce and R. W. Willson.

Presented March 13, 1889.

I. The Use of Water Cells.

The different methods which are commonly used for comparing the capacities of condensers often lead to widely different results.

Several condensers may be apparently of the same capacity when tested by one process, while each differs from all the others under a second set of conditions. Every condenser has its own characteristics, and these must be specially studied before it can be used in accurate work.

The present investigation grew out of the discordant results which one of us obtained in attempting to compare condensers made in different ways. Our experiments have removed some of our own difficulties, and we think that an account of our work may prove useful to others.

We shall begin by considering the behavior of different batteries when they are suddenly called on to furnish definite quantities of electricity in definite short times, and in this first paper we shall give some results which we have obtained in using water cells.

These results are interesting, because the water battery possesses in an exaggerated degree some properties which are common to all batteries, and which may seriously affect* the quantity of electricity furnished to a large condenser by a cell with which it is connected for a short time only.

The cells that we used were made of ordinary "$2\frac{1}{2}$ ounce wide mouth flint glass bottles," filled to the neck with faucet water, and containing each a strip of zinc and a strip of copper placed vertical and nearly parallel to each other, at a distance apart of about two centimeters. The

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* Von Beetz, Wied. Ann., xxvi. p. 24, 1885.

cylindrical part of each bottle under the neck was about six centimeters high, and four centimeters in diameter, and each strip of metal was of such a size as to expose a surface of seven square centimeters on each of its sides to the liquid. The resistance of each cell as measured by the use of alternating currents* was nearly 1200 ohms. Of a large number of such cells at our disposal, we found 240 sufficient for our purpose, and a switch-board enabled us to arrange these easily in various combinations of groups of twenty cells each.

The condensers which we used in this part of our work were nine in number, including one of a capacity of one microfarad subdivided into fractional parts. This condenser, which was made by Messrs. Elliott Brothers and marked by them No. 72, we took as a standard.

As we shall show when we come to discuss the characteristics of different condensers, the ratios of the capacities of the other condensers to the capacity of this one varied somewhat with the time of charging, but, when this remained constant, were the same, whatever the kind of battery used.

The capacity of each of the condensers for each time of charging was measured in terms of the capacity which No. 72 has when charged for one second by a battery of small internal resistance. The capacities of five of the other condensers, as determined in the manner just described, did not vary on the average by more than two per cent when the time of charge was decreased from 2.0 seconds to 0.01 second, that is, in the ratio of 200 to 1. By combining the different condensers, we were able to get within one twentieth of a microfarad any capacity from 0 to 11 mf., a range which was amply sufficient for our purposes.

Most of our work on water cells was done with the help of a four-coil mirror galvanometer (A), of 3300 ohms' resistance. For some purposes, however, only one of the coils was used. The period of the complete swing of the galvanometer needles was 27 seconds, and the ratio of two successive swings 1.058. Unlike some of our other galvanometers, this one, when used ballistically, within the limits which we set for our experiments, gave throws which seemed to be functions only of the quantity of electricity† discharged through it, that is, independent of the tension of this electricity at the instant of discharge. A minute coil of wire, placed in the core of one of the

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* F. Kohlrausch, Wied. Ann., xi. p. 653, 1880.

† See Lord Rayleigh, Phil. Trans., Pt. 2, p. 619, 1882.

galvanometer coils, through which by means of a double key the current from a small thermopile could be sent in either direction, served to damp the oscillations of the needle after a throw had been given.

A few of our measurements were made with the help of another four-coil galvanometer (B), of 3000 ohms' resistance. The period of a complete swing of its needle was 52.7 seconds, and the ratio of successive swings 1.068. With scale placed at a distance of one meter from the mirror, one microcoulomb when discharged through this galvanometer gave a throw of 45 mm.

For intervals between 0.01 sec. and 0.5 sec., the apparatus shown in Figure 1 was used. It consists of a pendulum with an iron bob, A, eight inches long, two inches in diameter, and weighing 7 lb., and a brass rod $\frac{1}{2}$ inch in diameter weighing 2.8 lb. The axis of suspension is formed by a brass rod $2\frac{1}{2}$ inches long held between pointed screws.

Upon this axis and concentric with it are placed two ebonite disks, F, 6 inches in diameter and $\frac{3}{8}$ inch thick. The face of each of these disks is armored through about half of its circumference with a strip of German silver $\frac{1}{32}$ inch in thickness, held by rivets passing through the disk, and the edge of the armature is turned true with the edge of the disk.

The disks are placed with their armored faces adjacent, but separated by an ebonite washer 5 inches in diameter and $\frac{1}{32}$ inch in thickness. One of the disks is fixed to the pendulum rod, while the other can be revolved about their common axis so that the two German silver strips may overlap to any desired extent; the arc *a*, attached to the movable disk, serves to clamp the two disks firmly together, and also to determine approximately the amount of the overlapping. To each of the German silver strips is joined a wire, *b*, which dips in a mercury cup, *g*, connected with one of the two points between which the circuit is to be made; to avoid as far as possible any interference with the motion of the pendulum, these mercury cups are placed very close to the axis of suspension.

The pointed screws upon which the pendulum swings are held in a frame, *c c*, of wrought iron, which is itself swung between two pointed screws, *d d*, perpendicular to the axis of suspension of the pendulum. By rotation of the frame *c c* upon these screws, the axis of the pendulum is easily levelled.

To the frame *c c* is attached a pillar, *e*, carrying a copper wire, *f*, $\frac{1}{20}$ of an inch in diameter, in such a position that its end runs with

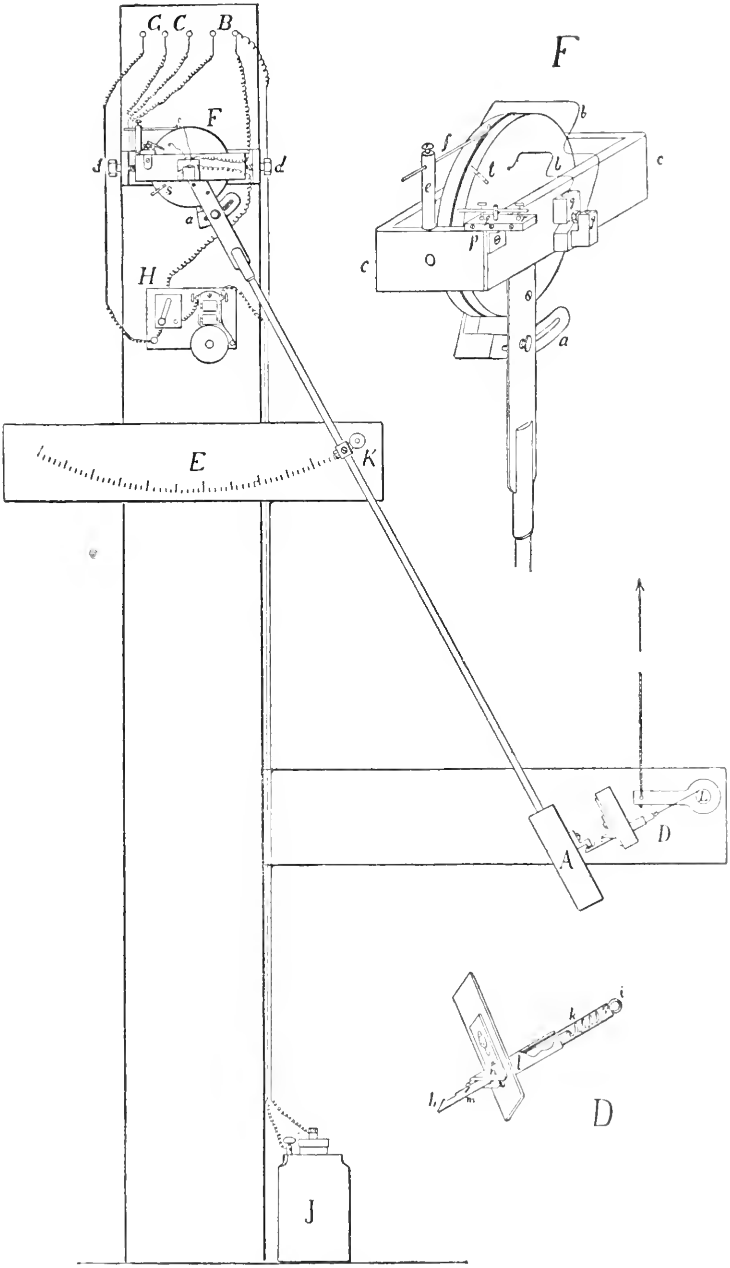


FIG. 1.

light friction in the narrow groove between the two disks as the pendulum swings; both the end of the wire and the sharp edges of the disks are somewhat rounded to prevent undue wear. If the two disks are clamped together in a position such that the unarmored part of one is opposite the armored part of the other, and that as the pendulum swings the wire leaves one German silver strip just as it reaches the other, it will be in contact with each armature successively, but will establish metallic contact between them and close the circuit between the mercury cups at most for a very short interval; if, however, the armatures overlap for a certain number of degrees, contact will be maintained while the pendulum swings through just that number of degrees of its arc. The front disk, which is rigidly fixed to the pendulum rod, is so placed that it comes in contact with the copper wire just as the pendulum reaches its lowest point. If therefore the armatures overlap, for instance, 10°, and if the pendulum is drawn out to a known point upon one side of its arc so that the copper wire rests upon the unarmored side of the "fixed" disk, then, when the pendulum is allowed to fall, metallic connection will exist between the disks while it is rising through 10° from its lowest point. From this "arc of contact" the time of contact is easily determined. The time of vibration of the pendulum is 1.181 sec., and the arc of initial displacement 28° 56′; the decrease of arc in one complete vibration is about 30′.

The length of the arc of contact may easily be determined within one minute. This uncertainty may give rise to an error in the computed time varying from 0.00022 sec. for an arc of 1°, to 0.00042 sec. for an arc of 25°.

The errors arising from a wrongly assumed value of the initial displacement, and from decrease of arc, are in no case greater than one fourth of one per cent of the computed time, and are here neglected.

Since the copper wire does not touch each of the armatures in a single point, the arc of contact will obviously not be exactly equal to the angle of overlap, but its value may be easily determined by direct observation. By throwing the switch at H to the right, the circuit through the bell and battery, J, is made complete, except for the break at the disks. The pendulum is then lowered, and the readings on the divided arc E of the microscope K are noted when the bell begins and stops ringing, as the pendulum is moved through its ascending arc; the former must nearly correspond with the reading when the pendulum is in its position of rest. To facilitate this latter adjustment the wire *f* is made movable in the direction of its length.

For releasing the pendulum and catching it at the end of its spring, the contrivance shown at D is used. The latch *h* is firmly fastened to the spring *i*, which serves the double purpose of giving the upward force upon the latch-bar to cause it to engage with the catch upon the pendulum bob, and also of lessening the shock produced upon the whole apparatus by the arrest of the pendulum. The spring *i* is fixed inside the tube *k*, which, sliding inside the sleeve *l*, serves as guide and stop for the motion of the latch. To operate the mechanism, the tube *k* is drawn out by the cord attached, and the pendulum drawn with it by the latch: at a certain point, however, the pin *m*, which passes through the latch, is brought against the wedge *n*, and a slight further motion trips the latch, and the pendulum is released. The point at which the pendulum is released is so adjusted, by sliding the wedge *n*, that the arc through which the bob is lifted is slightly greater than the loss of the arc through friction, etc. in a complete vibration. The latch is drawn up by a cord passing around an axis, L, which is turned by a lever and cord pulled by the observer at the galvanometer. This is to insure that the pendulum is dropped from nearly the same height at each observation, the multiplying arrangement serving to decrease the velocity with which the pendulum is raised, so that it rises an exceedingly small distance beyond the point where the latch is tripped. As soon as the pendulum falls, the latch, being at once released by the observer, is drawn back to its lowest position by a spring, not shown in the figure, and the pendulum returning is caught by the latch, and thus, having made a complete swing, is left in its original position ready for the next observation.

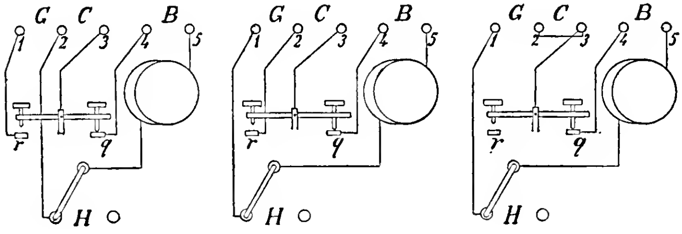
Attached to the frame in which the pendulum swings is a balanced rocking key, *p*, with two adjustable screws making contact in mercury cups. When the pendulum hangs by the latch, the key rests in contact with the left-hand mercury cup *q*, through the left-hand screw: but as the pendulum completes its half-vibration, the pin *s*, attached to the "fixed" ebonite disk for this purpose, throws the lever over upon the right-hand contact, *r*, where it remains during the second half-vibration of the pendulum, being replaced in its original position by the pin *t*, as the pendulum is caught by the latch.

The cycle of operations performed by the pendulum is explained by the diagram below, which shows the connections as made for the three different kinds of observation: —

(1.) Charge of the condenser for a short measurable interval followed by discharge through the galvanometer, the discharge occurring about 0.6 sec. after the commencement of the charge, and the contact between condenser and galvanometer lasting about 1.2 sec.

(2.) Charge of the condenser through the galvanometer for a short measurable interval; discharge (not measured) about 1.8 sec. after commencement of charge, the condenser remaining short-circuited 1.2 sec. This is the arrangement shown in Fig. 1.

(3.) Current flowing directly through the galvanometer for a short measurable interval of time.



I. II. III.

Fig. 2.

The switch H is always turned to the left except when the arc of contact is to be measured as before described.

For all the observations on condensers referred to in this paper, the first figure is applicable; the action is then as follows.

When the pendulum rests in the latch, one terminal of the condenser, C, attached to the binding screw 3, is in connection, through the rocking key, with the mercury cup, *q*, and therefore with one pole of the battery, B, at 4. When the pendulum is released, contact is made between the disks during a certain arc of swing, and the current then flows from the binding screw 5, through the disks and switch H, to the other terminal of the condenser at 2.

On the pendulum's arriving at the end of its swing, the key is shifted from contact with 4 to contact with 1, causing the condenser to be discharged through the galvanometer; returning, the pendulum returns the rocking key to its initial position, ready for the next observation. It may be noted that the battery is permanently connected with one pole of the condenser except during the return swing of the pendulum, but we have found no trouble from leakage in these experiments. The action in cases (2) and (3) will be sufficiently evident from the above description.

The weight of the pendulum rod being considerable, we found that it was somewhat bent by its own weight when the pendulum bob was supported by the latch, and when released a vibration was set up in the rod on its own account, which caused a rapid vibration of the disks in addition to the motion due to the pendulum. The result of this was to produce an uncertainty in the beginning and end of contact, depending upon the relative phase of the two vibrations at the beginning and end of the arc of contact; the amount of this uncertainty was less than 0.0005 sec., and was greatly lessened by adding steel wire stays to the rod when it became desirable to use the pendulum for times approaching 0.001 sec. in magnitude.

A similar effect, probably attributable to the same cause, was noticed as producing a considerable error in a much larger pendulum of similar construction, when used for times approaching 0.001 sec., although the rod was of wood $1\frac{7}{8}$ inches square in section, the bob weighing 40 lb. and the time of swing being 1.8 sec., with an initial displacement of 26°.

We have used a more simple apparatus, shown in Fig. 3, in cases where it was desired to charge a condenser for a definite interval of time, the absolute value of which is required to be known with a higher degree of accuracy. With the pendulum already described, the time is liable to considerable error when determined by an arc of contact nearly equal to the half arc of swing; that is, when the time of contact is in the neighborhood of 0.5 sec.

Where different times are not to be experimented upon, a greater degree of accuracy may be attained if the contact existing through the upward swing be maintained through the downward swing as well, beginning and ceasing nearly at the lowest point of the swing. The time of contact is then equal to the time of vibration, affected by a very small correction, which depends upon the departure of the beginning and end of contact from the lowest point, and which may be determined with considerable accuracy.

The pendulum bob is of iron, and is held displaced from its position of rest by one pole of a horseshoe magnet *b*, in contact with it at its middle point; this magnet is attached to the plate *c*, which turns on the screw *d*, so that the magnet may be moved in the plane of vibration of the pendulum by a cord leading to the observer at the galvanometer. The pin *e* acts as a stop limiting this motion of the

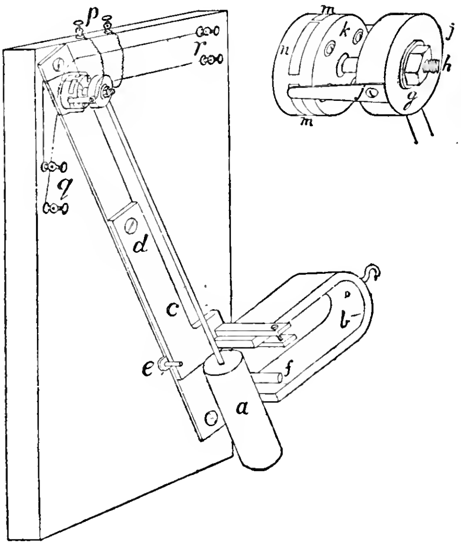


Fig. 3.

magnet towards the left. If the magnet is pulled out a certain distance toward the right, the pendulum bob is brought against the stop *f*, and any further motion of the magnet detaches the pendulum; the magnet is at once released by the observer, and falls back to a point fixed by the stop *e*, so as to arrest the pendulum at the completion of its first swing. The pendulum rod is screwed into the edge of an ebonite disk, *g*, three eighths of an inch thick and one inch in diameter, through the centre of which passes the pin *h*, which forms the axis of suspension. Attached to the disk *g* are two copper strips, *j*, of which one is shown in the figure, and which, as the pendulum swings, rub lightly upon the edge of the fixed disk *k*. Inserted in the latter are four pieces of copper *m*, *n*. In the ordinary position of the pendulum as shown in the figure, the copper strips *j j*, which are connected with the condenser by the binding screws at *p*, rest upon the opposite copper pieces *m m*, and through them are in circuit with the binding screws at *q*, which are connected with the galvanometer. The condenser is thus short circuited through the latter.

When the pendulum swings, the strips *j j* make contact at the lowest point of the swing with *n n*, which are connected through the binding screws at *r* with the battery; and this connection is maintained until the pendulum reaches its lowest point on the return swing, when the strips *j j* pass to the copper pieces, and the condenser is discharged through the galvanometer. It is hardly necessary to say, that the width between the pieces *m* and *n* is made slightly greater than the width of *j*, to prevent a direct current from the battery through the galvanometer.

The method above described has been found very satisfactory for the purpose of obtaining a single swing of a not too heavy pendulum; it is essential that the stop *e* should be somewhat elastic; a short piece of soft rubber tubing slipped over the pin answers well.

The upper pole of the magnet is brought quite near the upper part of the pendulum bob to strengthen the induction.

The motion of the magnet is so slight, that its direct effect upon the galvanometer is negligible. No great care is necessary in the release, as, even if the bob is brought up against the stop *f*, so as to rebound, the time of describing the second and third quarters of the complete vibration is altered by an inappreciable amount.

With the apparatus described a great many measurements were made, and these all gave concordant results. The following tables give, in microcoulombs, the charges which variously arranged batteries of water cells gave, in the times named, to condensers of different capacities. Each number in the body of a table is the mean of a set of closely agreeing observations. In the cases of many of the combinations of cells we have used a much greater number of different capacities than is indicated in the tables, but the results given below are representative.

Whereas in studying certain other cells we have found it desirable to use times shorter than the ten-thousandth of a second, it is evident, from the results in Table I., that in the present instance it was not worth while to use charging times smaller than the hundredth of a second.

TABLE I.

Quantity of Electricity delivered in 0.01 *seconds by different Batteries of Water-cells to Condensers of various Capacities.*

Battery.	Capacities of Condensers in Microfarads.						
	0.1	0.3	0.5	1.0	1.87	3.06	9.58
	mc.	mc.	mc.	mc.	mc.	mc.	mc.
20 cells in series	0.9	1.0	1.0	1.1	....	....	1.1
4 parallel 20's	....	....	3.1	3.4	....	3.8	4.0
8 parallel 20's	1.6	3.5	4.6	5.8	6.3	6.8	7.9
12 parallel 20's	1.7	4.2	5.8	7.9	9.1	9.7	10.8
6 parallel 40's	2.6	4.6	5.2	5.3	5.5	5.5	5.8
60 cells in series	1.1	1.2	....	1.3	....	....	1.3
4 parallel 60's	....	3.5	3.5	3.8	4.1	4.4	4.4
3 parallel 80's	....	3.0	....	3.3	....	3.3	3.6
2 parallel 120's	2.4	....	2.6	2.7	....	2.8	3.2
240 cells in series . . .	2.4	....	....	2.7	....	2.7	2.8

TABLE II.

Quantity of Electricity delivered in 0.19 *seconds by different Batteries of Water-cells to Condensers of various Capacities.*

Battery	Capacities of Condensers in Microfarads.					
	0.5	1.0	1.87	3.06	6.82	10.70
	mc.	mc.	mc.	mc.	mc.	mc.
20 cells in series . .	5.4	7.3	8.7	8.9	9.6	9.6
3 parallel 20's . .	7.2	12.3	17.1	20.1	23.8	25.3
12 parallel 20's . .	8.2	15.9	28.7	42.7	69.6	82.5
40 cells in series . .	7.1	8.4	8.8	9.6	....	9.8
6 parallel 40's . .	14.2	25.5	37.1	44.1	53.0	55.9
60 cells in series . .	7.6	8.9	9.1	9.0	....	9.6
4 parallel 60's . .	18.5	26.6	31.0	35.7	38.5	40.1
3 parallel 80's . .	18.7	24.6	26.7	29.7	30.3	31.0
2 parallel 120's . .	17.3	19.0	20.1	20.7	....	21.5
240 cells in series .	10.9	11.2	11.3	11.3	....	11.8

TABLE III.

Quantity of Electricity delivered in 0.37 *seconds by different Batteries of Water-cells to Condensers of various Capacities.*

Battery.	Capacities of Condensers in Microfarads.					
	0.5	1.0	1.88	3.07	6.86	10.85
	mc	mc.	mc.	mc.	mc.	mc.
20 cells in series . .	7.1	10.9	13.0	15.1	17.4	17.4
2 parallel 20's . .	8.0	14 0	20.6	26.0	31.8	33.9
3 parallel 20's . .	8.1	14 6	24.1	31.7	42.3	46.8
4 parallel 20's . .	8.1	15.5	....	38.0	55.6	64.5
6 parallel 20's . .	8.6	16.6	....	43.6	70.5	83.0
8 parallel 20's . .	9.0	16.7	30.3	46.8	80.4	98.9
12 parallel 20's . .	....	17.0	31.7	50.3	94.8	119.3
40 cells in series . .	10.8	13.3	16.4	17 5	18.9	20.0
2 parallel 40's . .	14.6	22.4	29.2	32 9	37.0	39.2
3 parallel 40's . .	15.0	25.1	36 2	43 2	50.3	52.6
4 parallel 40's . .	16.4	28 1	42.4	52.1	66.7	71.6
5 parallel 40's . .	....	29.6	46.4	60.3	78.2	85.5
6 parallel 40's . .	16.6	31.6	51.5	68.2	91.3	100.2
60 cells in series . .	12 0	14 9	....	....	....	19.2
2 parallel 60's . .	18.5	26.2	....	....	....	38.4
3 parallel 60's . .	20.8	32.9	....	49.3	51.4	57.5
4 parallel 60's . .	22.8	38.3	52.9	63.2	73.0	77.0
80 cells in series . .	14.1	16 6	18.7	19.8	20.0	20.7
2 parallel 80's . .	22 1	29.0	33.9	36.2	38.9	39.5
3 parallel 80's . .	26.1	39.1	47.4	53.5	58.6	62.1
120 cells in series .	16.4	17.8	19.1	20.2	20.4	20.7
2 parallel 120's . .	26.2	33.6	37.3	38.8	41.0	42.4
240 cells in series .	18.9	20.2	....	21.9	21.7	

TABLE IV.

Quantity of Electricity delivered in 0.93 seconds by different Batteries of Water-cells to Condensers of various Capacities.

Battery.	Capacities of Condensers in Microfarads.					
	0.5	1.0	1 89	3.11	7 18	11.41
	mc.	mc.	mc.	mc.	mc.	mc.
20 cells in series	7.2	13.0	19.2	24.6	29 6	32 2
3 parallel 20's	7 3	14.2	....	38.6	61.8	72.8
6 parallel 20's	7.6	....	....	46.3	89 7	
12 parallel 20's	....	16.1	....	51.0	103.9	
40 cells in series	14.4	21.5	26.2	28 9	....	32.9
6 parallel 40's	16.0	31.1	56.8	84.6		
80 cells in series	21 0	27.6	32.9	35 1	36 5	37.0
3 parallel 80's	29.7	50.7	71 7	85.3		
120 cells in series	24.3	30.0	33.5	34.1	....	36.3
2 parallel 120's	35.6	51.1	61.9	68.2	72.3	74.1
240 cells in series	31.6	34.9	37.2	37.9	....	39.0

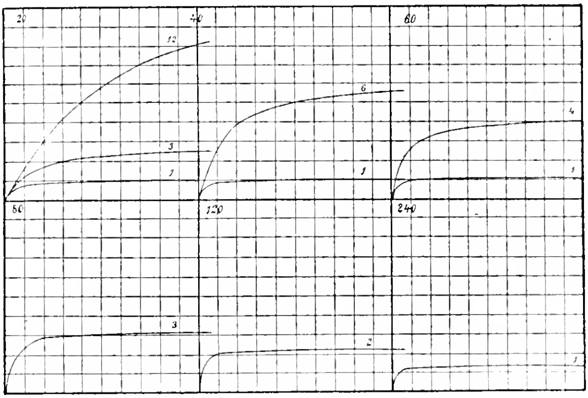
TABLE V.

Quantity of Electricity delivered in 2.0 seconds by different Batteries of Water-Cells to Condensers of various Capacities.

Battery.	Capacities of Condensers in Microfarads.					
	0.5	1.0	1.89	3.11	7.19	11.74
	mc.	mc.	mc	mc.	mc.	mc.
20 cells in series	7.3	14.4	24.9	35.1	52.9	57.7
2 parallel 20's	....	14.3	26.8	42.3	75.5	93.8
4 parallel 20's	....	15.2	....	48.8	96.1	
40 cells in series	14.8	26 2	40.0	50.1	59.3	64.1
2 parallel 40's	....	30.1	51 4	72.6		
4 parallel 40's	....	31.0	56 7	87.6		
60 cells in series	20 0	33.1	....	53.6	62.3	65.0
3 parallel 60's	....	44.5	77.1			
80 cells in series	25 8	40.8	53.6	59.8	68.5	69.8
2 parallel 80's	28 5	53.0	78.7	97.4		
3 parallel 80's	30.4	58.2	94.2			
120 cells in series	33.8	47 4	57.8	63.9	71.9	75.6
2 parallel 120's	....	73 5	100.0			
240 cells in series	49.8	63.6	71.0	78.0	....	83.8

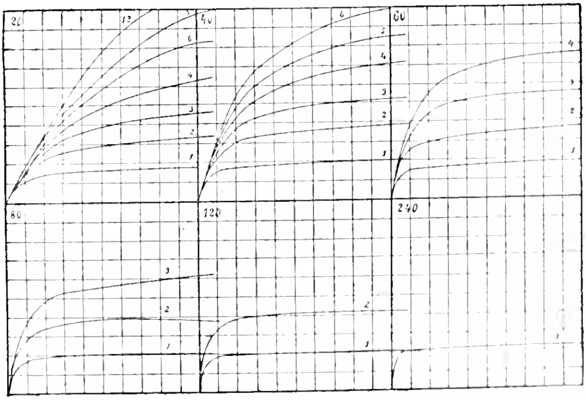
The results given in Tables II., III., IV., and V. have been used in plotting the subjoined curves. In each curve the ordinates represent the charges on a scale of 10 microcoulombs to a division, and the abscissas represent the capacities of the charged condensers in microfarads. Attached to each curve is a number (m), and at the upper left-hand corner of the square in which the curve is drawn is another number (n). These denote that a battery made up of m parallel groups, each consisting of n cells in series, was used in obtaining the results from which the curve has been plotted.

FIG. 4.



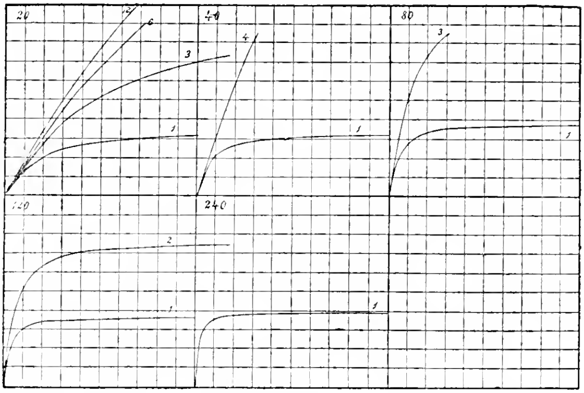
Time of charge, 0.19 sec. Unit of abscissas, 1 mf. Unit of ordinates, 10 mc.

FIG. 5.



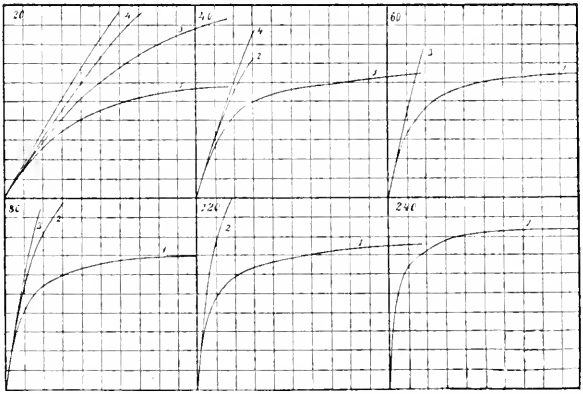
Time of charge, 0.37 sec. Unit of abscissas, 1 mf. Unit of ordinates, 10 mc.

Fig. 6.



Time of charge, 0.93 sec. Unit of abcissas, 1 mf. Unit of ordinates, 10 mc.

Fig. 7.



Time of charge, 2 sec. Unit of abscissas, 1 mf. Unit of ordinates, 10 mc.

It will be noticed that all the curves in all those squares which have any one number in their upper left-hand corners, have the same slope at the origin. This slope is numerically equal to one tenth* of the electromotive force in volts of the charging batteries, as computed from measurements of such cells in open circuit made with a Quadrant Electrometer.

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* Each vertical unit corresponds to ten microcoulombs.

So far as we can judge from our observations with limited capacities, each curve has as an asymptote a line parallel to the axis of x, and at a distance from it which represents the quantity of electricity which the charging battery would yield if joined up for the time given in simple circuit with a trifling outside resistance. Direct experiment shows that this quantity is almost exactly proportional to the number of cells joined up parallel to each other.

The general effect of interposing a large resistance wound bifilar between the battery and the condenser which it is charging is shown by the following diagram, in which the curves are drawn in the same way as in Figures 4, 5, 6, and 7. The two upper curves represent observations taken with a battery of twelve parallel groups of 20 water cells each, first with no interposed resistance and then with 247,000 ohms inserted. The two lower curves represent similar observations made with a single group of 20 cells joined up in series.

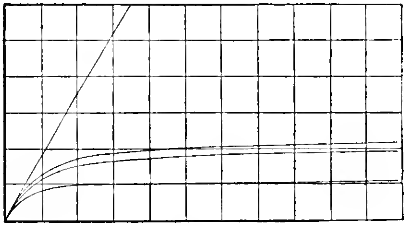

Fig. 8.

For purposes of comparison with the numbers in Tables I., II., III., IV., and V., we give some results obtained with a battery consisting of 20 water cells arranged in series. The poles of this battery were connected together, through various outside resistances, for given short intervals of time, and the quantities of electricity which traversed the circuit during these intervals were measured.

The three curves of Fig. 9 were plotted by using as abscissas the times * during which the battery circuit was closed, and as ordinates the quantities of electricity which passed through the circuit in these times. The observations represented by points in the upper curve were made when the resistance in the circuit outside the battery was 3,000 ohms. The corresponding resistances for the other two curves were 102,000 ohms and 250,000 ohms respectively. It will be

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* Each vertical unit corresponds to 1 microcoulomb. Each horizontal unit corresponds to 0.01 sec.

noticed that the curvature near the origin is considerable, but that after about one tenth of a second each line becomes nearly, though not quite, straight. If the internal resistance of the battery is assumed to be 24,000 ohms, the effective electromotive forces in the circuit after one tenth of a second are about 1.2 volts, 4.5 volts, and 7.4 volts, respectively. The electromotive force of the open battery was a little over 16 volts.

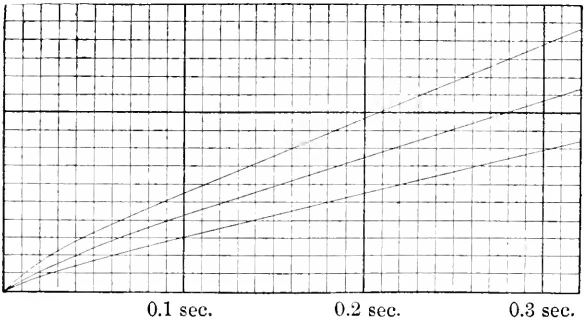

Fig. 9.

The results in Table VI. were obtained with another battery of 20 water cells which had been resting for one month. The numbers in the body of the table give in microcoulombs the quantity of electricity which passes through the circuit when the poles of the battery were connected for the times named through various external resistances.

TABLE VI.

Duration of Current.	Resistance of Outside Circuit in Ohms.		
	3,000	102,000	250,000
sec.	mc.	mc.	mc.
.0025	0.34	0.21	0.12
.011	0.94	0.59	0.41
.034	2.50	1.73	1.22
.077	4.94	3.59	2.52
.1033	6.43	4.64	3.34

After the poles of a battery of these water cells joined up in series have been connected together for a short interval only (say for one second or less), the battery seems to regain almost instantly its original electromotive force. Indeed, it is evident from the numbers given in Tables I., II., III., IV., and V., that the polarization — which, as is well known, increases and diminishes in the case of any given simple element with the intensity of the currents which pass through the cell — must almost instantly respond to any decrease in the density of the current. Of course, if a battery of water cells is short-circuited for a number of seconds or minutes, the polarization slowly increases, and the battery becomes "tired," and after the circuit is broken it must be allowed to rest for a number of minutes, or even hours, before it gets back its lost power.

From the fact that the lines in Fig. 9 are not straight, it appears that the sudden falling off in the electromotive force of the cells when the circuit is closed is not wholly due to a polarization, which is at every instant simply proportional to the density of the current then flowing.

We shall not discuss further the subject of polarization in water cells until we have published the results of some observations made with other kinds of battery.

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XIV.

CLASSIFICATION OF THE ATOMIC WEIGHTS IN TWO ASCENDING SERIES, CORRESPONDING TO THE GROUPS OF ARTIADS AND PERISSADS.

By W. R. Livermore, *Major of Engineers, U. S. Army.*

Presented by the Corresponding Secretary, April 10, 1889.

If the atomic weights of all chemical elements are arranged in a single ascending series, it will take the following form if expressed in whole numbers:

1, — 7, 9, 11, 12, 14, 16, 19, — 23, 24, 27, 28, 31, 32, 35, — 39,
40, 44, 48, 51, 52, 55, 56, 59, etc.;

corresponding to the elements,

H, — Li, Be, B, C, N, O, F, — Na, Mg, Al, Si, P, S, Cl, — K,
Ca, Sc, Ti, V, Cr, Mn, Fe, Co, etc.

The well known "Law of Octaves" calls attention to the fact that each element bears a strong resemblance to that seven places from it in this series, and the "Periodic Law" states that the properties of elements stand in periodic relation to their atomic weights. These laws have been enunciated and illustrated by Newlands, Mendeléeff, Lothar Meyer, and others, and are now familiar to all students of chemistry.

Referring to these laws, Wurtz in his "Atomic Theory" says: "Though it may be generally true that the properties of bodies are subject to periodic modifications with the increase of their atomic weights, the law of these modifications escapes our observation, and seems to be of a complicated nature; for, on the one hand, the atomic weights of successive elements vary within considerable limits without displaying any regularity in these variations; on the other hand, we must confess that the gradations of properties, in other words the greater or less divergencies between properties of successive elements, do not appear to depend upon the degree of the differences between the atomic weights. These are real difficulties." *

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* The Atomic Theory, 1881, p. 162.

Lothar Meyer on the same general subject says, "There can be no doubt as to the fact that these differences are subject to law";[*] and, "There is still much work for the hands and mind; but it will be thoroughly rewarded. The prize is a systematic inorganic chemistry which will bear comparison with the thoroughly developed system of organic chemistry."[†]

The object of this paper is to contribute to the removal of these difficulties, by showing that the increase in the atomic weights of the elements follows a law of the utmost simplicity in its general form, and identical with that of the series of organic compounds.

Let us take the series above mentioned and consider whether any of its terms can be classed in a series of constant increase. Beginning with 2 as a modulus, we find that it applies to 7, 9, and 11, with no recurrence of this difference except for the terms 12, 14, 16; 3 applies only to 9, 12, — 24, 27, — 48, 51, and to 16, 19 * * 28, 31 * * * * * 52, 55; 4 however applies to 7, 11 * 19, 23, 27, 31, 35, 39 * * 51, 55, 59, and to 12, 16 * 24, 28, 32 * 40, 44, 48, 52, 56; thus embracing in two parallel series all the terms of the first three periods of Newlands and Mendeléeff, with the exception of 9 and 14, i. e. 22 out of 24. The probability that these numbers would so far coincide with the regular series from the result of chance, is too slight to be entertained. If now, in addition to this coincidence, any points of resemblance can be discovered among several of the elements in each series, such resemblances are significant; but when it appears that all or nearly all in each series fall into a distinct group that has already been recognized as such by chemists, there is scarcely room for doubt that the regularity of the series is connected with the intrinsic nature of the elements.

Those of the first series are all Perissads and those of the second Artiads, or elements of uneven and even quantivalence respectively, with the single exception in one case of scandium, a newly discovered element whose atomic weight has never been so accurately determined as to throw it out of its group, and cobalt and nickel, which apparently belong to another group. For the present, therefore, the law of regular increase in the atomic weight of the parallel series is spoken of as the Law of Artiad and Perissad Increase, or more briefly as the Perissad Law.

By similar methods, we find that the numbers between 70 and 100

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[*] Modern Theories of Chemistry, English Translation, 1888, p. 160.

[†] Ibid., p. 170.

fall naturally into two series, with the common difference of 5 for the perissads and perhaps 4 for the artiads. The latter series, however, is somewhat indefinite.

Between 100 and 150 the perissads increase regularly, with a common difference of about $6\frac{1}{4}$, and the artiads less regularly, with the same difference, as shown in Tables I. and II.

Too little is known of the atomic weights between 150 and 190, and of those above 210, to justify their classification. Between 190 and 210, we find that 4 applies to 195, 199 * 207, and to 196, 200, 204, 208.

All of the first series are artiads, and in the second all except 200, or Hg, are recognized as perissads, and this element is so similar in many respects to Cu, Ag, and Au that for the present it is allowed to remain in its place. There only remain unclassified 9, 14, 59, 104, and 193. Of these numbers, 9 is the atomic weight of Be and appears to differ too much from 8, the serial number of this element, to be recognized in its natural place.

The remaining numbers, 14, 59, 104 * 193, form a series by themselves, with a difference of a little less than 45. Ni and Co correspond to 59, Ru and Rh to 104, and Ir to 193. These elements are always classified together, and this regularity of increase has often been noticed. But perhaps 14, or N, falls into this series accidentally.

In Tables I. and II. the first column shows the symbols for the elements; the second column, the serial numbers derived from the formula; the third column, the observed atomic weights; and the fourth column, the deviations from the serial numbers. The next columns show the specific gravity, the atomic volume, the fusibility, malleability, and place in an electro-chemical series for each element, and the last column the group in the classification of Newlands and Mendeléeff to which the element has been assigned. The horizontal lines divide the series and periods of this system.

The observed atomic weights are taken from the lists of Clarke,* L. Meyer,† and Van der Plaats,‡ and in most cases by selecting for each element that one of the values that differs least from the mean, taking oxygen at 16 for a standard, and expressing but one place of decimal fractions. The data for the next four columns are taken from Meyer's "Modern Theories." To express their fusibility, the elements are divided into seven classes, that represented by 1 being the most fusible. The brittle and malleable elements are distinguished

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* The Constants of Nature. A Recalculation of Atomic Weights, 1882.

† Modern Theories of Chemistry, English Translation, 1888.

‡ Verification of the Atomic Weights of M. Stas.

by the initial letters B and M. In the electro-chemical series taken from Barker's "Text-Book of Chemistry,"* 1 is the most electro-positive in an acid solution, and 63 the most negative.

It appears from these tables that none of the deviations from the serial numbers exceed 0.6 excepting that for Cb among the perissads, and Zn and Mo among the artiads; Zn differs by just a unit, and seems to form an exception to the regularity.

In his account of the Discovery of the Periodic Law,† Newlands points out the irregularity of the single series, illustrating it by several tables, and the data are clearly set forth and tabulated in a recent paper by Venable, on the Recalculation of the Atomic Weights.‡

In the artiad grand group no atomic weight corresponds to 20, 36, 83, or 131, and a reference to the electro-chemical series will show that these are the points at which the elements change from a negative to a positive maximum, corresponding also to the maximum atomic volumes, and to the end of the Mendeléeff periods.

These points are marked with asterisks in the table.

Analogy points to the possibility of elements with atomic weights of 15, 43 or 44, 47, 60, and perhaps of 99, 100, and 143.5.

The newly discovered philippium and praseodymium may perhaps correspond to 47 and 143.5, respectively, but there appears to be no place in either series for neodymium or 140.3.

In each of the grand groups, perissads and artiads, the breaks between the minor groups of common difference occur at or near the minimum points of the series of atomic volumes, and therefore midway between the dividing lines above mentioned.

The first term of each of the groups of common difference, except the first, viz. Ga, Ag, Au, Ge, Pd, and Pt, appears to be a heavy malleable metal, electrically neutral, and with an atomic volume a little above 9 in the artiad, and 10 in the perissad groups.

With the increase of atomic volume is generally associated an increase in electro-negative properties, and, as a rule, the elements become fusible, brittle, and diamagnetic.

With the maximum atomic volume, the elements change from the extreme of negative to positive, from diamagnetic to magnetic, from brittle to malleable; and with the decrease of volume, they lose their electro-positive properties, and, as a rule, become at last brittle and infusible.

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* Text-Book of Chemistry, p. 16.

† The Periodic Law, p. 27.

‡ Journal of Analytical Chemistry, January, 1889, p. 48.

TABLE I. — PERISSADS.

El.	Atomic Weights.			Physical Properties.					Gr.
	Ser.	Obs.	Dev.	Sp. Gr.	At. Vol.	Fus.	Mal.	Elec.	
H	1	1.0	0.0	....	....	..	..	..	I
	$+ 6 + n \times 4$								
Li	7	7.0	0.0	0.59	11.9	1	M	5	I
B	11	11.0	0.0	2.68	4.0	6	B	49	III
	15	?							
F	19	19 0	0.0	....	....	1	B	60	VII
Na	23	23 1	+0.1	0.97	23.7	1	M	4	I
Al	27	27.1	+0.1	2.56	10.6	3	M	13	III
P	31	31.0	0.0	2.30	13.5	2	B	55	V
Cl	35	35.5	+0.5	1.38	25.6	1	B	59	VII
K	39	39 1	+0.1	0 86	45.4	1	M	3	I
Sc	43	44.?	....	....	....	..	..	..	III
	47	?							
V	51	51.3	+0.3	5.50	9.3	7	B	52	V
Mn	55	55.0	0.0	8.00	6.9	5	B	19	VII
Co ?	59	(59.0	0 0	8.50	6.9	5	M	23)	
Cu	63	63.5	+0.5	8.80	7.2	3	M	31	I
	$+ 7 + n \times 5$								
Ga	70.0	70.0	0.0	5.96	11.7	1	?	?	III
As	75.0	75.0	0.0	5.67	13.2	2	B	54	V
Br	80.0	80.0	0.0	2.97	26.9	1	B	58	VII
Rb	85 0	85.4	+0 4	1.52	56 1	1	M	2	I
Y	90.0	89.8	—0.2	....	....	..	..	11	III
Cb	95.0	94.2	—0.8	6.27	15.0	7	B	44	V
	100.0								
	$+ 7\ 5 + n \times 6.25$								
Ag	107.5	107.9	+0.4	10.50	10.2	3	M	32	I
In	113.7	113.7	0.0	7.43	15.3	1	M	27	III
Sb	120.0	120.1	+0.1	6.70	17.9	2	B	47	V
I	126.3	126.8	+0.5	4.94	25.6	1	B	57	VII
Cs	132.5	132.9	+0 3	1.88	70 6	1	M	1	I
La	138 8	138.8	0.0	6.20	22.3	3 ?	..	18	III
Di	145.0	145.0	0.0	6.50	22.3	3 ?	..	17	V
	$? + n \times 4$								
Au	196.0	196.6	+0.6	19.30	10.2	3	M	40	I
Hg	200.0	200.2	+0.2	13.59	14.7	1	M	33	II
Tl	204.0	204 2	+0 2	11.86	18.1	2	M	24	III
Bi	208.0	208.0	0.0	9 82	21 1	2	B	29	V

TABLE II. — ARTIADS.

El.	Atomic Weights.			Physical Properties.					Gr.
	Ser.	Obs.	Dev.	Sp. Gr.	At. Vol.	Fus.	Mal.	Elec.	
	$12 + n \times 4$								
		?							
C	12.0	12.0	0.0	0.33	3.6	7	B	54	IV
O	16.0	16.0	0.0	....	....	1	B	63	VI
	20.0	*							
Mg	24.0	24.0	0 0	1.74	13.8	3	M	9	II
Si	28.0	28.1	+0.1	2.49	11.2	6	B	42	IV
S	32.0	32.1	+0.1	2.04	15.7	1	B	62	VI
	36.0	*							
Ca	40.0	40.0	0.0	1.57	25.4	2	M	8	II
	44.0	?							
Ti	48.0	48.1	+0.1	....	....	..	B	43	IV
Cr	52.0	52.3	+0 3	6.80	7.7	5	B	53	VI
Fe	56.0	56 0	0.0	7.80	7.2	5	M	21	VIII
	60.0	?							
Zn	64.0	65.0	+1.0	7.15	9.1	2	M	20	II
	$+ 7 + n \times 4$								
Ge	71.0	?	....	?	....	?	..	?	IV
As	75.0	75.0	0.0	5.67	13.2	2	B	54	V
Se	79.0	79.0	+0.0	4 60	17.1	1	B	56	VI
	83.0	*							
Sr	87.0	87.5	+0.5	2.50	34.9	2	M	7	II
Zr	91.0	90 6	—0.4	4.15	21.7	6	B	14	IV
Mo	95.0	95.9	+0.9	8.60	11.1	6	B	51	VI
	99.0	?							
	$+ 7 + n \times 6.25$								
Pd	106.0	106 0	0.0	11.50	9.2	4	M	34	VIII
Cd	112.2	112.2	0.0	8.65	12.9	2	M	25	II
Sn	118.5	118.0	+0.5	7.29	16.1	2	M	28	IV
Te	124.8	125.0	—0.2	6.25	20.2	2	B	46	VI
	131.0	*							
Ba	137.2	137.1	—0.1	3.75	36.5	2	M	6	II
Ce ?	143.5	?	?	6.70	21.0	3 ?	..	16	IV
	$? + n \times 4$								
Pt	195.0	194.9	—0.1	21.50	9.1	5	M	37	VIII
Os	199 0	198.9	— 0.1	22.50	8 7	5	B	39	VIII
	203.0	?							
Pb	207.0	206.9	—0 1	11.38	18.1	2	M	26	IV
	$14 + n \times 44.8$								
Ni	58.8	58.7	—0 1	8.80	6.7	4	M	22	VIII
Co	58 8	59.0	+0.2	8.50	6.9	5	M	23	VIII
Ru	103.6	104.0	+0.4	12.26	8.4	5	B	35	VIII
Rh	103.6	104.2	+0.6	12.10	8.6	5	M	36	VIII
	148.4	?							
Ir	193.2	193.0	—0.2	22.46	8.6	5	B	38	VIII

The study of the periodic law has directed attention to the relations between the atomic weights and these properties, many of which were previously treated as functions of the electro-chemical order.

When the exact atomic weights are all determined with sufficient accuracy, it is natural to infer that the deviations from the regular increase will show a law as significant as the approximate coincidence with the serial numbers, and even now we see clear evidences of this law. To make it more apparent, it will first be necessary so to adjust the formula as to reduce these differences to a minimum, and in the low atomic weights to take account of smaller fractions.

The formula $a + n\,d$ then has the following values for the several groups of common difference: —

$$\begin{array}{rr} 6.99 + n \times 4.02 & 12.00 + n \times 4.01 \\ 70.25 + n \times 4.85 & 74.88 + n \times 4.12 \\ 107.85 + n \times 6.20 & 105.98 + n \times 6.22 \end{array}$$

Table III. shows the deviations, arranged in the groups and series of the periodic law; the lower division shows the electro-chemical numbers in the same form.

Neglecting insignificant deviations, we find the positive results, or those where the atomic weight is slightly in excess of the serial number, either near the extremes of the electric series, in elements of maximum atomic volume, etc., or in the very centre of this series. The negative results occur half-way between the centre and the extremes. Of the perissads, 1, 2, — 31, 32, — 57, 59, are positive, and 17, 18, 19, 21, — 44, 47, 54, 55, are negative; of the artiads, 7, — 46, 51, 53, are positive, and 8, 14, 21, 23, 28, are negative.

In the periodic arrangement, the first and second groups show positive deviations in the high series of this arrangement; the third, fourth, and fifth, negative in the high series; the sixth, positive in the high series; and the seventh, positive in two terms, and insignificant in two. The seventh and eighth groups are negative in the third series. The deviation of Zn is not included in these calculations, nor is the cause of its deviation yet apparent. Perhaps the perissads of the second group are formed from an artiad nucleus, and the artiads of the second group from a perissad nucleus, thus: * 65, 70, 75, 80, etc., and 63 * 71, 75, 79, etc. The last line shows the algebraic mean of the deviations in each group, which, as might be expected, corresponds nearly to the relative atomic volumes.

To do justice to the bearing of these results on the physical question of the ultimate nature of "atoms" would involve a mathematical

TABLE III. — DEVIATIONS.

Gr.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Ser.								
1	—.03	?	—.03	.00	?	—.01	—.03	
2	—.02	—.02	.00	+.02	—.08	+.01	+.32	
3	—.02	—.08	?	.00	+.05	+.19	(—.26)	—.11
4	+.06	?	—.30	?	—.06	+.03	+.01	
5	+.64	+.28	+.01	—.80	—.30	+.47		+.02
6	+.08	+.03	—.36	—.42	—.14	+.31	+.41	
7	+.25	+.02	—.18	?	—.05			
	+.14	+.05	—.14	—.25	—.09	+.17	+ 18	—.05

ELECTRO-CHEMICAL ORDER.

1	5	?	49	48	?	63	60	
2	4	9	13	42	55	62	59	
3	3	8	?	43	52	53	(19)	21
4	31	20	?	?	54	56	58	
5	2	7	11	14	44	51		34
6	32	24	27	28	47	46	57	
7	1	6	18	16	17			

discussion too prolonged for this paper; but the subject cannot be completed without a brief statement of its relation to well known systems and theories of Chemistry. A few extracts will serve as a basis to show what the perissad law is intended to contribute to the solution of the all-important problem.

In 1854, in a paper read before the American Academy on "The Numerical Relation between the Atomic Weights," Professor Cooke announced the character of the problem as follows: —

"Numerical relations between the atomic weights of the chemical elements have been very frequently noticed by chemists. One of the fullest expositions of these relations was that given by M. Dumas, of Paris, before the British Association for the Advancement of Science, at the meeting of 1851. This distinguished chemist at that time pointed out the fact, that many of the elements might be grouped in triads, in which the atomic weight of one was the arithmetical mean of those of the other two. Thus the atomic weight of Bromine is the mean between those of Chlorine and Iodine; that of Selenium is the mean between those of Sulphur and Tellurium; and that of Sodium, the mean between those of Lithium and Potassium.

"M. Dumas also spoke of the remarkable analogies between the properties of the members of these triads, comparing them with similar analogies observed in Organic Chemistry, and drew, as is well known, from these facts arguments to support the hypothesis of the compound nature of many of the now received elements. Similar views to those of Dumas have been advanced by other chemists.

"The doctrine of triads is, however, as I hope to be able to show in the present memoir, a partial view of this subject, since these triads are only parts of series similar in all respects to the series of homologues of Organic Chemistry, in which the differences between the atomic weights of the members is a multiple of some whole number. All the elements may be classified into six series, in each of which this number is different, and may be said to characterize its series. In the first it is 9, in the second 8, in the third 6, in the fourth 5, in the fifth 4, and in the last 3." (See Table IV.)

The paper speaks of the properties of the elements which are functions of the atomic weights, and says that it does not seem bold theorizing to suppose that the atoms of the members of the same series are formed of a common nucleus, to which has been added one or more groups of atoms, or perhaps one or more single atoms, to which the corresponding element has not been discovered.

Referring to this subject in 1857,* M. Dumas said: "I have often tried, as Mr. Josiah Cooke has on his part, to compare them, to combine them, and to discuss them, with the hope of drawing some conclusion from them with certainty, but I have been unable to draw from them anything but doubt. The formula deduced from the above simple progression" $(a + n\,d)$ "would not account for the generation of simple bodies, as Cooke had supposed, but organic radicles are not always formed by addition, they are also produced by substitution, as we see in the compound ammoniums." Dumas proposed to substitute a formula like $n\,a + n'\,d + n''\,d'$; a being the nucleus; d and d', the common differences; and n, n', n'', whole numbers. Table IV. shows the series of Cooke and Dumas.

Following in their footsteps, Professor Newlands extended their principles to include newly discovered elements. Employing Cannizzaro's atomic weights instead of those of the old system, and collating his own results and all discovered up to 1864, he arranged the groups in horizontal lines instead of vertical columns, and then discovered the "Law of Octaves," as shown in Table IV. The coincidence of the ordinal numbers led him, in 1865, to express the following opinion: "I will

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* Comptes Rendus, 1857, p. 709.

TABLE IV.

Cooke, 1854.

Ser.	III.		IV	V.	VI.	VIII.	IX.	IV.
Gr.	3.	2. 1.	3, 2. 1.					2. 1. 3.
	H Li Na K Ag	Ca Mg Sr Zn Ba Cd Pb	Al Ti Cr Pd Mn Sn Fe Pt Co Ir Ni Os U Au Cu Hg	C B Si	O N P As Sb Bi	O S Se Mo Te V W Ta	O F Cy Cl Br I	Al Ti Cu Cr Pd Hg Mn Sn Fe Pt Co Ir Ni Os U Au
	Cu Mn			Ti	Cr V	As Mn	Cr Mn Os Au	

Dumas, 1857.

Form.	$7 + n\ 8$	$12 + n\ 8$	$25 + n\ 34$	$6 + n\ 5$	$14 + n\ 17$	$8 + n\ 8$	$19 + n\ 16.5 + n'\ 28$	
	L Na K	Mg Ca Sr Ba Pb	Ti Sn Ta	C B Si Zr	N P As Sb Bi	Cr O Mo S V Se W Te	F Cl Br I	

Mendeléeff, 1869.

Gr.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Ser.								
1	H							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni Cu
5	(Cu)	Zn	Ga	—	As	Se	Br	
6	Rb	Sr	?Y	Zr	Nb	Mo	—	Ru Rh Pd Ag
7	(Ag)	Cd	In	Sn	Sb	Te	I	
8	Cs	Ba	?Di	?Ce				
9	(—)							
10			?Er	?La	Ta	W		Os Ir Pt Au
11	(Au)	Hg	Ti	Pb	Bi			
12				Th		U		

TABLE IV. — *Continued.*

NEWLANDS, 1865.

	No.		No		No.		No		No.		No.		No.		No.
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Tl	53
G	3	Mg	10	Ca	17	Zn	25	Sr	31	Cd	38	Ba & V	45	Pb	54
Bo	4	Al	11	Cr	19	Y	24	Ce & La	33	U	40	Ta	46	Th	56
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Hg	52
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Os	51

endeavor to show that all the numerical relations among the equivalents pointed out by M. Dumas and others, including the well known triads, are merely arithmetical results flowing from the existence of the 'law of octaves,' taken in connection with the fact of the equivalents forming a series of numbers approaching to the natural order." And in 1866: "The fact that such a simple relation exists now, affords a strong presumptive proof that it will always continue to exist, even should hundreds of new elements be discovered. For, although the difference in the numbers of analogous elements might, in that case, be altered from 7, or a multiple of 7, to 8, 9, 10, 20, or any conceivable figure, the existence of a simple relation among the number of analogous elements would be none the less evident." * The law of regular increase, however, points to a relationship far more significant than the identity of their ordinal numbers.

Working independently of Newlands, Mendeléeff discovered the periodic law in 1869. It has offered a grand incentive to new discoveries and received well merited recognition throughout the world. The extracts from Wurtz and Meyer, at the beginning of this paper, show what it left to be desired.

A paper by Rev. Dr. Haughton, and an abstract of one by Mr. Stoney, have recently appeared in "The Chemical News." Each gives a clear enunciation of the nature of the problem. Dr. Haughton discovers some of the regular intervals noticed here. Unfortunately, the paper of Stoney, on "The Logarithmic Law of Atomic Weights" † is so abridged, that it is hard to determine how his results may compare with those herein discussed. The abstract states, that, in plotting the atomic volumes as ordinates of a diagram, the effort to

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* The Periodic Law, p. 20.

† The Chemical News, vol. lvii. p. 163.

extract information from the resulting curves was a failure ; in plotting their cube roots, however, he found a logarithmic curve with perturbations which showed a distinct law of increase for perissads and artiads. The abstract was not discovered until most of this paper was written, and, from its indefinite statements, it would require much time to construct the curves and divine the inferences.

At the close of his paper of 1854, Professor Cooke said : " To my conceptions Chemistry will then have become a perfect science, when all substances have been classed in series of homologues, and when we can make a table which shall contain, not only every known substance, but also every possible one, and when by means of a few general formulæ we shall be able to express all the properties of matter, so that, when the series of a substance and its place in the series are given, we shall be able to calculate, nay predict, its properties with absolute certainty. . . . Then the dreams of the ancient alchemist will be realized, for the problem of the transmutation of metals will have been theoretically, if not practically, solved."

XV.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

NEUTRALIZATION OF INDUCTION.

By John Trowbridge and Samuel Sheldon.

Presented May 28, 1889

The invention of the telephone drew attention to the extraordinary sensitiveness of Faraday's electrotonic state, and immediate attempts were made to construct induction balances, so called, which might serve for quantitative measurements. Thus we have Hughes's induction balance, which had its prototype in the balance described in Maxwell's "Electricity and Magnetism," Vol. II. § 636, due to Felici,[*] and which differs from Hughes's balance merely in the employment of a galvanometer instead of a telephone. By substituting the latter instrument, Hughes showed that great sensitiveness could be obtained, and even proposed to adopt an instrument for measuring minute amounts of impurities in coins arising from alloys.

The great difficulty, however, in the employment of Hughes's induction balance in quantitative work arises from the difficulty of getting a good minimum of tone in the telephone. The method that Hughes employed was, briefly, to employ four coils, — two in a circuit through which an alternating current or an interrupted current was passed, and two other coils placed contiguous to the coils which were in the interrupted circuit, but in another circuit. By interposing a telephone in the last mentioned circuit, and by properly placing the coils in this circuit with reference to those in the circuit through which the interrupted current was passed, a balance could be obtained, or an imperfect minimum of sound in the telephone, when the induction between the sets of coils was neutralized. In order to obtain a standard, Hughes employed a wedge of zinc, which was thrust between one of the coils in the interrupted circuit and one of the coils in the telephone circuit, in order that the mutual induction between these coils might balance

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[*] Nuovo Cimento, vol. ix. p. 345, 1859

that arising between the other two similarly placed coils when a coin or sheet of metal was placed between these last mentioned coils. Other devices have also been employed by various investigators who have endeavored to use the apparatus for quantitative measurement. Alexander Graham Bell employed a modification of Hughes's induction balance for the detection of the presence of a bullet in the human body. In the form employed by him, one coil, which was a closely wound flat copper band, was made to slide over a similar one by means of a screw, one coil being placed in the telephone circuit and the other in a circuit containing a current-breaker. The induction arising from a similar pair of coils moved over a mass of metal like a bullet could thus be neutralized by this sliding coil arrangement. In no form, however, of Hughes's induction apparatus can one obtain a satisfactory minimum of tone in the telephone. There is never absolute silence, and no two observers can obtain the same point at which the sound seems to be a minimum. The failure to obtain this minimum is thus a radical defect in the instrument. It is doubtless very sensitive, but it cannot be called a quantitative instrument.

To remedy this defect, A. Overbeck and J. Bergmann* substituted an electro-dynamometer for the telephone, and worked out a method of obtaining the resistances of metals when they are in the form of thin circular plates. The standard of comparison they employed was a thin layer of mercury between disks of glass in a cylindrical reservoir. Preliminary investigations had shown the authors that a certain relation existed between the thickness and specific resistance and coefficient of induction of metals in the form of thin disks, which were placed between the coils of the induction balance. In a subsequent paper,† A. Overbeck gives the mathematical theory of the induction balance, which in the main is Maxwell's theory of current sheets applied to Arago's disk.‡ In employing the instrument to measure the effect of change of temperature on induction in copper plates, or, in other words, temperature coefficients, in which we found that Messrs. Overbeck and Bergmann had anticipated us,§ we were led to adopt the following form of the instrument, which differed entirely from that of these authors. Four coils were employed, as in the Hughes form of instrument. One of the coils in the telephone circuit was fixed upon a horizontal axis which was at right angles to the axis of the

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* Annalen der Physik, xxxi., 1887, p. 792.

† Ibid., p. 812.

‡ Maxwell's Electricity and Magnetism, vol. ii. § 668 *et seq.*

§ Annalen der Physik, xxxvi., 1889, p. 783.

coil. The coil could therefore be moved through all positions, from perfect parallelism to its neighboring coil in the interrupted circuit to a position at right angles to this coil. The horizontal axis was provided with an index arm which moved over a graduated circle. Calling θ the angle of inclination of the axis of the movable coil with the axis of the fixed coil in the interrupted circuit, and N the strength of the induction current in the movable coil, we have evidently, on the supposition that the strength of the alternating current remains constant,

$$N = \text{constant} \times \text{cosine } \theta.$$

When the axes of the coils are at right angles, cosine $\theta = 0$, and we should have silence in the telephone. Since adopting this arrangement we have discovered that Dr. Bowditch, of the Harvard Medical School,* has employed this arrangement of a movable coil placed in front of a fixed coil as a modification of Du Bois Reymond's apparatus for controlling induction currents so that they may be administered by known amounts for physiological purposes. In Du Bois Reymond's apparatus one induction coil was simply moved away from a fixed coil through which an interrupted current was passed, much in the same manner as the coils in Wiedemann's form of galvanometer are moved. Here no minimum could be obtained. In Dr. Bowditch's form of this apparatus, theoretically a minimum should be obtained, that is, when cosine $\theta = 0$, or when the axes of the coils were at right angles. An indication of an electrical current is obtained even when the axes of the coils are at right angles, on account of the windings of the coil not being perfectly at right angles to those of the stationary coil.

That no minimum should be obtained when the axes of the coils are at right angles, and when induction arises from all parts of the circuit, is evident upon an elementary consideration of the subject. We have to deal in this form of instrument with the mutual induction which arises between the fixed coil and the movable one, and also with the self-induction which arises between the spires of the movable coil in the telephone circuit. The mutual induction can be reduced theoretically to zero by placing the movable coil of the telephone circuit at right angles to the fixed coil. The self-induction can be estimated as follows. Taking Maxwell's discussion for the induction between parallel circuits of radii A and a, we have the coefficient of mutual induction,

$$M = \int\int \frac{\cos e \, ds \, ds'}{r}.$$

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* Proc. Am. Acad., vol. xi. p. 281.

Projecting one circle upon the plane of the circle of greater radius, A, we have

$$M = \int_0^{2\pi} \int_0^{2\pi} \frac{A a \cos(\phi - \phi') \, d\phi \, d\phi'}{\sqrt{A^2 + a^2 + b^2 - 2 A a \cos(\phi - \phi')}} .$$

Making b the distance between the planes of the circles $= 0$, we pass from the case of mutual induction to that of self-induction between two spires of a coil which may be considered approximately circular. The form of M adapted for calculation is then

$$M = 4 \pi \sqrt{Aa} \left\{ \left(c - \frac{2}{c} \right) F + \frac{2}{c} E \right\},$$

where $c = \frac{2 \sqrt{Aa}}{(A + a)}$, and F and E are complete elliptic integrals to modulus c.

If we make $A - a = D$, or $A = D + a$, in which D is the distance between the spires at which the self-induction becomes insensible, the most perfect minimum can be attained. We have found that copper wire of 2 mm. diameter, wound in a flat loose spiral, the spires of which from centre to centre of the wire are 4 mm. apart, gives no sensible self-induction for spirals of eight to ten spires. On turning a movable coil of this form so that its axis may be perpendicular to the axis of the fixed coil, a perfect minimum can be obtained. A slight movement to the right or left of this position is quickly made evident by the note of the interrupted circuit which is heard in the telephone. It is evident that, if four coils are employed, as in Hughes's form of induction balance, the two coils in the telephone circuit should be wound in the manner we have indicated, to avoid self-induction. On placing a plate of metal between one set of the coils of this balance, the movable coil no longer gives a minimum at the position where its axis is at right angles to that of the fixed coil, but at some point removed a few degrees from this. By placing a mirror upon the movable coil, and by observing its deflection with a telescope, a greater refinement of reading is possible.

This instrument in its modified form suggests the possibility of neutralizing induction upon telephone circuits. The extension of the various systems for transmitting power by electricity, especially the electric car system, has led to great disturbances in the telephone circuits. These disturbances are due both to leakage from the power circuit into the telephone circuit, since the earth is used partially by the electric power companies in their return circuits, and to actual induction. The best remedy for these disturbances is doubtless the adoption by either the power companies or the telephone companies of entire metallic circuits, in which the earth plays no part. If this is not possible, a system of neutralization for the inductive disturbances might be adopted as follows. Let a shunt circuit from the electric light wire or the wire carrying the current for motors be led into a station through which also passes the telephone wire. The resistance of this shunt or derived circuit can be made suitable for the purpose. In all cases it reduces the resistance of the main line, and is therefore not prejudicial. On this shunt can be arranged a fixed coil, and on a neighboring telephone wire a movable coil of no self-induction. Let this movable coil be placed in front of the fixed coil in the motor circuit, and let it be turned until the mutual induction between it and the fixed coil neutralizes the induction produced at all points along the telephone circuit. Each telephone wire would need its movable coil, and to every movable coil would correspond a fixed coil in the shunt of the motor circuit. The operator at the central station could adjust the movable coils until the disturbances arising from induction at various points along the line are neutralized.

XVI.

THE MAGNETISM OF NICKEL AND TUNGSTEN ALLOYS.

By John Trowbridge and Samuel Sheldon.

Presented May 28, 1889.

Introductory.

The fact that different kinds of steel, alloyed in small proportions with Tungsten or Wolfram, and magnetized to saturation, increase in specific magnetism,* has long been known. Whether the same effect would result from the use of Nickel alloyed with Tungsten has never been investigated. This paper has for its object a partial answer to the query. It was instigated by Mr. Wharton, proprietor of the American Nickel Works, whose chemist, Mr. Riddle, kindly prepared the alloys which have been employed. These alloys were in two groups. The first, received in November, 1888, consisted of three bars of the same shape, one being of pure nickel and the other two having respectively 3 and 4 per cent of tungsten in alloy. These bars were rolled from cast ingots, which were toughened by the addition of magnesium after Fleitmann's method, the magnesium being added just before pouring. They were hot when rolled. The one of pure nickel was afterwards planed into regular shape. Those containing tungsten were too brittle to allow of this manipulation. They were, however, of sufficient regularity to permit accurate measurements. This group contained also an octagonally shaped bar with 8 per cent of tungsten, which was prepared like the others, and was afterwards ground into shape.

The second group, received in May, 1889, contained bars which were simple castings, made without the addition of magnesium, and consisted of pure nickel and alloys with 1, 2, 3, and 6 per cent of tungsten. All the bars in this group were extremely hard and brittle. In making them, tungsten oxide, of weight calculated to yield the desired percentage of tungsten in the resulting alloy, was placed with

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* Jour. Chem. Soc., 1868, xxi. 284, says 300 per cent.

adequate carbon in the bottom of a graphite crucible and covered by the proper weight of pure grain nickel. All was then covered with borax, the lid of the crucible was placed on, and the crucible was heated until reduction and fusion were completed.

Method.

As the suspected influence of the tungsten would be to affect the magnetic moment of the bars, these were magnetized to saturation and their specific magnetism then determined, i. e. the magnetic moment for each gram of metal.

The magnetization was effected by placing the bars separately in a hollow coil whose length was 15 cm. and outside and inside diameters respectively 6 and 3 cm. It consisted of 6 layers of wire having 63 turns each. A dynamo current of 40 ampères was then sent through the coil for one minute, and the circuit then broken and the bars removed.

For the determination of the magnetic moment, use was made of a reflecting magnetometer, and deflections were observed with a telescope and scale at a scale-distance of 100 cm. Measurements of the horizontal intensity, H, of the earth's magnetism were first made. The results from these determinations by means of the first and second Gauss arrangements were, respectively,

$$H = 0.1724 \text{ cm. g. s.}$$
$$H = 0.1720 \quad \text{“}$$

The freshly magnetized bars were then placed in the second Gauss position relative to the magnetometer, and the angular deflection determined. The specific magnetism, S, was then calculated by the formula

$$S = \frac{r^3 H \tan \phi}{m},$$

where

r = distance from bar to magnetometer = 72.68 cm.
H = earth's horizontal intensity = 0.1722.
m = mass of the bar.
ϕ = angular deflection of magnetometer.

Results.

The mean results of two sets of observations on Group I., and also upon a similar bar of soft tool steel are given in the following table.

GROUP I.

Composition.	Size in cms.	Mass in grams.	$S\ [\text{cm.}^{\frac{5}{2}}\,\text{g.}^{-\frac{1}{2}}\,\text{sec.}^{-1}]$.
Pure Nickel	18 × 2.7 × 0.65	284.5	1.23
Ni + 3% W	" " "	286.5	10.60
Ni + 4% W	" " "	283.5	10.40
Tool Steel	15 × 2.5 × 0.5	159.5	7.46
Ni + 8% W	(Octagonal 13 × 1.5)	144.0	5.25

Group II., of cast bars, gave the following results.

GROUP II.

Composition.	Size in cms.	Mass in grams.	$S\ [\text{cm.}^{\frac{5}{2}}\,\text{g}^{-\frac{1}{2}}\,\text{sec.}^{-1}]$.
Pure Nickel	18 × 1.8 × 1.6	459	1.05
Ni + 1% W	" " "	455	1.92
Ni + 2% W	" " "	454	1.70
Ni + 3% W	" " "	463	1.75
Ni + 6% W	" " "	465	1.15

The bars of both groups were, subsequent to the above observations, completely demagnetized, and then freshly magnetized. New determinations gave the same results as before. The demagnetization was accomplished by placing the bars inside two coils, which were traversed by currents from an alternating dynamo. The coils were then slowly drawn apart, and the bars maintained at a position central between them. After treatment in this manner, they showed no appreciable deflection when placed in position relative to the magnetometer.

The results tabulated indicate that tungsten greatly increases the magnetic moment of nickel, if the alloy be forged and rolled, but on the other hand has but small influence if they be simply cast. Furthermore, changes in the amount of tungsten do not appear to cause corresponding changes in the magnetic properties.

To see whether the remarkable effect in bars 2 and 3, as compared with bar 1, of Group I. was owing to some molecular condition of their surfaces induced by rolling, two bars from the same steel, one rolled and the other pressed, were magnetized and then measured. The ratio of the specific magnetism of pressed to rolled was as 9 to 5, the rolled having the smaller amount. The existing difference, in this case, is probably owing to a difference in hardness, rather than to any molecular condition of the surfaces.

The specific magnetisms of all the bars are small when compared with good steel magnets. Kohlrausch says that good magnets, of common form, should have $S = 40$. The bar of ordinary tool steel, however, retained but 7.46. Still it was soft, and by tempering would doubtless have doubled this value.

If forged nickel and tungsten can be made to maintain a specific magnetism of 10, it will form a useful addition to the resources of physical laboratories. From the high polish of which it is susceptible and its freedom from damaging atmospheric influences, it will be most happily suited for the manufacture of mirror magnets where magnetic damping is to be employed.

JEFFERSON PHYSICAL LABORATORY.

XVII.

THE MÉCANIQUE CÉLESTE OF LAPLACE, AND ITS TRANSLATION WITH A COMMENTARY BY BOWDITCH.

By Joseph Lovering.

Presented June 8, 1889.

Laplace was born in Beaumont-en-Auge on March 28, 1749. The early years of his life are hidden in the obscurity of his humble origin. It is only known that he was the son of a small farmer. He first gained distinction in a theological controversy. After attending some of the classes in a military school in Beaumont, he taught mathematics there. At the age of eighteen, he approached the great D'Alembert with the hope of finding some career in Paris, and was rebuffed. Afterwards, Laplace sent to him a letter on the *Principles of Mechanics.* D'Alembert wrote back: "You see that I make little enough of the matter of recommendations. You have no need of them. You have done better: to know. This is enough for me: my support is your due." Thus he mounted at once to the position of Mathematical Professor in the Military School at Paris. Before entering the Paris Academy, at the age of twenty-four, he began his career of investigation by which he won the title of the Newton of France, having made a capital discovery relating to the mean distances of the planets from the sun. Laplace was also an investigator in physics and chemistry, working with Lavoisier and Berthollet. Only fifteen days before his last sickness, he communicated to the Memoirs of the Academy a paper on the oscillations of the earth's atmosphere, which was printed in the same volume which contained Poisson's funeral oration.

Of his three great works, the five volumes of the *Mécanique Céleste* were published between 1799 and 1827; the *Exposition du Système du Monde* in 1796; and the *Théorie analytique des Probabilités* in 1812. Arago reported, in 1842, that not a copy of the last work was in the libraries of Paris, although three editions had been published, and that the two other works were almost out of print, so that he feared that it would be necessary to order from America Bowditch's translation. In this emergency Madame de Laplace, always devoted to the reputation and memory of her dead husband, was negotiating for the sale of a small farm in order to provide the means of republishing his works, when the government of Louis Philippe took the matter in hand and appropriated forty thousand francs for a new edition. This appeared, in seven quarto volumes, between 1843 and 1847. At a later period, when this edition was nearly exhausted, General Laplace, the distinguished son of the mathematician, and his granddaughter, the Marquise de Colbert, expended seventy thousand francs on a third edition, which appeared between 1878 and 1886.

Laplace was the friend of young mathematicians and physicists, such as Arago, Poisson, and Biot, who were called "the adopted children of his thought." At an early age, while still a pupil in the Polytechnic School, Arago was attached to the Paris Observatory as secretary. He has given in his Autobiography the following interesting sketch of Laplace. He says: "I entered this establishment, then, on the nomination of Poisson, my friend, and through the intervention of Laplace. The latter loaded me with civilities. I was happy and proud when I dined in the Rue de Tournon with the great geometer. My mind and my heart were much disposed to admire all, to respect all, that was associated with one who had discovered the cause of the secular acceleration of the moon, had found in the movement of this satellite the means of calculating the ellipticity of the earth, had traced to the laws of gravitation the long inequality of Jupiter and Saturn, etc., etc. But what was my disenchantment when, one day, I heard Madame de Laplace approach her husband, and say to him, 'Will you intrust to me the key of the sugar?'"

Another anecdote told by Arago is not so complimentary to Laplace. Delambre, the Perpetual Secretary of the Academy of Paris, died on the 19th of August, 1822. A committee was appointed to present candidates for the succession. The choice lay between Fourier and Biot. The election was always by secret ballot, — Arago frankly saying that no one wished to incur the disaffection of a successful candidate against whom he had voted. Laplace wrote the *same* name upon two ballots, put them in his hat, and shook them up. He took one out and tore it, and put the other in the urn, pretending not to know for whom he had voted, though an indiscreet neighbor did. No calculus of probabilities, Arago says, was needed for this problem.

Twenty-three years after the death of Laplace, Biot confided to the Academy of Paris these interesting reminiscences of him. "Every one," he says, "will understand how valuable to a young man were these familiar and intimate interviews with a genius so powerful and so comprehensive. But what he might not imagine were the sentiments of affectionate and paternal delicacy which attended them, unless he himself had been the object of them. Shortly after I was permitted to approach him, I had the good fortune to take a step, which seemed to me new and unexpected, in a field of mathematics hitherto scarcely invaded. In 1766, Euler had treated a peculiar class of geometrical questions by an indirect method in a paper entitled *De insigni promotione methodi tangentium inversæ.** Subsequently, he attacked a more difficult problem of the same kind, to which he repeatedly returned with different solutions, but always indirect. The singularity of the problem originated in the nature of the curve, the geometrical characters being of different orders, — some belonging to points infinitely near, others to distant points separated by finite differences. I succeeded in rendering a complete statement of the problem in analytical language, applying to each part appropriate symbols. The realization of this idea surpassed my expectations.†

"After I had found the key to a solution of the problem, I spoke to Laplace about it. He listened with attention and with some surprise, and then said, 'It seems all very well; come to-morrow morning and bring your memoir; I shall be glad to see it.' After hearing it, discussing it, and suggesting certain omissions, he told me to present it to the Academy the next day, and, after the session, come and dine with him. 'Now,' said he, 'let us lunch.'"

Biot communicated his paper to the Academy in the presence of Monge, Lagrange, Laplace, and of Bonaparte who had just returned from Egypt. Bonaparte pretended to recognize the diagrams, though no one had ever seen them before except Laplace. "I had more fear of Lagrange," said Biot, "than of Bonaparte, with all his military glory."

After Biot had read his paper, and received the congratulations of the Academicians, he accompanied Laplace home. As soon as they had entered the house, Laplace took Biot into his study, unlocked a closet, took out a copy-book, yellow with age, and showed him all

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* Nov. Comment. Petrop., x.

† Considerations sur les équations aux différences mêlées; Mém. Savants Etrangères, i 296–328.

the problems resolved by the method which Biot had supposed to be original with himself. When Biot read his paper to Laplace he was cautioned against certain inferences at the end which Laplace thought too remote. "Go not," he said, "beyond the results which you have actually obtained. You will probably meet difficulties more serious than you suppose: the actual state of analysis cannot furnish you the means of surmounting them." And Biot struck out his hazardous inferences. It now appeared that Laplace had been arrested by the same obstacle which he had signalized to Biot. Hoping to surmount it later, he had said nothing about it to any one, not even to Biot, when he came to bring him his own work as if it were a novelty. Biot does homage to the abnegation of Laplace in allowing him to make his communication without the consciousness of having been anticipated. Laplace would allow no allusion to be made to the transaction when Biot's paper was printed. No mention of it appears in the records of the Academy. Not until after fifty years did Biot feel at liberty to mention it. "This discovery, the first I had made, was everything for me. It was little for him who had made so many. Would he always have been so just? Would he be so generous to a rival? I have no occasion to examine that here. He was all this for me, and for many others who began their career in this way."

Biot has described the country-seat of Laplace in Arcueil, adjoining that of the eminent chemist, Berthollet. "It was acquired by him in 1806, two years after the Emperor, Bonaparte, had promoted him to the first dignities of the Senate. He bought it without having seen it, on the report of Madame Laplace, being contented to know that it was adjacent to that of his friend Berthollet. A simple garden wall separated them. Berthollet had cut an opening in it and placed a gate there before Laplace arrived. Then he came to receive him with ceremony at the boundary of their domains, bringing the keys which would give them free access to each other. It was in this delicious retreat that Laplace spent every day, every moment, of liberty that his business left to him, — not to give himself to indolent repose, but to continue, with unwearied passion, his great labors on mathematical physics and the system of the world, emerging from these meditations only to converse with his friend on physics and chemistry. Here he also welcomed a retinue of zealous young men, whom he condescended afterwards to call his colleagues, and who always were proud of this association. Around him, in a more elevated sphere, were seen continually Berthollet, Lagrange, Cuvier, etc., to whom he introduced his young protégés. Here Laplace died, on March 5, 1827.

His last words were, 'Ce que nous connaissons est peu de chose; ce que nous ignorons est immense.' This sanctuary of sciences has been preserved, with a religious respect, by Madame Laplace, to whom it belongs to-day (1850). The house, the gardens where he walked, are as they were then. The study in which he composed so many noble works remains untouched, with the same furniture and books that served him in the state in which he left them. He alone is wanting, to the profound regret of those who knew him and will never see his equal."

If we turn from this attractive picture of the domestic and scientific life of Laplace to his public career, the contrast is not pleasant. Living in the most disturbed period of France, he managed to keep himself always in the ascendency. After the *coup d'état* of Napoleon, in 1799, his republican ardor was replaced by devotion to the First Consul. But his incapacity as Minister of the Interior led to his removal in six weeks. It was charged against him that he brought into his administration the principles of the infinitesimals. As a consolation, he was given a place in the Senate, of which he was made Chancellor in 1803. He was also Grand Officer of the Legion of Honor. On the erection of the Imperial throne, in 1804, he was made a Count. In 1814, he gave his voice for the Provisional Government, the deposition of Napoleon, and the restoration of the Bourbons. Louis XVIII. rewarded him by a seat in the Chamber of Peers, and in 1817 by a Marquisate.

The first edition of the *Exposition du Système du Monde* was inscribed to the Council of Five Hundred. The third volume of the *Mécanique Céleste*, published in 1802, was a tribute to the Pacificator of Europe. In the edition of the *Théorie analytique des Probabilités*, published after the restoration, the dedication to the Emperor in an earlier edition was suppressed.

Bonaparte recognized the splendor which the great intellect of Laplace shed upon his administration. On October 19, 1801, having received a volume of the *Mécanique Céleste*, he wrote to the author: "The first six months at my disposal will be employed on your beautiful work." On November 26, 1802, after reading some chapters of a new volume dedicated to himself, he refers to "the new occasion for regret that the force of circumstances had directed him to a career which led him away from that of science. At least, he added, I desire ardently that future generations, reading the *Mécanique Céleste*, should not forget the esteem and friendship I have borne to the author." On June 6, 1805, the General having become Emperor, he wrote from Milan: "The *Mécanique Céleste* seems to me called to give a new splendor to the age in which we live." On August 12, 1812, he wrote from Witepsk: "There was a time when I should have read with interest your *Traité du Calcul des Probabilités.* To-day, I must limit myself to testifying to you the satisfaction I experience every time I see you communicate new works which perfect and extend the first of the sciences and contribute to the glory of the nation. The advancement and perfectionation of mathematics are bound to the prosperity of the state."

Arago did not imitate the political subserviency of Laplace, much as he admired his genius. In early life he went to Spain with Biot, to complete a geodesic operation. This expedition, though full of adventure and danger, had a successful issue, by giving a more precise value to the magnitude of the earth. On his return he was made a member of the Paris Academy when scarcely twenty-three years old. His scientific career was brilliant, and in 1830 he replaced Fourier as Perpetual Secretary. In 1848 he espoused the cause of the second republic, with Louis Bonaparte as President. After the second *coup d'état*, he refused to take the oath of allegiance to the new government, required of all officials. Nevertheless, he was allowed to retain the post of astronomer in the *Bureau de Longitude*, the new Emperor "making an exception in favor of a savant whose works had thrown lustre on France, and whose life his government would regret to embitter." As Minister of the Marine, Arago had originated and carried an act for abolishing slavery in the French colonies. Being urged to delay the change and make it gradually, he declared, "I will not postpone till to-morrow an act which sets free the oppressed."

Poisson was of humble origin, but rose to be Peer of France. He befriended Arago, who was five years younger, and who describes him in his youth as of delicate complexion, slight figure, and childish manner. At the age of eighteen, he submitted to his teacher, Lagrange, some amelioration in the method of demonstrating the binomial theorem, which his teacher read publicly in his lectures, and said he should adopt. Laplace wished to know a geometer who had made such a beginning. Poisson was one of the earliest and the most powerful in applying Fourier's definite integrals and periodic series to physical problems. He extended the conclusions of Lagrange and Laplace on the stability of the solar system, adding millions of years to its probable duration. As there was no vacancy in the French Academy in his proper section, he was placed in that of Physics. Afterwards much of his work was upon physical problems, such as electricity, magnetism, and capillarity. By common consent, he stood at the head of European analysts, after the death of Laplace, whom he succeeded as geometer in the *Bureau de Longitude.*

The publication of Dr. Bowditch's great work, a translation of four volumes of Laplace's *Mécanique Céleste*, with an ample commentary, was heralded by an article which he wrote for the North American Review in 1820. After describing the works of Olbers and Gauss in mathematical astronomy, the three principal publications of Laplace, and especially his discovery of the great equation in the motions of Jupiter and Saturn, with its long period of 917 years, and the neglect by men of science in Great Britain of the vigorous science upon the Continent, he thus expresses his admiration of Laplace: "These discoveries, together with a multitude of improvements in analysis and in every branch of mathematical knowledge, place this immortal man far above any of his contemporaries in the walks of science."* Fourier had called Laplace's works the *Almagest* of the eighteenth century.

Professor John Playfair, having alluded to the absence of diagrams and geometrical figures in the writings of the great mathematicians of France, says: "If we come to works of still greater difficulty, such as the *Mécanique Céleste*, we will venture to say that the number of those in this island who can read that work with any tolerable facility is small indeed. If we reckon two or three in London and the military schools in its vicinity, the same number at each of the two English Universities, and perhaps four in Scotland, we shall not hardly exceed a dozen: and yet we are fully persuaded that our reckoning is beyond the truth."†

On the appearance of the first volume of Bowditch's translation, a writer in the London Quarterly Review expresses his admiration in these words: "The idea of undertaking a translation of the whole *Mécanique Céleste*, accompanied throughout with a copious running commentary, is one which savors, at first sight, of *gigantesque*, and is certainly one which, from what we have had hitherto reason to conceive of the popularity and diffusion of mathematical knowledge on the opposite shores of the Atlantic, we should never have expected to have found originated, or at least carried into execution, in that quarter. Meanwhile, the part actually completed (which contains the first two books of Laplace's work) is, with few and slight exceptions, just what we could have wished to see, — an exact and careful

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* North American Review, 1820, vol. x. pp. 260–272.

† Edinburgh Review, 1808, vol. xi. p. 281.

translation into very good English, — exceedingly well printed, and accompanied with notes appended to each page which leave no step in the text, of moment, unsupplied, and hardly any material difficulty of conception or reasoning unelucidated." Referring to the continuance of the work, the writer adds: "Should this unfortunately not be the case, we shall deeply lament that the liberal offer of the American Academy of Arts and Sciences to print the whole at their expense, was not accepted." *

In 1838, after three volumes of the translation and commentary had been published, a writer in the London Athenæum expresses himself in these words: "Dr. Bowditch rose, like Franklin, from humble life, and had much to struggle with, and did struggle manfully, and did succeed. He was, in other words, an illustrious instance of a *self-educated man*. . . . No matter what a man's facilities may be, without this (the possession and use of the appropriating and incorporating power) he can never be educated, any more than he can be healthy without sound bodily organs.

"The lack of facilities is not, however, to be spoken of lightly, though it must not be confounded, nor yet compared, with the lack of the power that uses them: nor must it be supposed that such a thing as an absolute lack of facilities can exist. Nature herself has provided facilities, food for education, materials for self-making men to rise up, in times and places when and where no other facilities may be had. She opens the great school-room of creation for them. She gives them homes, society, the world at large. Above all, she gives them eyes to see, and ears to hear, and an all-availing and available spirit within them: the intellectual, immortal instinct, the thirst for knowledge, and the faculty of finding it, in earth, and air, and sea. No loads of appliances can surfeit such a mind on the one hand; no lack of them can starve it on the other.

"Let us not be supposed, then, to use the words as abusing them, when we call Dr. Bowditch an illustrious instance of a self-educated man. He was, in other words, as *we* understand it, an educated man: his intellect informed and trained, his character seasoned and consummated, and this under those circumstances of extraordinary self-dependence, which, it is well known, are so admirably suited to bring out and give their finest play to minds of a high order, on the very same principle that they prove fatal to weaker ones. . . .

"Dr. Bowditch's great scientific work — the one on which his

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* Quarterly Review, vol. xlvii., 1832, pp. 558, 559.

European reputation rests and will rest — was a translation of the *Mécanique Céleste* of Laplace, accompanied with an extensive explanatory commentary, making a work, which existed one may say in mere abstraction before, as accessible to all public and popular purposes as its essential nature would permit."*

Dr. Bowditch's work was not that of a mere translator and commentator. The subject was brought down to the date of publication, and was illustrated by the labors of geometers and astronomers who had succeeded Laplace. Such mathematicians as Lacroix, Legendre, Bessel, and Puissant recognized the great value of these additions. Mr. Babbage, in a letter to Dr. Bowditch, under date of August 5, 1832, wrote: "It is a proud circumstance for America that she has preceded her parent country in such an undertaking; and we in England must be content that our language is made the vehicle of the sublimest portion of human knowledge, and be grateful to you for rendering it more accessible." Letters of similar import were received by Dr. Bowditch from Airy, Francis Baily, Herschel, the Bishop of Cloyne (Dr. Brinkley), and Cacciatore.

The Council of the Royal Astronomical Society of London,† in noticing Dr. Bowditch's commentary and notes upon Laplace, expresses its appreciation in these terms: "An expert mathematician would find most of them (*the notes*) useless; but to the student who has sufficient knowledge to understand, without the habit of previous investigation which the reading of Laplace always requires, the work of Dr. Bowditch is invaluable. We see in it, not the performance of a practised analyst, but the record of the steps by which the translator became one; and a person more familiar with the most modern form of analysis than he appears to have been at the time when he wrote would probably have filled his commentary with difficulties of the same order as those of his author. This, however, was not done; and the work, as it stands, is most unquestionably fitted to bring the *Mécanique Céleste* within the grasp of a number of students exceeding five times, at least, that of those who could master Laplace by themselves.

"The name of Dr. Bowditch must be long remembered in the United States by the impulse which such a work as his commentary cannot fail to give to analysis in that country. The undertaking required sound knowledge, power of combining brevity and clearness,

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* London Athenæum, 1838, pp. 451, 452.

† Memoirs, vol. xi. pp. 300, 301.

an accurate remembrance of the nature of a beginner's difficulties, and determined perseverance. The congratulations which this society would so cordially have offered to the performer of this strikingly useful task can now only be forwarded, with expressions of sympathy and condolence, to his surviving relatives and friends; with the hope that astronomy, theoretical and practical, will flourish in the country which has produced so remarkable a facilitation of the study of the former, and so sound an example of the union of both."

In a note to the memoir of Dr. Bowditch by his son, it is stated that in America two, and perhaps three persons, besides Dr. Bowditch, were able to read the original work critically; but a competent judge has doubted whether the whole of it had been so read even by one. It is also known, on the authority of his son, that Dr. Bowditch was gratified whenever he received assurances that his work had made Laplace accessible to young students, — more even than he was by the approbation of his peers.

Benjamin Peirce, who was born in Salem, Mass., in 1809, and died at Cambridge in 1880, and who was Professor of Mathematics or Astronomy for forty-seven years, enjoyed the most intimate social and scientific relations with Dr. Bowditch. How these relations originated we are told by the writer of his obituary notice prepared for the American Academy of Arts and Sciences.*

"In his early years he had the good fortune to come under the influence of Dr. Nathaniel Bowditch. It is said that their first acquaintance was made while Dr. Bowditch's son, Ingersoll, and young Peirce were schoolmates. Ingersoll showed his comrade a solution which his father had prepared of a problem that the boys had been at work upon. Some error, real or conceived, was pointed out in the work, which was reported by Ingersoll to his father. 'Bring me that boy who corrects my mathematics!' was the invitation to an acquaintance, the importance of which, in Professor Pierce's own estimation, is told in the dedication, more than thirty years later, of his *Analytic Mechanics*: 'To the cherished and revered memory of my Master in Science, Nathaniel Bowditch, the father of American Geometry.'

"Peirce entered Harvard College in 1825. As Dr. Bowditch was now in Boston, having removed from Salem in 1823, and was preparing the first volume of his translation of Laplace's *Mécanique Céleste* for the press, it followed almost as a matter of course that the college student was more influenced in his studies by him than by

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* Proceedings, vol. xvi. pp. 443, 444.

the college course. Dr. Bowditch's first volume was completed, and the second entered for copyright, in 1829, the year of Peirce's graduation; and the proof-sheets were regularly read by him." *

That it should have been left to this country to open a way to English-speaking nations for the study of the transcendental mathematics of France and Germany may be explained by the following lamentation of the younger Herschel, printed as late as 1845.† After acknowledging the celerity with which everything valuable in British journals is republished, examined, and criticised in those on the Continent, he writes: —

"This ought to encourage our men of science. They have a larger audience, and a wider sympathy than they are, perhaps, aware of; and however disheartening the general diffusion of smatterings of a number of subjects, and the almost equally general indifference to profound knowledge in any, among their own countrymen, may be, they may rest assured that not a fact they may discover, nor a good experiment they may make, but is instantly repeated, verified, and commented upon in Germany, and we may add too in Italy. We wish the obligation were mutual. Here, whole branches of Continental discovery are unstudied, and indeed almost unknown even by name. It is in vain to conceal the melancholy truth. We are fast dropping behind. In mathematics we have long since drawn the rein, and given over a hopeless race. In chemistry the case is not much better."

At the present day Great Britain no longer lies under this severe reproach. In pure mathematics there have been Boole, Hamilton, Cayley, H. J. S. Smith, Clifford, and Sylvester; and in applied mathematics, Adams, Stokes, Sir William Thomson, Lord Rayleigh, Challis, and Powell. But the highest mathematical faculty will be always the prerogative of the few. Not many can say with Lagrange, "I found chemistry as easy as algebra!"

The contrast is not less striking in this country between the present condition of mathematical taste and acquirement and what they were at the time of Bowditch's translation. This change has been largely

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* In the memoir of Dr. Bowditch by his son it is said: "Whenever one hundred and twenty pages were printed, Dr. Bowditch had them bound in a pamphlet form, and sent them to Professor Peirce, who, in this manner, read the work for the first time. He returned the pages with the list of errata, which were then corrected with a pen or otherwise in every copy of the whole edition."

† On Sound. Encyclo Metropolitana, vol. iv. p. 810

due to the example and inspiration of Peirce. Though he was a poor teacher for indifferent students, he was the best for superior intellects. He simply led, and charmed them into following him as far and as fast as they could. While his text-books were an enigma to those who had little mathematical capacity, they fascinated minds of the highest order in this direction. Hence, in every class in college, a very few were found competent to read Bowditch's version of Laplace, and obtain glimpses of the meaning of Peirce's ideal algebras. Observatories, the United States Coast Survey, the Nautical Almanac, the Smithsonian Institution, and schools of science exist, partly as cause and partly as effect of this new development. Bowditch's Practical Navigator, first published in 1802, has carried his name, long ago, over every ocean and into every port in the civilized world, and his scientific reputation, as the earliest American expounder of the higher geometry, is slowly following after.

The four volumes of Dr. Bowditch's Translation and Commentary were published successively, in 1829, 1832, 1834, and 1839, at the sacrifice of one quarter of hi whole property. The expense was largely increased by the voluminous commentary. This was really of the nature of an original work, and was rendered necessary by the frequent gaps which Laplace had left in his own publication. Mr. N. I. Bowditch says, in his biography of his father, that Dr. Bowditch himself was accustomed to remark, "Whenever I meet in Laplace with the words, *Thus it plainly appears*, I am sure that hours, and perhaps days, of hard study will alone enable me to discover *how* it plainly appears."

The attention of Mr. James B. Francis of Lowell was attracted by the following passage in a recent work of W. W. R. Ball of London: "The *Mécanique Céleste* is by no means easy reading. Biot, who assisted Laplace in revising it for the press, says that Laplace himself was frequently unable to recover the details in the chain of reasoning, and, if satisfied that the conclusions were correct, he was content to insert the constantly recurring formula, *Il est aisé à voir*." *

Mr. Ball refers to the *Journal des Savants*, February, 1850. Mr. Francis has found the volume in the Boston Public Library. The title of the paper, translated, is, "An anecdote relating to Laplace: read to the French Academy at its special session, on February 5, 1850, by Mr. J. B. Biot." I find that Biot reprinted the paper in 1858, in his *Mélanges Scientifiques et Littéraires*. As Mr. Francis

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* A Short Account of the History of Mathematics. London, 1888, p. 387.

has been at the pains of obtaining a translation of the paper by a lady. I shall adopt that with a few trifling changes.

"When a man of order prepares to depart on a long journey, he arranges his affairs, and is careful to discharge all the debts he may have contracted. This is why I am going to tell you how, some fifty years ago, one of our scientists, the most distinguished, received and encouraged a young débutant who had come to show him his first attempts.

"This young débutant was myself, with your leave. Notice, to excuse the epithet, that this goes back to the month Brumaire of the year VIII. of the French republic, first edition.* Some months later, they did me the signal honor of electing me an associate of the National Institute; but at that date, and especially at the little earlier period when my story begins, I found myself completely unknown. I was then quite a small professor of mathematics in the Central School of Beauvais. Having recently left the Polytechnic School, I had much zeal and less science. At that time, little was demanded of young men but zeal. I was impassioned for geometry and many other things. Fortune rather than reason saved me from yielding to tastes too diverse. Bound from that time by the sweetest ties to the interior of the family which had adopted me, happy in the present and counting on the future, I only thought of following with delight the bent of my mind towards all kinds of scientific studies, and of doing for pleasure what the interest of my career would have prescribed to me as a duty. I had, above all, an unbounded ambition to penetrate into the high regions of mathematics, where men discover the laws of the universe. But these grand theories, still scattered in the collections of academies, were almost unapproachable, except to a small number of superior men who had co-operated in establishing them; and to launch into them without a guide over their footsteps, this would be an enterprise in which one would have every chance of wandering for a long time before rejoining them. I knew that Laplace had labored in unifying this magnificent *ensemble* of discoveries in the work which he has very justly called the *Mécanique Céleste*. The first volume was in press; the others would follow, at long intervals, agreeably to my desires. A step which might appear very hazardous opened to me a privileged entrance into this sanctuary of genius. I ventured to write directly to the illustrious author, and beg him to permit his

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* Brumaire began in 1799 on October 23: Biot was then twenty-five years old.

publisher to send me the sheets of his book as they were printed. Laplace replied to me with no less ceremony than if I had been a real savant. However, as the end of the story, he refused my request; not wishing, he said, that his work should be presented to the public before it was completed, that it might be judged as a whole. This polite refusal was doubtless very obliging in its form; but, at bottom, it badly suited my business. I was not willing to accept it without appeal. I immediately wrote again to Laplace to represent to him that he did me more honor than I merited, and than I desired. I am not, I said to him, of the public who judge, but of the public who study. I added, that, wishing to follow and make again all the calculations throughout, for my own instruction, I might, if he yielded to my request, discover and indicate the errors of press which may have slipped into them. My respectful persistence disarmed his reserve. He sent to me all the sheets already printed, adding thereto a charming letter; this time not at all ceremonious, but filled with the most lively and precious encouragements. I need not say with what ardor I devoured this treasure. I could well apply to myself the maxim, *Violenti rapiunt illud.*

"After this, every time I went to Paris, I carried my work of typographical revision, and presented it in person to M. Laplace. He received it always with kindness, examined it, discussed it; and that gave me an opportunity to submit to him the difficulties which too frequently baffled my weakness. His condescension to remove them was without bounds. But he himself could not always do it, without giving attention to them; sometimes pretty long. That happened usually in places where, to save himself from the details of a too expanded exposition, he had employed the expeditious formula, *Il est aisé de voir.* The thing, in fact, had appeared at the moment very clear to his eyes. But it was not so always, even for him, some time afterwards. Then, if you asked him the explanation of it, he sought it patiently, by different ways, on his own account as well as yours; and *there* was, without doubt, the most instructive of commentaries. Once I saw him pass almost an hour trying to seize again the chain of reasoning which he had concealed under this mysterious symbol, *Il est aisé de voir.* It must be said, for his acquittal, that if he had wished to be completely explicit, his work would have required eight or ten quarto volumes instead of five; and perhaps he would not have lived long enough to finish it."

These minute details relating to the intellectual life of Laplace, so sacredly preserved by Biot, the eminent mathematician and physicist, were not published until twenty-three years after the death of Laplace, and twelve years after the death of Bowditch. They must be taken into account when the mathematical powers of the author of the *Mécanique Céleste* and of its translator and commentator are compared. There can be no doubt that a higher order of mind is demanded for originating a profound analysis, than for understanding it when it is once made. Dr. Bowditch said to one of his sons: "My order of talent is very different from that of Laplace. Laplace originates things which it would have been impossible for me to have originated. Laplace was of the Newton class; and there is the same difference between Laplace and myself as between Archimedes and Euclid." This confession, taken in connection with Bowditch's estimate of Euclid, erred on the side of excessive modesty. For he was able not only to detect and point out to Laplace accidental errors in his work, but to provide an original commentary upon it more voluminous than the work itself. If this required a great expenditure of time and thought, it was no easy matter for Laplace himself. It was, in fact, so hard, that Laplace was not willing to undertake it a second time, after the subject had passed out of his mind; and he left the abyss open, with no stronger bridge to cross it than the simple formula, *Il est aisé de voir.*

The circumstances under which Laplace and Bowditch did their work are in striking contrast. Laplace was a favored child of fortune. He was able to give his long life of seventy-eight years to his noble task, breathing an intensely intellectual atmosphere, and surrounded by men of science only a little less distinguished than himself. Bowditch's knowledge of affairs was as remarkable as his science. He was weighted all his life with heavy cares and trusts, and could spare only his hard-earned leisure for scientific work, dying at the age of sixty-five. His intellect worked on a solitary height, admired but not fully comprehended by those about him. For example, instruction, and inspiration, he did as much for science in America, and wherever the English language is read, as Laplace did for that of France. It would be unjust to his memory, and to his own great modesty, to make any other comparison.

No names more illustrious adorn the two original branches of membership in this Academy than those of Laplace and Bowditch. Laplace was elected a Foreign Honorary Member in 1822, when he had published only four volumes of the *Mécanique Céleste.* Bowditch became a Resident Fellow in 1799, fifteen years before he had begun his translation of Laplace's greatest work. He contributed twenty-three valuable papers to the Memoirs, chiefly on Astronomy and the Physics of the Globe. Having succeeded John Quincy Adams as President of the Academy in 1829, he died in office, in 1838. An elaborate eulogy was pronounced before the Academy, May 29, 1838, by Mr. John Pickering, the Corresponding Secretary.

After the death of Laplace, his widow recognized the value of Bowditch's labors, in extending the usefulness and enlarging the fame of her husband's greatest work, by presenting to his translator and commentator his marble bust. In the fourth volume of the last edition of Laplace's work, fifty-two corrections are specified as having been made by Dr. Bowditch.

Dr. Bowditch's strength held out until he had corrected the proof-sheet of the thousandth page of the fourth volume of his translation. That was the last page his eye was to rest on. Eighteen more pages remained. The incident has its parallel in the death of Copernicus. He had spent twenty-three years in writing his book *De Orbium Cœlestium Revolutionibus*, but delayed its publication for fear of a popular outcry against his scientific doctrines. The book had been printed at Nuremberg under the care of his disciple, Rheticus. A few hours before he died, a copy arrived which was placed in his hands. He touched it, and seemed to recognize it, and then relapsed into unconsciousness.

No less suggestive was the death-bed of Lagrange. Though of French extraction, he was born in Turin in 1736. His father lost his property in speculation, — an event which the son did not regret. "Had I been rich," he said, "I might never have known mathematics." At the age of twenty-six, Lagrange had reached the summit of fame, though at the sacrifice of his health. In 1766, he was brought to Berlin by Frederick the Great, "the greatest king in Europe wishing to have the greatest mathematician at his court." Afterwards, various other courts competed for him. In 1787, he selected Paris. He was patronized by Marie Antoinette, and lodged in the Louvre. In the Revolution, when other scientific men were victims, his name commanded respect. In reply to a petition in favor of Lavoisier it was said, "The republic has no need of savants." Bonaparte called Lagrange "La haute pyramide des sciences mathematiques," and loaded him with offices and distinction. The first edition of his *Mécanique Analytique* appeared in 1788. In 1811, he published the first volume of another edition. The second volume, which was on *Dynamics*, required more serious changes, and its preparation was too much for his failing strength. On April 8, he had a conversation with Monge and other friends, and looked forward to another early interview, when he would complete some autobiographical details. But what he intended to say was never spoken. He died two days afterwards, and was buried in the Pantheon.

Only one Fellow of this Academy is now living who was elected before the death of Dr. Bowditch; and there must be very few in its present membership who knew him or ever saw him. But his work and his reputation are their common inheritance. To keep alive his memory, and do justice to his gigantic undertaking, is the loving service of one who, in early life, was welcomed to the hospitality of his thoughts and his books.

XVIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON A NEW METHOD OF DETERMINING GAS DENSITIES.

By Josiah Parsons Cooke.

Presented June 12, 1889.

In the well known method employed by Regnault for determining the density or specific gravity of air, oxygen, nitrogen, hydrogen, and carbonic acid, we deal primarily with tares, of which the weights to be determined are the differences. The glass balloon which holds the gas is tared by a similar balloon of exactly the same volume and of nearly equal weight, suspended from the opposite pan of the balance. The small difference of weight required to establish perfect equilibrium is alone measured with standard brass or platinum weights. Whatever may be the form of the subsequent calculation, the primary object is to obtain the tare of the empty balloon when absolutely vacuous. This known, the differences between such tare and the tare of the balloon filled with various aeriform substances, gives the weights of equal volumes of these substances under the temperatures and pressures at which the balloon was filled. The volume of the counterpoise is exactly adjusted to that of the balloon by the aid of a small subsidiary glass bulb (Plate II.); and by sealing up more or less mercury in this bulb it is easy to make the difference of weight such that the standard weights required to complete the equilibrium will measure the differences of tare to be determined, and no more.

In the method of Regnault the tare of the empty balloon, or what was equivalent to it, was found by exhausting the balloon with an air-pump and weighing it after measuring the tension of the residual gas while the glass was surrounded by ice. But it has been shown by Agamennone * and Lord Rayleigh † that the results thus obtained are

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* Atti (Rendiconti) d. R. Accad. dei Lincei, 1885.

† Proceedings of the Royal Society, vol. xliii. p. 362. 1888.

vitiated to a small extent by the circumstance that when the balloon is exhausted the pressure of the atmosphere determines a slight shrinkage of the external volume, which naturally disturbs the exactness of the compensation between the buoyancy of the air on the balloon and on its counterpoise. Although this shrinkage can be readily measured, as was done by Dr. T. W. Richards under my direction,* and still more recently by Professor Crafts,† who experimented on the balloon used by Regnault, which fortunately has been preserved, it seemed desirable to develop a method by which this correction could be avoided. For even if the new method should lead to no more accurate results than before obtained, it might serve to confirm the validity of the correction in question, and at least would give additional data towards establishing the value of important physical constants.

The new method we have devised for the purpose consists in first taring the balloon when filled with carbonic acid gas, and then drawing the gas through absorption tubes and determining its weight, as in the well known method of organic analysis. This weight known, the tare of the empty balloon is obviously the difference between the first tare and the weight in question. The practical problem here presented is, however, far more difficult than that of organic analysis. In the last, we expect to determine the weight of only a few decigrams of carbonic acid within a few tenths of a milligram, while in the problem now before us we must weigh at least nine or ten grams of carbonic acid, not simply to a proportional, but to an equal, degree of accuracy. We only succeeded in securing such accuracy after many trials and a careful study of all the conditions involved, and our primary object in this paper will be to describe the precautions which are essential to the success of the new experimental method. Incidentally it will appear that our results confirm in a most striking manner the high value of the specific gravity of hydrogen found by Lord Rayleigh,‡ and the low value of the atomic weight of oxygen found by ourselves.

THE BALANCE AND WEIGHTS.

The balance and weights were the same as those used by us in our previous work.§ The disposition of the apparatus which, after many trials, we have found most suitable for accurate work, is shown in

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* These Proceedings, vol. xxiii. p. 177. 1888.

† Comptes Rendus, vol. cvi. p. 1662. 1888.

‡ Proceedings of the Royal Society, vol. xlv. p. 426. 1889.

§ These Proceedings, vol. xxiii. p. 159. 1888.

Plate II. The balance rests on the plank shelf of a wooden case, whose glazed doors are shown open in the drawing; and as this shelf is firmly secured to a thick brick partition wall behind, great steadiness is secured for the instrument. Around the inside of the wooden case are hung folds of drapery, which surround the balance case and protect the beam from radiations, while a curtain rolling on a spring fixture enables the experimenter to uncover the front as necessary. Fastened by flanges and screws to the under side of the same shelf is a box made of tinned sheet iron, of somewhat larger dimensions than the balance case. The front of this box can be almost wholly uncovered by means of two large doors made of the same metal sheet, and secured when closed by turning buttons, but shown open in the drawing. In the metal top are two circular holes about half an inch in diameter, corresponding to holes through the shelf and the base of the balance case, and directly under the centres of the balance pans. From hooks soldered to the under side of the pans the globe and its counterpoise are suspended by means of brass wires, and the lengths of the wires are so adjusted that the two glass vessels shall hang midway in the metal box. The globe is hung from a wire stirrup, Plate I., which swings from an eye at the end of one wire; while on the neck of the counterpoise is cemented a brass cap and hook, and both it and the small subsidiary bulb are hung on an eye at the end of the other wire. Of course these details might be varied. It is only important that the whole system should swing freely, with as little friction as possible, and that the balloon should be easily removed and replaced.

Through a third hole in the top of the metal box and shelf, placed just in front of the balance case, passes a thermometer (not shown in the drawing) by which the temperature may be watched, and the inside of the box is painted with lamp-black so as to secure a uniform temperature throughout the interior. In our previous paper we spoke of the disturbance sometimes caused by currents of air within the box, but we found on further experience that these currents could be prevented by keeping the interior of the box as nearly as possible at the temperature of the external air. For this purpose it is important that the air of the room should circulate as freely as possible around the box, and the required condition is more easily secured if the box is made of thin metal sheet. It is also important that the temperature of the room should not be constantly changing, and that all circumstances should be avoided which would cause a flow of heat either into or out from the box. Sitting in front of the box in the process of weighing immediately causes a disturbance, and hence the division of the outer wooden case below the shelf is provided with wooden doors, which should be shut in front of the metal box before approaching the balance. When the thermometer hanging with its bulb inside the box indicates the same temperature as one hanging from the balance case outside within one tenth of a centigrade degree, the conditions are most favorable for accurate weighing.

In order to maintain the atmosphere within the box in a constant hygrometric condition, we placed in it four large open dishes of sulphuric acid, two on the bottom of the box and two on a shelf near the top, as described in our previous paper. The acid was first boiled with a fraction of a gram of ammonic sulphate, to remove the last traces of nitrous fumes, and renewed as occasion required.

We have found that we can most accurately estimate slight differences of weight with a balance thus loaded by observing the amplitude of the first swing of the pointer when the pans are relieved. With the balances of Becker, after the beam has been set on its bearings by the usual cam motion, the pans are still supported by two delicate arms, which are held by a weighted lever against the under side of the pans, but which can be pressed down by pushing against the button shown in the drawing on the front of the balance case. Such a mechanical arrangement is peculiarly adapted to this method of weighing, as it relieves the pans suddenly and under the same conditions, so that the amplitude of the subsequent swing is an accurate measure of the difference of weight acting at the two ends of the balance beam; and in this case the inertia of the heavy load renders the effects surprisingly uniform. We give these details, not because they involve any new principles, but because the results have been reached after a long series of experiments, and our experience may save others much loss of time. With the apparatus arranged as we have described it, a difference of weight amounting only to one tenth of a milligram was distinctly indicated, although the load exceeded half a kilogram on each pan, and the compensation was made so perfect that the equilibrium was not perceptibly altered by any ordinary changes of atmospheric conditions.

In order to reach such compensation, a counterpoise is first selected which on rough measurement appears to be nearly of the same volume as the balloon, and at the same time a little lighter in weight. The apparatus is then mounted with this counterpoise as described, the stopcocks of the balloon being closed. A series of observations are then made of the variations of weight arising from changes of atmospheric pressure and temperature, as carefully measured as possible. From such observations we can readily calculate, by the method we have previously described in these Proceedings,* the volume of the small bulb required to make the compensation perfect, and an experienced glass-blower can readily make a bulb of the size indicated, which, before it is sealed, may be adjusted as to weight by loading with mercury as above described.

The weights used in connection with the balance had been adjusted for our previous work with the greatest care, and not only compared with each other, but also compared with a copy of the Washington standard. Although we shall deal in this paper solely with relative weights, yet the absolute values that may be deduced from our results must be correct far within the limits of the experimental errors of our own work. The sum of the weights required to measure the differences of tare never exceeded twelve grams, and of this small mass any possible difference between our copy and the Paris standard kilogram must be wholly inappreciable.

THE GLASS BALLOON.

We have used in this investigation the same glass balloon that was fitted up for a somewhat different purpose in our work on the atomic weight of oxygen, but which has proved equally well adapted to determinations of gas density. Regnault in his work on the same subject used a balloon of ten liters' capacity, having its neck closed with a brass cap and stop-cock, and filled it by alternately exhausting the interior with an air-pump and refilling from a gasometer until the complete purity of the enclosed gas was assured. After long experience with this mode of experimenting, we have found it more convenient to fill the balloon by displacement directly from the generator, and we have found that we can reach a satisfactory result with least labor in this way.

Our balloon is represented in Plate I., which shows all the details of its construction. It was made by Emil Greiner of New York, and all the joints are so finely ground that when properly lubricated they will hold a vacuum indefinitely. The peculiar form of the stop-cocks enables the experimenter to shut into the globe a definite volume of gas and at the same time open a vent to the generator through the side tube; or to allow the gas to flow through the side tube until the current is perfectly pure before it is admitted to the balloon; and again, when the stop-cocks are both closed and the balloon disconnected,

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* Vol. xviii. p. 55.

all the gas left in the connecting tubes will soon be replaced by air. At the freezing point the internal volume of the balloon, as nearly as we have been able to measure it, is 4961.5 cubic centimeters, and the weight of the glass 570.5 grams. After much experimenting, we have concluded that as great accuracy in determinations of gas density can be obtained with a balloon of this size as with a larger one. The advantage to be derived from the greater mass of gas experimented on is more than compensated by the greater liability to error which the weighing of larger vessels and the longer duration of all the processes involve.

The extent to which this balloon is actually compressed by the tension of the atmosphere when a vacuum is made in the interior has been carefully measured,* and amounts to 1.66 cubic centimeters for a difference of tension of 760 mm. between the interior and exterior of the glass vessel; and this corresponds to a loss of buoyancy of 1.96 milligrams in the air at 760 mm. and 22° C.

When the balloon was not hanging on the balance, it was always protected by a metal case (see Plate II.), from which the neck and connecting tubes alone protruded, and in transferring the balloon to and from the balance it was handled only by the neck.

In Regnault's experiments the balloon was filled with the gas under examination at the temperature of 0° C. by surrounding the glass with melting ice. This necessitates a careful cleaning of the globe at least twice during each determination, and thus may arise slight variations of condition to impair the accuracy of the results. We have found with Lord Rayleigh that it is preferable to fill the balloon at the temperature of the laboratory, but we must then observe the temperature with very great accuracy. It is important to know the temperature to the one hundredth of a centigrade degree, for even so small a difference of temperature as this causes a change in the amount of carbonic acid gas which our balloon will hold under ordinary atmospheric conditions corresponding to three tenths of a milligram.

We have found it possible to secure even such constancy of temperature as this delicate measure implies by placing the balloon while filling in a calorimeter case, and observing the temperature with a calorimetric thermometer divided to the fiftieth of a centigrade degree. The calorimeter case consists of a cylindrical vessel of sheet zinc wide enough to receive the balloon with its tube and leave a play of less than an inch on either side. This vessel is fastened by metal stays

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* These Proceedings, vol. xxiii. p. 182.

inside a second cylindrical vessel of the same material, leaving an annular space about two inches wide and an equal space between the bottoms of the two vessels, all of which is filled with water. In addition, the water vessel is further protected by a layer of felt one inch thick kept in place by an outer covering of the same sheet metal. When in use, the top is covered by a cap made also of thick felting, and in the crown of the cap is a slit, through which a thermometer may be inserted or the hand passed to turn the stop-cocks. The gas to be used is conducted into the calorimeter through a very small lead tube, which is connected with the lower tubulature of the stop-cock by a rubber connection, and the balloon is so placed that the current shall enter either at the top or at the bottom of the vessel, according as the gas is lighter or heavier than the atmosphere. The calorimeter case stands about four feet high, and the balloon rests in it on a down cushion, with the connecting tubes fully six inches below the surface of the water in the annular space above mentioned. With this apparatus it was possible to keep the temperature of the balloon constant within the one hundredth of a centigrade degree for an hour at a time, unless the temperature of the laboratory suddenly and greatly changed.

The general arrangement for filling the balloon was then as follows. The gas delivered from the drying tubes of one of the generators hereafter to be described passed through the lead tube of which we have spoken to one or the other, as the case might be, of the tubulatures of the balloon standing in the calorimeter. Passing out by the opposite tubulature, the current was conducted by a similar lead tube to a second but much larger balloon serving as a gasometer, and from the last vessel through a gas wash-bottle to the atmosphere. The bottom of the wash-bottle was covered with strong sulphuric acid to dry any returning air, but not deep enough for the inlet tube to dip under the liquid. The current was continued until the proper test showed that the gas issuing from the end of the apparatus was perfectly pure. Then the inlet cock of the balloon was turned, and the temperature of the calorimeter case watched until constant, and a sufficient time had elapsed to establish a perfect equilibrium with the atmosphere through the connecting tubes and vessels. This, as we found by experience, often requires longer time than we were led to anticipate, and when experimenting with carbonic acid gas it is not safe to allow less than twenty or thirty minutes; and now the large balloon and wash-bottle come into play to prevent air diffusing into the balloon, or being drawn back in consequence of changing pressure.

When all the conditions seemed to be satisfactory, the temperature of the calorimeter and the height of the barometer were accurately observed, the first to the hundredth of a centigrade degree and the last to the twentieth of a millimeter, noting always the height of the attached thermometer. The hand was then quickly thrust into the calorimeter, and the outlet cock at once closed. The balloon was now removed, dusted with a large camel's-hair brush, and hung in its place on the balance. When, however, the atmosphere is very dry, as it often is in this climate during the winter months, it may happen that the surface of the glass acquires a charge of electricity from the friction of the cushion in the calorimeter or of the brush just mentioned; and if there is any suspicion of such an effect, the best way to dissipate the charge is to stand the balloon for a few minutes in its metal case (shown in Plate III.), after covering the bottom of the case with a thin layer of water. If the balloon is hung on the balance with a charge of electricity on its surface, however small, it will be unequally attracted by the surrounding metallic walls, and most confusing anomalies of weight will be noticed. Moreover, in the very dry atmosphere of the case the charge will last for days, or even weeks, as on the insulated vanes of an electrometer.

THERMOMETERS AND BAROMETERS, AND THEIR CORRECTION.

The thermometers on whose indications we have relied in this investigation are two of small range, but divided into fiftieths of a centigrade degree and made by the house of the late Dr. H. Geissler of Bonn. We were obliged to use the two, for our investigation was continued into summer weather, which exceeded the range of the thermometer first selected. As should always be the case with such instruments, the zero point is given in each case on a short subsidiary scale, separated from the main scale by an enlargement of the tube. Careful observation showed that the zero point of the instrument we will designate as No. 1, was depressed 0.02 of a centigrade degree, while the zero point of No. 2 was raised 0.28 of a degree. Making the correction thus indicated, to be added to all temperatures observed with No. 1, and subtracted from all observed with No. 2, the two instruments were found to agree exactly through all portions of the scale common to both. Obviously, therefore, the differences of temperature observed are perfectly trustworthy to the one hundredth of a degree, but how far the absolute values — counting from the freezing point of water — can be relied on when compared with the observations of other experimenters, we have no means of determining. Of course, it will be understood that all temperatures hereafter given have been corrected for the variation of the zero point. At the close of the investigation the zero points were again tested and found to be unchanged.

The barometer used was a large standard instrument of the familiar mountain form, made by Greene of New York. Hanging at the side of it was a smaller instrument of the same maker, whose indications agreed with the first within the tenth of a millimeter. Here again, as in the case of the thermometer, there can be no question as to the accuracy of the differences of tension observed within moderate limits; but how far the absolute heights can be compared with those observed by Regnault and others is also a problem that cannot be readily solved, and one not within the means of a single experimenter to determine. All heights of barometer given hereafter have been reduced to 0° by the tables of Guyot.*

TARE OF THE EMPTY BALLOON BY REGNAULT'S METHOD.

In the method of experimenting devised by Regnault the tare of the empty glass globe used, although not explicitly given, was implicitly determined. His arrangement for filling the globe, shown by Figure 1, has already been referred to, and his general method of experimenting consisted in taking the tare of the globe when filled with the same gas at the temperature of melting ice under as different tensions as possible. The tensions were found by measuring with a cathetometer the difference of height, $\alpha\,\beta$ (see Fig. 1), under each condition, and the tares were found by means of the balance by the system of compensation already described. The difference of tare gives the weight of gas which the globe contains at 0° at the tension $H - h$, and from this may readily be deduced the weight at any other tension; as, for example, at the standard tension of 760 mm. The calculated weight at either of the tensions H or h, deducted from the corresponding tare, gives what we have called the tare of the empty globe; but obviously with Regnault's method this value is not needed in the calculations of specific gravity or density.

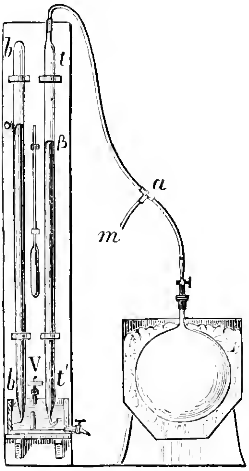

FIG. 1.

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* Published by the Smithsonian Institution, Washington.

When the globe is filled by displacement it conduces to greater accuracy to determine independently the tare in question; and as soon as the details of the new method had been worked out, we began our final determinations by taking according to the old method the tare of the balloon above described when empty, so as to obtain a definite standard of comparison for further results. We however varied the method of Regnault in so far that we always filled the globe with hydrogen before exhausting the interior. As with this exceedingly light material the weight of the residual gas seldom exceeded one half a milligram, an error as great as one fifth in the capacity of the balloon or in the tension of the residual gas would cause no appreciable difference in the value of the small weight we sought to estimate. The details of a single example will be sufficient to illustrate the procedure.

DETERMINATION No. 1.

A current of hydrogen gas from the electrolytic generator described in our previous paper* was run through the balloon from Saturday, May 25th, at 4 o'clock P. M., to Monday, May 29th, at 10 o'clock A. M., 1889, the balloon standing in calorimeter case connected with larger balloon to receive overflow. At moment of closing, the height of barometer and temperature of the case were observed, but these data are not required for the present determination, and will be given hereafter when used for calculating the specific gravity of hydrogen. The balloon was exhausted with an excellent mechanical air-pump,† and the tension of the residual gas measured by means of a siphon manometer interposed between the balloon and the pump. The form of manometer used is shown by Figure 2. It was made in the laboratory, and in filling it with mercury the liquid metal, purified by repeated distillation, was boiled in the tube with the greatest care. For convenience, the difference of level of the mercury in the two arms was measured with a cathetometer constructed by the Société Genevoise, but it might have been estimated with sufficient accuracy by the millimeter scale of the instrument. Tension in balloon after exhaustion 456.95 — 455.55 = 1.40 mm.

Assuming 0.4164 as the approximate value of the weight of hydrogen gas filling the balloon at 763.10 mm. and 21°.08 C. (p. 227), the weight of the residual gas at 1.4 mm. and same temperature would be

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* These Proceedings, vol. xxiii. p. 168.

† Author's Chemical Physics, p. 331.

0.00076 gram or 0.76 m.g. No exact observation of the temperature of the balloon was necessary; for a difference of 4° C. would not alter the above value more than $\frac{1}{100}$ m.g., and we may therefore assume that the temperature of the balloon was the same as that of the laboratory, which at the time was 21° C. The correction for lessened buoyancy (increased weight) on account of the contraction of the balloon by atmospheric pressure amounts, as has been shown, to 1.98 m.g.,* and this added to 0.76 makes the total correction 2.74 m.g. When the balloon was hung on the balance, the weight required to complete the tare was 2.5600 grams. Hence we have, —

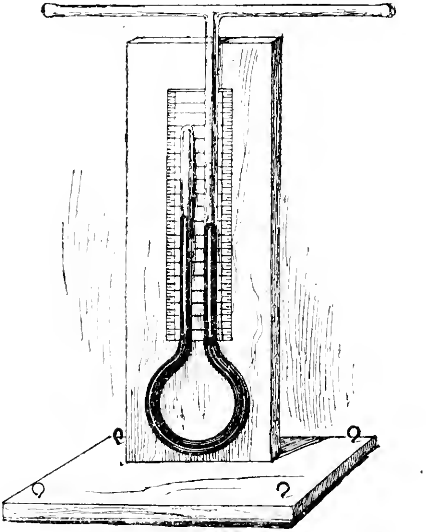

Fig. 2.

Weight of balloon exhausted		2.5600 grams.
Correction for residual gas . . .	0.76 m.g.	
" " lessened buoyancy .	1.98 "	27 "
Tare of empty balloon		2.5573 "

Two other determinations were made in the same way, and the three results are united in the following table.

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* These Proceedings, vol. xxiii. p. 184.

Summary.

Tare of empty balloon,	1st value	. . . . .	2.5573 grams.
" " "	2d "	. . . . . .	2.5572 "
" " "	3d "	. . . . . .	2.5574 "
Mean value,	. . . .		2.5573 "

TARE OF THE EMPTY BALLOON BY CHEMICAL METHOD.

The general theory of this method has already been stated. The balloon is filled with carbonic acid gas by displacement, and the tare taken. The gas is then drawn through a series of absorption tubes, as in the process of organic analysis, and the sum of the increased weights of these tubes gives the weight of the total contents of the balloon at the time the tare was taken. The weight of the balloon filled with carbonic acid gas less the weight of the carbonic acid thus determined is obviously the tare of the empty balloon required. In attempting to perfect this apparently simple experimental method we met with unexpected difficulties, arising from several circumstances.

In the first place, in order to wash out from the balloon the last traces of carbonic acid, it was necessary to draw through the apparatus a very large volume of air, and the system of purifiers and desiccators needed absolutely to free the atmospheric air from the least admixture of carbonic acid or aqueous vapor was found to be far more extensive than we anticipated. In the second place, since the globe held, at the ordinary temperature of the laboratory and at the average pressure of the atmosphere, no less than nine grams of gas, the common potash bulbs used in organic analysis were wholly inadequate for our requirements, and we only succeeded after many trials in finding a form of apparatus by which so great an amount of carbonic acid could be determined with the necessary accuracy, that is, within a few tenths of a milligram. The arrangement finally adopted is shown in Plate III. The balloon is represented standing in its covered metallic case, in which it is placed the moment it is taken from the balance. On the right of the balloon and below it is a system of tubes for purifying and drying the atmospheric air which enters from outside the laboratory by the flexible tube on the extreme right. On the left of the globe is a system of tubes for absorbing the carbonic acid. The flexible tube on the left is connected with a Bunsen pump through a form of Mariotte's flask,* and by this means a current is maintained through the whole system, under constant pressure.

Purifying and Drying Apparatus.

The air entering as we have described passed first through a wash-bottle of familiar construction containing a solution of potassic hydrate, Sp. Gr. = 1.44, and then through a similar wash-bottle containing a concentrated solution of baric hydrate; and if the rapidity of the current was not greater than two bubbles a second, this double washing was found sufficient to remove the last traces of carbonic acid. Indeed, as soon as the baryta water showed the least indications of cloudiness, the solutions were renewed. It was not so easy to remove the last traces of moisture.

After the air had passed the washing flasks it entered a system of desiccators, shown in the lower half of the plate, where in small bubbles it travelled up first one tube, and then a second tube, both 5½ feet long, and filled with concentrated sulphuric acid previously boiled with a small amount of ammonic sulphate to remove all nitrous fumes. Leaving the second of these tubes it entered an elongated bulb four inches long by two inches in diameter filled with phosphoric anhydride; and the fact that prolonged contact with sulphuric acid is not sufficient to remove the last traces of moisture was shown by the circumstance that after the current has passed for several days the dry white powder at the opening of the bulb showed signs of deliquescence.

Our phosphoric anhydride was prepared by burning common yellow phosphorus in a large sheet iron drum, through which a current of dry air was drawn with sufficient rapidity to maintain the phosphorus in rapid combustion, and the bottom of the drum was made tunnel-shaped so that the anhydride could be shaken down into a self-sealing fruit jar as fast as it formed. As thus prepared the anhydride has a slight odor, which it loses after a prolonged current of dry air has been drawn through the powder; and after our drying tubes had been filled their contents were submitted to a preliminary treatment of this sort, and not until long after all perceptible odor had disappeared were they used in our work. We noticed that after the anhydride had been used for some time it appeared more granular and lost in part its hygroscopic power. In order to make sure of this point, the apparatus as far as described having been in use for several weeks, we connected with the first phosphoric anhydride tube a weighed tube

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* These Proceedings, vol. xxiii. p. 163.

containing fresh anhydride. After drawing air through the system at the same rate and during the same time as in a carbonic acid determination, we reweighed this second tube and found that it had gained 5.5 m.g. We next added to our system the U tube filled with phosphoric anhydride, which is shown in Plate III. immediately before the balloon, and repeated the experiment. There was then no gain in weight perceptible. The observations were as follows.

Before interposing the U Tube.

		H	T°	R
1st weight P_2O_5 tube	25.9212 grams	295.7	20.0	302.7
2d " "	25.9267 "	295.2	20.8	301.4
	0.0055 "			1.4

After interposing the U Tube.

		H	T°	R
1st weight P_2O_5 tube	25.9268 grams	299.3	19.6	306.7
2d " "	25.9268 "	299.2	21.6	304.6
				2.1

In this table the column headed H contains the barometric pressure at time of weighing in tenths of an inch; that headed T° gives the corresponding temperatures of the balance case in centigrade degrees. By adding to the values H the quantities $(27 - T)°$ we obtain the values R, and these are the barometric heights which would give an atmosphere of the same density, and therefore exerting the same buoyancy, as the atmosphere at the time of weighing if the temperature were uniformly 27° C. The correction that should be made for differences of temperature and pressure at successive weighings can at once be calculated from these values. We found by experiment that for the phosphoric anhydride tube used in these and in subsequent determinations the correction amounted to 0.04 m.g. for each tenth of an inch change of pressure, and hence in the above weighings the correction is too small to be appreciable. This simple method of correcting weights for changes in the buoyancy of the atmosphere has been described in a previous paper in these Proceedings.* In order to apply it readily, the barometrie heights, although usually read in millimeters, were often also noted, as here, in tenths of inches, and the instrument we used was provided with both scales.

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* Vol. xviii p. 55.

It is obvious from the above experiments that the hygroscopic power of phosphoric anhydride becomes impaired before the powder actually deliquesces, and we have dwelt on the point because the experience was of great importance in our investigation by leading us to add the second anhydride tube to our system, and also to watch carefully the condition of its contents and to replace the tube as soon as the least change was perceptible. We attribute the change to a glazing of the amorphous grains due to the forming of a coating of glacial phosphoric acid, but the effect is one that would not be noticed except under such extreme conditions as existed in our work. We now pass to the system of absorption tubes on the other side of the balloon.

Absorption Apparatus.

The apparatus for the absorption of the carbonic acid gas must meet very opposite requisitions. In the first place, it must offer a sufficiently large mass of absorbent to the pure gas which first comes to prevent overheating from the rapid chemical combination. In the next place, it must be capable of removing the last traces of carbonic acid from the air which is afterwards drawn through the tubes. Lastly, it must not be so heavy or so complicated that it cannot be promptly and sharply weighed, and the correction for changes of temperature and pressure between successive weighings accurately estimated.

After trying in various ways to enlarge and modify the different forms of potash bulbs and spiral tubes in general use, (and in these attempts we had the aid of a skilful glass-blower,) we found that we could reach a more accurate result with a system of separate tubes, in spite of the number of weighings they involved. To absorb the great mass of the carbonic acid we used the simplest form of gas washer, shown in Plate III. at A. The bulb had a capacity of 200 c.c., and in this we placed 75 c.c. of a solution of potassic hydrate having Sp. Gr. = 1.443. When empty the bulb weighed only 57 grams, and when filled about 165 grams. Assuming that the potash was fully neutralized, less than one half of this amount would be sufficient to combine with nine grams of carbonic acid; but to insure prompt action and avoid excessive heating the amount given is required.

The potash tube was followed by a small U tube, four inches long, with ground caps filled with finely granulated soda lime, and weighing when full about 40 grams. (See B, Plate III.) To this was united a similar U tube containing phosphoric anhydride to hold the aqueous vapor, which is brought over by the gas current in no inconsiderable amount from the potash solution and the soda lime, in consequence of the heat set free by the absorption. The anhydride tube weighed when full about 25 grams, and is shown at C. Next was a third U tube filled with glass beads and having a few drops of strong sulphuric acid at the bend. This tube, D, was not weighed, but was necessary in order to indicate any sucking back of the air and to prevent any vapor from thus reaching the phosphoric anhydride. The double bulb forming the end of the system, shown at E, was made by melting together the usual inlet tubes of two gas washers like A. In this we placed 50 c.c. of a standard solution of baric hydrate, and the peculiar construction was necessary in order to provide against regurgitration in consequence of back pressure. The solution is easily washed out of the bulbs, and when retitrated at the end of the process gives the amount of carbonic acid, if any, which escaped the other absorbents. All of these tubes were united into one system by rubber connections carefully lubricated both inside and out with vaseline, a soft paraffine which had previously been melted and heated to remove every trace of moisture.

The manipulation of this apparatus was an interesting experiment. When all had been set up as shown in Plate III., the globe being full of carbonic acid, the Bunsen pump was first started, and after a constant suction (regulated by the Mariotte's flask before described) had been established, we cautiously opened the cock of the balloon, which connected with the potash bulb, closely watching the flow of gas. As soon as this flow began to slacken, we as cautiously opened the farther cock, by which air was admitted to the balloon through the line of purifiers, still closely watching and regulating the flow. We then noticed a striking phenomenon. As pure carbonic acid was now passing into the potash bulb, the air mixing but slowly with the heavy gas at the surface of contact as the level sunk in the balloon, the absorption at first was complete. If the air supply from behind was not sufficient, a partial vacuum formed in A, and air was drawn back through the tubes in front, as indicated at once by the bubbles at the bend of D; but if the supply was carefully regulated, a perfect equilibrium could be maintained in the tubes beyond, and we have seen the carbonic acid flow into the potash bulb for half an hour without more than a few bubbles of air passing through the sulphuric acid at the bend of D in either direction.

After a while, however, when the great mass of the carbonic acid has been absorbed, bubbles of air begin to pass through D, and also bubble through the baryta water beyond, and soon a steady current is established throughout the whole apparatus, which may then be left to take care of itself. If the current does not exceed in rapidity two bubbles a second, it may be allowed to flow for twenty-four hours without risk, and in that time every trace of carbonic acid will have been washed out of the balloon. The suction should now be stopped, and the cocks of the balloon closed. The tubes A, B, and C may then be disconnected, and after they have come to equilibrium in the balance case reweighed. The double bulb E must also be disconnected, the baryta washed out into a suitable bottle, and the solution retitrated with oxalic acid.

As the weights of the tubes A, B, and C must be corrected for the buoyancy of the air, it is essential to note the temperature of the balance case and the height of the barometer at the time of each weighing. The corrections in question may be considered under two heads; first, that made necessary by a change of temperature or pressure between successive weighings; secondly, that required to eliminate the effect of atmospheric buoyancy on the total weight of carbonic acid absorbed.

The first correction is best made by the method already described, and the application of this method was greatly facilitated in the present investigation by the circumstance that the same tubes, with the same weights of contents, were used in all the carbonic acid determinations made. We were able to determine once for all for each tube the correction required for a variation of one tenth of an inch in the barometric height reduced to 27° C.,* and then the correction in any case could be found by a simple multiplication. Thus we estimated that the correction for one tenth of an inch in the barometric height reduced to 27° C. was, —

For the potash bulb before absorption, . . .	0.306 milligram.
" " " after " . . .	0.321	"
" soda lime tube	0.067	"
" phosphoric anhydride tube	0.040	"

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* That is, reduced to the height which would be required to give at the temperature of 27°, an atmosphere of the same density and buoyancy as that at the temperature of the balance case when the tube was weighed. These Proceedings, vol. xix. p. 55.

Calculation of Correction for Potash Bulb.

	Before Absorption.	After Absorption.
Weight of glass	57.45 grams.	57.45 grams.
Volume of glass = 57.45 ÷ 2.5	23 c. c.	23 c. c.
" KOH solution	75 "	80 "
	98	103
" brass weights, 164 ÷ 8.2	20 "	
" " " 173 ÷ 8.2		21 "
Uncompensated volume	78 "	82 "
Air displaced at 27° C. and 300 tenths of an inch		
1.176 × 78	91.928 m. g.	
1.176 × 82		96.332 m. g.
Variation for $\frac{1}{300}$	0.306 "	0.321 "

The correction of the total weight of carbonic acid for the buoyancy of the atmosphere was not so simple a problem; but by using the same bulb and nearly the same volume of the same solution of potassic hydrate in every case, it was sensibly the same for all the determinations. The specific gravity of the solution of potassic hydrate before the absorption was 1.443, and tested in two separate determinations after absorption it was found to be 1.464 in each case. Using now the arithmetical means of the weights of the potash bulb in the three determinations under consideration, it was easy to find an average value for the correction thus.

Average weight of potash bulb before absorption	165.02 gr.
Weight of glass	57.45 "
" solution of KOH	107.57 "
Volume of solution of KOH = 107.57 ÷ 1.443	74.55 c. c.
Average weight of potash bulb after absorption	173.57 gr.
Weight of glass	57.45 "
	116.12 "
Volume of solution of KOH = 116.12 ÷ 1.464	79.32 c. c.
Difference of volume = 79.32 − 74.55	4.77 "
Weight of CO_2 absorbed in potash bulb = 173.57 − 165.02	8.55 gr.

Volume of brass weights $= 8.55 \div 8.2$	1.04 c. c.
Uncompensated volume $= 4.77 - 1.04$	3.73 "
Weight of 3.73 c. c. of air at 300 tenths inch and 27° C. $= 1.176 \times 3.73 =$ corr. required . .	4.39 m. g.

In this calculation we have necessarily left out of the account both the small amount of carbonic acid absorbed by the soda lime and the water carried by the current from the potash bulb to the connecting tubes; for the increased weight of these tubes results from both these causes, whose relative effects or whose influence on the correction we cannot estimate. That they would tend to raise slightly the value of the correction is obvious; and if we assume, as we have in the following calculations, that the value is 4.5 milligrams we shall approximate as nearly to the precise amount as circumstances will permit. For all these corrections the data are only known within certain narrow limits; but the total uncertainty thus arising does not exceed two or three tenths of a milligram in the final result.

In weighing the potash bulb and U tubes it is of course essential that they should be left in the balance case until a perfect equilibrium of temperature has been reached, and then they must be weighed when open so that a perfect equilibrium of pressure on the inside and outside of the glass may be secured. And since we were here aiming at very great accuracy, we felt it important to inquire further whether any gain of weight from hygroscopic moisture was possible during the time necessary to verify the weight while the tubes remained open on the scale pan. We therefore carefully investigated this point. The air in the balance case was kept as dry as possible by an open dish of sulphuric acid, and the experiments were made under such conditions. It was found that the weight both of the potash bulb and of the soda lime tube remained absolutely constant, hour and hour together, except so far as they were influenced by changes of temperature and pressure, but the weight of the phosphoric anhydride tube slowly but uniformly increased at the rate of 0.025 m.g. per hour. We followed the change on one occasion from $10^{\text{h.}}\ 45^{\text{m.}}$ A. M. to $6^{\text{h.}}\ 15^{\text{m.}}$ P. M., and during these seven hours and a half the gain was 1.9 m.g., while the changes of temperature and pressure meanwhile were not enough to cause a sensible difference in the atmospheric buoyancy. Such experiments were continued for a sufficient length of time to enable us to confirm the values of the corrections above given, and they gave us great confidence in our weights. They showed that the only precaution necessary for accuracy was to close the tubes as soon as they were disconnected, and to leave each of them closed in the balance case until it was time to take the weight. The U-shaped tubes with perforated ground stoppers, by which connection with the lateral tubes can be instantly opened or closed, are admirably adapted to this work. As an example, we give next the details of one determination of carbonic acid by the method we have described.

Details of a Determination of Carbonic Acid.

The gas was generated from statuary marble and dilute hydrochloric acid in an apparatus precisely similar to that described and figured by us in a previous paper.* It was first washed by a solution of potassic bicarbonate, and then, having passed in succession over calcic chloride, sulphuric acid, and phosphoric anhydride, it was conducted into the balloon and overflow in the manner already described. The gas was tested by leading the current from the overflow into a familiar form of nitrogen apparatus filled with a solution of potassic

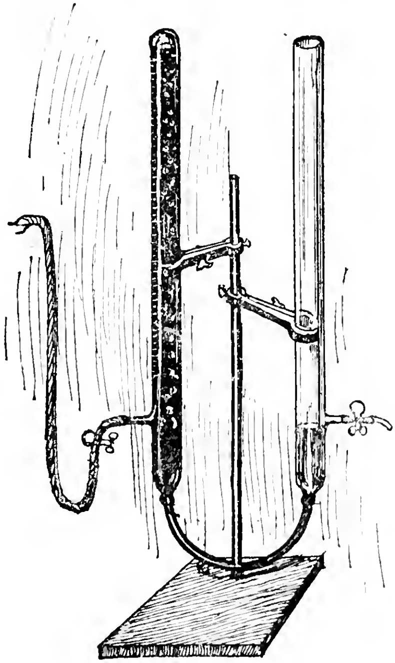

Fig. 3.

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* These Proceedings, vol. xxiii. p. 166.

hydrate (Fig. 3), and not until no measurable residue was left by a full liter of gas was its condition regarded as satisfactory. The balloon stood in the calorimeter case, and when the cocks were closed with the precautions already described the temperature of the case and the height of the barometer were observed, and although these values are not needed for determining the tare of the empty balloon, they will be used for determining the density of carbonic acid hereafter. The balloon was then disconnected and hung on the balance, and its tare found to be

$$W = 11.5907 \text{ grams.}$$

The balloon was then transferred to its metal case, and, having been mounted as shown in Plate III., the determination of the weight of its contents proceeded as just described.

Potash Bulb.

	Grams.	H	T°
1st weight of potash bulb	165.3388	299.99	25.8
2d " " "	174.0132	299.83	27.0
	8.6744		
Correction* for change of H and T	4		
	8.6740		

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* Since the volume and density of the potash solution used were closely the same in all the determinations, whether compared before or after the absorption, the value of the correction may be assumed to be the same in all cases, and, as has been shown at page 218, amounts to 0.306 m.g. before absorption and 0.321 m.g. after absorption for every change of one tenth of an inch pressure or 1° centigrade temperature from the standard of 300 tenths inch and 27° C. or 300° absolute temperature. The correct mode of calculating the correction in any case is to reduce both weights to what they would appear to be at $H = 300$ and $T_0° = 300 = 27°$ C. before taking their difference, using the value 0.306 for the smaller of the two, and 0.321 for the larger.

299.89 at 25°.8 corresponds in buoyancy to 301.09 at 27°
299.83 at 27° " " " 299.83 "

$301.09 - 300 = 1.09$ and $1.09 \times 0.306 = 0.33$ addative.
$299.83 - 300 = -0.17$ and $-0.17 \times 0.321 = -0.05$ subtractive.

Then $165.3388 + 0.33 = 165.33913$
$174.0132 - 0.05 = 174\ 01315$
8.67402 as before.

As regards the sign of the correction, notice that, when reduced to $H = 300$, the buoyancy becomes less and the *apparent* weight greater if the previous pressure was above 300, and *vice versa*.

Soda Lime Tube.

	Grams.	H	T°
1st weight of soda lime tube	42.8731	299.54	26.6
2d " " " "	43.1857	299.87	27.4
Correction insensible	0.3126		

Phosphoric Anhydride Tube.

1st weight of anhydride tube	39.5196	299.50	27.0
2d " " " "	39.5493	300.00	27.2
Correction insensible	0.0297		

Standard Solution of Baric Hydrate.

Before absorption, 50 c. c. required 46.60 c. c. solution of oxalic acid.
After " " " 43.65 " " "
2.95

One c. c. of decinormal solution of oxalic acid contains 0.0126 gram of $H_2C_2O_4 . 2 H_2O$, corresponding to 0.0044 gram of CO_2.

$$2.95 \times 0.0044 = 0.0130 \text{ gram of } CO_2.$$

Total Weight of Carbonic Acid.

	Grams.
From potash bulb	8.6740
" soda lime tube	0.3126
" anhydride tube	0.0297
" titration	0.0130
	9.0293
Reduction to vacuum	45
	9.0338
Tare of balloon and gas	11.5907
Tare of empty balloon	2.5569
Value by Regnault's method	2.5573

The value of the tare of the empty balloon found by the new chemical method is directly comparable with that obtained by the Regnault method, since there was no change in the balloon meanwhile. But after this determination was finished, the balloon, as it remained standing in its case, having been exposed to the direct sunshine of an unusually hot June day, some of the cerate lubricating the stop-cocks melted and ran down into the tubulatures below, from which it had to be removed. Thus the tare was lessened by nearly a centigram. It was easy, however, to determine the exact loss, and as in a like investigation, even when using the greatest care, one must ever be liable to accidents of this sort, it is important to dwell on this point.

In losing the tare we had apparently lost the thread of our investigation, but we were readily able to recover this thread without interrupting the general course of the work. It must be borne in mind that our immediate object was to obtain by the chemical method a series of results for the tare of the empty globe which could be compared with the mean value 2.5573 obtained by the method of Regnault. Here had come a change of tare, and we could obviously find a new standard of comparison by redetermining the new value by the old method. But this was not necessary. In the first determination by the chemical method, we had observed with great precision the pressure and temperature at which the balloon was filled. We do the same in the second determination, to which we next proceed, although these values are not needed in this determination, by itself considered, any more than they were in the first. If now from the tare of balloon and gas in the first determination (11.5907) we deduct 2.5573, we have the weight of carbonic acid which the balloon contains at a known temperature and pressure as found by the method of Regnault. If we deduct the same quantity from the tare found in the second determination, we have the weight of gas which the balloon holds at another temperature and pressure by the same method. If now there has been no change of tare, these two weights ought to agree exactly when one is reduced to what it would have been under the conditions at which the other was taken; and if there has been a change of tare, the difference of the weights thus reduced will give the exact amount of the loss, on the basis solely, let it be noticed, of results obtained after the method of Regnault. Thus we have, —

				Grams.
By No. 1, weight of CO_2 at	763.85	mm. and	25°.08	9.0273
“ No. 2, “ “	756.73	“ “	22°.40	9.0334
Weight No. 1 reduced at	“	“ “	“	9.0241
Loss of tare				9.3 m.g.

Obviously the accuracy of this result depends upon the accuracy with which the observations of temperature and pressure were made, and upon the correctness of the data on which the reductions are based. That the accuracy is extreme will appear from a comparison of the values of the specific gravity of carbonic acid, given on page 229, which were deduced from the same elements. And although in such work as this there is an obvious liability to error from just such a change of tare as we have been discussing, yet the loss or gain thus resulting is usually of such a magnitude that it cannot be overlooked.

Besides the one of which the details have been given, we made by the chemical method two other determinations of the tare of the empty globe in precisely the same manner as before described, and obtained the values 2.5481 and 2.5475 respectively. In order to bring these results into comparison with that obtained by the first determination, or those obtained by the method of Regnault, we must add 9.3 m. g. to each value. We then have for

Tare of Empty Balloon.

	Regnault's Method.	Chemical Method.
No. 1	2.5573	2.5569
No. 2	2.5572	2.5574
No. 3	2.5574	2.5568
Average	2.55730	2.55703

These results are essentially identical, and the two methods confirm each other. But having reached this important conclusion, which was the main object of our investigation, we freely concede the preference to Regnault's method. The difference between the results of the two methods, as here exhibited, is insignificant; but so long as the validity and value of the correction for the contraction of the balloon on exhaustion has been thus established, Regnault's method will be preferred because it is practically more simple, and hence the results are more accordant than those obtained by the chemical method first described in this paper.

During the course of our investigation there were two marked changes in the tare of our balloon. One of these has been described. The other arose from the circumstance that the thin paraffine (vaseline) which was most suitable for lubricating the stop-cocks during the winter no longer kept the joints tight when the heat of approaching summer rendered the material more liquid; and it became necessary to remove the stoppers and relubricate them, and it was the excess of cerate then used which melted and ran into the tubulatures subsequently.

There are then three separate values of the tare of the empty balloon to be used in our further calculations, all determined by or dependent upon Regnault's method, and all known with equal accuracy. These values we shall distinguish by the letters A, B, and C, and we shall designate by the same letters the experimental data or calculated results into which these values enter as elements.

Tare of Empty Balloon.

Values.	
A	2.5098 grams.
B	2.5573 "
C	2.5480 "

DENSITY OF AIR FREED FROM MOISTURE AND CARBONIC ACID.

In these determinations the balloon was placed in the calorimeter case and connected with the Bunsen pump through an overflow jar. Air was then drawn into it through the purifiers we have described, and the reflux current which followed for a moment when the inlet cock was closed was supplied from the previous overflow. In other respects the determinations were made as before described, and we obtained the following data for the weight of air held in the balloon at different temperatures and pressures.

Summary of Air Weights.

A No. 1, weight of air at 762.63 mm. and 18°.52 = 6.0347 grams.
A No. 2, " " 758.71 " " 19°.96 = 5.9745 "
B No. 1, " " 750.30 " " 23°.32 = 5.8411 "

Reducing now these weights to what they would have been at the temperatures and pressures we have assumed as standards, we obtain the following comparable values.

Reduced Air Weights for

H = 761.99 mm. = 300 d. in.* and
T = 27° C. = 300° absolute temperature.

A No. 1	5.8584 grams.
A No. 2	5.8588 "
B No. 1	5.8586 "
Average value	5.8586 grams.†

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* We shall use the abbreviation d. in. for tenths of an inch, after the analogy of d. m. for tenths of a meter.

† In the calculations of density and specific gravity, a still further, although wholly unimportant, correction has been made for the buoyancy of the air on the *brass* weights used to complete the tare in weighing the balloon, and in this connection it must be borne in mind that the *platinum* or *aluminum* fractions of a gram in a set of weights have always been adjusted to the larger *brass* weights in the air, and are therefore the equivalent of *brass* weights of the same denomi-

DENSITY OF HYDROGEN.

We have for the weight of hydrogen held by the balloon the following data.

B No. 1, weight of hydrogen at 763.10 mm. and 21°.08 = 0.4164 gr.
B No. 2, " " 764.92 " " 20°.52 = 0.4178 "
B No. 3, " " 758.96 " " 22°.75 = 0.4123 "

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nations. The volume of the counterpoise was adjusted when the balloon was full of air; but although the compensation may be perfect through all ordinary changes of temperature and pressure, it cannot be regarded as absolute. In a laboratory, such changes seldom amount in the aggregate to more than the equivalent of one twentieth of the normal atmospheric pressure; and although such a variation might not produce a sensible effect on the apparent weight of the small amount of brass used in our weighings, twenty times this effect, which we should have if the brass weights were wholly uncompensated, might be an appreciable quantity. In weighing the balloon the largest amount of brass weights used was about 11.5 grams, which at 300 d. in. and 27° C. displace 1.6 m.g. of air. One twentieth of this value would be barely, if at all, perceptible, but the whole quantity might cause a serious error in our results.

The tare of the empty balloon as first found by Regnault's method was 2.5573 grams; and we must assume that in the system consisting of balloon counterpoise and weights there may be outstanding a very small uncompensated volume, so that the true tare would be represented by

$$W_R = 2.5573 \pm w.$$

We next find the weight of the balloon filled with hydrogen gas, and it is obvious that under standard conditions the true weight, or

$$W' = 2.5573 \pm w + 0.4076 - w',$$

where w' represents the buoyancy of air on 0.4076 gram of brass. So the true weight of the balloon filled with air must be

$$W'' = 2.5573 \pm w + 5.8594 - w'',$$

where w'' represents the buoyancy of air on 5.8594 grams of brass. In like manner, the true weight of the balloon filled with carbonic acid gas is

$$W''' = 2.5573 \pm w + 8.9564 - w''',$$

where w''' is the buoyancy of air on 8.9564 grams of brass.

Taking 1.176 m.g. as the weight of 1 c.c. of air at 300 d. in. and 27° C., the standard conditions to which the weights have been reduced, we have

$w' = 0.05$ m. g., $w'' = 0.84$ m g., $w''' = 1.28$ m. g.;

and further,

$W' - W_R = 0.4076 - 0.00005$ gram. True weight of hydrogen.
$W'' - W_R = 5.8594 - 0.00084$ " " " air.
$W''' - W_R = 8.9564 - 0.00128$ " " " carbonic acid.

These corrections should be applied to the weights before calculating the specific gravities, although they only alter the last values one or two units in

Reduced Weights.

H = 300 d. in.	T = 27° C.
B No. 1	0.4076
B No. 2	0.4072
B No. 3	0.4081
Average	0.4076

SPECIFIC GRAVITY OF HYDROGEN.

Air = 1.

The values were obtained by dividing each of the weights of hydrogen above given by the average weight of air (5.8586), after reduction for the temperatures and pressures at which the hydrogen weights were observed. The calculations were verified by dividing each of the reduced weights of hydrogen by the average reduced weight of air as above, and the same figures were obtained in both ways.

B No. 1	0.06957
B No. 2	0.06951
B No. 3	0.06966
Average	0.06958
Average using values of tare by chemical method	0.06962

SPECIFIC GRAVITY OF OXYGEN.

Hydrogen = 1.

In this investigation we have not made an additional determination of the specific gravity of oxygen gas referred to air, for the causes of error which are serious in the case of hydrogen are not appreciable when working with the heavier gas, and we cannot expect to improve

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the last decimal place; and in this paper, as is usual, the decimals are carried out one figure beyond the limits of accuracy.

In the chemical method we also took the weight of the balloon filled with carbonic acid gas, and, as before, we have

$$W''' = 2.5573 \pm w + 8.9564 - w'''.$$

Then by chemical means we determined the absolute weight (*in vacuo*) of the carbonic acid which the vessel held, that is, the quantity represented by $8.9564 - w'''$. Subtracting this value from the total weight, we obtained the tare of the empty balloon by the chemical method, and this obviously is

$$W_C = 2.5573 \pm w.$$

Thus, the buoyancy of the air on the weights is eliminated, and W_C is directly comparable in all its relations with W_R.

on the results of Regnault. Assuming, then, for the specific gravity of oxygen gas referred to air the value 1.10562, as obtained by Regnault and corrected by Crafts, and dividing this value by each of the values for the specific gravity of hydrogen gas given above, we have the following values for the specific gravity of oxygen referred to hydrogen.

B No. 1	15.892
B No. 2	15.907
B No. 3	15.873
Average	15.891
Average of chemical method	15.882
Value found by Lord Rayleigh	15.884

DENSITY OF CARBONIC ACID.

For the weight of carbonic acid gas held in the balloon at different temperatures and pressures we have the following data.

B No. 1,	weight of CO_2 at	756.73	mm. and	22°.40	9.0334	gr.
C No. 1,	" "	760.50	" "	25°.56	8.9821	"
C No. 2,	" "	759.13	" "	26°.60	8.9348	"

Taking now the average value of the weight of air held in the balloon at 300 d. in. = 761.99 mm. and 27° (viz. 5.8586 grams), and reducing this weight to what it would have been under the condition at which each of the four weights just given was observed, and then dividing each of these weights (corrected as by previous note) by the weight of air under the same conditions, we obtain the following results.

Specific Gravity of Carbonic Acid. Air = 1.

	Wt. of CO_2.	Wt. of Air.	H	T	Sp. Gr.
B No. 1	9.0321	5.9088	756.73	22°.40	1.52858
C No. 1	8.9808	5.8753	760.50	25°.56	1.52855
C No. 2	8.9335	5.8445	759.13	26°.60	1.52855
	Average value				1.52856
	Average value by chemical process				1.52854

Taking lastly the average value of the weight of hydrogen held in the balloon at 761.99 mm. and 27° (viz. 0.4076 gram), and dividing the several weights of carbonic acid by this weight reduced to the same conditions, we have, —

Specific Gravity of Carbonic Acid. Hydrogen = 1.

	Wt. of CO_2.	Wt. of H_2.	H	T	Sp. Gr.
B No. 1	9.0321	0.4111	756.73	22°.40	21.971
C No. 1	8.9808	0.4088	760.50	25°.56	21.971
C No. 2	8.9335	0.4066	759.13	26°.60	21.971
	Average value				21.971
	Average value by chemical process				21.957

The close agreement, indeed the essential identity, of these results should be noticed, as this fully substantiates the extreme accuracy of the method of recovering the lost tare of the empty balloon described on page 224. It is true that, as the values of the specific gravity of carbonic acid have been calculated with an average value of the several reduced weights of hydrogen or air, an error in these data would not affect the results; but any error in the observed weights of carbonic acid would appear to its full extent.

Moreover, the striking fact should not be overlooked that the specific gravity of carbonic acid gas referred to hydrogen approaches much more nearly 22, the half molecular weight of carbonic acid gas as generally assumed, than does that of oxygen gas when referred to the same standard, the corresponding whole number 16, and the significance of the circumstance is obvious. If we assume that the atomic weight of oxygen as determined by Dr. Richards under my direction is 15.87,* then the corresponding atomic weight of carbon would be 11.90, and the half molecular weight of carbonic acid 21.82. Theoretically, this number ought also to define the specific gravity of carbonic acid gas referred to hydrogen gas, if the two gases were compared under the same conditions of high temperature and indefinite expansion. But under the great pressure of our atmosphere the molecular volume of carbonic acid gas is known to be condensed to a measurably greater degree than the potentially equal molecular volume of hydrogen gas, and the result must be a proportionally increased density; and, moreover, the inequality in the condensation of the two gases must be increased by the circumstance that at the ordinary temperature of the air carbonic acid gas is below the critical point, while hydrogen gas is very far above it. If, however, this is true in the case of carbonic acid gas, our knowledge of the deviations from Mariotte's law compels us to infer that the same must be true in some small measure, although in a much less degree, in the case of oxygen gas;

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* These Proceedings, vol. xxiii. p. 185.

and it would lead us to expect that the specific gravity of oxygen gas referred to hydrogen gas would be slightly greater, certainly not less, than the corresponding half molecular weight. Now we have from the results published in this and our preceding paper, —

Half molecular weight of carbonic acid gas	21.82
Sp. Gr. of carbonic acid gas (referred to hydrogen gas) .	21.96
Half molecular or atomic weight of oxygen gas . . .	15.87
Sp. Gr. of oxygen gas (referred to hydrogen gas) . . .	15.88

It has been thought to discredit the low value of the atomic weight of oxygen we have found by the very easy but wholly gratuitous assumption that the hydrogen gas on which we experimented was impure, and we had intended in this investigation to demonstrate the identity of the gas from the several sources employed by a comparison of their specific gravities. We are under great obligations to Lord Rayleigh, who has relieved us from this necessity by anticipating the work. He has experimented on hydrogen gas, not only from all the sources we used, but also on gas which had been occluded by palladium, and has obtained the same result in all cases; namely, the value 15.884,* essentially identical with that which we have found in this investigation with the hydrogen gas from our electrolytic apparatus.†

This point, however, had not been overlooked in the previous paper. It was there shown that the results obtained, in *three distinct series of experiments*, with hydrogen gas prepared by *three different processes* and with *three different forms of apparatus*, were essentially identical.‡ On the doctrine of chances, such an agreement would have been practically impossible had there been an appreciable amount of accidental impurities, in the gas from either of the sources. We say accidental impurities, for there may be inherent impurities common to the gas from all sources, of which we as yet know nothing; and, as we wrote before, "The question still remains, Is the hydrogen gas thus prepared the typical hydrogen element? But this is the same question which must arise in regard to any one of the elementary substances; and all that we can say is, that the evidence in regard to the purity of the hydrogen we have used is as good as any that can be adduced in regard to any one of the elementary substances whose atomic weight has been most accurately determined." §

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* Proceedings of the Royal Society, vol. xlv. p. 425.

† These Proceedings, vol. xxiii. p. 168.

‡ See table, these Proceedings, vol. xxiii. p. 173.

§ These Proceedings, vol. xxiii. p. 174.

It is not to be expected that our results, or those of our contemporaries, are final. The most that has been accomplished by recent investigation is to show that the ratio of the atomic weight of oxygen to that of hydrogen, deduced from the elementary substances, as we know them in their purest condition, is decidedly less than that of 16 to 1. The evidence as to the exact value of this ratio is still conflicting, and although after our experience we cannot see how greater accuracy could be gained by any variation of our process, we are far from claiming that our results have not been vitiated by unknown constant errors. Fortunately, an exact knowledge of the ratio is at present of no practical importance in chemical analysis. The only question on which the actual small indefiniteness has a bearing is the unit of atomic weights, a question that has been much discussed of late; but here, as it seems to us, one consideration should be conclusive.

Every one who has worked on the oxygen and hydrogen ratio knows that the resources of experimental science have been taxed to the utmost in these investigations. Greater accuracy is not to be expected with our present appliances, and yet there is an outstanding uncertainty amounting to more than one half of one per cent of the value. This corresponds to a variation of more than one unit in many of the higher atomic weights: and unless we are willing that these *chemical constants* should fluctuate to this extent with every new determination of the fundamental ratio, we must seek a more invariable basis. The most natural and stable unit is the atomic weight of oxygen, not only on account of the wonderful combining power of this element, but also because the ratio of the combining weights of most of the elements to that of oxygen are known with great precision; and many cogent reasons could be urged for returning to the system of Berzelius, which referred all the other weights to that of oxygen, assumed to be 100. But this system would not exhibit to advantage the numerical ratios on which modern chemical classification is based. Hence for a provisional system we most warmly approve of that which assumes O = 16 as its basis, and of the best known atomic weights leaves only the value of H to vary with our changing knowledge. This system has all the stability it is possible at present to secure, and exhibits to advantage the relations which are important in classification. Moreover, it is no small recommendation to this system that a large number of the weights are whole numbers, within the limits of error of ordinary analytical work, and for this reason can be easily remembered.

In conclusion, I would express my obligations to my nephew, Dr.

PLATE I.

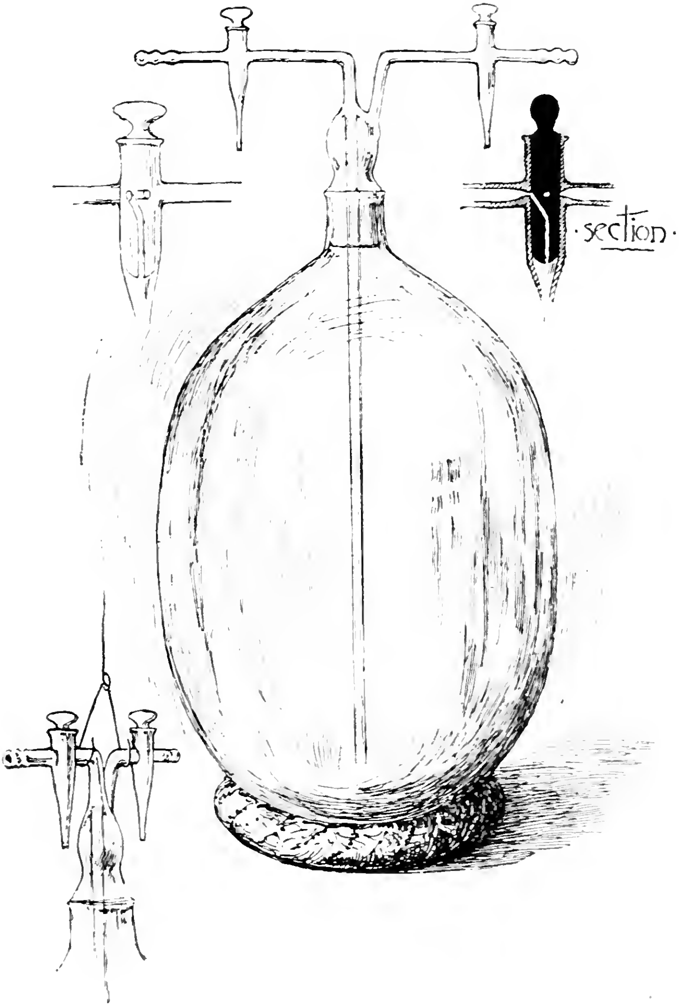


PLATE II.

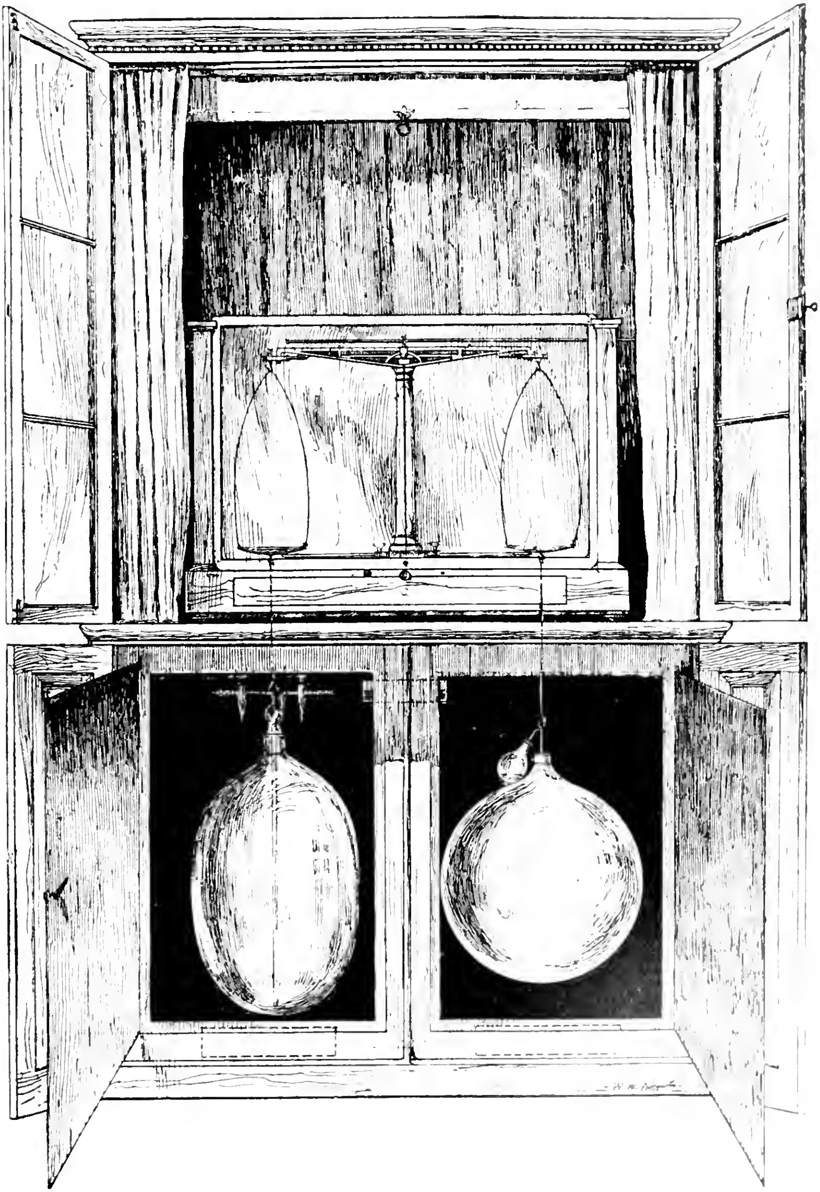
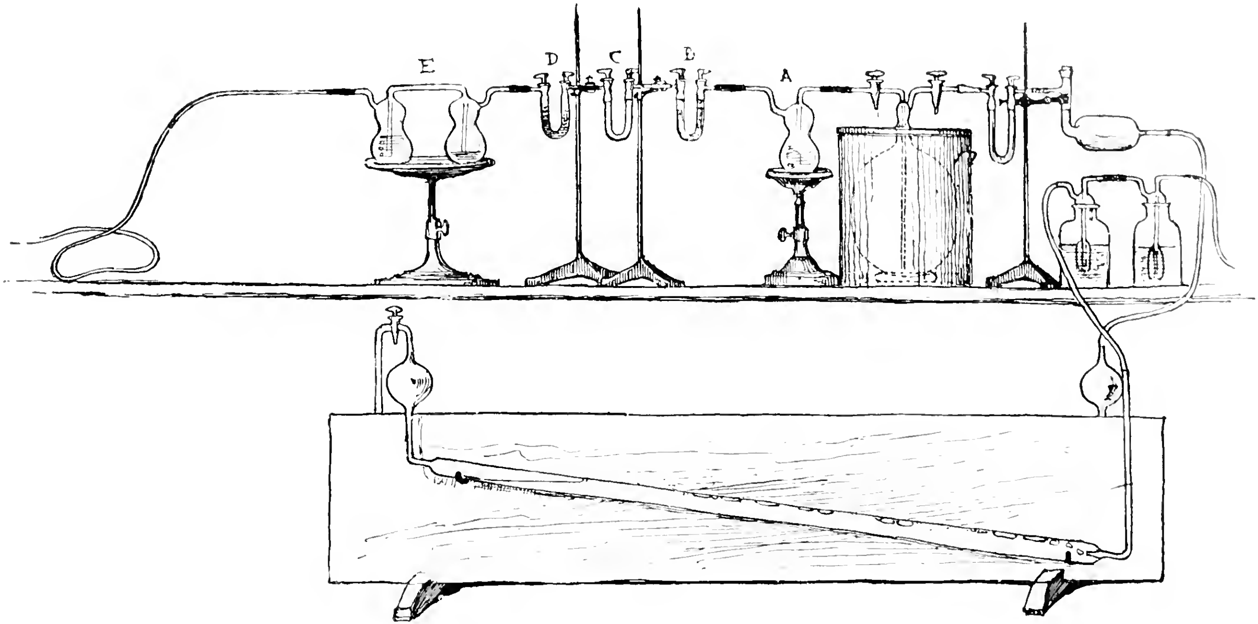


PLATE III.



Oliver W. Huntington, for the great aid he has given throughout this investigation. With the help of his skill in glass-blowing I have been able to secure all the connections of my gas generators with melted or cement joints, except the direct connections with the globe, where india-rubber could not be avoided. He has also constantly assisted my impaired eyesight in the observations with barometer and thermometer on which the accuracy of the work greatly depended. I have likewise been indebted to Dr. Arthur M. Comey for making the titrations required, and to Mr. W. W. Bosworth for the drawings with which this paper is illustrated.

XIX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF SODIUM MALONIC ESTER ON TRIBROMDINITROBENZOL.

SECOND PAPER.

By C. Loring Jackson and W. S. Robinson.

Presented May 28, 1889.

In a previous paper * on this subject we were obliged to publish several results in an unfinished condition, because at the time we saw no chance of being able to continue the work together. Since then, however, unforeseen circumstances have allowed us to go on with the research, and in this paper we describe work which fills up most of the gaps in our former publication.

The most important results contained in this paper may be stated briefly as follows. The reactions by which the bromdinitrophenylmalonic ester is formed have been made out to be the following: —

I. $C_6HBr_3(NO_2)_2 + CHNa(COOC_2H_5)_2 =$
$NaBr + C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2.$

II. $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + CHNa(COOC_2H_5)_2 =$
$C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2.$

III. $C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 =$
$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2.$

IV. $CHNa(COOC_2H_5)_2 + H_2O = NaOH + CH_2(COOC_2H_5)_2.$

V. $CHBr(COOC_2H_5)_2 + NaOH = NaBr + CHOH(COOC_2H_5)_2.$

The proof of these reactions consisted in the isolation of tartronic acid from the mixture obtained by the saponification of the oily secondary product with hydrochloric acid.

The action of concentrated hydrochloric acid, or, better, sulphuric acid of specific gravity 1.44, upon the bromdinitrophenylmalonic ester

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* These Proceedings, xxiv. 1.

has been studied, and we are able to correct some of the preliminary statements made on this subject in our first paper. The product is the bromdinitrophenylacetic acid

$$C_6H_2Br(NO_2)_2CH_2COOH,$$

which melts at 177°, and is formed, when hydrochloric acid is used, by the following reactions:—

$$\begin{aligned} &C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2 + 2\,HCl = \\ &\quad 2\,C_2H_5Cl + C_6H_2Br(NO_2)_2CH(COOH)_2 = \\ &\quad 2\,C_2H_5Cl + CO_2 + C_6H_2Br(NO_2)_2CH_2COOH. \end{aligned}$$

The crystalline silver salt of this acid was analyzed, and proved to have the formula

$$C_6H_2Br(NO_2)_2CH_2COOAg\,.\,H_2O.$$

With sodic hydrate a deep Prussian green or with an excess a yellowish brown solution is formed, from which acids throw down a pale crimson precipitate, or a white one which becomes pale crimson when moistened with alcohol; none of these substances could be brought into a state fit for analysis, but we found that bromine was removed in their formation.

The bromdinitrophenylacetic acid is broken up when boiled with alcohol into bromdinitrotoluol and carbonic dioxide; boiling with water produces the same effect, but much more slowly. A few drops of sulphuric acid prevent the decomposition by boiling water. This conversion into bromdinitrotoluol gave us the means of determining the constitution of the bromdinitrophenylmalonic ester and its derivatives; as Messrs. W. B. Bentley and W. H. Warren have, at our request, worked out the constitution of the substituted toluol, and found that it is as follows:

$$CH_3\,.\,Br\,.\,NO_2\,.\,NO_2\,.\,1\,.\,3\,.\,4\,.\,6.$$

It follows, therefore, that all the substances mentioned in this and our former paper must have a similar constitution, and that in making the bromdinitrophenylmalonic ester from bromdinitrobenzol the bromine atom replaced by the malonic radical is one of those which is at the same time para and ortho to the nitro groups, the one replaced by hydrogen is ortho to the two nitro groups, while the third atom of bromine, which remains unaltered, occupies exactly the same position as that replaced by the malonic ester radical,—certainly a curious result.

Preparation of Bromdinitrophenylmalonic Ester.

Our longer experience in the preparation of bromdinitrophenylmalonic ester has led us to introduce several improvements into the process, which now we carry on as follows. A strong benzol solution of 20 grs. of tribromdinitrobenzol (benzol is to be preferred to the ether used formerly, because the tribromdinitrobenzol is more soluble in it) is mixed with 16 grs. of malonic ester previously converted into sodium malonic ester by treatment with the sodic ethylate from 2.3 grs. of sodium and about 100 to 125 c.c. of alcohol, and the mixture allowed to stand over night at ordinary temperatures. The red solution thus obtained is treated with water, which separates it into two layers, a dark red aqueous solution containing the sodium salt of bromdinitrophenylmalonic ester and sodic bromide, and a benzol solution of the unaltered tribromdinitrobenzol with the oily product of the reaction. The two layers are separated with a drop-funnel, and the lower aqueous one acidified with dilute sulphuric acid; this throws down a yellowish white precipitate of the bromdinitrophenylmalonic ester, which is purified by crystallization from hot alcohol, until it shows the constant melting point 76°.

In this way 20 grs. of tribromdinitrobenzol gave 7.9 grs. of the bromdinitrophenylmalonic ester,* and 5.1 grs. of tribromdinitrobenzol were recovered from the benzol solution. Subtracting this from the 20 grs. there are left 14.9 grs. of tribromdinitrobenzol, which entered into the reaction, and should have given the same weight, 14.9 grs., of the product, so that the yield was 53 per cent of the theory, or about the same as that obtained by the process as given in our first paper, which calculated in the same way becomes 50 per cent.

In the course of some other experiments the curious observation was made that it is not necessary to use sodic ethylate to bring about the action of malonic ester on the tribromdinitrobenzol, as a little of the red salt of bromdinitrophenylmalonic ester was formed when *aqueous* sodic hydrate was added to a mixture of the two organic

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* Dr. G. D. Moore, in his work with me on the action of sodium acetacetic ester on tribromdinitrobenzol, has found that a much better yield is obtained if the mixture is boiled for an hour under a return condenser. This observation was not made until the work described in this paper was finished and Mr. Robinson had left Cambridge, so that it was not convenient to try the experiment of boiling the solution of sodium malonic ester and tribromdinitrobenzol, nor did it seem very desirable to do so, as when we first took up the subject such an experiment was tried, and seemed to yield very unfavorable results. I propose, however, to repeat the experiment next year, if I return to the study of these compounds. C. L. J.

substances. This recalls the observation of Victor Meyer,* that homologues can be obtained from benzylcyanide by using the alkylhaloid with powdered solid sodic hydrate instead of sodic ethylate, or from desoxybenzoin by the use of an alcoholic solution of an alkaline hydrate.

Study of the Reactions by which the Bromdinitrophenylmalonic Ester is formed.

One of the most important points, which want of time prevented us from considering in our first paper, was the mechanism of the reactions by which the bromdinitrophenylmalonic ester was formed from the tribromdinitrobenzol, and accordingly this was one of the first points to which we turned our attention in taking up the subject again. The reaction consists essentially, as our analyses of the product showed, in the replacement of one of the bromine atoms in the tribromdinitrobenzol by the malonic ester radical $CH(COOC_2H_5)_2$, and of a second by hydrogen forming $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$, and the obscure part of it is the manner in which this second atom of bromine is replaced by hydrogen. The first step toward clearing up this obscurity was obviously to make out whether this atom of bromine was eliminated in the form of some organic compound, or as sodic bromide, which was done by the following quantitative determinations of the amount of sodic bromide formed in the reaction.

I. 20 grs. of tribromdinitrobenzol were treated with the sodium malonic ester from 16 grs. of malonic ester in the way already described, and, after precipitating the bromdinitrophenylmalonic ester from the aqueous solution with dilute nitric acid, and filtering it out, the amount of sodic bromide was determined by precipitation of argentic bromide from an aliquot part of the filtrate, and calculating the amount in the entire solution. In this way the whole solution was found to yield 13.81 grs. of argentic bromide, corresponding to 5.88 grs. of bromine. The benzol solution on evaporation yielded 5.1 grs. of tribromdinitrobenzol, which had not taken part in the reaction, leaving 14.9 grs. which had acted, and which would yield 5.89 grs. of bromine, if two of the atoms of bromine had been removed from each molecule as sodic bromide.

II. 20 grs. of tribromdinitrobenzol gave under the same conditions 13.8 grs. of argentic bromide corresponding to 5.87 grs. of bromine, but only 4.9 grs. of tribromdinitrobenzol were recovered unaltered.

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* Ber. d. ch. G. 1888, p. 1291.

The 15.1 grs. of tribromdinitrobenzol which entered into the reaction should have lost 5.96 grs. of bromine.

Percentage of the theoretical amount of bromine removed from tribromdinitrobenzol in the form of sodic bromide: —

I.	II.
99.86	98.49

These numbers agree as closely as could be expected, when the necessary sources of error in the process are considered, and prove that all the bromine removed by the reaction is converted into sodic bromide.

The second point to be determined was from what source the atom of hydrogen was obtained which replaced the atom of bromine. For this purpose we investigated the oily product of the reaction, and, after we had found that nothing definite could be obtained from it by distillation under ordinary pressures, or with steam, and that sodic hydrate or other alkaline saponifying agents gave most unpromising results, we tried heating it with strong hydrochloric acid in a sealed tube to 130° for 20 hours, as the bromdinitrophenylmalonic ester which was dissolved in the oil would be converted by this treatment into the corresponding phenylacetic acid, with the properties of which we were familiar, and which therefore we thought could be removed easily from the other products of the reaction. The tubes after heating contained an aqueous solution and a small amount of viscous matter, which gradually changed into an amorphous solid. These were separated by filtration, and the filtrate evaporated to dryness on the water bath, leaving a crystalline residue, which was extracted with cold water to leave behind the bromdinitrophenylacetic acid present. The extract after being evaporated again on the water bath gave crystals, which made up about one half the amount of the residue from the first evaporation. They were freely soluble in water or alcohol, nearly insoluble in ether, and could be sublimed at temperatures below their melting point forming glassy white thick needles or prisms, which melted at 185°. These properties prove that the crystals are tartronic acid, as they are identical with those given by Conrad and Bischoff for that substance.* We tried also to confirm this inference by an analysis, but the small amount of the acid which after some unsuccessful experiments remained at our disposal. little more than 0.1 gr., prevented us from purifying it thoroughly, as sublimation,

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* Ann. Chem., ccix. 222.

which had given the substance melting at 185°, turned out to be too wasteful a process for working up large amounts; we were not surprised, therefore, that our analysis of the silver salt gave 62.82 per cent of silver, instead of the 64.69 per cent calculated for argentic tartronate. This result, however, bad as it is, comes nearer to that for argentic tartronate than to that for any other substance which could well be formed, and therefore gives us the desired confirmation.* The small amount of tartronic acid obtained, less than 0.5 gr. from about 10 grs. of the oil, may be accounted for on the supposition that the larger part of the tartronic acid was decomposed by the strong hydrochloric acid used in the saponification of the oil, as Conrad and Bischoff† have observed that tartronic acid is decomposed very easily by hydrochloric acid, and we also were unable to obtain a trace of the acid from the filtrate after argentic chloride had been precipitated from the silver salt by a slight excess of hydrochloric acid. In fact, we should not have thought it worth while to try to obtain tartronic acid by the action of hydrochloric acid on our oil, if it had not been for the fact that tartronic ester has been made from calcic tartronate by the action of hydrochloric acid gas and alcohol,‡ which would seem to show that the tartronic acid is more stable in presence of strong than of dilute hydrochloric acid, improbable as this sounds. This view is in harmony with our observations detailed above, and Conrad and Bischoff state that even very dilute acid decomposes it readily; but even granting this, a large proportion of the tartronic acid must have been decomposed during the treatment with hydrochloric acid, and this seems to us sufficient to make it more than probable that the tartronic acid is the product of the principal reaction, and not formed in a secondary one taking place only to a limited extent. If this is admitted, the following reactions would give the most probable explanation of what takes place.

I. $C_6HBr_3(NO_2)_2 + NaCH(COOC_2H_5)_2 =$
$C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + NaBr.$

II. $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + NaCH(COOC_2H_5)_2 =$
$C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2.$

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* No attempt was made to obtain a better analysis of the tartronic acid, because the work upon the corresponding trinitro compound described in another paper furnished a complete confirmation of the theory of the reactions given here.

† Ann. Chem., ccix. 223.

‡ Freund, Ber. d. ch. G., xvii. 786. Pinner, Ibid., xviii. 757.

III. $C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 =$
$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2.$

IV. $NaCH(COOC_2H_5)_2 + H_2O = NaOH + CH_2(COOC_2H_5)_2.$

V. $CHBr(COOC_2H_5)_2 + NaOH = CHOH(COOC_2H_5)_2 + NaBr.$

Of these reactions, I., II., and III. take place before, IV. and V. after, the addition of the water used in working up the product. That Reaction III. takes place we infer from our discovery of tartronic acid among the products of saponification of the oil, as Conrad and Bischoff [*] have proved that brommalonic ester is decomposed by sodic hydrate, according to Reaction V.[†]

The experiments of one of us with G. D. Moore upon the action of sodium malonic ester on tribromtrinitrobenzol have shown that these reactions take place in a way analogous to that just worked out. For the details we would refer to the paper on this subject.

The objection which might be raised against these reactions, that the yield of bromdinitrophenylmalonic ester is at best only about 50 per cent of that required by theory, and therefore that some other substance may be formed from the tribromdinitrobenzol in addition to it, is disposed of by the fact that on making the dibromdinitrophenylmalonic ester from tetrabromdinitrobenzol by exactly analogous reactions, the yield rose to 80 per cent of the theoretical.[‡] It follows, therefore, that the 47 to 50 per cent unaccounted for in our preparations remained dissolved in the oily secondary product; but although we have made many attempts to recover it, none of them have been crowned with success.

The absence of malonic acid in the product of the action of hydrochloric acid on the oil seems to us extraordinary, as we purposely kept the temperature of the saponification at 130°, in order to avoid decomposing the malonic acid, which we expected from the excess of malonic ester undoubtedly present in the oil. We can account for this only by supposing that malonic acid is decomposed in presence of strong hydrochloric acid at a lower temperature than when heated alone.

Saponification of Bromdinitrophenylmalonic Ester.

In our previous paper we stated that strong hydrochloric acid decomposed bromdinitrophenylmalonic ester, when the two substances

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[*] Ann. Chem., ccix. 222.

[†] A fuller discussion of these reactions will be found in the general paper at the end of this series.

[‡] These Proceedings, xxiv. 295.

were heated together to 140°–145° in a sealed tube, and described the product formed, stating, however, that all our results up to that time must be regarded as preliminary. Upon taking up the subject again, we studied in the first place the gas evolved when the tube was opened, and found that, in addition to the gas already mentioned burning with a green-bordered flame (which is undoubtedly ethylchloride), carbonic dioxide was given off, as was proved by the precipitate formed when the gas was passed through lime-water. It is to be observed, however, that if the temperature to which the tubes were heated was 140°, or a little lower, very little, if any, carbonic dioxide was given off, and the product insoluble in the hydrochloric acid was oily; on the other hand, when a crystalline product was obtained at a somewhat higher temperature, carbonic dioxide was given off freely. We next attempted to prepare the substance in open vessels by substituting for strong hydrochloric acid dilute sulphuric acid boiling at about the temperature to which we heated the tubes, and found that not only did we obtain the product in this way, but that it was much purer than that made in the sealed tubes with hydrochloric acid. We have arrived accordingly at the following method as the most convenient for saponifying the bromdinitrophenylmalonic ester. 2 grs. of the ester are mixed with about 100 c.c. of dilute sulphuric acid, specific gravity 1.44 and boiling point 132°, and the mixture boiled in a flask with a return condenser, until the oily drops of melted bromdinitrophenylmalonic ester have all gone into solution, which usually takes about an hour and a half. After this the solution, as it cools, deposits long, pale yellow needles of the new substance, which, if the preparation has succeeded well, melt at 177° at once. If, however, the action has not run so well, and the melting point is somewhat lower than this, the substance can be easily purified by crystallization from boiling water acidified with a few drops of dilute sulphuric acid, but in no case should it be crystallized from pure water, or alcohol, as these solvents decompose it in the curious way described later in this paper, when we consider its properties.

Metabromdinitrophenylacetic Acid, $C_6H_2Br(NO_2)_2CH_2COOH$.

The substance prepared in the manner just described, and showing the constant melting point 177°, was dried at 100°, and analyzed with the following results: —

I. 0.2106 gr. of the substance gave on combustion 0.2426 gr. of carbonic dioxide, and 0.0420 gr. of water.

II. 0.1933 gr. of the substance gave 15.6 c.c. of nitrogen at a temperature of 15°.5, and a pressure of 759.2 mm.

III. 0.1821 gr. of the substance gave, according to the method of Carius, 0.1152 gr. of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2H$.	Found. I.	II.	III.
Carbon	31.47	31.43		
Hydrogen	1.64	2.21		
Nitrogen	9.18		9.42	
Bromine	26.23			26.93

These analyses supersede those already published,* which were made with a substance prepared by crystallization from dilute alcohol, before we had found that this solvent decomposed the compound; it was therefore decidedly impure, as indeed was shown by its melting point, which was 170° instead of 177°.

The yield of the bromdinitrophenylacetic acid is essentially quantitative, as 2 grs. of the bromdinitrophenylmalonic ester gave, after treatment with dilute sulphuric acid, 1.4 grs. of bromdinitrophenylacetic acid melting at 177°, instead of the calculated amount, 1.56 grs., that is, 90 per cent of the theory; the missing 10 per cent without doubt remained dissolved in the dilute sulphuric acid, in which the substituted acetic acid is not wholly insoluble, as the 1.4 grs. were obtained by simple filtration, no attempt being made to recover the organic substance from the filtrate.

In view of the observations described above, there can be no doubt that the following reactions take place when bromdinitrophenylmalonic ester is saponified by heating it with hydrochloric acid at temperatures in the neighborhood of 145°:

$$\begin{aligned} &C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2 + 2\,HCl = \\ &\quad C_6H_2Br(NO_2)_2CH(COOH)_2 + 2\,C_2H_5Cl = \\ &\quad C_6H_2Br(NO_2)_2CH_2COOH + CO_2 + 2\,C_2H_5Cl. \end{aligned}$$

And there can be no question that a similar reaction takes place when dilute sulphuric acid is substituted for strong hydrochloric acid. In fact, this was so obvious that we have not thought it worth while to try to isolate the sulphovinic acid which must be formed in this case instead of the ethylchloride.

Properties. — The metabromdinitrophenylacetic acid crystallizes from an aqueous solution containing a little sulphuric acid in yellowish

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* These Proceedings, xxiv. 11.

white needles, often one to two centimeters long, which appear under the microscope as tolerably thick prisms frequently tapering owing to modification by the planes of a pyramid with a very acute angle, but almost always, even in addition to this tapering, terminated bluntly by the planes of another very obtuse pyramid. Occasionally the termination is a single plane at a moderately acute angle to the sides, but this looked as if it were due to cleavage. The crystals are generally very well developed, but if they are small, a tendency to twin longitudinally is observed. If the substance is crystallized from alcohol, the forms like feathers, or half-feathers, described in our previous paper, and groups of branching needles looking like certain feathery seaweeds, appear; but as the alcohol decomposes the substance, these forms can hardly be ascribed to the substituted acetic acid itself. It melts at 177°; and is essentially insoluble in ligroine or carbonic disulphide; very slightly soluble in chloroform, slightly in benzol, more soluble in both of these solvents when hot; tolerably soluble in ether, separating from the solution in a liquid form, which solidifies on stirring; easily soluble in acetone or glacial acetic acid; soluble in cold alcohol, more freely in hot, but the alcohol decomposes it, as is indicated by the change in the appearance of the crystals, the long yellowish prisms of unaltered bromdinitrophenylacetic acid becoming roughly studded with fine needles of another substance, and by the lowering of the melting point, when the substance is crystallized from alcohol; evaporation to dryness of the alcoholic solution, if repeated three times, reducing the melting point from 177° to 147°; while after two more evaporations, making five in all, the melting point had sunk to 103°–104°, at which point it remained constant after repeated crystallization. The substance obtained in this way crystallized in rectangular prisms, or plates, was not acted on by alkalies, and was recognized as Grete's metabromdinitrotoluol.* For greater certainty it was analyzed, with the following results: —

I. 0.1690 gr. of the substance gave by the method of Carius 0.1210 gr. of argentic bromide.

II. 0.2185 gr. of the substance gave 20.3 c.c. of nitrogen at a temperature of 22°.5 and a pressure of 773.3 mm.

	Calculated for $C_6H_2Br(NO_2)_2CH_3$.	Found.	
		I.	II.
Bromine	30.65	30.47	
Nitrogen	10.73		10.69

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* Ann. Chem., clxxvii. 258.

This conversion of the metabromdinitrophenylacetic acid into the corresponding toluol by boiling with alcohol, when it is so stable in presence of boiling dilute sulphuric acid, seemed to us so interesting that we have examined it more carefully. Having in the first place determined that the alcohol was neutral to test papers, to prove that the reaction could not be due to a trace of alkali, or acid in it, a quantity of the substance melting at 177° was boiled in a flask under a return condenser with a little alcohol for three hours, and pure air occasionally drawn through the apparatus to sweep out its contents into a set of absorption bulbs filled with lime-water; in this way a heavy precipitate was obtained, which consisted in great part of calcic hydrate precipitated by the alcohol vapor, but also contained calcic carbonate, as was shown by effervescence when it was dissolved in an acid, thus proving that carbonic dioxide had been given off. The alcoholic solution, after it had been boiled for an hour and a half longer, gave crystals, melting at 103° to 104°. It seems evident, therefore, that the reaction runs as follows,

$$C_6H_2Br(NO_2)_2CH_2COOH = C_6H_2Br(NO_2)_2CH_3+CO_2,$$

and the alcohol seems to take no part in it. Methyl alcohol, in which the substance is more soluble than in ethyl alcohol, brings about a similar decomposition, but more slowly. In boiling water the metabromdinitrophenylacetic acid is tolerably soluble, but nearly insoluble in cold water. The decomposition produced by alcohol also takes place when the aqueous solution is boiled, but very slowly, so that long boiling is necessary to convert the substance completely into the substituted toluol; nevertheless, after distilling with steam for several hours, the whole of the substance had passed over into the receiver as metabromdinitrotoluol, since none of the substituted acetic acid. which does not distil with steam, was left in the flask. The presence of a very small amount of sulphuric acid (two or three drops of the dilute acid to 100 c.c. of water) is sufficient to prevent this decomposition entirely, as a specimen of the substituted acetic acid showed no signs of decomposition, even after having been distilled with steam for three hours with only the amount of dilute sulphuric acid which remained adhering to it after the excess of acid used in its preparation had been removed by filtration. The best solvent for the bromdinitrophenylacetic acid therefore is boiling water containing a few drops of sulphuric acid. If the substance has become contaminated with the substituted toluol, it can be purified conveniently by distillation with steam in presence of a few drops of sulphuric acid, when the toluol passes over, and the acetic acid remains behind in the flask.

Ammonic hydrate dissolves the metabromdinitrophenylacetic acid, forming a colorless solution if the acid is in excess; but if the ammonic hydrate is added in slight excess, a green solution is obtained, which turns dark brown if a large excess of ammonic hydrate is added, but regains its green color on dilution with water. Both the colorless and green solutions smell of ammonia, and this smell could not be removed by gentle boiling, or by allowing the solution to stand over sulphuric acid, from which we infer that the ammonium salt is a decidedly unstable substance. When either solution is warmed on the water bath for some time it is partially decomposed with formation of a precipitate of metabromdinitrotoluol, and the green solution turns yellow even when allowed to evaporate spontaneously. Hydrochloric acid threw down from the solution a precipitate of metabromdinitrophenylacetic acid. The ammoniacal solution, prepared with an excess of the acid and freed as completely as possible from an excess of ammonia, gave no precipitate with baric, strontic, or calcic chloride, but with the salts of many of the heavy metals it gave precipitates, of which the following were the most characteristic: —

Aluminic chloride, heavy, white.

Ferric chloride, heavy, very pale buff.

Cupric sulphate, heavy, pale blue.

Mercuric nitrate, heavy, yellowish white.

Mercuric chloride, a very slight precipitate, probably white precipitate from the slight excess of ammonic hydrate.

Mercurous nitrate, heavy, white.

Plumbic acetate, heavy, white.

Argentic nitrate, heavy, white.

The behavior with argentic nitrate is especially characteristic; if the solutions are strong, the mixture becomes nearly solid from the formation of a white flocculent precipitate, which frequently swells up, forming a little heap or pyramid, and after standing for some hours becomes converted into good-sized crystals. The analysis and properties of this salt are described more in detail below.

With sodic hydrate a solution of the acid turns a deep Prussian green color, which passes in time into a yellowish brown, this latter color appearing at once when an excess of sodic hydrate is added. If the green solution is acidified, a precipitate is obtained, which, although nearly colorless when dry, becomes purple when moistened with alcohol. This precipitate was oily at first, and, although it solidified later, we did not succeed in finding any solvent from which it could be crystallized. That the sodic hydrate had acted on the bromine was shown by an actual experiment, which gave the following results.

0.67 gr. of the acid yielded by treatment with sodic hydrate so as to form the green salt 0.1136 gr. of argentic bromide, which corresponds to 0.0483 gr. of bromine instead of the 0.1757 gr. contained in the amount of acid taken; that is, 27.5 per cent of the whole had been removed.

The yellowish brown solution obtained, when a large excess of sodic hydrate was used, or the mixture of sodic hydrate and metabromdinitrophenylacetic acid was boiled for some time, gave on addition of an acid a viscous red substance, which was exceedingly unmanageable. That bromine was removed in quantity in this way is shown by the following determination.

0.2412 gr. of the metabromdinitrophenylacetic acid was boiled with sodic hydrate for three quarters of an hour; the product, after acidifying with nitric acid, and filtering out the precipitate, gave 0.1180 gr. of argentic bromide, corresponding to 0.0502 gr. of bromine instead of the 0.0632 gr. contained in the weight of acid taken; that is, 79.4 per cent of the whole.

It is evident, therefore, that the original compound has undergone a deep-seated alteration, and the new crimson substance is probably a phenol. This view of its nature receives some confirmation from the fact that it is decomposed with the greatest ease by even somewhat dilute nitric acid. We have not yet succeeded in bringing either of the products derived from sodic hydrate into a state fit for analysis, although the slight solubility of the barium salt of the crimson acid awakened hopes of success; but these ended in disappointment, as the salt proved quite as viscous as the free acid.

Potassic carbonate gives with the metabromdinitrophenylacetic acid results similar to those obtained with sodic hydrate, but less marked.

We hoped to be able to throw some light on this action of alkalies on the metabromdinitrophenylacetic acid by the study of the corresponding anilido compound, but have not succeeded as yet in preparing it, as aniline converts the free acid direct into metanilidodinitrotoluol,* $C_6H_2CH_3(C_6H_5NH)(NO_2)_2$, melting point 142°, and the saponification of anilidodinitrophenylmalonic ester with sulphuric acid yielded only uninviting viscous products.

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* Hepp, Ann. Chem., ccxv. 371.

Radziszewski,* Gabriel and R. Meyer,† and Heckmann,‡ have prepared a dinitrophenylacetic acid which differs from that just described only in containing no bromine. This substance also loses carbonic dioxide easily, passing into dinitrotoluol, but none of the chemists who have worked with it describe a decomposition by solvents similar to that observed by us; in fact, they crystallized it for analysis from boiling water, but, as in all their methods of preparation acids were used, it is possible that a sufficient amount of sulphuric acid was present during the crystallization to prevent the decomposition. It appears that none of them tried to crystallize it from alcohol. The statement is made, however, that the sodium or potassium salt of the acid decomposes slowly on standing, instantly on boiling giving carbonate and dinitrotoluol; from this it would seem probable that our bromine acid was more stable than that containing no bromine, as our ammonium salt (the sodium or potassium salt could not be obtained) stood unaltered for many days, and even could be warmed on the water bath for some minutes with only slight decomposition. The curious change of color with sodic hydrate observed by us did not occur with the dinitro body, confirming our conclusion that this action was due to the removal of bromine by the sodic hydrate.

Argentic Metabromdinitrophenylacetate, $C_6H_2Br(NO_2)_2CH_2COOAg . H_2O$.

This substance was prepared by adding a solution of argentic nitrate to a solution of the acid in ammonic hydrate, which had been freed from the excess of ammonia as completely as possible, best by using an excess of the acid in preparing the salt. The heavy flocculent precipitate, which, if the solutions were strong, entirely filled the liquid, and even piled up above its surface, became crystalline on standing, and was purified by washing with cold water. Some of the salt is also formed when argentic nitrate is added to an aqueous solution of the free metabromdinitrophenylacetic acid. The analysis of the salt gave the following results.

0.3530 gr. of the air-dried salt lost, when heated to 100°, 0.0149 gr.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2Ag . H_2O$.	Found.
Water	4.19	4.22

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* Ber. d. ch. G., ii. 210.

† Ibid., xiv. 823.

‡ Ann. Chem., ccxx. 134.

I. 0.1674 gr. of the salt dried at 100° gave, after being heated with fuming nitric acid in a sealed tube * and precipitated with potassic bromide, 0.0761 gr. of argentic bromide.

II. 0.1556 gr. of the salt treated in the same way gave 0.0707 gr. of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2Ag$.	Found.	
		I.	II.
Silver	26.21	26.11	26.10

Properties. — The argentic bromdinitrophenylacetate forms white flat prisms terminated by a single plane at an oblique angle; the terminated end is somewhat broader than the other, so that the crystals look like a flattened base-ball bat. They have also a tendency to twin longitudinally. When put in the flame of a Bunsen lamp, they burn with a sparkling flame, but when heated carefully on a piece of porcelain, decompose quietly leaving a residue of silver. The substance is very slightly soluble in cold water, so that it can be washed without too great loss; more soluble in hot water, from which it crystallizes apparently without decomposition; insoluble in cold alcohol, but slowly decomposed, if heated with it.

Constitution of Bromdinitrophenylmalonic Ester.

The formation of metabromdinitrotoluol from bromdinitrophenylmalonic ester by a series of reactions giving essentially a quantitative yield and taking place at temperatures not above 150°, throws a great deal of light on the nature of this substance. In the first place, its conversion into a toluol derivative is a welcome confirmation of the formula which we have given it, and which did not rest on the most secure experimental foundations. In our first paper it was stated that the analysis left the choice open between the following formulas,

$$\text{I. } C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2,$$
$$\text{II. } C_6HBr(NO_2)_2C(COOC_2H_5)_2,$$

and we decided in favor of the first on account of the analyses of the sodium salt, an amorphous substance for the purity of which we had no guaranty, and also on account of the ease with which this salt was formed and decomposed, the product of the decomposition being the original ester. Against this formula stood only our inability at the

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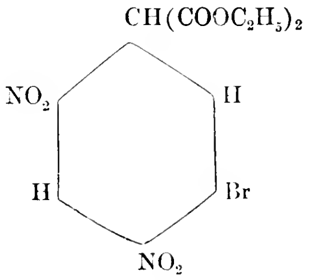
* We had hoped in this way to determine both the silver and bromine in one operation, but found that the filtrate gave a precipitate with potassic bromide. It would seem, therefore, that the presence of an excess of argentic nitrate is necessary to retain all the bromine.

time to explain the reactions by which it was formed, an objection which is removed by this paper. The easy conversion of a substance having Formula I. into a toluol compound is to be expected, whereas with one having Formula II. it would be necessary to add two atoms of hydrogen, an action which could hardly take place quantitatively by boiling with dilute sulphuric acid, or distillation with steam, the two processes employed in converting the bromdinitrophenylmalonic ester into the bromdinitrotoluol. This formation of the substituted toluol therefore establishes Formula I. beyond question.

In the second place, the way is opened to the determination of the position of the substituting radicals upon the benzol ring in all these compounds, as their position must be the same as in the bromdinitrotoluol. Messrs. W. B. Bentley and W. H. Warren have accordingly, at our request, determined the constitution of the bromdinitrotoluol by replacing its bromine successively by the amido group and by hydrogen, and have found in this way that its constitution is

$$CH_3 . Br . NO_2 . NO_2 . 1 . 3 . 4 . 6.$$

For the details of their work we would refer to their paper, which follows immediately after this. It follows from this that in the tribromdinitrobenzol $Br . H . Br . NO_2 . Br . NO_2 . 1 . 2 . 3 . 4 . 5 . 6$, the bromine numbered 1, which stands in the ortho position to one nitro group and the hydrogen, in the para position to the other nitro group, has been replaced by the malonic ester radical $CH(COOC_2H_5)_2$; that the bromine replaced by hydrogen is the one between the two nitro groups; and that the third bromine, which is in exactly the same relation to the nitro groups as the one replaced by the malonic ester radical, is left entirely unaltered. This last fact seems very strange to us. The constitution of our bromdinitrophenylmalonic ester is therefore represented by the following graphical formula:—



XX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON SOME NITRO DERIVATIVES OF METABROMTOLUOL.

By W. B. Bentley and W. H. Warren.

Presented May 28, 1889.

Determination of the Constitution of Metabromdinitrotoluol, $C_6H_2CH_3Br(NO_2)_2$.

Our attention was first called to this subject by Prof. C. Loring Jackson, who, having with W. S. Robinson* obtained the metabromdinitrotoluol by the decomposition of their bromdinitrophenylmalonic ester, asked us to determine its constitution.

This metabromdinitrotoluol, melting point 103°–104°, was discovered by Grete,† who made it by the action of fuming nitric acid on metabromtoluol, or metabrommononitrotoluol, and assigned to it the constitution CH_3, NO_2, Br, NO_2, 1, 2, 3, 4, although he was very doubtful about the position of the second nitro group, giving it the para position without any experimental reason for doing so. His proof that one of the nitro groups was in the ortho position consisted in establishing the identity of the bromtoluidine made by the reduction of his bromnitrotoluol with that obtained by the action of bromine on orthoacettoluid; ‡ but this obviously leaves it doubtful whether this nitro group stands in the position 2 or 6 to the methyl of the toluol, and in fact later work has shown that Grete was wrong in ascribing to it the position 2, as his mononitro compound really has the constitution CH_3, Br, NO_2, 1, 3, 6. The proof of this was given by Nevile and Winther,§ who, by replacing the amido group in the metabromorthotoluidine (melting point 55°–56°) already mentioned by bromine,

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* See preceding paper.

† Ann. Chem., clxxvii. 258.

‡ Wroblewsky, Ann. Chem., clxviii. 161.

§ Ber. d. ch. G., xiii. 962.

obtained a liquid dibromtoluol, which on oxidation with nitric acid yielded the dibrombenzoic acid melting at 151°–153° previously made by Von Richter[*] from paradibrombenzol.

The only point therefore not settled in regard to the constitution of Grete's metabromdinitrotoluol was the position of the second nitro group, which might be either para or ortho to the methyl. To determine this the metabromdinitrotoluol was heated with alcoholic ammonia[†] in sealed tubes to 100° for 12 hours, when it was found to be converted into a yellow substance, which had partly separated in the solid state, and partly remained in solution in the alcohol, from which it was obtained by evaporation. The product was purified by washing with water to remove the ammonic bromide, and crystallization from hot glacial acetic acid, until it showed a constant melting point (193°–194°), when it was dried at 135°, and the following analysis showed that a dinitrometatoluidine had been formed.

0.2658 gr. of the substance gave 51.2 c.c. of nitrogen at a temperature of 24° and a pressure of 767.5 mm.

	Calculated for $C_6H_2CH_3NH_2(NO_2)_2$.	Found.
Nitrogen	21.31	21.71

The melting point showed that this substance is identical with the dinitrotoluidine made by Hepp[‡] by the action of alcoholic ammonia on his γ trinitrotoluol, but the constitution of this trinitrotoluol had not been determined. Staedel[§] has also announced recently that one of his students, Herr Adalbert Kolb, has prepared a dinitrotoluidine from dinitrokresolether and determined its constitution as CH_3, NH_2, NO_2, NO_2, 1, 3, 4, 6; but, as he neglected to give the melting point, we were unable to tell whether it was identical with ours or not, and have been forced to work out the constitution of our dinitrotoluidine by the replacement of the amido group by hydrogen. In doing this some difficulty was encountered because of the very slight solubility of the dinitrotoluidine in alcohol, but we found on experiment that the Griess reaction would take place satisfactorily in a mixture of acetone and alcohol, and accordingly proceeded as follows. 2 grs. of the dinitro-

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[*] Ber. d. ch. G., vii. 1146.

[†] When metabromdinitrotoluol was allowed to stand with alcoholic ammonia in the cold, a dark blue solution was formed at first, but the color gradually changed to reddish brown.

[‡] Ann. Chem., ccxv. 371.

[§] Ber. d. ch. G., xxii. 215.

toluidine were dissolved in about 12 c.c. of acetone, 8 c.c. of common alcohol added, and the mixture acidified with strong sulphuric acid, after which 1.5 grs. of sodic nitrite, about twice the calculated amount, was added in small portions at a time, and the liquid warmed gently until the evolution of nitrogen ceased, when the larger part of the acetone and alcohol was distilled off at first on the water bath, finally on the sand bath, and the residue distilled with steam; the dinitrotoluol passed over into the receiver in small white crystals, which were removed by filtration, and crystallized from hot alcohol until they showed the constant melting point 71°. It was not worth while to dilute the distillate of acetone and alcohol, as no precipitate was obtained in that way. For greater certainty the product was analyzed, with the following results: —

0.2456 gr. of the substance gave 33.1 c.c. of nitrogen at a temperature of 22° and a pressure of 764.2 mm.

	Calculated for $C_6H_3CH_3(NO_2)_2$.	Found.
Nitrogen	21.31	21.71

There is no question therefore that the substance is the orthoparadinitrotoluol, CH_3, NO_2, NO_2, 1, 2, 4, and the bromdinitrotoluol accordingly has the following constitution: CH_3, Br, NO_2, NO_2, 1, 3, 4, 6. It follows also that our dinitrotoluidine is identical with that described by Kolb, and, if Staedel had given its melting point, it would not have been necessary for us to determine its constitution. As has been already stated, this dinitrotoluidine melts at the same point as that made by Hepp from alcoholic ammonia and his γ trinitrotoluol. To establish the relation between these substances more firmly, we made the dinitrophenyltoluidine by treating our dinitrobromtoluol with aniline, and found that the product showed the same melting point, 142°, as that of the compound made by Hepp from γ trinitrotoluol and aniline. The γ trinitrotoluol of Hepp therefore has the following constitution: CH_3, NO_2, NO_2, NO_2, 1, 3, 4, 6; which is in harmony with Laubenheimer's rule,* that a nitro group is removed by the action of alcoholic ammonia only when it is in the ortho position to another nitro group.

Metabromtrinitrotoluol, $C_6HCH_3Br(NO_2)_3$.

In preparing the metabromdinitrotoluol, we found, if a mixture of fuming nitric acid and sulphuric acid was used, that a new substance

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* Ber. d. ch. G., ix. 766, 1828.

melting above 104° was obtained, which turned out to be the as yet undescribed metabromtrinitrotoluol. This compound is most easily prepared from the metabromdinitrotoluol, when it is convenient to proceed as follows. 5 to 10 grs. of metabromdinitrotoluol were placed in a flask, and 10 to 20 c.c. of a mixture of two volumes of fuming nitric acid and one of strong sulphuric acid added. The whole was then boiled until the evolution of red fumes had nearly ceased, when, after it was cool, it was poured in a fine stream into a beaker of cold water, stirring the liquid vigorously during the addition of the acid solution, as in this way the product is precipitated in a granular form much more easy to manage than the large compact lumps obtained if the stirring is neglected. The product was then washed with cold water till free from acid, and purified by crystallization from alcohol, until it showed the constant melting point 143°. The residue from the mother liquors, consisting of a mixture of metabromtrinitrotoluol and the corresponding dinitro compound, can be advantageously used for preparing a fresh quantity of the trinitro body. The pure substance was dried at 120°, and analyzed with the following results: —

I. 0.3372 gr. of the substance gave on combustion 0.3356 gr. of carbonic dioxide and 0.0453 gr. of water.

II. 0.2651 gr. of the substance gave 32.9 c.c. of nitrogen at a temperature of 21° and a pressure of 761.5 mm.

III. 0.1830 gr. of the substance gave, by the method of Carius, 0.1120 gr. of argentic bromide.

	Calculated for $C_6HCH_3Br(NO_2)_3$.	Found. I.	II.	III.
Carbon	27.46	27.14		
Hydrogen	1.31	1.49		
Nitrogen	26.14		26.04	
Bromine	13.73			14.09

The yield was about 60 per cent of the theoretical.

Properties. — The metabromtrinitrotoluol crystallizes from alcohol in small white needles, which melt at 143°. They are insoluble in water, or ligroine; nearly insoluble in cold alcohol, only sparingly soluble in hot; slightly soluble in carbonic disulphide; soluble in ether, methyl alcohol, benzol, chloroform, glacial acetic acid, or acetone. Boiling alcohol we found the best solvent for it, although it is so slightly soluble in it. Aqueous sodic hydrate seemed to have no action upon it, nor was it affected by the strong acids. The bromine is removed easily, which we proved by the action of alcoholic ammonia or aniline on it, as will be described later in this paper.

Constitution of Metabromtrinitrotoluol.

As the metabromtrinitrotoluol is made from the metabromdinitrotoluol, the only point to be determined is the position of the third nitro group; for this purpose we converted it into the corresponding trinitrotoluidine by treatment with alcoholic ammonia in the cold. The mixture was allowed to stand in a corked flask for about twelve hours; at first a dark blue color appeared in the liquid, but on longer standing this turned to a deep reddish brown, and a precipitate was deposited, which with the supernatant liquid at the end of the twelve hours was poured into a dish, and the solvent allowed to evaporate spontaneously. The residue, which was red and yellow, was washed till free from ammonic bromide, and then purified by crystallization from hot glacial acetic acid, until it showed the constant melting point 136°, when it was dried at 120°, and analyzed with the following result: —

0.1144 gr. of the substance gave 24.2 c.c. of nitrogen at a temperature of 23° and a pressure of 754.7 mm.

	Calculated for $C_6HCH_3NH_2(NO_2)_3$.	Found.
Nitrogen	23.14	23.51

The melting point of this trinitrotoluidine shows that it is identical with that prepared by Nölting and Salis* by the action of alcoholic ammonia on trinitrometakresolethylether, to which they assign the constitution CH_3, NO_2, NH_2, NO_2, NO_2, 1, 2, 3, 4, 6, on the ground that the alcoholic ammonia did not remove any of the nitro groups, and therefore, according to Laubenheimer,† no two of them could be in the ortho position to each other, and this is the only possible arrangement in which no two nitro groups are in the ortho position. Our metabromtrinitrotoluol must consequently have the constitution CH_3, NO_2, Br, NO_2, NO_2, 1, 2, 3, 4, 6; and this conclusion is confirmed by the fact recently discovered in this laboratory,‡ that the bromtrinitrophenylmalonic ester is converted by boiling with sulphuric acid of specific gravity 1.44 into this metabromtrinitrotoluol melting at 143°. As the bromtrinitrophenylmalonic ester is made from the symmetrical tribromtrinitrobenzol, Br, NO_2, Br, NO_2, Br, NO_2, 1, 2, 3, 4, 5, 6, it can have only the constitution $CH(COOC_2H_5)_2$, NO_2, Br, NO_2, NO_2,

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* Ber d. ch. G., xv. 1864.

† Ber. d. ch. G., ix. 766, 1828.

‡ C. Loring Jackson and G. D. Moore. These Proceedings, xxiv. 268.

1, 2, 3, 4, 6, which leads to the constitution of our metabromtrinitrotoluol given above.

Anilidotrinitrotoluol, $C_6HCH_3(C_6H_5NH)(NO_2)_3$.

This substance was prepared by treating metabromtrinitrotoluol with aniline in the proportion of two molecules of the base to one of the nitro compound; the action is violent, accompanied with considerable evolution of heat, and the product was easily purified by crystallization from a mixture of alcohol and benzol, until it showed the constant melting point 151°, when it was dried at 120°, and analyzed with the following results: —

I. 0.2804 gr. of the substance gave on combustion 0.5031 gr. of carbonic dioxide and 0.0936 gr. of water.

II. 0.2777 gr. of the substance gave 43.2 c.c. of nitrogen at a temperature of 27°.5 and a pressure of 772 mm.

	Calculated for $C_6HCH_3(C_6H_5NH)(NO_2)_3$.	Found. I.	II.
Carbon	49.06	49.03	
Hydrogen	3.14	3.71	
Nitrogen	17.61		17.41

Properties. — The metanilidotrinitrotoluol crystallizes from a mixture of alcohol and benzol in well developed shining yellow plates, which melt at 151°. The substance is insoluble in water or ligroine; sparingly soluble in ethyl or methyl alcohol; soluble in ether, chloroform, benzol, carbonic disulphide, glacial acetic acid, or acetone. The most convenient solvent for it is a mixture of five parts of alcohol with one of benzol. Aqueous sodic hydrate dissolves it with a red color, and hydrochloric acid throws down from this solution the original substance apparently unaltered. Strong sulphuric or strong nitric acid dissolves it, but strong hydrochloric acid does not.

The constitution of this substance is CH_3, NO_2, C_6H_5NH, NO_2, NO_2, 1, 2, 3, 4, 6, as is shown by its preparation from the metabromtrinitrotoluol, the constitution of which has been determined, as given earlier in this paper.

XXI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF SODIUM MALONIC ESTER UPON TRIBROMTRINITROBENZOL.

By C. Loring Jackson and George Dunning Moore.

Presented May 28, 1889.

In a previous paper [*] one of us with J. F. Wing described the preparation of tribromtrinitrobenzol, and announced that its action with sodium malonic ester would be studied. This work promised to be of especial interest, because we hoped that each of the bromine atoms would be replaced by the radical $CH(COOC_2H_5)_2$, and that by the reduction of the substance thus formed a compound might be obtained consisting of three pyrrol molecules united to form a central benzol ring, a sort of triple indol. Our first experiments, however, showed that the reaction did not run in the way we had expected, but instead of the removal of all three of the bromine atoms only two were replaced, one by the radical $CH(COOC_2H_5)_2$, the other by hydrogen giving a product with the following formula,

$$C_6HBr(NO_2)_3CH(COOC_2H_5)_2,$$

that is, bromtrinitrophenylmalonic ester. After we had established the composition of this substance, we decided that it was unwise to undertake a complete study of this trinitro compound, which can be obtained only with a very considerable outlay of time and material, when the corresponding dinitro compound can be made much more easily, and resembles it closely in most respects. We have accordingly confined our work principally to those properties of the trinitro compound in which we have observed marked differences from the corresponding ones of the dinitro body, and for a fuller discussion of those properties which the two substances have in common would

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[*] These Proceeding, xxiii. 138.

refer the reader to a paper "On the Action of Sodium Malonic Ester on Tribromdinitrobenzol" by one of us and W. S. Robinson.*

The results described in this paper can be briefly stated as follows. Sodium malonic ester forms in the cold with tribromtrinitrobenzol bromtrinitrophenylmalonic ester,

$$C_6HBr(NO_2)_3CH(COOC_2H_5)_2, \text{ melting point } 104^\circ\text{–}105^\circ,$$

which has acid properties forming salts even with aqueous solutions of the alkaline carbonates. Of these the red soluble sodium salt has been studied, and its analysis led to the formula

$$C_6HBr(NO_2)_3CNa(COOC_2H_5)_2.$$

The yellow insoluble copper salt, on the other hand, gave no constant result on analysis, but on several occasions, in trying to make it from a solution of cupric chloride in alcohol and the sodium salt, a crystalline substance free from copper was obtained melting in the neighborhood of 75°. Unfortunately the end of the term has prevented us from studying this substance, which is the more interesting because no similar compound has been obtained from the corresponding dinitro body.

The reactions by which the bromtrinitrophenylmalonic ester is derived from tribromtrinitrobenzol have been made out as follows: —

$$\begin{aligned}
&C_6Br_3(NO_2)_3 + 3\ CHNa(COOC_2H_5)_2 = \\
&\quad NaBr + C_6Br_2(NO_2)_3CH(COOC_2H_5)_2 + 2\ CHNa(COOC_2H_5)_2 = \\
&\quad C_6Br_2(NO_2)_3CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 \\
&\qquad\qquad + CHNa(COOC_2H_5)_2 + NaBr = \\
&\quad C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2 \\
&\qquad\qquad + CHNa(COOC_2H_5)_2 + NaBr = \\
&\quad C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + 2NaBr + C_2H_2(COOC_2H_5)_4.
\end{aligned}$$

The acetylentetracarbonic ester formed according to the last reaction was obtained from the oily secondary product of the action by distillation under diminished pressure, and identified by its melting point and analysis.

Perhaps the most striking difference between the dinitro and trinitro compounds consisted in the fact that the trinitro ester, or its salts, when heated with an excess of common strong nitric acid, turned bright blood-red, whereas no such action could be obtained from the dinitro compound. The red product, on crystallization from alcohol,

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* These Proceedings, xxiv. 1.

was converted into colorless crystals melting at 125°, and as they melted becoming blood-red and increasing very much in volume. The study of this curious substance is still unfinished: we have only established the fact that it is an ester. If the action of the nitric acid is long continued, another body is formed melting at 156° to a colorless liquid, and dissolving in aqueous sodic hydrate with a red color.

Sulphuric acid of specific gravity 1.44 converts the ester into the metabromtrinitrotoluol melting at 143°–144°, recently discovered in this laboratory by Bentley and Warren.

The trinitrophenylendimalonic ester (melting point 123°),

$$C_6H(NO_2)_3[CH(COOC_2H_5)_2]_2,$$

was also obtained by the further action of sodium malonic ester on bromtrinitrophenylmalonic ester; strangely enough, it has less marked acid properties than the bromine compound, from which it is derived.

Preparation of Bromtrinitrophenylmalonic Ester.

The tribromtrinitrobenzol used for this purpose was prepared according to the method already given by one of us and J. F. Wing;* we have found, however, that if the proportion of fuming sulphuric acid is increased, a better yield is obtained. The proportions finally used were, 20 grs. of tribromdinitrobenzol, 500 c.c. of the nitric acid of 1.52 specific gravity, and 200 c.c. of fuming sulphuric acid, instead of one third the volume of the nitric acid as previously recommended. The yield obtained from the new proportions was in the neighborhood of 40 per cent of the theory, running in one case as high as 45 per cent, whereas the proportions recommended by one of us and Wing gave on the average from 15 to 20 per cent, and only in a single instance ran as high as 40 per cent.

To convert the tribromtrinitrobenzol into bromtrinitrophenylmalonic ester, one molecule of it must be treated with about three molecules of sodium malonic ester. In practice we found it convenient to proceed as follows. 10 grs. of tribromtrinitrobenzol were dissolved in about 200 c.c. of benzol with the aid of heat, mixed, while the solution was still moderately warm, with 10.6 grs. of malonic ester previously converted into the sodium compound by treatment with the sodic ethylate from 1.7 grs. of sodium (a slight excess over the calculated amount) and about 15 c.c. of absolute alcohol, and the mixture

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* These Proceedings, xxiii. 139.

allowed to stand 40 to 60 hours in a corked flask at ordinary temperatures. As soon as the sodium malonic ester was added, the liquid became dark blood-red, and on standing this color gradually increased in intensity, while at the same time a precipitate of sodic bromide was thrown down. The product of the reaction was mixed with about three quarters of a litre of water, and acidified with dilute sulphuric acid,* which decomposed the red salt, setting free the ester. Ether was then added, and, after shaking thoroughly, the ethereal and benzol solution separated from the aqueous liquid, which was extracted once more with ether. On distilling off the ether and benzol from the extract, a dark oily residue was left, which was mixed with a little alcohol, when, upon stirring, it solidified to a mass of prismatic crystals. These were sucked out on the pump, washed with a little cold alcohol to remove the adhering oil, and purified by crystallization from hot alcohol, till they showed the constant melting point 104°–105°. The oil which was sucked out from the crystals, or removed from them by alcohol, upon standing, deposited an additional amount of the substance, which was purified in the same way as the main portion. The substance, after being dried *in vacuo*, was analyzed with the following results: —

I. 0.2235 gr. of the substance gave on combustion 0.2860 gr. of carbonic dioxide, and 0.0629 gr. of water.
II. 0.1930 gr. of the substance gave 16.2 c.c. of nitrogen at a temperature of 21°, and under a pressure of 775.9 mm.
III. 0.2548 gr. gave 20.1 c.c. of nitrogen at 18°.5, and 784 mm. pressure.
IV. 0.2080 gr. gave by the method of Carius 0.0870 gr. of argentic bromide.
V. 0.2512 gr. gave 0.1034 gr. of argentic bromide.

	Calculated for $C_6HBr(NO_2)_3CH(COOC_2H_5)_2$.	Found.				
		I.	II.	III.	IV.	V.
Carbon	34.67	34.89				
Hydrogen	2.67	3.13				
Nitrogen	9.33		9.75	9.38		
Bromine	17.78				17.80	17.52

The yield was good, when compared to that obtained in similar preparations from other substances; the best result was as follows:

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* Dilute nitric acid, which was used in some of the earlier preparations, seemed to diminish the yield.

10 grs. of tribromtrinitrobenzol, treated as described above with 10.6 grs. of malonic ester, gave 6.4 grs. of bromtrinitrophenylmalonic ester. The amount required by theory, if all the tribromtrinitrobenzol had been converted into bromtrinitrophenylmalonic ester, is 10 grs.; therefore the yield is 64 per cent of the theoretical. The average yield was between 50 and 60 per cent of the theoretical.

Properties. — The bromtrinitrophenylmalonic ester crystallizes in white slender needles arranged in radiating groups, which, when examined with the microscope, are seen to be flat needles, or long plates terminated by one plane, or, as commonly, by two at an obtuse angle to each other. The crystals seem to belong to the monoclinic system. The melting point is 104° to 105°, and if heated to 160° the substance becomes dark red, and gives off gas. It is essentially insoluble in cold water, very slightly soluble in hot; insoluble in ligroine; slightly soluble in ether; not very soluble in cold, freely in hot ethyl or methyl alcohol; freely in benzol, carbonic disulphide, or glacial acetic acid; very freely in chloroform or acetone. Hot alcohol is the best solvent for it. Strong hydrochloric acid has no action upon it, even when the substances are warmed together in open vessels; it is probable, however, that in sealed tubes the same decomposition would take place as that observed with the corresponding dinitro body. Strong sulphuric acid dissolves a little in the cold, more when hot, forming a colorless solution. Strong nitric acid has little or no action in the cold, but, if warmed with it, converts it into an intensely red viscous substance swimming in the red acid liquid, which by further action of strong nitric acid becomes solid and crystalline. A fuller discussion of the action of strong nitric acid and that of dilute sulphuric acid will be found later in this paper.

As was to be expected from the position of one of its hydrogen atoms on a carbon surrounded by two carboxylester radicals and a trinitrophenyl group, the substance possesses marked acid properties. Sodic hydrate in excess gives only a pale red color with the solid ester, owing to the very slight solubility of the sodium salt in sodic hydrate, but upon adding water the coloration increases, and the addition of a few drops of alcohol produces a very dark red solution. Potassic carbonate in aqueous solution gives a slight red color, on the addition of a little alcohol a dark red solution; acid sodic carbonate acts in much the same way, but the color produced by the aqueous solution is paler than that given with potassic carbonate. Ammonic hydrate gives a red color at once, but this cannot be obtained free from ammonia by evaporation on the water bath, or by using an excess of the ester. The behavior of such a solution made by using an excess of the ester with ammonic hydrate was studied nevertheless, and the following are the more characteristic precipitates which were obtained : —

Magnesium salt, pale rust-colored.

Calcium salt, pale red flocks.

Strontium salt, like that obtained from calcium, but not so heavy a precipitate.

Barium salt, an even less heavy precipitate than that obtained with strontium, also less flocculent.

Manganese salt, yellowish brown.

Zinc salt, pale red.

Cobalt or Nickel salts, yellowish.

Ferric salt, rust-colored.

Cupric salt, a rusty red to orange.

Mercuric chloride, yellowish brown.

Mercuric nitrate, rust-colored.

Mercurous salt, rusty precipitate mixed with the black product from the excess of ammonic hydrate.

Cadmium salt, yellowish red.

Lead salt, brilliant rust-color.

Silver salt, vivid brown (" Bismarck brown").

The most characteristic point in its behavior with reagents is that the magnesium and calcium salts are less soluble than the strontium and barium salts, the order of solubility being magnesium and calcium least soluble, strontium more soluble, barium the most soluble. A similar observation has been made by Bischoff* in regard to the salts of orthonitrobenzoylmalonic ester, and the bromdinitrophenylacetacetic ester also exhibits the same peculiarity, as we mention in detail in the next paper of this series.

Salts of Bromtrinitrophenylmalonic Ester.

We had intended at first to make a rather thorough study of the salts of the bromtrinitrophenylmalonic ester, but after a few experiments became convinced that this would be a waste of time, as, owing to the ease with which the atom of bromine can be removed, no very satisfactory analytical results could be obtained ; and we were the more ready to give up this part of the work, because our investigation of the secondary oily product of the reaction, by which the bromtrini-

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* Ann. Chem , ccli. 362.

trophenylmalonic ester is formed, had settled beyond a doubt the composition of the ester, which before this and the similar investigation made by one of us and W. S. Robinson had rested principally on the analyses of its salts (see these Proceedings, xxiv. 4). We have confined ourselves therefore to a single analysis of the sodium salt, and a preliminary study of the copper salt, the results of which are given below.

Sodium Salt, $C_6HBr(NO_2)_3CNa(COOC_2H_5)_2$. — This substance was made in two ways. First, by digesting solid pure sodic carbonate with a solution of bromtrinitrophenylmalonic ester in absolute alcohol. The red solution was filtered from the excess of sodic carbonate, evaporated to dryness on the water bath, and dried at 100°, when it gave the following result on analysis: —

0.2373 gr. of the salt gave after being heated with sulphuric acid 0.0418 gr. of sodic sulphate.

	Calculated for $C_6HBr(NO_2)_3CNa(CO_2C_2H_5)_2$.	Found.
Sodium	4.87	5.71

The bad result is probably due to a slight excess of sodic carbonate, which dissolved in the alcohol. The salt looked black and somewhat decomposed.

The second and better method was that used for making the salt of the corresponding dinitro compound, that is, by the action of an alcoholic solution of sodic hydrate or ethylate on an alcoholic solution of the ester, taking care that the ester is in excess. For the necessary precautions see these Proceedings, xxiv. 7. No analysis was made of this preparation, as from our experience with the acetacetic compound we were sure that no accurate analytical results would be obtained.

Properties. — The sodium salt forms an amorphous blackish red mass, soluble in ethyl or methyl alcohol, water, or acetone; tolerably soluble in ether; slightly in chloroform; insoluble in benzol or ligroine. All the solutions have a deep blood-red color. When the salt is treated with an excess of strong nitric acid (of specific gravity 1.36), it is at first decolorized, but almost immediately turns vivid red owing to the formation of the substance produced by warming the free ester with nitric acid. This behavior is characteristic, as it appears with none of the similar substances which we have studied.

Copper Salt. — We took up the study of this salt in the hope of throwing light on the composition of the ester, but after analyzing several samples were convinced that the precipitate had a varying composition, and therefore describe our work only because of a curious observation made in the course of it. The salt was made by adding a solution of cupric sulphate to an alcoholic solution of the sodium salt, which need not be free from sodic hydrate; the copper salt was extracted with ether, and obtained on evaporating the ethereal solution as an orange mass, which when heated exploded with a blue flame. It was insoluble in water, nearly insoluble in cold alcohol, soluble in hot, and the yellow solution deposited the salt in rhombic crystals; very soluble in benzol or chloroform; insoluble in ligroine.

We next substituted an alcoholic solution of cupric chloride for the cupric sulphate, in hopes of getting a better result, when to our surprise a product was obtained crystallizing from alcohol in long white prisms, and melting in the crude state at 75°. This product was obtained more than once, but as frequent crystallization was necessary to purify it, we did not at first have enough to bring it into a state fit for analysis; and, on returning to the subject after some months, we obtained under the same conditions nothing but the orange explosive copper salt. Unfortunately, we had postponed work on this subject till so near the end of the term that we were unable to give it the careful study it seems to deserve, but its investigation will be continued in this laboratory next year.

Study of the Reactions by which Bromtrinitrophenylmalonic Ester is formed.

The reactions by which the bromtrinitrophenylmalonic ester is formed from the tribromtrinitrobenzol must consist in the replacement of one of the atoms of bromine by the malonic ester radical $CH(COOC_2H_5)_2$, and of another by hydrogen. The first of these processes needs no explanation, but the mechanism of the second, the replacement of the bromine by hydrogen, could be made out only by experiment. Obviously, the first point to be settled was the form in which the bromine was eliminated; that is, whether as sodic bromide alone, or partly as sodic bromide and partly as an organic compound. For this purpose the following quantitative determinations were made: —

I. 10 grs. of tribromtrinitrobenzol, treated with the sodium malonic ester from 15 grs. of malonic ester, gave after standing two days and a half 8.83 grs. of argentic bromide, corresponding to 3.76 grs. of bromine.

II. The same weights under the same conditions gave 9.08 grs. of argentic bromide, corresponding to 3.86 grs. of bromine.

If two atoms of bromine had been removed, the amount of bromine should have been 3.55 grs. Therefore the percentages of the theoretical bromine removed as sodic bromide were, —

I.	II.
105.9	108.8

It appears, therefore, that a little more than the amount calculated for two atoms of bromine has been removed as sodic bromide, and this is easily explained by the observation described later in this paper, that sodium malonic ester can act on the bromtrinitrophenylmalonic ester even in the cold to form the trinitrophenylendimalonic ester, a small quantity of which was undoubtedly formed in these two experiments by the large excess of sodium malonic ester present. At any rate, there can be no question that all the bromine was removed in the form of sodic bromide.

The next step consisted in determining the nature of the organic secondary product. For this purpose, the oil, separated from the bromtrinitrophenylmalonic ester by sucking out the crude product on the pump and treatment with alcohol, was allowed to stand till it ceased to deposit crystals of the ester, and then submitted to distillation under diminished pressure. The pressure varied from 22 to 25 mm., and a distillate began to appear when the thermometer inside the flask stood at 98°, and was collected until the temperature had reached 160°, when about one third of the total volume had passed over. In this way a clear yellow liquid was obtained, which distilled unaltered at ordinary pressure between 197° and 206°. We therefore inferred it was mostly malonic ester, boiling point 197°.7, a view of its nature which was confirmed by its smell. As the whole of the distillate passed over below 206°, there could be no large amount of tartronic ester (boiling point 220°) present, which we had expected after the work of one of us and W. S. Robinson on the corresponding dinitro compound, and the secondary product of the reaction must be looked for in the residue which had been left behind in the flask after the distillation under diminished pressure. This was a thick blackish brown oil, which on standing for about a week deposited crystals all over its surface; these were removed and allowed to stand on filter paper until a large part of the oil had been sucked out, when they were purified by washing with a small quantity of cold alcohol, and then crystallizing from boiling alcohol, until they showed the constant melting point 76°. The substance formed long glittering colorless needles or prisms, and contained no bromine; we decided accordingly that it was the acetylentetracarbonic ester (melting point 76°), and this conclusion was confirmed by the following analysis: —

0.2270 gr. of the substance gave on combustion 0.4384 gr. of carbonic dioxide, and 0.1506 gr. of water.

	Calculated for $C_2H_2(CO_2C_2H_5)_4$.	Found.
Carbon	52.83	52.67
Hydrogen	6.92	7.36

The amount of acetylentetracarbonic ester was so considerable, that there can be no doubt it was a principal product of the reactions by which the bromtrinitrophenylmalonic ester is formed, and these must therefore be written thus: —

$$\begin{aligned}
&C_6Br_3(NO_2)_3 + 3\,CHNa(COOC_2H_5)_2 = \\
&\quad C_6Br_2(NO_2)_3CH(COOC_2H_5)_2 + NaBr + 2\,CHNa(COOC_2H_5)_2 = \\
&\quad C_6Br_2(NO_2)_3CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 \\
&\qquad\qquad + CHNa(COOC_2H_5)_2 + NaBr = \\
&\quad C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2 \\
&\qquad\qquad + CHNa(COOC_2H_5)_2 + NaBr = \\
&\quad C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + C_2H_2(COOC_2H_5)_4 + 2\,NaBr.
\end{aligned}$$

The only objection which could be urged against this series of reactions is that the yield of bromtrinitrophenylmalonic ester is only 64 per cent of the theoretical, from which it might be argued that nearly half of the tribromtrinitrobenzol may have undergone some different transformation. This objection is disposed of, however, by the fact that W. D. Bancroft and one of us * have succeeded in getting a yield of 80 per cent of the dibromdinitrophenylmalonic ester from tetrabromdinitrobenzol by a series of reactions exactly analogous to those just given. The missing 36 per cent of the bromtrinitrophenylmalonic ester must therefore have remained dissolved in the oil, and have been destroyed by the distillation even under the diminished pressure used by us.

Action of Nitric Acid.

The intense red color produced by the action of nitric acid of specific gravity 1.36 on the sodium, or copper salt of the bromtrinitrophenylmalonic ester in the cold, or on the ester itself at 100°, seemed to

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* These Proceedings, xxiv. 295.

us of great interest, and we laid out what we thought would be time enough for its investigation; unfortunately, however, this was not the case, since, after the work had been going on for some time, we found that at least two substances were formed by this reaction, and consequently the end of the term surprised us before we had reached any definite results. We have decided, however, to publish here what results we have obtained, as we are unable to go on with this work together, but wish it to be understood that all these statements are to be taken as preliminary.

If about 1 gr. of bromtrinitrophenylmalonic ester was mixed with 2–3 c.c. of strong nitric acid (specific gravity 1.36), no change took place in the cold; but if the mixture was warmed gently on the water bath for less than five minutes, an intense vivid red color appeared in both the acid liquid and the organic substance, which melted and became converted into a viscous mass. If now the acid was poured off, a fresh quantity added, and the gentle warming repeated, the viscous drop became converted into a red crystalline mass, and by continuing this treatment with successive portions of nitric acid the red color could be removed partially, so that the product had a spotted red and white appearance. This frequent treatment with nitric acid was, however, unnecessary, as the red crystalline product after the second warming with nitric acid gave, when crystallized from alcohol, well formed white prisms, and a reddish mother liquor. The red nitric acid poured off from the principal part of the product gave with water a red precipitate, but a better mode of treatment seemed to be to evaporate this red acid to dryness on the water bath. The residue, or precipitate obtained with water, was partly viscous, partly crystalline, and by treating it again with warm strong nitric acid a new quantity of the red crystalline substance was obtained, but the amount recovered in this way was so small that it hardly paid for the trouble. The white crystals, after purification by crystallization from alcohol, showed the constant melting point 125°, and their behavior in melting was very characteristic, as they turned from white to bright red, and swelled to many times their original volume. They were not affected by sodic hydrate in aqueous solution. Supposing that the substance was homogeneous because of its constant melting point, we analyzed it, but on studying its properties more carefully we began to doubt its purity for the following reasons: — First. Although the microscopic examination showed that the substance consisted principally of white, short, rather thick monoclinic prisms, usually with both terminations well developed and made up of two planes, there were mixed with these longer prisms, and we could not decide whether these latter were a different substance or merely a different habit of the same. Second. When the crystals were treated with sodic hydrate and alcohol a little of a soluble red salt was formed around each crystal, but we could not convert the whole of the crystals into this salt. This seemed to point to the presence of an impurity, from which the salt was formed. Third. We found almost at the very end of the term, that by warming the bromtrinitrophenylmalonic ester with strong nitric acid for three hours, instead of a few minutes, a red substance was obtained, which crystallized from alcohol, became white, and melted at 156° instead of 125°, and, what was as distinctive as the different melting point, fused to a colorless liquid, and gave a red solution with aqueous sodic hydrate. This substance was discovered so late that we had no time to investigate it, but some of it seemed to be formed even on shorter heating (15 minutes) with the nitric acid. For these reasons, we have decided that it is wiser to postpone the publication of our analyses of the substance melting at 125° until the work has been repeated with samples in regard to the purity of which there can be no doubt. We add such results of our work as are established with certainty. The analyses made by us showed that there were three atoms of nitrogen to one of bromine in the substance, and therefore the action of the nitric acid did not consist in the introduction of another nitro, or nitroso group. The fact that it is insoluble in aqueous sodic hydrate shows that it is not a free acid, and its action with hydrochloric acid would indicate that it was an ester, as, when heated to 135°–140° with this acid in a sealed tube for 36 hours, a gas was given off burning with a green-bordered flame, and giving a white precipitate with lime-water, which therefore must have contained ethyl chloride and carbonic dioxide. The solid product of this action was partly viscous and partly crystalline; the latter melted in the crude state above 180°. It has been stated already that the substance melting at 125° turns red and increases in volume when it melts; this change, which takes place to a limited extent even when it is kept at 100° for some time, is accompanied by loss of weight, as a sample kept at its melting point for some days lost at least 17 per cent, and gave a residue consisting of two or more substances, one white and crystalline, the other red and viscous.

Action of Sulphuric Acid. — Constitution of the Bromtrinitrophenylmalonic Ester.

The action of dilute sulphuric acid upon the bromtrinitrophenylmalonic ester was studied in the hope of obtaining the as yet unknown bromtrinitrophenylacetic acid, as it had been found by one of us and W. S. Robinson † that the corresponding dinitro compound was decomposed in this way. For this purpose, about 2 grs. of the ester were boiled in a flask under a return condenser with sulphuric acid of specific gravity 1.44 and boiling point 132° until the ester had dissolved; the liquid was then allowed to cool, when it deposited crystals, which, after recrystallization from alcohol, were recognized by their melting point 143°–144°, their appearance, and the absence of acid properties, as the metabromtrinitrotoluol discovered in this laboratory by Bentley and Warren.

It is evident therefore that the bromtrinitrophenylacetic acid is less stable than the corresponding dinitro compound, as indeed was to be expected, and was broken up as soon as formed into the substituted toluol and carbonic dioxide according to the following reaction:

$$C_6HBr(NO_2)_3CH_2COOH = C_6HBr(NO_2)_3CH_3 + CO_2.$$

The formation of this substance would settle the constitution of the bromtrinitrophenylmalonic ester, if that were necessary, but the preparation of the ester from symmetrical tribromtrinitrobenzol leaves no doubt as to its constitution, which must be as follows, $CH(COOC_2H_5)_2$, NO_2, Br, NO_2, H, NO_2, 1, 2, 3, 4, 5, 6, and Bentley and Warren have established the corresponding constitution for their substituted toluol.

Trinitrophenylendimalonic Ester, $C_6H(NO_2)_3[CH(COOC_2H_5)_2]_2$.

This substance was formed by the further action of sodium malonic ester on bromtrinitrophenylmalonic ester. For this purpose, 1 gr. of bromtrinitrophenylmalonic ester dissolved in ether was mixed with 1.5 grs. of malonic ester previously converted into sodium malonic ester and dissolved in much absolute alcohol, and the mixture boiled in a flask with a return condenser for an hour. The product, which was very dark brown, almost black, was treated with water, acidified with dilute sulphuric acid avoiding a large excess, the ether removed with a drop funnel, and the aqueous liquid shaken out twice with ether. The extract, after distilling off the ether and allowing it to

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† These Proceedings, xxiv. 240.

get perfectly cool, was treated with a little alcohol, when crystals separated on standing, which were purified by recrystallization from alcohol, until they showed the constant melting point 123°. They gave no test for bromine when heated on a copper wire, and, after drying *in vacuo*, were analyzed with the following results: —

I. 0.3004 gr. of the substance gave on combustion 0.5043 gr. of carbonic dioxide, and 0.1230 gr. of water.

II. 0.2392 gr. of the substance gave 16.8 c.c. of nitrogen at a temperature of 25° and a pressure of 768 mm.

	Calculated for $C_6H(NO_2)_3[CH(COOC_2H_5)_2]_2$.	Found.	
		I.	II.
Carbon	45.37	45.78	
Hydrogen	4.35	4.55	
Nitrogen	7.94		7.92

A small quantity of this substance can also be formed in the cold, and more than once some of it has been obtained in making the bromtrinitrophenylmalonic ester by the process described earlier in this paper (compare pages 258 and 264).

Properties. — The trinitrophenylendimalonic ester crystallizes from alcohol in long colorless prisms, terminated by a single rhombic plane at a tolerably sharp angle to the sides; less frequently, the termination consists of two planes at an obtuse angle to each other, so that the general effect is as if the prisms had rounded ends. They are frequently grouped, or twinned, parallel to their long axes, so that often there are two or more terminations at one end of a group. The substance melts at 123°; and is very nearly, if not quite, insoluble in water, whether cold or boiling; essentially insoluble in ligroine; not very soluble in cold ethyl or methyl alcohol, freely in either of these solvents when hot; very slightly soluble in carbonic disulphide; soluble in ether or glacial acetic acid; and freely soluble in benzol, chloroform, or acetone. Its acid properties are not so strongly developed as we expected. An aqueous solution of sodic hydrate turns the solid pale red, but does not dissolve it to any extent; if, however, sodic hydrate is added to its alcoholic solution, it at once takes on a dark brownish red color, much browner than any of the similar salts which we have studied, — in fact it would be possible to recognize the salt by this color. An aqueous solution of potassic carbonate gives a very faint red color with it, which is increased, but not to a great extent, by adding alcohol to the aqueous solution. The action was incomplete at best; acid sodic carbonate had no action on it in aqueous solution, but on the addition of alcohol a barely perceptible red color appeared. Ammonic hydrate even in dilute aqueous solution dissolved it easily with a brown color; the solution turned blacker when the attempt was made to drive off the excess of ammonia on the water bath, and a white scum formed on the surface, probably the original substance. The behavior of this solution was studied with some of the commoner reagents; but, as it showed such evident signs of decomposition, we did not think it worth while to extend this work to salts of all the basic radicals.

Ferric salt, *cupric salt*, *silver salt*, and *lead salt* all gave brown flocculent precipitates.

Calcium salt gave no precipitate.

Barium salt, a very slight dirty brown precipitate, but none if the solution had not been warmed on the water bath in the vain attempt to drive off the excess of ammonia.

Strong sulphuric acid dissolved the dimalonic ester, giving a colorless solution. Strong hydrochloric acid had no action upon it, whether hot or cold. Strong nitric acid dissolved it partially in the cold, giving a yellowish solution, which when warmed became darker yellow; but if the warming on the water bath was continued for some time, the acid liquid became red, and a red viscous substance was also obtained, which, after washing with water and crystallization from alcohol, was converted into yellow plates melting at 104°–105° in the crude state. It is evident that the action here is similar to that of bromtrinitrophenylmalonic ester with strong nitric acid, but the end of the term has prevented us from continuing the study of this substance at present.

XXII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF SODIUM ACETACETIC ESTER UPON TRIBROMDINITROBENZOL.

By C. Loring Jackson and George Dunning Moore.

Presented May 28, 1889.

After the action of sodium malonic ester on tribromtrinitrobenzol and on tribromdinitrobenzol had been studied, it seemed of interest to determine whether sodium acetacetic ester acted in the same way, and the following paper contains the results of experiments undertaken with this intention upon the tribromdinitrobenzol, which was selected because it can be prepared so much more easily than the corresponding trinitro compound. These results can be summarized briefly as follows. Tribromdinitrobenzol behaves with sodium acetacetic ester in the same way that it does with sodium malonic ester; that is, one atom of its bromine is replaced by the acetacetic radical

$$CH_3COCHCOOC_2H_5,$$

and a second by hydrogen, while the third remains unaltered; so that the product of the action is the bromdinitrophenylacetacetic ester,

$$C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5,$$

or to speak more accurately its sodium salt,

$$C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5,$$

The bromdinitrophenylacetacetic ester melts at 96°, and possesses marked acid properties, forming the sodium salt whose formula has just been given, even with acid sodic carbonate in aqueous solution. The salt has a red color, and is soluble in water; in fact, it resembles the sodium salt of the corresponding malonic compound most closely.

The bromdinitrophenylacetacetic ester is saponified and decomposed by heating with sulphuric acid of specific gravity 1.44, giving the bromdinitrobenzylmethylketone,

$$C_6H_2Br(NO_2)_2CH_2COCH_3,$$

but no trace of the corresponding acetic acid. This ketone melts at 112°–113°, and also possesses acid properties, giving a purplish red salt soluble in alcohol, but decomposed almost completely by water. The acid properties of the ketone are less marked than those of the acetacetic ester, as was to be expected, since the hydrogen, which is replaced by basic radicals, is subject to the influence of an acetyl, a carboxylester, and a dinitro phenyl group in the acetacetic compound, only to those of an acetyl and a dinitro phenyl group in the ketone.

The bromine of the ketone can be replaced easily by the aniline radical C_6H_5NH, forming anilidodinitrobenzylmethylketone,

$$C_6H_2(C_6H_5NH)(NO_2)_2CH_2COCH_3,$$

which melts at 131°, and has not lost all acid properties, although they have been much weakened by replacing the bromine atom by the basic radical C_6H_5NH. It cannot form an ammonium salt, but the sodium salt can be easily obtained in alcoholic solution, and on analysis gave a number corresponding to the formula

$$C_6H_2(C_6H_5NH)(NO_2)_2CHNaCOCH_3.$$

It is completely decomposed by water, but dissolves in alcohol with a brown color.

Both these ketones, therefore, show stronger acid properties than desoxybenzoine $C_6H_5COCH_2C_6H_5$, the metallic compounds of which, according to Victor Meyer,* could not be isolated; we are inclined to ascribe this to the presence of the nitro groups in the phenyl, which would heighten its acid-producing power, but it may also be due in part to the fact that these ketones contain the acetyl group, which, as Claisen and Ehrhardt † have pointed out, has a greater influence in producing acidity than the benzoyl radical contained in desoxybenzoine.

The hydrazone of the anilidodinitrobenzylmethylketone,

$$C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(NNHC_6H_5)CH_3,$$

was also prepared, and melted at 110°.

The full details of the work will be found in the remainder of the paper.

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* Ber. d. ch. G. 1888, p. 1231.

† Ber. d. ch. G. 1889, p. 1019.

Preparation of Tribromdinitrobenzol.

The method used by us for preparing tribromdinitrobenzol differs from that formerly in use only in certain details, but, as careful attention to these details insures a purer product at much less expense of time and labor, we have thought it best to give a full account of our mode of procedure.

To make the tribromaniline, 60 grs. of aniline were dissolved in dilute hydrochloric acid, and, the solution having been made up to a volume of about 3 litres, a rapid stream of air saturated with bromine vapor was sucked through it by means of a Bunsen pump, until the liquid assumed a distinct yellow color. The precipitate of tribromaniline was then removed by straining through cheese-cloth, and washed with a stream of common water, until free from acid, when the greater part of the water was squeezed out with a screw press, and the product thoroughly dried on a steam radiator. In this way a quantitative yield of the tribromaniline was obtained, and it was free from colored by-products.

In order to convert the tribromaniline into tribrombenzol, 50 grs. of it, after being pulverized, were dissolved with the aid of heat in about 300 c.c. of common alcohol, and a concentrated aqueous solution of 21 grs. of sodic nitrite poured in slowly, but not in successive portions. The hot mixture was then acidified with dilute sulphuric acid, and allowed to stand over night, when it was filtered, and the precipitate washed with hot water to remove the sodic sulphate and leave the tribrombenzol. An additional quantity of this was obtained by concentrating the alcoholic filtrate, when it separated as an oil, that solidified on standing, and was then crystallized from alcohol. The yield was nearly quantitative, as 45.50 grs. of tribrombenzol were obtained instead of the 47.77 required by the theory, that is 95 per cent. When made by this method, the tribrombenzol was usually pure enough to be nitrired directly in spite of its brownish color.*

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* The amount of sodic nitrite used in the process described above (two molecules of nitrite to one of the base) is twice that required by the theory, but we have found that this large excess was necessary to bring all the tribromaniline into the reaction. When a smaller amount of nitrite was used, the product was much less pure, as shown by its lower melting point; it was necessary in this case to distil it from a little retort, and crystallize several times from alcohol, to obtain pure tribrombenzol. The crystals obtained on evaporating the alcoholic mother liquors, which made up about two thirds of the entire amount, were distilled with steam, pushing the distillation as rapidly as possible, when tribrombenzol passed over, and tribromaniline was left in the retort; but all this tedious purification can be avoided by using the excess of nitrite recommended above.

To convert the tribrombenzol into the dinitro compound, 25 grs. of it were added to 100–120 grs. of nitric acid* of specific gravity 1.52, (made from potassic nitrate and sulphuric acid in the laboratory.) warmed gently until the solid had dissolved, and allowed to stand about two hours, when the tribromdinitrobenzol crystallized out in large white prisms. The yield was essentially quantitative.

Bromdinitrophenylacetacetic Ester,
$C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5$.

Preparation. — This substance was made by the action of an alcoholic solution of sodium acetacetic ester on a benzol solution of the tribromdinitrobenzol in the proportion of about four molecules of the former to one of the latter. For this purpose 15 grs. of tribromdinitrobenzol were dissolved in about 200 c.c. of benzol, and mixed with 20 grs. of acetacetic ester previously treated with 3 grs. of sodium dissolved in about 20 c.c. of absolute alcohol. At first there was very little change of color, but on standing at ordinary temperatures the liquid turned first yellow and then red (whereas with malonic ester the red color appeared instantaneously). In order to complete the reaction, the mixture was heated on the steam bath for about one hour, at the end of which time it had become nearly black, and a considerable precipitate of sodic bromide had formed. It was then mixed with from one and a half to two litres of water, and the reddish benzol solution, which was precipitated, removed from the dark red aqueous liquid; the latter was then acidified with dilute sulphuric acid; taking care to avoid a large excess; this decomposed the red sodium salt of the new substance, which was set free in the form of a yellowish oil, and extracted by shaking the liquid with ether twice. On distilling off the ether a dark reddish brown oil was left, which, when cold, was treated with very little alcohol, and upon stirring became filled with crystals, the quantity of which increased on standing for twelve or more hours. When the quantity of the crystals did not increase further, the pasty mass was sucked out on the pump, first adding a little alcohol, if necessary, and by washing with a small quantity of cold alcohol all the very soluble red oil was removed from the crystals, which were nearly or quite insoluble in cold alcohol, and were next purified by crystallization from hot alcohol until they showed the constant melting point 96°. An additional quantity of the substance can be obtained from the benzol solution by distilling off the benzol

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* These Proceedings, xxii. 374.

and treating the residue with sodic hydrate and a little alcohol, which convert the new substance into its sodium salt, and this can be removed from the unaltered tribromdinitrobenzol by washing with water; when the wash-waters were acidified, and the precipitate purified in the same way as the main portion, the substance was dried *in vacuo*, and analyzed with the following results: —

I. 0.2683 gr. of the substance gave on combustion 0.3788 gr. of carbonic dioxide, and 0.0748 gr. of water.

II. 0.2512 gr. of the substance gave 16.7 c.c. of nitrogen at a temperature of 22° and a pressure of 759.7 mm.

III. 0.2067 gr. of the substance gave, according to the method of Carius, 0.1041 gr. of argentic bromide.

IV. 0.2141 gr. of the substance gave 0.1059 gr. of argentic bromide.

	Calculated for	Found.			
	$C_6H_2Br(NO_2)_2CH_3COCHCO_2C_2H_5$.	I.	II.	III.	IV.
Carbon	38.41	38.50			
Hydrogen	2.93	3.09			
Nitrogen	7.47		7.33		
Bromine	21.33			21.43	21.05

The yield of bromdinitrophenylacetacetic ester, prepared by the method described above, is satisfactory on the whole, the best result being as follows: —

15 grs. of the tribromdinitrobenzol yielded 6.5 grs. of the ester, and 3.1 grs. of unaltered tribromdinitrobenzol were recovered, leaving 11.9 grs. which had entered into the reaction. 11.9 grs. of tribromdinitrobenzol should yield 11.0 grs. of bromdinitrophenylacetacetic ester. The actual yield, therefore, was 59 per cent of the theoretical. In other preparations the yield varied from 54 to 34 per cent, the lowest which was obtained from this process. The yield was not improved by increasing or by diminishing the proportion of acetacetic ester to the tribromdinitrobenzol. In our first preparations the reaction was allowed to run in the cold, as an experiment, in which the mixture had been heated less than one hour, seemed to give a very unmanageable product; in this case, however, the yield was very much less than that obtained by the process described above, in which the mixture was heated one hour.

In order to throw light on the way in which the reaction runs, we determined the amount of bromide of sodium formed in two preparations as follows: —

I. 12 grs. of tribromdinitrobenzol yielded 4.43 grs. of bromine in the form of sodic bromide.

II. 12 grs. of tribromdinitrobenzol yielded 4.40 grs. of bromine in the form of sodic bromide.

If two atoms of bromine are removed from each molecule by this reaction, 12 grs. of tribromdinitrobenzol would lose 4.74 grs. of bromine.

Percentage of bromine removed as sodic bromide, —

I.	II.
93.5	93.0

From this it appears that all the bromine removed from the tribromdinitrobenzol is finally in the state of sodic bromide, as the slight loss of 7 to 6.5 per cent is not greater than would be expected when it is considered that the aqueous solution containing the sodic bromide was shaken out twice with ether. These determinations show also that in these cases the whole of the tribromdinitrobenzol entered into the reaction, and in fact none of it could be found unaltered in the products of these two preparations; but this was not always the case, as, for instance, in the preparation described on page 275.

The full explanation of the reaction, however, was to be found in the study of its secondary product, the red oil removed from the crystals by washing with cold alcohol. This, upon long standing exposed to the air, threw down a few more crystals of bromdinitrophenylacetacetic ester, which would raise the yield a little above that given, but the amount obtained in this way was very small. The oil, after no more crystals could be obtained from it, was distilled under diminished pressure and yielded some acetacetic ester, leaving in the flask a tarry mass which has shown no signs of giving crystals even after long standing. This part of the work therefore was not carried further, as from the formula of the ester and the removal of all the bromine as sodic bromide there can be no doubt that the reaction with acetacetic ester runs in the same way as that with malonic ester, and in this latter case the reaction has been fully explained.* Reasoning on this analogy, the following reactions may be taken as expressing what takes place in the formation of the bromdinitrophenylacetacetic ester.

$$
\begin{aligned}
&C_6HBr_3(NO_2)_2 + 2\,CH_3COCHNaCOOC_2H_5 = \\
&\quad C_6HBr_2(NO_2)_2CH_3COCHCOOC_2H_5 + NaBr \\
&\qquad\qquad\qquad + CH_3COCHNaCOOC_2H_5 = \\
&\quad C_6HBr_2(NO_2)_2CH_3COCNaCOOC_2H_5 + CH_3COCH_2COOC_2H_5 \\
&\qquad\qquad\qquad + NaBr = \\
&\quad C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5 + CH_3COCHBrCOOC_2H_5 \\
&\qquad\qquad\qquad + NaBr.
\end{aligned}
$$

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* These Proceedings, xxiv. 238, 265.

The bromacetacetic ester being afterward attacked either by a molecule of sodium acetacetic ester or by sodic hydrate.

The only question with regard to these reactions, which might arise would be due to the fact that only a little over 50 per cent (59 per cent) of the ester was obtained, which might lead to the hypothesis that nearly half of the tribromdinitrobenzol went to form another substance; but this objection is removed by the fact that in another analogous case as much as 80 per cent of a corresponding ester has been found. We consider, therefore, that the missing 41 per cent of the ester remained dissolved in the oily secondary product, but should state, on the other hand, that upon treating the oil with sulphuric acid of specific gravity 1.44 in hopes of decomposing the secondary products and converting the bromdinitrophenylacetacetic ester into bromdinitrobenzylmethylketone, we obtained nothing but black tarry substances, from which no substance fit for analysis could be obtained.

Properties. — The bromdinitrophenylacetacetic ester crystallizes well, usually in forms looking like a rhombohedron with a very acute angle, less frequently in prismatic forms, which are twinned on a central line parallel to their longer axis, the termination being in shape either like a simple gable, or one with a notch in its point. The crystals show a great tendency to twin, or group, often in forms like those of frost, and are sometimes from 2 to 3 mm. long. The substance has a yellow color of about the shade of potassic chromate, which is characteristic, as the corresponding malonic compound is nearly white. Heckmann * has observed a similar deep yellow color in the orthoparadinitrophenylacetacetic ester. It melts at 96°; is very slightly soluble in water, rather more so in hot than in cold; essentially insoluble in ligroine; not very soluble in cold alcohol, but freely in hot; if anything less soluble in methyl than in common alcohol both cold and hot, but the solubility is much greater in the hot methyl alcohol than in the same solvent when cold; tolerably soluble in carbonic disulphide, or ether; soluble in glacial acetic acid; and freely in benzol, chloroform, or acetone; from ether, benzol, or chloroform it is deposited as an oil. The best solvent for it is hot alcohol. Strong sulphuric acid does not act upon it in the cold, but when warm dissolves it, forming a slightly yellowish solution. Strong hydrochloric acid has no action with it in open vessels, even if heated. The decomposition of the substance by these two acids under proper conditions is described later in this paper. Strong nitric acid has no action

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* Ann. Chem., ccxx. 133.

on it in the cold, but dissolves it when warm; there is, however, no marked change of color in which respect this substance shows a striking difference from the bromtrinitrophenylmalonic ester, but resembles the bromdinitrophenylmalonic ester.

The bromdinitrophenylacetacetic ester shows marked acid properties, as was to be expected from the position of one of its hydrogen atoms upon a carbon adjacent to an acetyl, a carboxylester, and a phenyl group, the latter rendered still more efficient by the presence of two nitro groups, and also from the acid properties of the corresponding malonic compound. Aqueous sodic, or ammonic hydrate dissolves it forming a red solution of the corresponding salt; an aqueous solution of potassic carbonate acts upon it in the same way giving, however, a somewhat fainter color, but, if alcohol is added to the solution, it turns at once dark red; acid sodic carbonate in aqueous solution gives a very faint red color which is much intensified by addition of alcohol to the solution. The red solution of the ester in ammonic hydrate is decomposed by heating, or even by exposure to the air at ordinary temperatures, and we were not able to obtain a solution, which did not smell of ammonia, even when a large excess of the ester was used, it is evident therefore that its ammonium salt is very unstable. We have, however, tried the action of a solution prepared from an excess of the ester and ammonic hydrate with various reagents, and found the following characteristic reactions.

Magnesium or Calcium salt, heavy flocculent precipitate of the color of chrome yellow.

Strontium salt, a less heavy precipitate of a redder color.

Barium salt, a still smaller precipitate, also reddish.

Zinc salt, a pale yellow precipitate.

Cupric salt, a pale yellow precipitate.

Lead salt, a dark yellow precipitate.

Silver salt, a yellowish white precipitate.

The most striking thing about these salts is that the calcium salt is less soluble than that of strontium, and this less soluble than the barium salt. Bischoff* has observed a similar peculiarity in the salts of orthonitrobenzoylmalonic ester, and we have found it in the salts of bromtrinitrophenylmalonic ester.

With aniline the bromdinitrophenylacetacetic ester gave only a waxy yellow mass, from which there seemed little chance of obtaining a substance in a state fit for analysis. We have, therefore, abandoned

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* Ann. Chem., ccli. 362.

the further study of this reaction, in which undoubtedly the aniline acted on the acetacetic ester radical as well as on the bromine in the benzol ring. That this bromine had been removed we proved by detecting aniline bromide among the products of the reaction.

Sodium Salt, $C_6H_2Br(NO_2)_2CH_3COCNaCOOC_2H_5$.

In the earlier portions of our work on the bromdinitrophenylacetacetic ester and allied bodies the determination of the composition of the salts was of the greatest importance, as this was the only experimental method which we had found for deciding between the formulas,

$$\text{I.}\quad C_6H_2Br(NO_2)_2CH_3COCHCOOC_2H_5,$$
$$\text{II.}\quad C_6HBr(NO_2)_2CH_3COCCOOC_2H_5.$$

This, at present, is no longer the case, as the discovery of acetylentetracarbonic ester or tartronic acid as a secondary product in the formation of the corresponding malonic compounds can be explained only if a formula similar to I. is adopted, and the easy conversion of bromdi- (or tri-) nitrophenylmalonic ester into the corresponding toluol compound also could hardly be brought into harmony with a formula like II. No similar proof has been applied to the acetacetic compound, it is true; but when the close resemblance between this and the malonic compounds is considered, there can be no doubt that they are similarly constituted. The composition of the sodium salt therefore becomes of secondary importance, and this is fortunate, as we have not succeeded in preparing it in a state of purity sufficient to decide between the salts derived from formulas I. and II., although our analyses leave no doubt as to its composition, if the first formula is adopted as correct.

The salt was prepared by adding to a solution of the bromdinitrophenylacetacetic ester in absolute alcohol a solution of sodic hydrate or ethylate also in absolute alcohol, taking care that the ester was in decided excess. The deep red alcoholic solution thus obtained was evaporated rapidly to dryness in a narrow beaker sunk throughout its whole height in a water bath, some ether having been added previously in order that its vapor might protect the solution from the carbonic dioxide of the air until the alcohol began to boil. The excess of ester was washed out of the dry residue with benzol, and the salt dried at 100°, and analyzed with the following results: —

I. 0.2102 gr. of the salt gave after treatment with sulphuric acid 0.0361 gr. of sodic sulphate.

II. 0.2056 gr. of the salt gave 0.0407 gr. of sodic sulphate.
III. 0.2531 gr. of the salt gave 0.0390 gr. of sodic sulphate.

	Calculated for $C_6H_2Br(NO_2)_2CH_3COCNaCO_2C_2H_5$.	Found.		
		I.	II.	III.
Sodium	5.79	5.56	6.41	4.99

It is evident from these results that the method of preparation is unsatisfactory, and we ascribe this to the action of the sodic hydrate (or ethylate) on the bromine, and perhaps also on the acetacetic radical, as, when these two sources of error were removed by using the anilidodinitrobenzylmethylketone, an excellent result was obtained. Bad as these analytical results are, they show that the salt contains but one atom of sodium, and therefore must have the formula which we have ascribed to it.

Properties. — The sodium salt of the bromdinitrophenylacetacetic ester forms a brick-red amorphous mass, easily soluble in water, alcohol, or ether, but insoluble in benzol. Much less freely soluble in a solution of sodic hydrate than in water. Strong nitric acid decomposes it, giving apparently the unaltered ester.

Bromdinitrobenzylmethylketone (*Bromdinitrophenylacetone*), $C_6H_2Br(NO_2)_2CH_2COCH_3$.

This substance can be made from the bromdinitrophenylacetacetic ester by the action of dilute sulphuric acid in open vessels, or of strong hydrochloric acid in sealed tubes. The method of preparation which gave us the best results was as follows: 2 to 2.5 grs. of bromdinitrophenylacetacetic ester were boiled with about 200 c.c. of sulphuric acid of specific gravity 1.44, boiling point 132°, in a flask with a return condenser, until all the solid was dissolved, which took usually from one hour to an hour and a half. The yellow solution was then allowed to cool, when it deposited a heavy white flocculent precipitate, which was increased in quantity by diluting largely with water; it was filtered out, and after thorough washing with water was purified by crystallization from alcohol until it showed the constant melting point 112°–113°, when it was dried at 100° for analysis. If the ester used in this process was not perfectly pure, a tarry impurity was formed which could be removed only with great difficulty; the best plan in such a case was to wash the product with a small quantity (20–30 c.c.) of benzol, which dissolved the ketone more readily than its impurity, but even after this treatment tedious crystallization from alcohol was necessary to obtain a pure substance.

The formation of this substance by heating the bromdinitrophenylacetacetic ester with hydrochloric acid is not a good method of preparing it, because the process must be carried on in sealed tubes, and also because the product is apt to be contaminated with the tarry impurity just mentioned; but as it throws light on the reaction which takes place, we will describe it briefly: 1 gr. to 1.5 grs. of the ester were sealed in a tube with 20–30 c.c. of pure strong hydrochloric acid, and heated from 130°–150° for two or three hours. Upon opening the tube a gas was evolved, which burnt with a smoky green-bordered flame (ethylchloride), and also contained carbonic dioxide, as shown by its giving a precipitate with lime-water. The contents of the tubes consisting, in addition to the acid liquid, either of tufts of brownish acicular crystals, or a brown oily semi-solid mass, were poured into a large volume of cold water, and the insoluble portions purified as already described.

The following analyses were made in part with substance prepared by the hydrochloric acid process, and in part with that made with sulphuric acid: —

I. 0.2312 gr. of the substance gave on combustion 0.3005 gr. of carbonic dioxide, and 0.0546 gr. of water.

II. 0.1638 gr. of the substance gave 14 c.c. of nitrogen at a temperature of 23° and a pressure of 755 mm.

III. 0.1862 gr. of the substance gave, according to the method of Carius, 0.1173 gr. of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2COCH_3$.	Found.		
		I.	II.	III.
Carbon	35.64	35.44		
Hydrogen	2.31	2.62		
Nitrogen	9.24		9.57	
Bromine	26.40			26.81

It is evident from the analyses and observations given above that the reaction with hydrochloric acid runs as follows: —

$$C_6H_2Br(NO_2)_2CH_2COCHCO_2C_2H_5 + HCl = \\ C_2H_5Cl + CO_2 + C_6H_2Br(NO_2)_2CH_2COCH_3;$$

and that the reaction with sulphuric acid must be similar. We had expected that bromdinitrophenylacetic acid would be formed also by these processes, but after a most careful search for it not a trace could be detected; and as its properties are so striking that we could not have overlooked it, the conclusion is forced upon us that the reaction consisted only in the formation of the ketone. This result is the more remarkable because Heckmann* obtained from the orthoparadinitrophenylacetacetic ester by treatment with sulphuric acid of about 10 per cent exclusively the dinitrophenylacetic acid without a trace of the corresponding ketone. As the presence of bromine in our compound could hardly have caused such a great difference in the action of the sulphuric acid, we infer that it must have been caused by the difference in strength of the sulphuric acid, Heckmann's containing about 10 per cent of H_2SO_4, while ours contained 54 per cent. This inference will be tested by experiment in the coming year.

Properties. — The bromdinitrobenzylmethylketone crystallizes from hot alcohol by cooling in white rectangular plates, often with a right-angled notch in one corner, sometimes also in plates with parallel sides and a deep notch in each end, which makes them look like reels. If crystallized by the evaporation of its alcoholic solution, it forms cylindrical tufts of needles looking like spires of moss, or much branched forms resembling certain seaweeds. Both the plates and the branching needles commonly occur together. It melts at 112°–113° and is essentially insoluble in ligroine; nearly insoluble in cold water, more soluble in hot, but still very sparingly; slightly soluble in ether, carbonic disulphide, benzol, or methyl alcohol, its solubility in the last two solvents is increased by heat; tolerably soluble in ethyl alcohol in the cold, freely when hot; ethyl alcohol dissolves it more freely than methyl alcohol; tolerably soluble in glacial acetic acid; soluble in chloroform; and freely soluble in acetone. Hot alcohol is the best solvent for it. Strong sulphuric acid has no action on it in the cold, but when warmed dissolves it, forming a colorless solution from which water precipitates the ketone essentially unaltered, although it appears at first in spherical groups of thickly set radiating needles, a form in which it is also obtained sometimes when prepared by the action of sulphuric acid on bromdinitrophenylacetacetic ester, but these crystals are converted by crystallization from alcohol into the rectangular plates described above. Strong nitric acid acts like strong sulphuric acid.

The bromdinitrobenzylmethylketone has well marked acid properties, and in this respect far surpasses the desoxybenzoine from which according to Victor Meyer† no sodium compound could be isolated. In alcoholic solution the ketone gives a dark purplish red color with sodic hydrate or ethylate. Aqueous ammonic hydrate gives only a slight red color with it, which is increased by warming for a short

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* Ann. Chem., ccxx 134.

† Ber. d. ch. G. 1888, p. 1291.

time, and still more by the addition of alcohol, but the color disappears if the heating is long continued. Aqueous potassic carbonate gave no action, but on the addition of alcohol a very dark purplish red solution of the salt. Acid sodic carbonate had no action in aqueous solution, and only very slight on addition of alcohol. The dark red alcoholic solution of the ammonium or sodium salt, if made with an excess of the ketone, is decomposed by water, giving a white precipitate of the ketone. The decomposition is not complete, however, as the liquid retains a pale red color. In the presence of an excess of sodic hydrate, the salt is much more stable. An attempt was made to study the action of the pale red aqueous solution of the ammonium salt with various reagents, but no characteristic precipitates were obtained, probably on account of the small amount of salt left in solution.

We tried also to prepare and analyze the sodium salt, the method being that adopted for the sodium salt of the bromdinitrophenylacetacetic ester; but the results of the analyses came much too high, 9.73 and 8.64 per cent of sodium, instead of the 7.07 per cent required by the formula. The reason for this difference is that the sodic hydrate or ethylate removed a portion of the bromine from the ketone, and the benzol, dissolving the organic product, left the sodic bromide formed with the salt of the ketone, as was proved by dissolving the salt in water, and acidifying with nitric acid, when, after removing the precipitate by filtration, argentic nitrate gave a heavy precipitate of argentic bromide in the filtrate. We accordingly turned our attention to the anilidoketone, our work on which is described later in this paper. We add here the *properties* of the *sodium salt of bromdinitrobenzylmethylketone.* It is a purplish black amorphous substance, very easily soluble in alcohol forming a dark claret-red solution, the color of which is so much more purple than that of the salt of the corresponding acetacetic ester, that the two substances can be easily distinguished in this way; it is decomposed almost, but not quite, completely by water, and is insoluble in benzol.

The ketone is a decidedly reactive substance. When treated with aniline, it gives aniline bromide and the anilidodinitrobenzylmethylketone, which is described later. With phenylhydrazine it appears to form a hydrazone, but at the same time the bromine was removed from the benzol ring, so that the product seemed to be a phenylhydrazidohydrazone. It was free from bromine, and exploded when touched with a hot wire; but as its purification offered considerable difficulties, we did not try to investigate it thoroughly. The ketone seems to react in the same way with hydroxylamine, since in this case also bromine seemed to be removed; but as the product did not have inviting properties, we have not attempted to isolate the oxime. If the ketone is dissolved in chloroform, the solution mixed with bromine, and allowed to stand at ordinary temperatures, hydrobromic acid is given off in considerable quantity, and a new substance melting at least 10° higher than the original is formed, which will be investigated in this laboratory next term. It is a curious fact, that, if a solution of the ketone in carbonic disulphide instead of chloroform was treated with bromine, no hydrobromic acid was given off, so far as we could find.

Anilidodinitrobenzylmethylketone, $C_6H_2(C_6H_5NH)(NO_2)_2CH_2COCH_3$.

This substance is prepared easily by the action of aniline on the bromdinitrobenzylmethylketone. The substances were mixed in the proportion of one molecule of the ketone to two of the base, and the mixture, which had a bright red color, warmed for 15 to 20 minutes on the water bath. The product was then freed from the aniline bromide and any slight excess of aniline by washing with water to which a little hydrochloric acid was added, the residue, which contained no bromine, purified by crystallization from hot alcohol till it showed the constant melting point 131°, dried at 100°, and analyzed with the following result: —

0.1980 gr. of the substance gave 23.2 c c. of nitrogen at a temperature of 25° and a pressure of 771.2 mm.

	Calculated for $C_6H_2C_6H_5NH(NO_2)_2CH_2COCH_3$.	Found.
Nitrogen	13.33	13.26

Properties. — The anilidodinitrobenzylmethylketone forms, when crystallized from alcohol, bright yellow groups of curving needles, which look at first like two heads of palm trees cut off at the point where the leaves grow out of the trunks, and put with the stumps together. As more crystals are formed, the groups develop into irregular chestnut burs. It melts at 131°; is essentially insoluble in ligroine; nearly insoluble in cold water, slightly soluble in hot, forming a pale yellow solution; slightly soluble in ether; soluble in cold ethyl or methyl alcohol, more freely in either of these solvents when hot; soluble in benzol, carbonic disulphide, or glacial acetic acid; freely soluble in chloroform or acetone. Alcohol is the best solvent for obtaining crystals. Strong sulphuric acid dissolves it, forming a brown solution. Strong nitric or hydrochloric acid dissolves it with a yellow color, but it is very slightly soluble in hydrochloric acid.

The acid properties of this substance are much less marked than those of the corresponding bromine compound, as was to be expected from the substitution of bromine by the basic radical C_6H_5NH. Aqueous sodic hydrate has no action on it in the cold, and but slight when warm, but if alcohol is added a brownish red solution of the sodium salt is obtained. Ammonic hydrate, on the other hand, could not be made to act on it, even by warming in presence of a large excess of alcohol. Potassic carbonate in aqueous solution had no action on it, either cold or hot, but gave a very slight action when a large quantity of alcohol was added. The behavior of the solution of a soluble salt with various reagents could not be studied, as the alcoholic solution of the sodium salt was decomposed completely by diluting it with water. But in spite of these weaker acid properties we selected the sodium salt of this substance for analysis, as there was no danger of a decomposition of this ketone by the alkali used, such as had prevented us from getting good results with the corresponding bromine compound. For the same reason, the hydrazone for analysis was prepared from this substance instead of from the bromdinitrobenzylmethylketone.

Sodium Salt of Anilidodinitrobenzylmethylketone,
$C_6H_2(C_6H_5NH)(NO_2)_2CHNaCOCH_3$.

This substance was prepared by adding an alcoholic solution of sodic ethylate to an excess of the ketone also dissolved in absolute alcohol. The narrow beaker containing the mixture, after the addition of a little ether, was sunk to its rim in a steam bath. In this way, at first the ether, and later the alcohol vapor, prevented the carbonic dioxide of the air from acting on the salt during the evaporation. The dry residue was thoroughly washed with benzol to remove the excess of the ketone, and the salt thus purified dried at 100°, and analyzed with the following result: —

0.2380 gr. of the salt gave after evaporation with sulphuric acid 0.0500 gr. of sodic sulphate.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2C_3OH_4Na$.	Found.
Sodium	6.82	6.80

Properties. — A brownish black mass, soluble in alcohol, giving a much browner solution than any of the other salts described in this paper, so that it could be recognized with ease by its color. It is decomposed at once by water, the brown alcoholic solution being turned yellow and turbid. It seems to be nearly or quite insoluble in ether, and is insoluble in benzol.

Anilidodinitrobenzylmethylketonehydrazone, $C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(N_2HC_6H_5)CH_3$.

This substance was made by warming for 20–30 minutes on the water bath in an open dish a mixture of anilidodinitrobenzylmethylketone with phenylhydrazine in the proportion of one molecule of the former to about one and a half of the latter, so as to have a decided excess of the hydrazine. At the end of this time the mixture had changed from yellow to dark carmine red, and solidified to a tarry mass, which was crystallized once or twice from alcohol to bring it into a finely divided state, and washed with water containing a little hydrochloric acid till the excess of phenylhydrazine had been removed, after which it was boiled with alcohol on the water bath, and while boiling enough benzol added cautiously to effect the solution; the mixture was then boiled for about a minute, when upon cooling crystals were deposited, and this crystallization was continued until the substance showed the constant melting point 140°, when it was dried at 100°, and analyzed with the following result: —

0.2177 gr. of the substance gave 32.5 c.c. of nitrogen at a temperature of 22° and a pressure of 763 mm.

	Calculated for $C_6H_2(C_6H_5NH)(NO_2)_2CH_2C(N_2HC_6H_5)CH_3$.	Found.
Nitrogen	17.28	16.97

Properties. — The hydrazone crystallizes well in reddish brown scales, resembling strongly in general appearance the official ferric citrate. The scales often reach a diameter of 3 to 4 millimeters. Under the microscope plates were observed which seemed to belong to the monoclinic system, but with these were very irregular forms, often serrated on one or both sides, or irregularly diamond-shaped with re-entering angles, usually either grouped in radiating masses, or in crowded branching collections of thick needles. It melts at 140°, but, as it seems to be slightly decomposed by crystallization, it was difficult to determine the melting point with perfect exactness. It is essentially insoluble in ligroine or cold water; very slightly soluble in boiling water or in ether; slightly soluble in cold alcohol, more soluble, but still not freely, in hot; more soluble in methyl than in ethyl alcohol; slightly soluble in cold glacial acetic acid, freely in hot; soluble in cold benzol or carbonic disulphide, freely soluble in these solvents when hot; easily soluble in chloroform or acetone, even in the cold. As the benzol solution deposits the substance in a viscous state, it is best to crystallize from a mixture of alcohol and benzol, as described above in speaking of its preparation. Strong hydrochloric acid has no action upon it. Strong nitric acid seems to decompose it, dissolving a little of the product. Strong sulphuric acid dissolves it with a yellowish brown color.

Neither sodic or ammonic hydrate, nor potassic carbonate, nor acid sodic carbonate, gives any action with it in aqueous solution, hot or cold, or even on addition of alcohol; but if it is warmed with sodic hydrate, water, and alcohol, a little dissolves with a brown color, and if a drop of sodic hydrate is added to an alcoholic solution, a dark brownish red solution is formed, which is decomposed by water. It may be, therefore, that the substance has not lost completely the power of forming salts, but it is on the whole more probable that the salt is derived from anilidodinitrobenzylmethylketone formed by the action of the sodic hydrate on the hydrazone, as the action was certainly accompanied by decomposition, since there was a smell of isocyanphenyl, and the hydrazone could not be recovered from the solution in sodic hydrate.

The study of the bromdinitrobenzylmethylketone will be continued in this laboratory.

XXIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON TETRABROMDINITROBENZOL.

By C. Loring Jackson and W. D. Bancroft.

Presented May 28, 1889.

After it had been determined that the tribromdinitrobenzol, melting at 192°, reacted easily with a variety of substances, it seemed of interest to try similar experiments with a tetrabrom compound, and we selected for this purpose the tetrabromdinitrobenzol, melting at 228°, and describe in this paper the results of our work, which may be briefly summarized as follows. Tetrabromdinitrobenzol is not acted on by alcoholic ammonia in open vessels, but, if heated with it in a sealed tube, is converted into a yellow substance insoluble in all the common solvents, which seems to be the bromtriamidodinitrobenzol. With aniline the bromtrianilidodinitrobenzol, melting at 175°–176°, is formed. With sodium malonic ester it gives in the cold dibromdinitrophenylmalonic ester, melting point 89°, which possesses acid properties forming a red sodium salt, and is converted by aniline into the bromanilidodinitrophenylmalonic ester, melting at 127°. The action of these reagents on the tetrabromdinitrobenzol is therefore similar to their behavior with tribromdinitrobenzol, the fourth atom of bromine remaining unaffected in all these reactions. We were prevented by want of time from trying to remove this fourth atom of bromine by reactions carried on at higher temperatures. We have studied also the reduction of the dibromdinitrophenylmalonic ester with tin and hydrochloric acid, and have obtained in this way the bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$, melting at about 212°, and its chloride, $C_6H_2BrNH_2(CH_2CONH)HClH_2O$. We may add, that in preparing the tetrabromdinitrobenzol from somewhat impure tetrabrombenzol we obtained the as yet undescribed pentabromnitrobenzol, which melts at 248°, and on another occasion the hexabrombenzol.

Preparation of Tetrabromdinitrobenzol.

Our starting point in the manufacture of the tetrabrombenzol was tribromaniline, which we prepared as follows. 60 grs. of aniline were dissolved in dilute hydrochloric acid, and the solution, having been made up to a volume of about three litres, a rapid stream of air saturated with bromine vapor was sucked through it by means of a Bunsen pump, until the liquid assumed a distinct yellow color. The precipitate of tribromaniline was then removed by straining through cheese-cloth, washed with a stream of common water until free from acid, when the greater part of the water was squeezed out with a screw press, and the product thoroughly dried on a steam radiator. In this way a quantitative yield of tribromaniline free from colored by-products was obtained at a much less expense of time and labor than by the method formerly in use.

To convert the tribromaniline into tetrabrombenzol we used the method of V. von Richter* slightly modified, which left nothing to be desired so far as the yield was concerned, when the process was successful; this, however, was not always the case, as frequently the product was a substance melting in the neighborhood of 87°, from which tetrabrombenzol melting at 98° could be obtained only by repeated crystallization from a mixture of alcohol and benzol, and even then not in large quantity.† In spite of many experiments, we have not succeeded in determining with certainty the conditions under which this mixture was formed, or the nature of the impurity which it contained, and can give only the conditions which usually gave a good result. 25 grs. of the tribromaniline were dissolved in a small quantity of glacial acetic acid with the aid of heat, and, after the solution had cooled, a concentrated aqueous solution of hydrobromic acid ‡ was added, which threw down a precipitate of tribromaniline bromide; the mixture was stirred vigorously, and, disregarding the precipitate, a concentrated aqueous solution of about the theoretical amount of sodic nitrite added in small portions, keeping the solution cool by immersing the beaker containing it in cold water; the beaker was then warmed gently on the water bath, and solid sodic nitrite added in small pieces

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* Ber. d. ch. G , viii. 1428.

† Owing to this uncertainty in our modification of Von Richter's process, we made two attempts to use Sandmeyer's method, but encountered such difficulties in applying it to tribromaniline that we decided it was easier to prepare our material by Von Richter's process than to overcome these difficulties.

‡ An attempt to substitute potassic bromide and sulphuric acid for hydrobromic acid gave a much poorer yield; less than 50 per cent instead of 90.

until the proportion of the total sodic nitrite to the tribromaniline was three molecules to one (this very large excess of sodic nitrite being found necessary to complete the reaction). The liquid on cooling deposited a tarry mass, which was extracted repeatedly with small quantities of hot alcohol, until it was converted into crystals (melting at about 95°). An additional amount of these crystals was obtained by pouring into water the red liquid from which the tar had been deposited, but this amount was not large. The product, after purification by one or two crystallizations from hot alcohol, showed a yield of from 89 to 93 per cent of the theoretical.

To convert the tetrabrombenzol into tetrabromdinitrobenzol, 10 grs. of it were dissolved with the aid of heat in nitric acid of specific gravity 1.52, prepared in the laboratory from nitre and sulphuric acid; then the same volume of strong sulphuric acid was added, about 200 c.c. of the mixture of the two acids being used, and, after standing in the cold for ten minutes, the whole was boiled for about an hour in a flask closed with a glass bulb. If the tetrabrombenzol was sufficiently pure there was little foaming and no violent action, and on cooling a white crystalline solid separated, which was nearly pure tetrabromdinitrobenzol, and, after crystallization from benzol with a little alcohol, or from chloroform, showed the right melting point 228°.*

If, on the other hand, a tetrabrombenzol was used containing some of the impurity already mentioned, which, when present in quantity, lowered the melting point to the neighborhood of 87°, the action was violent, the boiling being accompanied by much foaming, the product was often oily, and, after most of the solid had been precipitated by water, the aqueous liquid contained decomposition-products, as was shown by the blackish precipitate formed in it on the addition of sodic carbonate. The main product in this case was a mixture of the tetrabromdinitrobenzol and another substance, which was obtained by treatment with aniline or sodium malonic ester, and subsequent separation of the derivative of the tetrabromdinitrobenzol by crystalliza-

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* One of us and J. F. Wing (These Proceedings, xxiii. 148) some years ago obtained tetrabromdinitrobenzol as a secondary product in the manufacture of tribromtrinitrobenzol, but we were unable to raise its melting point above 224°; this was ascribed at the time to the presence of a little tribromtri- (or di-) nitrobenzol, an opinion which is confirmed by the fact mentioned above that tetrabromdinitrobenzol prepared by us according to the usual method showed the melting point 228° given by Von Richter (Ber. d. ch. G., 1875, p. 1427). The difficulty in removing the tribrom compound can be accounted for by supposing that it forms the addition-product observed by one of us and G. D. Moore (Ber. d. ch. G. 1888, p. 1707), or an analogous one with the trinitro compound.

tion out of alcohol from the unaltered second product, which was then purified by crystallization from boiling alcohol, or better chloroform, until it showed the constant melting point 248°, when, after drying at 100°, it was analyzed with the following results: —

I. 0.1711 gr. of the substance gave on combustion 0.0855 gr. of carbonic dioxide and 0.0151 gr. of water.
II. 0.2100 gr. of the substance gave 0.1075 gr. of carbonic dioxide and 0.0103 gr. of water.
III. 0.1846 gr. of the substance gave 3.5 c.c. of nitrogen at a temperature of 17° and a pressure of 773 mm.
IV. 0.1881 gr. of the substance gave, according to the method of Carius, 0.3418 gr. of argentic bromide.

	Calculated for $C_6Br_5NO_2$.	Found.			
		I.	II.	III.	IV.
Carbon	13.90	13.63	13.96		
Hydrogen	0.00	0.98	0.54		
Nitrogen	2.70			2.24	
Bromine	77.23				77.34

There can be no doubt, therefore, that this is the as yet undescribed pentabromnitrobenzol.

Properties. — The pentabromnitrobenzol crystallizes in very slender little white needles, which melt at 248°. The substance is essentially insoluble in water or ligroine; nearly insoluble in cold ethyl or methyl alcohol, more soluble when hot, but still sparingly; the solubility in glacial acetic acid or acetone is similar, except that it is much more soluble in either of these solvents when hot than it is in alcohol; readily soluble in hot benzol or chloroform; very soluble in ether or carbonic disulphide.

Although pentabromnitrobenzol was the usual impurity, on one occasion a different product was obtained, which consisted of small needles melting, after crystallization from benzol, at about 312°, essentially insoluble in alcohol or sodic hydrate, and containing no nitrogen. We inferred therefore that this was the hexabrombenzol, which is said to melt above 315°, and to be almost insoluble in boiling alcohol, and this inference was proved to be correct by the following analysis: —

0.1303 gr. of the substance gave, by the method of Carius, 0.2666 gr. of argentic bromide.

	Calculated for C_6Br_6.	Found.
Bromine	86.96	87.10

Preliminary Experiments.

After the tetrabromdinitrobenzol had been prepared, the following experiments were tried to determine the ease with which it reacted with various substances.

As has been stated in an earlier paper, alcoholic ammonia has no action on tetrabromdinitrobenzol in the cold, or even if the substances are heated together in open vessels. If however the mixture is heated to 100° in a sealed tube for four or more hours, a reaction takes place giving an orange precipitate and a red alcoholic solution in addition to some unaltered tetrabromdinitrobenzol. The orange insoluble substance was undoubtedly the bromtriamidodinitrobenzol, but, as it was insoluble in all the common solvents, we could only try to purify it by washing, and even after repeated treatment with water, alcohol, chloroform, and benzol were unable to obtain a substance giving constant results on analysis; the bromine varied in different samples from 25.34 to 29.07 per cent, the amount required by the formula,

$$C_6Br(NO_2)_2(NH_2)_3,$$

being 27.39. Although it is probable that further work on this substance would have enabled us to find a method of purifying it, we did not think it worth while to sacrifice the time, as these analyses show that the reaction has run in the same way as that between tribromdinitrobenzol and alcoholic ammonia, and nothing of interest was likely to be found in its investigation. The substance is an orange-yellow powder, insoluble in all the common solvents, and not melting even at 285°. The alcoholic filtrate contained a yellow substance melting at 185° in the crude state, but we did not obtain enough of it for investigation. With aniline a more favorable result was obtained, which is described fully in the next section of this paper.

When boiled with potassic sulphocyanate in alcoholic solution in a flask with a return condenser, there was very little action, but, if amyl alcohol was substituted for ethyl alcohol, so that the action would take place at a higher temperature, a dark red substance was formed insoluble in all the common solvents. In this respect the tetrabromdinitrobenzol behaved exactly like the tribromdinitrobenzol, and, as it had been found impossible to purify the corresponding product from the tribrom compound, we did not think it worth while to continue work in this direction.

With sodium malonic ester or sodium acetacetic ester it behaves like the tribromdinitrobenzol. The action with sodium malonic ester is described in detail later in this paper.

In all the derivatives of tetrabromdinitrobenzol which were analyzed it was found that only three of the atoms of bromine had been attacked. We had hoped to try some experiments at higher temperatures for the purpose of replacing the fourth atom of bromine, but the work described in this paper has taken so much time that we have been unable to take up this branch of the subject.

Bromdinitrotrianilidobenzol, $C_6Br(NO_2)_2(C_6H_5NH)_3$.

To prepare this substance tetrabromdinitrobenzol was heated with aniline in the proportion of one molecule of the former to a little more than six of the base. Convenient amounts were 7 grs. of tetrabromdinitrobenzol to 8.3 grs. of aniline. When the mixture was heated on the water bath, the solid dissolved after some time, the solution being accompanied by a change of color from yellow to bright red, and on cooling the whole solidified to a mass of red needles; but in order to get even a tolerable yield of the new substance the heating on the water bath must be continued for at least four to six hours, and then it is not by any means complete. A higher heat than the water bath should not be used, as then the mixture shows a tendency to pass into a purplish coloring matter, resembling impure rosaniline in appearance, and similar to the substance obtained in the same way from tribromdinitrobenzol,* and like that undoubtedly produced by the nitro groups taking part in the reaction. If the reaction had run properly, the product consisted of a viscous or crystalline mass of the color of red lead, from which in the first place the aniline bromide and excess of aniline were removed by washing with water containing a little hydrochloric acid, leaving a brick-red powder. The purification was completed by crystallization from alcohol, and afterward from a mixture of alcohol and chloroform, until it showed the constant melting point 175°–176°. If there was difficulty in obtaining crystals of the proper melting point, it was found advisable to warm the substance again with aniline for two or more hours, and then purify again in the manner just described. In addition to unaltered tetrabromdinitrobenzol a small amount of an impurity was found, which melted in the crude state between 120° and 140°, but we did not succeed in isolating a substance fit for analysis from it. The main product, when pure, was dried at 100°, and analyzed with the following results: —

I. 0.1667 gr. of the substance gave 20.4 c.c. of nitrogen at a temperature of 25° and a pressure of 768.4 mm.

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* These Proceedings, xxiii. 145.

II. 0.1624 gr. of the substance gave, by the method of Carius, 0.0578 gr. of argentic bromide.

	Calculated for $C_6Br(NO_2)_2(C_6H_5NH)_3$.	Found. I.	Found. II.
Nitrogen	13.46	13.81	
Bromine	15.38		15.15

Properties. — Bromtrianilidodinitrobenzol forms a brilliant but rather dark red crystalline powder, which, when examined with the microscope, consists of crystals of two forms, rather short prisms terminated by an obtuse angle, and thick groups shaped like an hour-glass and made up of short prisms, which seem to have the same terminal angles as those which are not in groups; the groups are rather darker in color than the free prisms, but this is probably due to their being thicker. When crystallized from hot alcohol, instead of the usual mixture of alcohol and chloroform, characteristic forms like sheaves were obtained, also a small quantity of red nearly square plates. It melts at 175°–176°; is essentially insoluble in ligroine, or in water either cold or boiling; very slightly soluble in cold alcohol, more soluble in hot; more soluble in methyl than in ethyl alcohol; slightly soluble in cold ether, freely in hot; moderately soluble in glacial acetic acid; freely soluble in benzol, chloroform, or carbonic disulphide; very freely in acetone. The best solvent for it is a mixture of alcohol and chloroform, as it tends to separate in a viscous state from the solution in chloroform alone. Strong sulphuric acid dissolves it slightly, forming a pale yellow solution. Strong nitric acid acts in the same way, but less energetically; fuming nitric acid acts upon it violently even in the cold. Hydrochloric acid has no action either hot or cold. The absence of basic properties is accounted for by the presence of the two nitro groups. We tried also the action of sodic hydrate, as certain nitroamido compounds possess weak acid properties, — for instance, the trinitrotoluidine of Nölting and Salis,* — but found that it produced no effect.

Dibromdinitrophenylmalonic Ester, $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$.

This substance was prepared by acting on one molecule of tetrabromdinitrobenzol with about four molecules of sodium malonic ester, as follows: 15 grs. of tetrabromdinitrobenzol dissolved in about 20–30 c.c. of benzol were mixed with 20 grs. of malonic ester previously converted into sodium malonic ester by treatment with the sodic ethyl-

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* Ber. d. ch. G., xv. 1864.

ate made from 3 grs. of sodium dissolved in 100 to 150 c.c. of absolute alcohol. The action began at once, as shown by the appearance of a dark red color and a considerable evolution of heat, so that the flask became too hot to hold in the hand with comfort; in this respect it differed from that with the tribromdinitrobenzol, as, although in that case the red color appeared at once, no perceptible rise of temperature was observed in any part of the reaction. To make certain that the reaction had run as far as possible, the mixture was allowed to stand in the cold for three or four days. At the end of this time the product was diluted with about half a litre of water, and the benzol separated from the red aqueous solution of the salt of the new substance. Upon adding dilute sulphuric acid to this aqueous solution, the new substance was precipitated, and after washing with water was purified by crystallization from alcohol until it showed the constant melting point 89°, when it was dried *in vacuo* for analysis. The benzol solution, which separated on the addition of water, was evaporated to dryness, and the residue, consisting of the new substance, a little unaltered tetrabromdinitrobenzol, and an oil, after being freed from the oil on the pump, was treated with alcohol, in which the tetrabrom compound is essentially insoluble, and the small amount of the new substance thus obtained was added to that from the aqueous solution.

I. 0.2183 gr. of the substance gave on combustion 0.2568 gr. of carbonic dioxide and 0.0528 gr. of water.

II. 0.2144 gr. of the substance gave 11.4 c.c. of nitrogen at a temperature of 23°.1 and a pressure of 763.4 mm.

III. 0.2372 gr. of the substance gave, by the method of Carius, 0.1833 gr. of argentic bromide.

	Calculated for $C_6HBr_2(NO_2)_2CH(CO_2C_2H_5)_2$.	Found.		
		I.	II.	III.
Carbon	32.23	32.07		
Hydrogen	2.48	2.69		
Nitrogen	5.78		6.02	
Bromine	33.06			32.91

The yield of dibromdinitrophenylmalonic ester was very satisfactory. On one occasion 5 grs. of tetrabromdinitrobenzol gave 4 grs. of the dibromdinitrophenylmalonic ester, instead of the 5 grs. required by the theory, that is, 80 per cent of the theoretical yield. This large yield proves conclusively that dibromdinitrophenylmalonic ester is the only aromatic product of the reaction, a point which before this observation seemed somewhat doubtful in the analogous preparations described in other papers from this laboratory, as in them the yield rose but little above 50 per cent of the theory.

The amount of bromine separated as bromide of sodium in the preparation of the substance was determined in two cases as follows: —

I. 5 grs. of tetrabromdinitrobenzol yielded 3.707 grs. of argentic bromide, corresponding to 1.578 grs. of bromine.
II. 5 grs. of tetrabromdinitrobenzol yielded 3.631 grs. of argentic bromide, corresponding to 1.545 grs. of bromine.

The theoretical yield, if two of the atoms of bromine had been removed, would be 1.653 grs.

Percentage of bromine found as bromide of sodium, —

I.	II.
95.43	93.48

From these numbers it appears that essentially all the bromine is removed as sodic bromide.

The oil which formed the secondary product of the reaction was not investigated further, as from the composition of the ester, and the fact that all the bromine appeared as sodic bromide, there could be no question that the nature of this action is the same as that with the tribrom compounds; and in those cases* the study of the oils has shown conclusively the mode of formation of the substances. There can be no doubt, therefore, that the reactions which take place in this case should be written as follows: —

$$\begin{aligned}&C_6Br_4(NO_2)_2 + 2\,CHNa(COOC_2H_5)_2 = \\ &\quad NaBr + C_6Br_3(NO_2)_2CH(COOC_2H_5)_2 + CHNa(COOC_2H_5)_2 = \\ &\quad C_6Br_3(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 = \\ &\quad C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2.\end{aligned}$$

The brommalonic ester being converted afterward into tartronic or acetylentetracarbonic ester.

Properties. — The dibromdinitrophenylmalonic ester crystallizes from alcohol usually in slightly yellow to colorless needles, which unite into groups like pompons if the solution is dilute; seen under the microscope they consist of rather long rhombic plates with a decidedly acute angle, about six times as long as their breadth, or even slenderer, either free or in radiating groups, the crystals branching so as to give the effect of being arranged in curved lines. When less well developed, the groups are made up of fine needles very much

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* These Proceedings, xxiv. 238, 265.

branched, like certain feathery seaweeds. From the oil which forms the secondary product in its preparation, the substance crystallizes in flattened prisms, often two centimeters in length, arranged in slightly radiating groups. The melting point is 89°. It is essentially insoluble in water or ligroine; slightly soluble in cold, freely in hot methyl, or ethyl alcohol; freely soluble in carbonic disulphide, glacial acetic acid, or acetone; very freely in ether, benzol, or chloroform. Strong sulphuric acid has little, if any, action on it in the cold, but dissolves it slightly without change of color when hot. Strong nitric acid also seems not to act upon it in the cold, but, when warmed with it, turns yellow and imparts a yellow color to the drops of the melted substance which swim on its surface. Hydrochloric acid does not seem to act on it in open vessels either cold or warm, although from analogy with the corresponding monobrom compound it is fair to suppose that it would decompose it if the two substances were heated to 150° in a sealed tube.

The dibromdinitrophenylmalonic ester has well marked acid properties, as was to be expected from the fact that one of its atoms of hydrogen is attached to a carbon atom in direct contact with two carboxylester radicals and a dinitrophenyl. An excess of sodic hydrate in aqueous solution has but little action on the solid, turning it pale red; if, however, a drop of alcohol is added, it turns a very dark red at once, and the salt begins to dissolve. Potassic carbonate acts in much the same way. Acid sodic carbonate in aqueous solution has no effect, but if alcohol is added there is a slight action shown by formation of a little of the red salt. Ammonic hydrate in aqueous solution has but little action, but turns red if a little alcohol is added, and upon warming this mixture a deep brownish red solution is obtained, which smells strongly of ammonia, even if an excess of the ester is used in making it. It seemed to be decomposed by heating, or by exposure to the air, so that the ammonium salt must be a very unstable substance. The solution of the ammonium salt made with an excess of the ester (but still smelling of ammonia) was treated with various reagents, and gave the following characteristic precipitates: —

With a salt of *magnesium*, *calcium*, *strontium*, or *barium*, very heavy pale red flocks.

With a *zinc* salt, pale yellow flocks.

With a salt of *manganese*, *cobalt*, or *nickel*, pale red flocks.

With a *ferric* salt, pale brownish purple.

With a *cupric* salt, bright yellow.

With salts of *mercury*, pale red.

With a *cadmium* salt, reddish yellow.

With a *lead* salt, whitish red.

With a *silver* salt, pale orange.

Strong nitric acid gave with the salts a white precipitate, probably the unaltered ester. In this respect it differs from bromtrinitrophenylmalonic ester.

Bromanilidodinitrophenylmalonic Ester,

$C_6HBr(C_6H_5NH)(NO_2)_2CH(COOC_2H_5)_2$.

This substance was made by adding aniline to the dibromdinitrophenylmalonic ester in the proportion of a little more than two molecules of the base to one of the ester. The reaction began in the cold, but was brought to an end by warming the mixture for a short time on the water bath. The product, after washing with water, to which a little hydrochloric acid was added to remove aniline bromide and the excess of aniline, was crystallized from hot alcohol, until it showed the constant melting point 127°, when it was dried at 100°, and analyzed with the following result: —

0.2003 gr. of the substance gave 14.85 c.c. of nitrogen at a temperature of 20°.5 and a pressure of 762 mm.

	Calculated for $C_6HBr(C_6H_5NH)(NO_2)_2CH(CO_2C_2H_5)_2$.	Found.
Nitrogen	8.47	8.49

Properties. — The bromanilidodinitrophenylmalonic ester crystallizes from alcohol in bright red needles, which under the microscope are seen to be slender prisms terminated usually by two planes, less commonly by one, and seeming to belong to the monoclinic system. The substance melts at 127°; and is essentially insoluble in cold water, very sparingly soluble in boiling water, as shown by the faint yellow color imparted to the liquid; insoluble in ligroine; very slightly soluble in cold ethyl or methyl alcohol, more freely in either of these solvents when hot; slightly soluble in ether; soluble in benzol or glacial acetic acid; freely soluble in chloroform, carbonic disulphide, or acetone. Strong sulphuric acid dissolves it slightly, forming a yellowish solution; the solubility did not seem to be increased by heat. Strong nitric acid dissolved it rather more freely than sulphuric acid, and the solubility was increased by heat. Strong hydrochloric acid had no action upon it, although it is probable that long heating in a sealed tube with this acid would have decomposed it in the way described * under the bromdinitrophenylmalonic ester.

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* These Proceedings, xxiv. 240.

The acid properties of this substance have been much weakened by the replacement of bromine by the basic aniline radical C_6H_5NH, but that they still exist is shown by the following observations. Sodic hydrate in aqueous solution has no action on the solid, but on the addition of a little alcohol a dark red solution of the salt is formed; sodic carbonate in aqueous solution produces no effect, but on the addition of alcohol a very slight red coloration appears; acid sodic carbonate produces no effect even in presence of alcohol. Ammonic hydrate in aqueous solution does not dissolve the solid substance, and, even if alcohol is added, the action is very slight; if, however, the mixture of aqueous ammonic hydrate, alcohol, and the solid is warmed on the water bath, a dark red solution is obtained, which smells of ammonia, even if a large excess of the ester is used. The behavior of such a solution with various reagents was studied with the following results: —

Salts of *magnesium*, *calcium*, *strontium*, or *barium* gave rusty brown precipitates.

The salts of the heavy metals gave yellow precipitates, except where the color was modified by the excess of ammonia which could not be removed from the solution of the salt.

Reduction of Dibromdinitrophenylmalonic Ester.

The investigation of this subject interested us especially, because it seemed probable that the diamidophenylmalonic or acetic acid, which would be the first product of the reaction, would lose water and become converted into an amidooxindol, especially since Bischoff[*] obtained from the reduction of his orthonitrobenzoylmalonic ester α-γ-dihydroxychinoline. As with zinc and alcoholic hydrochloric acid, or with zinc dust and acetic acid, he obtained more complex products, some of which it was almost impossible to purify, we decided to try first the action of tin and hydrochloric acid with alcohol upon our dibromdinitrophenylmalonic ester, and for this purpose proceeded as follows. 2 grs. of the dibromdinitrophenylmalonic ester were mixed with alcohol, strong hydrochloric acid, and tin, a piece of platinum foil being used to accelerate the action, and the mixture was kept upon a steam radiator at a temperature of from 50°–70° until the whole of the malonic compound had disappeared, which usually happened in an hour and a half. The clear solution was poured off from the excess of tin, and, after evaporation to dryness, dissolved again in water, and

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[*] Ann. Chem., ccli. 361.

freed from tin with sulphuretted hydrogen; upon concentrating the filtrate, long needles separated, which varied in color from brown to nearly white. By further concentration of the mother liquors a fresh crop of crystals was obtained, and the precipitate of sulphide of tin must be boiled out several times with water, as the reduction-product is but slightly soluble. As the substance seemed to be decomposed to a certain extent by our attempts to purify it by crystallization, we analyzed some of it without further purification, while other samples were crystallized once more from hot water, allowing the solution to cool *in vacuo* to avoid oxidation by the air. It was dried *in vacuo*, and analyzed with the following results: —

I. 0.0977 gr. of the substance gave on combustion 0.1224 gr. of carbonic dioxide and 0.0434 gr. of water.

II. 0.3108 gr. gave on combustion 0.3869 gr. of carbonic dioxide and 0.1128 gr. of water.

III. 0.1113 gr. of the substance gave 9.8 c.c. of nitrogen at a temperature of 25°.5 and a pressure of 763 mm.

IV. 0.1010 gr. of the substance treated with argentic nitrate and the precipitate washed with nitric acid and water gave 0.0498 gr. of argentic chloride.

V. 0.4762 gr. gave 0.2461 gr. of argentic chloride.

	Found.				
	I.	II.	III.	IV.	V.
Carbon	34.17	33.93			
Hydrogen	4.93	4.03			
Nitrogen			9.84		
Chlorine				12.19	12.77

The free base corresponding to this chloride was next prepared by adding ammonic hydrate to a strong solution of it, when a white precipitate swimming in a dark green liquid was obtained. It was purified by washing with cold water, in which it is as good as insoluble, until the wash water gave no test for a chloride, then dried *in vacuo*, and analyzed with the following results: —

I. 0.1690 gr. of the substance gave on combustion 0.2587 gr. of carbonic dioxide and 0.0580 gr. of water.

II. 0.2021 gr. of the substance gave 23.7 c.c. of nitrogen at a temperature of 24°.5 and a pressure of 768.5 mm.

	Found.	
	I.	II.
Carbon	41.75	
Hydrogen	3.81	
Nitrogen		13.28

The following comparison shows that the numbers obtained from the analyses of the chloride correspond to those calculated for the formula $C_8H_9BrN_2O_2HCl$ (with the exception of the hydrogen,[*] which was undoubtedly brought too high by the passing over of a part of the halogen into the sulphuric acid bulbs).

	Calculated for $C_8H_9BrN_2O_2HCl$.	Found.	
Carbon	34.12	34.17	33.93
Hydrogen	3.55	4.93	4.03
Nitrogen	9.95	9.84	
Chlorine	12.61	12.19	12.77

On the other hand, the numbers given by the analyses of the free base indicate a substance containing one molecule less of water.

	Calculated for $C_8H_7BrN_2O$.	Found.	Calculated for $C_8H_9BrN_2O_2$.
Carbon	42.30	41.75	39.17
Hydrogen	3.08	3.81	3.67
Nitrogen	12.34	13.28	11.43

The want of agreement between the percentages of hydrogen[†] is explained in the same way as in the analyses of the chloride. Otherwise the numbers come as near as could be expected, when it is remembered that the free base was so unstable that we did not dare to purify it except by washing, and that it gradually turned brown even when dry.

In order to harmonize these results and determine the nature of the substances we have found only three hypotheses.

First, and most obvious. The two substances belong to different classes, i. e. one is the chloride of the bromdiamidophenylacetic, acid $C_6H_2BrNH_3ClNH_2CH_2COOH$; the other is free bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$.

If, on the other hand, the substances belong to the same class, —

Second. They are the bromamidooxindol and its chloride. In this case the chloride must contain one molecule of water of crystallization.

Third. They are bromdiamidophenylacetic acid and its chloride. In this case our analyses of the free base are incorrect.

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[*] The formula $C_8H_{11}BrN_2O_2HCl$ requires 4.23 per cent of hydrogen, and is therefore distinctly too high for Analysis II., and the analysis of the "chloride of the free base" given later. The small amount of substance used in Analysis I. makes the per cent of hydrogen in it of no value.

[†] The formula $C_8H_9BrN_2O$ requires 3.93 per cent of hydrogen.

If the first of these explanations is the true one, the chloride made by adding hydrochloric acid to the free base would be the chloride of the bromamidooxindol, and therefore different from the original chloride of the bromdiamidophenylacetic acid. To settle this point, we set free the base with ammonic hydrate from a quantity of the original chloride, and, after washing until free from ammonic chloride, dissolved it in dilute hydrochloric acid and crystallized it from the slightly acid solution. The general habit of the crystals of the two chlorides (the original one and that made from the free base) was the same, but there were differences in the modifications on the ends of the prisms which made the identity of the two somewhat doubtful; we accordingly analyzed the chloride made from the free base, with the following results:—

0.1853 gr. of the substance gave on combustion 0.2328 gr. of carbonic dioxide and 0.0678 gr. of water.

	Calculated for $C_8H_7BrN_2OHCl$.	Calculated for $C_8H_9BrN_2O_2HCl$.	Found.	Analyses of Original Chloride.	
Carbon	36.43	34.12	34.26	34.17	33.93
Hydrogen	3.04	3.55	4.06	4.93	4.03

There can be no doubt, therefore, of the identity of the two chlorides, and the first explanation must be abandoned.

The second explanation requires that the chloride should contain one molecule of water of crystallization. This point was tested by heating the chloride with the following result:—

0.2517 gr. of the chloride heated for 6 hours at first at 110°, later to 135°, lost 0.0024 gr.

	Calculated for $C_8H_7BrN_2OHClH_2O$.	Found.
Water	6.42	0.95

From this it appears that, if the chloride contains water of crystallization, it does not lose it at 135°. The slight loss of only 2.4 mgrs. could be sufficiently accounted for by the decomposition of the salt, which had turned dark gray on the surface, and for this reason too the heating could not be repeated at a higher temperature.

This result, unfavorable to the second explanation, necessitates the discussion of the third,—that the free base is bromdiamidophenylacetic acid,—which otherwise we should not have thought worthy of consideration. As has been already stated, the analyses of the free base do not agree with this explanation, and in order to adopt it we must assume that the substance had undergone a decomposition sufficient to raise the carbon 2.58 per cent, an assumption improbable in itself, and not supported by the appearance of the preparation, which had only a slight dirty pink color. This we think is enough to condemn this third explanation, but we add the following considerations, all of which tell strongly in favor of the second, and against the third explanation. (1.) Gabriel and R. Meyer* by the reduction of dinitrophenylacetic acid with tin and hydrochloric acid obtained the paramidooxindol direct, and it does not seem possible that our bromdiamidophenylacetic acid, which differs from theirs only in containing an atom of bromine, should be so much more stable. (2.) Our free base agrees fairly well in properties with the paramidooxindol of Gabriel and R. Meyer. Both are easily oxidized, soluble in hot water or in alcohol, slightly soluble in benzol or carbonic disulphide, the only difference being that our base is nearly insoluble in ether, whereas theirs is soluble in it. The melting points also stand about where we should expect, amidooxindol about 200°, our bromamidooxindol about 212°; in both cases there was so much blackening that the melting point could not be accurately determined. (3.) Our base (or its chloride) gives the indol reaction, turning a piece of pine wood red if boiled with it and dilute sulphuric acid, or if the wood, after being saturated with a solution of the base, is soaked in strong hydrochloric acid. This seems to us conclusive. The color is rather dull, and appears only after some time; but the objection which might be urged against this argument on this account, that the bromdiamidophenylacetic acid was converted into the bromamidooxindol by treatment with the acids, has no weight, as in the preparation of the original chloride it was most thoroughly exposed to the action of strong hydrochloric acid, both hot and cold; and yet this chloride, as we have shown by the analyses, contained two atoms of hydrogen and one of oxygen more than is required by the chloride of the bromamidooxindol.

These arguments seem to us to prove conclusively that the two substances are bromamidooxindol $C_6H_2BrNH_2(CH_2CONH)$, and its chloride $C_6H_2BrNH_2(CH_2CONH)HCl \cdot H_2O$, in spite of the fact that we could not drive off the water of crystallization from the chloride even at 135°.

Properties of Bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$.

As precipitated from its chloride it forms a heavy flocculent white precipitate, which, when examined with the microscope, is seen to be

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* Ber. d. ch. G., xiv. 832.

a felt of small white needles, often arranged in fagots or groups like an hour-glass; it is not very stable, changing to a dirty pink on exposure to the air, even when dry. The substance analyzed melted at 212° with a good deal of blackening, but we do not place much reliance on this melting point, as the sample used was a good deal colored. It is almost insoluble in cold, soluble in hot water; soluble in hot alcohol; insoluble or nearly so in ether or chloroform; not freely soluble in benzol or carbonic disulphide, even when hot; freely soluble in hot glacial acetic acid. Sodic hydrate dissolves it, giving a pinkish or pale magenta solution; ammonic hydrate at first seems to have no action, but on standing the liquid and solid turn dark bluish green; potassic carbonate in aqueous solution does not dissolve it. It seems therefore to have the properties of a phenol. Neither picric acid in benzol solution, nor ferric chloride with an alcoholic solution of the base, produced any change of color. If some of the free base was boiled with dilute sulphuric acid and a piece of pine, the wood was turned a dull orange-red.

As to the constitution of this base, it has been determined by work* done in this laboratory on the bromdinitrophenylmalonic ester that the nitro group, from which the amido group is formed, is in the para position to the carbon side chain. The bromine is probably in the ortho position, since all our work with the tetrabromdinitrobenzol has shown that only three of its atoms of bromine can be replaced easily; and, as the compounds made from this substance are so closely analogous to those prepared from the tribromdinitrobenzol, it is fair to infer that the three symmetrical (meta) atoms of bromine are those which can be removed, and that the fourth more stable atom of bromine is the one in the unsymmetrical (ortho) position; the atom of bromine, therefore, which reduction takes away from the dibromdinitrophenylmalonic ester, would be that in the meta position, and the base would be accordingly *orthobromparamidooxindol.*

Properties of the Chloride of Bromamidooxindol,
$C_6H_2BrNH_2(CH_2CONH)HClH_2O$.

When crystallized from water, the substance forms needles, or prisms, sometimes as much as a centimeter long and a millimeter thick, which seem to belong to the monoclinic system, and usually have a yellowish color; we think, however, that this color is due to partial oxidation, and that the substance is white when pure. When

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* These Proceedings, xxiv. 249, 250.

examined with the microscope, the prisms are found to be arranged in globular radiating groups, and are terminated usually by a single rhombic plane at a not very oblique angle to the long sides of the prism; sometimes a number of other modifying planes are observed, giving a sharp end to the prism. From alcohol it crystallizes in branching needles set at a very acute angle to each other. It melts only at a very high temperature, probably above the range of the mercury thermometer. It is slightly soluble in cold water, freely in hot; soluble in alcohol; slightly soluble in cold benzol, chloroform, or glacial acetic acid, freely soluble in these solvents, when hot; almost insoluble in ether; very soluble in carbonic disulphide. The best solvent for the substance is boiling water. An excess of ammonic hydrate throws down from a concentrated solution a heavy precipitate of the free base, which is white, but the liquid turns dark green; potassic carbonate gives a similar precipitate, not soluble in an excess; sodic hydrate in small quantity gives a similar precipitate, but dissolves it when added in larger quantity, giving a reddish solution. It gives a dull orange-red indol reaction with pine wood.

XXIV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

GENERAL CONSIDERATIONS IN REGARD TO CERTAIN COMPOUNDS PREPARED FROM BROMNITROBENZOLS.

By C. Loring Jackson.

Presented May 28, 1889.

Several compounds derived from various bromnitrobenzols have been described recently by me in conjunction with other chemists in a number of papers * from this laboratory, but in the course of the work certain general observations were made in regard to them which could not conveniently be introduced in the separate papers, and are therefore collected here.

The Action of Sodium Malonic (or Acetacetic) Ester on certain Bromnitrobenzols.

The actions studied were the following: —

Sodium Malonic Ester on
  Tribromtrinitrobenzol, $C_6Br_3(NO_2)_3$, melting point 285°.
  Tribromdinitrobenzol, $C_6HBr_3(NO_2)_2$, melting point 192°.
  Tetrabromdinitrobenzol, $C_6Br_4(NO_2)_2$, melting point 227°.
Sodium Acetacetic Ester on
  Tribromdinitrobenzol, $C_6HBr_3(NO_2)_2$, melting point 192°.

In all these cases the action was essentially the same, and may be represented by the following reactions for tribromtrinitrobenzol: —

I. $C_6Br_3(NO_2)_3 + CHNa(COOC_2H_5)_2 =$
$NaBr + C_6Br_2(NO_2)_3CH(COOC_2H_5)_2.$

II. $C_6Br_2(NO_2)_3CH(COOC_2H_5)_2 + CHNa(COOC_2H_5)_2 =$
$C_6Br_2(NO_2)_3CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2.$

III. $C_6Br_2(NO_2)_3CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 =$
$C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2.$

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* These Proceedings, xxiii. 138; xxiv. 1, 105, 234, 256, 271, 288.

The formation of brommalonic ester in III., the only point in these reactions about which there was any doubt, was proved by the isolation of acetylentetracarbonic ester[*] or of tartronic acid[†] from the oily secondary product, as these substances could hardly have been formed otherwise than by the following reactions, —

$$CHBr(COOC_2H_5)_2 + CHNa(COOC_2H_5)_2 =$$
$$CHCH(COOC_2H_5)_4 + NaBr.$$
$$CHBr(COOC_2H_5)_2 + NaOH = CHOH(COOC_2H_5)_2 + NaBr.$$

Reactions I.–III. are given because they show more clearly what has taken place, but the discussion which follows does not depend on them alone, since the analyses of the products are sufficient to prove that in all the cases studied the action has consisted in the replacement of one atom of bromine by the malonic ester radical, and of the second by hydrogen, while the third (and fourth) has remained unaltered.[‡] This difference in the behavior of the three atoms of bromine is certainly very curious, and, so far as I can find, no case analogous to it has been described as yet. The strangeness of the replacement of bromine by hydrogen becomes especially evident when it is remembered that in every case there was a large excess of sodium malonic ester present, and that this second atom of bromine has therefore combined with the carbon of malonic ester (see Reaction III.) in preference to the sodium of sodium malonic ester, so that the tendency to introduce hydrogen rather than the malonic ester radical has been strong enough in this case to overcome the attraction of the bromine for the sodium, and to cause it to combine with carbon instead.

I have not succeeded in finding any explanation of these curious observations which satisfies me, but hope to be led to one by further experiment. It can be stated at present, however, that the difference of behavior in the three bromine atoms is not due to differences in their position on the benzol ring. This is shown easily in the case of the tribromtrinitrobenzol, as here the three atoms of bromine occupy exactly similar positions, each being ortho to two nitro groups and para to the third. In the tribromdinitrobenzol,[§] also, the first and

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[*] These Proceedings, xxiv. 265.

[†] Ibid., xxiv. 238.

[‡] In the trinitro compound the third atom of bromine is replaced by the malonic ester radical to a limited extent even in the cold, but it is acted on much less easily than the first.

[§] In the tetrabromdinitrobenzol the fourth atom of bromine seems to have no influence on the reaction, and therefore all I say about the tribromdinitrobenzol also applies to this substance.

third atoms of bromine are similarly placed (ortho to one, para to the other nitro group), but the second (that replaced by hydrogen) is peculiar in being ortho to both nitro groups. It is evident, then, that in these reactions both similarly placed bromine atoms are not replaced by the malonic ester radical; but it is also to be observed that the bromine which is replaced by hydrogen has in every case stood in the ortho position to two nitro groups, and this suggested to me that perhaps an atom of bromine in this position might be especially susceptible to the action of free malonic ester. To test this hypothesis I mixed some tribromdinitrobenzol dissolved in benzol with malonic ester, and, after the mixture had stood for some time in the cold, warmed it for about an hour on the water bath, but even after this treatment no action * had taken place, as the tribromdinitrobenzol melted unaltered at 192°. This result was confirmed by a similar experiment with acetacetic ester, which stood with tribromdinitrobenzol for six months without any action. It is evident, therefore, that this atom of bromine is not attached in an especially loose way to the molecule, and that its replacement by hydrogen does not depend only on its position with reference to the nitro groups, but is due also to the presence of the malonic ester radical.

On the Relative Ease with which the Reactions take Place.

This subject will I hope prove susceptible of quantitative treatment, and I propose next year to try some experiments of this sort; I shall therefore at present confine myself to two qualitative observations, which were so marked that a quantitative confirmation of them seems unnecessary.

The tribromtrinitrobenzol is distinctly more reactive than the tribromdinitro- or tetrabromdinitrobenzol, as it acts on alcoholic ammonia in the cold, whereas the other two must be heated to 100° in sealed vessels to bring about this reaction.

The sodium acetacetic ester acts much less energetically than sodium malonic ester upon tribromdinitrobenzol, since the red color of the product appears instantaneously with the malonic ester, but only after some time with acetacetic ester, and the yield of the acetacetic compound is much smaller than that of the malonic derivative, if the reactions are carried on under the same conditions.

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* The addition of a little aqueous sodic hydrate was enough to cause action at once, as shown by the appearance of the red color of the sodium salt.

On the Acidity of the substituted Malonic Esters, Acetacetic Ester, and Ketones described in the preceding Papers.

In order to determine the relative acidity of these substances, their action with the following reagents was studied: acid sodic carbonate, sodic carbonate, ammonic hydrate, sodic hydrate. Each reagent was added in aqueous solution to the solid organic substance, and, after observing what took place, alcohol was added, and any change in the behavior of the substance noted. All these experiments were tried at the same time, great care being used to make the conditions as nearly the same as possible. The results can be divided into those which were perfectly definite, that is, where the differences consisted in the fact that one compound formed a salt with the reagent, and another did not; and those depending to a certain extent upon my judgment, in which the differences were only in the amount of salt formed, as shown by the depth of color, or in the quantity of alcohol necessary to produce the salt. The differences of the first class can be described most clearly and succinctly by the following table, in which the substances are arranged in the order of their acidity, beginning with the most acid. The columns correspond to the reagents, and the word "Salt" indicates that a salt was formed, as shown by the color imparted to the solution, or solid.

	$NaHCO_3$		Na_2CO_3		NH_4OH		$NaOH$	
	Aqueous.	With Alcohol.	Aqueous.	With Alcohol.	Aqueous.	With Alcohol.	Aqueous	With Alcohol.
I. $C_6H_2Br(NO_2)_2C_2H_3OCH_2CO_2C_2H_5$	Salt	Salt	Salt	Salt	Salt	Salt	Salt	Salt
II. $C_6HBr(NO_2)_3CH(CO_2C_2H_5)_2$	Salt	Salt	Salt	Salt	Salt	Salt	Salt	Salt
III. $C_6H_2Br(NO_2)_2CH(CO_2C_2H_5)_2$	..	Salt	Salt	Salt	Salt	Salt	Salt	Salt
IV. $C_6H_2Br(NO_2)_2CH_2COCH_3$	..	Salt	*	Salt	Salt	Salt	Salt	Salt
V. $C_6HBr_2(NO_2)_2CH(CO_2C_2H_5)_2$	..	Salt	Salt	Salt	Salt	Salt	Salt	Salt
VI. $C_6H_2C_6H_5NH(NO_2)_2CH(CO_2C_2H_5)_2$	..	Salt	..	Salt	..	Salt	..	Salt
VII. $C_6HBrC_6H_5NH(NO_2)_2CH(CO_2C_2H_5)_2$	..	..	..	Salt	..	Salt	..	Salt
VIII. $C_6H_2C_6H_5NH(NO_2)_2CH_2COCH_3$	..	..	..	Salt	..	..	..	Salt

* No salt was obtained from IV. with aqueous sodic carbonate, but I ascribe this to a mistaken observation, probably due to the difficulty in moistening the ketone with the aqueous solution.

The observations recorded in this table divide these substances into the following groups (indicated by the lines): — I. and II., most acid; III., IV., and V., less acid; VI., less acid; VII., less acid; VIII., least acid. The relative acidity of I. and II. was determined by data of the second sort mentioned above, since I. gave a much stronger coloration than II. with aqueous sodic carbonate, ammonic hydrate, or sodic hydrate. The order of III., IV., and V. was determined by the following observations. With acid sodic carbonate and dilute alcohol, III. and IV. gave a stronger red color than V. With aqueous sodic carbonate, III. gave a pale red, V. a much paler, in fact barely perceptible color. With aqueous ammonic hydrate, III. gave a pale red, V. a very pale barely perceptible red, and IV. stood between III. and V. in color. With aqueous sodic hydrate, the color was confined to the crystals of the organic substance, owing to the slight solubility of the salt in a solution of sodic hydrate, and III. turned dark red, IV. pale red, while V. showed a mixture of pale red particles of the salt and white ones of the ester. Upon adding alcohol to the mixture of the substance and either aqueous sodic carbonate or ammonic hydrate, a dark red color was obtained from all three, but much more alcohol was necessary to produce this color with V. than with III. or IV. My observations on the intensity of the color with different reagents confirm the order of compounds VI., VII., and VIII., but I do not think it worth while to give the details. I should add, also, to show that the personal equation did not enter to any great extent into these observations, that the substances during the experiments were arranged in an order different from that of their acidity, and that the order of acidity given above derived from these experiments was a surprise to me in many particulars.

These experimental results justify the following inferences in regard to the effect of differences in composition upon the acidity of these substances.

(*a.*) The introduction of an additional nitro group (in the ortho position) increases the acidity, since II. is more acid than III.

(*b.*) The replacement of hydrogen (in the ortho position) by bromine diminishes the acidity, since V. is less acid than III.

(*c.*) The replacement of bromine (in the meta position) by the aniline radical C_6H_5NH reduces the acidity very considerably, since III., IV., and V. are much more acid than VI., VIII., and VII. respectively.

In all these cases the differences occur in the benzol ring, and the effects are very marked (especially in *c*) when it is considered that the hydrogen affected is attached to the side chain, and therefore more removed from the influence of the acid radicals than in most of the similar cases previously described, in which the element influenced was attached to the benzol ring. These observations recall some made by me several years ago, when I showed* that the ring bromine in the three brombenzylbromides had a marked influence in diminishing the ease with which the side-chain bromine was removed, varying with its position on the benzol ring, the para bromine having less influence than the meta, the meta than the ortho.

(*d.*) The nature of the side-chain also has a marked influence on the acidity; thus the substituted acetacetic ester I. is much more acid than the corresponding malonic ester III., a result in harmony with Claisen and Ehrhardt's† classification of the radicals according to their acid-producing power, since they give the following list beginning with that which has the least influence, "phenyl, carboxyl, benzoyl, acetyl, formyl." An approximate measure of the relative acid-producing power of carboxyl and acetyl is given by the comparison of III. and IV., which possess nearly the same degree of acidity, and therefore it follows that one acetyl has nearly, although not quite, the same effect as two carboxyls.

(*e.*) The comparison of a dimalonic with the corresponding monomalonic compound in this respect is of interest. Unfortunately I had none of the trinitrophenylendimalonic ester when the comparison described above was made, so that this substance does not appear in the table; but by comparing the observations made on it when its properties were studied with those on the bromtrinitrophenylmalonic ester, I have found that the dimalonic compound is much less acid than the brommonomalonic ester, since acid sodic carbonate in aqueous solution has no action upon it, and even aqueous sodic carbonate gives only a very faint red color.‡ This weaker acidity can be accounted for by the hypothesis, that the influence of the three nitro groups being divided between two malonic ester radicals, each will have the acidifying influence of only one and a half nitro groups, instead of the three, which act on the acid hydrogen in the monomalonic compound.

The stability of the salts of all these compounds is remarkable, the

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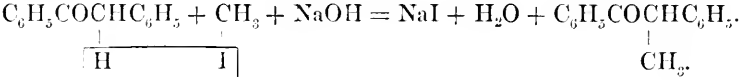
* These Proceedings, xvi. 241.

† Ber. d. ch. G. 1889, p. 1019.

‡ I should be inclined to place the trinitrophenylendimalonic ester between III. and V., although from the absence of comparative work its exact place cannot be determined with certainty; this, however, is of little importance, as the comparison of it with II. is the only one of especial interest.

sodium salt even of the anilidodinitrobenzylmethylketone (the least acid of all these substances) having been prepared and analyzed with no especial difficulty; it shows therefore a marked difference in this respect from desoxybenzoine ($C_6H_5COCH_2C_6H_5$), the sodium compound of which, according to Victor Meyer,* has not been isolated. In fact, he thinks it probable that it may not exist in the free state, and leaves it doubtful whether the syntheses of homologues of desoxybenzoine are preceded by the formation of a sodium compound, as with malonic or acetacetic ester, or whether the homologue is formed direct by the removal of hydrogen and the halogen by sodic hydrate, according to this reaction:



$$C_6H_5CO\underset{H}{\underset{|}{C}}HC_6H_5 + \underset{I}{\underset{|}{CH_3}} + NaOH = NaI + H_2O + C_6H_5CO\underset{CH_3.}{\underset{|}{C}}HC_6H_5.$$

The reason for this striking difference in acidity between the substituted benzylmethylketones and desoxybenzoine can hardly be due to the fact that the former contain the more active acetyl instead of the benzoyl contained in the latter, although this may have some influence, but in my opinion is rather to be ascribed to the heightening of the acid-producing power of the phenyl by the nitro groups which it contains. The salts of the acetacetic or malonic esters are much more stable than those of the ketones, as was to be expected, since in these cases the hydrogen is exposed to the acidifying power of three radicals (nitrophenyl and two carboxyls, or one carboxyl and an acetyl), and their stability almost equals that of the salts of Bischoff's † orthonitrobenzoylmalonic ester, in which the nitrophenyl of my compounds is replaced by the even more acid nitrobenzoyl.

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* Ber. d. ch. G 1888, p. 1291.

† Ann. Chem., ccli. 364.

XXV.

FEATURES OF CRYSTALLINE GROWTH.

By Oliver Whipple Huntington.

Presented June 12, 1889.

Variations in the Butcher Irons.

In a former paper * the author discussed in some detail the crystalline structure of iron meteorites, and in a second † described the cleavage exhibited by various specimens of the Coahuila group of irons, which are generally supposed to have come from the same original mass. It was then shown that in this group of irons the Butcher specimens differed so markedly from those of Saltillo (Santa Rosa) that the cleavage seemed to offer a conclusive means for separating the two falls, though the appearance of the etched surfaces failed to distinguish them.

As several very large individual masses of these irons are now in the Harvard Cabinet, under the general name of "The Butcher Irons," we were interested to see whether any peculiarity of structure would further distinguish them as independent meteorites, or whether on the contrary they could be identified as having unquestionably come from the same original body. A careful examination of the exterior of these irons showed that they had begun to break up since becoming the property of Harvard College, but this alteration had only taken place in certain parts of the specimens. The largest specimen seemed to have a zone running through the thickest part from which could be detached with little difficulty octahedral fragments of iron made up of distinct plates, showing a cleavage very similar to the well known Putnam County iron, while the rest of the mass was compact and unaltered. Thus certain parts of the Butcher specimens appeared to have an entirely different structure from what we are accustomed to associate with these irons. They have heretofore been known as typical "cubic irons," and, though it has been shown that all the twin

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* Proceedings of the American Academy, vol. xxi. p. 478, May, 1886.

† Ibid., vol. xxiv. p. 30, October, 1888.

members of the regular octahedron cube and dodecahedron appear on the surface of fracture, still the cube gives character to the iron, and, together with the etched surface, serves to connect it closely with the Braunau (Hauptmannsdorf) and other so called cubic irons.

In seeking to explain this apparent variation in the structure of the Butcher specimens, a number of large masses were polished and etched. The most striking result was obtained on a specimen which formed one end of a large mass originally cut up by Ward and Howell for the late J. Lawrence Smith. This surface as it appeared after etching is shown, one third the natural size, in Plate I., which was made directly from a photographic negative. The figure, although so much reduced, shows clearly a zone passing through the thickest part of the mass characterized by a very different crystallization from the rest of the piece. The greater portion of the etched surface is covered only with Neumann lines so characteristic of the Coahuila irons. These lines, although not well shown in the photograph, are plainly exhibited by the print from an etched plate previously published.* This last feature is characteristic of the outside of the mass, where the cooling must have been quicker and the crystallization more rapid and disturbed, though following, nevertheless, the fundamental forms of the regular system. In the central zone, however, corresponding to the thickest part of the specimen, the iron appears to have crystallized more slowly, and exhibits all the characters of Widmanstättian figures resulting from well marked crystal plates; and here the octahedron appears to predominate, though the presence or absence of the cube and dodecahedron cannot be established by the examination of only a single etched surface cut at random.

The etched surface of another portion of the same mass seemed to explain this contrast of coarse and fine grained crystallization. There is in the Harvard collection the largest slab ever cut from the Coahuila specimens, being a full section of the large mass which we have been discussing. The etched surface of this slab was fully as striking as that shown in Plate I., but exhibited more uniformity in the distribution of the figures. Unfortunately, the slab was too large to allow of its reproduction on paper within the limits of this publication, but the figures can be best described by their resemblance to the markings of frost on a large window-pane. Around the edge the crystals were so compact as to show no details, but these compact masses joined the inner portion on a curved outline, looking like cloud masses

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* Proceedings of the American Academy, vol. xxiii., Plate I.

which had floated in to the distance of from ten to one hundred millimeters from the crust, and on the inner edge of these cloudy portions the crystals became more distinct, and finally shot out in crystalline plates (which were seen of course only in section) some of them from fifty to one hundred millimeters in extent. These again were met and intersected by similar crystalline plates radiating from numerous centres through the mass, these centres being spots of more compact crystallization, like the cloudy masses around the edge, forming in the interior a network of plates producing skeleton crystals.

Thus the entire surface presented exactly the appearance that one might expect in a mass of iron which had slowly cooled. In such a mass, the surface cooling first would become compact, and exhibit only confused crystallization, while the interior, cooling more slowly, would allow time for isolated crystal plates to form; and at the same time local causes would start a simultaneous crystallization from other points in the interior, determined probably by the presence of nuclei of foreign matter.

The possible variation in the character of the figures brought out by etching different portions of the same iron, has been mentioned in a former paper,* but at that time no such striking example had been noticed as that now exhibited by the Coahuila irons. Specimens might be cut from the iron shown in Plate I. so selected that one piece when etched would give well marked Widmanstättian figures, with all the characteristic features which have commonly been associated with the so called typical octahedral irons, while another would show equally typical Neumann lines, and still a third piece would appear perfectly amorphous or made up of irregular grains.

Widmanstättian Figures on "Spiegel Eisen."

Hitherto Widmanstättian figures and Neumann lines have been considered the strongest characteristic of meteoric irons; but since it is merely the evidence of slow crystallization attended by the exclusion of foreign matter, one would expect that any impure iron, provided that it had cooled slowly from a state of fusion, would exhibit similar characters. From depending too much upon these features the Greenland iron was originally considered to be of meteoric origin, as some of the masses show very good Widmanstättian figures. Since specimens of cast iron have been frequently described as meteoric, and

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* Proceedings of the American Academy, vol. xxi. p. 478, May, 1886.

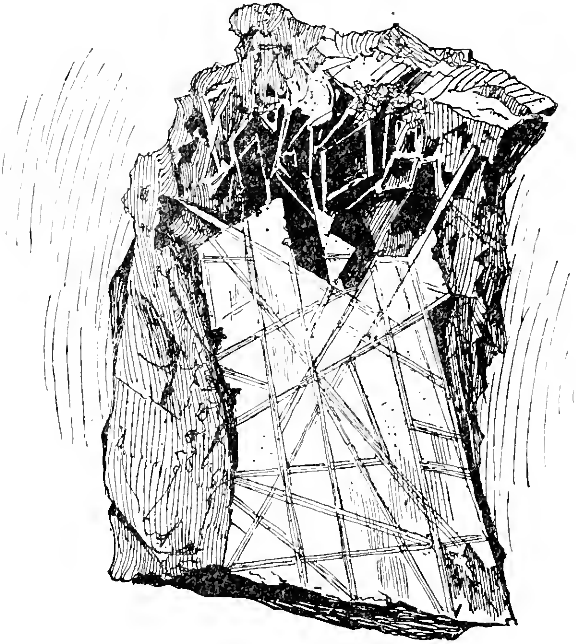

Fig. 1.

are to be found in all the large museums of the world. I was interested in examining specimens of "Spiegel Eisen," which contains so large an impurity of manganese, and is at the same time so strikingly crystalline. In the first place, the fracture somewhat resembles that of the Mexican irons which we have been discussing, as it shows cube faces, although the octahedron is dominant. Moreover, thin plates of "Spiegel Eisen" can in some cases be detached from the mass which would make it appear still more like meteoric iron, were it not for its great hardness. On a polished surface, however, the resemblance is far more striking, since etching or tempering brings out well defined Widmanstättian figures. These figures are shown of natural size in Figure 1, which is an exact sketch of the etched surface on a piece of this iron.

CRYSTALLINE PLATES IN GALENA.

In this connection it may be of interest to describe some specimens of galena which appeared among the minerals used for blowpipe analysis by the class in mineralogy at Harvard College, but whose origin is unknown.

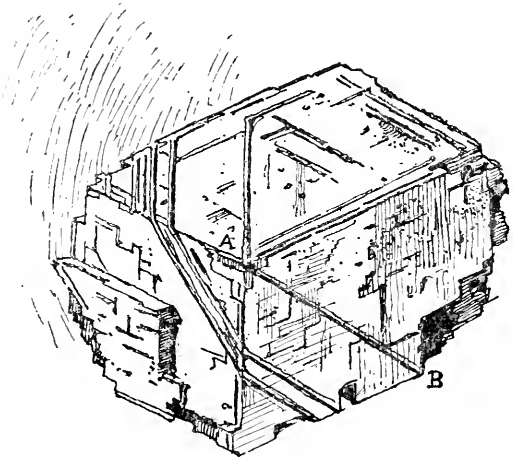

FIG. 2.

There were found three crystals very much alike, one of which is shown considerably enlarged in the accompanying sketch. On one side it showed the perfect cubic cleavage of ordinary galena, but the mass of the crystal consisted of a network of plates about 1 mm. thick, intersecting each other for the most part at right angles, and thus forming a skeleton cube. But that which makes the specimens of unusual interest is the fact that there are certain additional plates, following the direction of the faces of an octahedron, and thus running diagonally through the entire thickness of the crystals. Such a plate is shown at A B in the sketch (Fig. 2).

Moreover, the cleavage of the galena appeared to be due to some other cause than the form of the crystal, since the octahedral plates were as well marked and nearly as abundant as the cubic ones, while the cleavage was distinctly cubic. Thus it appears that when galena crystallizes, just as when iron crystallizes, plates form through the mass following the directions of both the cube and octahedron till the mass becomes solid, but that subsequently either cleavage may become so dominant as to wholly cover up all other crystalline structure.

Crystalline Concretions of Mica.

Some time ago I received from Dr. D. F. Lincoln of Boston some remarkable specimens of curved mica, one of which is shown of natural size in Figure 3. This crystal had its cleavage face very much curved, while the successive layers tapered back to an apex at the centre of curvature, the whole having the appearance of forming a portion of a sphere. The occurrence of these micas is very well described in a letter from Dr. Lincoln: —

Fig. 3.

"The specimens of mica were procured by me in 1885, from Mt. Apatite in Auburn, Maine. The rock of that locality resembles that

of Mt. Mica, being a granite, with all its components (quartz, orthoclase, clevelandite, muscovite, black tourmaline, etc.), in very large masses. At the eastern end of the ridge there are several places where a very pure quartz is quarried in immense quantities. The peculiar mica is found at one of these quarries at points on the border of the quartz deposit. The coarser and less well formed specimens are imbedded in quartz and feldspar ; the finer and well formed are usually enclosed in feldspar alone. One vertical face of the quarry presented a most interesting exposure. Here the mica stood out in bosses, or huge breasts, looking like broken spheres developed from numerous centres, and grouped very irregularly. The spherical surfaces, on analysis, consisted of groups of rhombic figures, each representing a crystal of mica, with curved cleavage and tapering to the centre of the sphere."

Thus it appears as if these crystals were the result of two distinct tendencies acting together, one concretionary, exerted to make the mass solidify from centres, and the other the crystallizing force, tending to form at the same time the rhombic prism of 60° and 120° so characteristic of the mineral.

XXVI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

I. ON CHLORPYROMUCIC ACIDS.*

By Henry B. Hill and Louis L. Jackson.

Presented May 28, 1889.

Many years ago Malaguti † found that dry chlorine gas was quickly absorbed by ethyl pyromucate, and that a thick viscous liquid was formed, the composition of which showed that four atoms of chlorine had been taken up. The oil was carbonized on distillation, and yielded with potassic hydrate decomposition products which were not further studied. Although Schmelz and Beilstein ‡ later found that chlorine converted pyromucic acid in aqueous solution into mucochloric acid, and this reaction was afterwards further studied by Hill and Bennett,§ no further experiments, as far as we could learn, had ever been made with dry chlorine on pyromucic acid or its ethers. In 1884, after it had been shown by investigations carried on in this laboratory that substitution products could readily be formed from pyromucic acid by the action of dry bromine, Mr. J. N. Garratt, at that time an assistant in the laboratory, undertook the investigation of the action of dry chlorine under similar conditions. Although he succeeded in isolating a dichlorpyromucic acid melting at 167–168° in a state of purity, he found that the reaction differed in many respects from the corresponding reaction with bromine, and that the matter deserved a more careful study than he was then able to bestow upon it. Mr. Garratt relinquished his investigation of this subject in order to continue his studies in Zurich, and in the following winter

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* A part of the work described in the following paper was presented in the form of a thesis to the Academic Council of Harvard University in May, 1888, by Louis L. Jackson, then candidate for the degree of Doctor of Philosophy.

† Ann. Chim. Phys., lxiv. 282; lxx. 371.

‡ Ann. Chem. u. Pharm., Suppl., iii. 276.

§ Berichte d. deutsch. chem. Gesellsch., xii. 655.

met with the fatal accident which so sadly ended his promising career.

The observations which already had been made interested us so much that in 1886 we undertook a more thorough study of the subject. We had already collected a great deal of material which we did not think it necessary to publish in a preliminary form, when Denaro * published in the Gazzetta Chimica a brief notice of a dichlorpyromucic acid melting at 167–168°, which was evidently identical with that prepared by Garratt. The paper contained a description of the acid and two of its salts, but the analyses of the latter did not agree with those which we had already obtained, and moreover contained such serious misprints or arithmetical errors, or both, as to be wholly without value. In consequence of the appearance of that paper, we thought it best to publish a preliminary account † of our work, so far as that one acid was concerned, more especially since our study of it was then essentially completed.

In repeating the experiments of Garratt, we had no difficulty in isolating the dichlorpyromucic acid which he had prepared, but we found that the reaction was still more complex than we had supposed. At ordinary temperatures chlorine was rapidly absorbed, but the pyromucic acid was soon so coated with the viscous addition product that a homogeneous product could not be obtained. On heating, the reaction could easily be pushed to the end, and the gain in weight closely corresponded with the addition of four atoms of chlorine. At the same time hydrochloric acid and carbonic dioxide were given off, and the resulting product contained a percentage of chlorine much larger than that demanded by any simple addition product. Under these circumstances it seemed advisable to return to the ethyl pyromucic tetrachloride of Malaguti, which, from his description and analyses, appeared to be homogeneous; and to take up the study of the more complex action of chlorine upon the acid itself after this investigation had made us better acquainted with some of the products likely to be formed. Although we were unable to prepare a perfectly homogeneous product by following the directions of Malaguti, we found no difficulty in so modifying the conditions that the resulting compound should give us pure $\beta\gamma$ dichlorpyromucic acid melting at 168–169°, δ chlorpyromucic acid melting at 176–177°, or trichlorpyromucic acid melting at 172–173°. The $\beta\delta$ dichlorpyromucic acid we were unable to prepare by direct substitution, or by saponification of ethyl pyromucic tetra-

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* Gazz. Chim., xvi. 333. † Berichte d. deutsch. chem. Gesellsch., xx. 252.

chloride; but by distillation of ethyl pyromucic tetrachloride, of the tetrachloride of pyromucyl chloride, or of ethyl δ chlorpyromucic tetrachloride, the βδ dichlorpyromucic acid melting at 155–156° may be obtained, and in the first two cases a third dichlorpyromucic acid melting at 197–198° is also formed. By careful reduction of the βδ or the βγ dichlorpyromucic acids, the β chlorpyromucic acid melting at 145–146° is formed.

Ethyl Pyromucic Tetrachloride.

The ethyl pyromucate which we have used in the course of our investigations we have made by warming a solution of pyromucic acid (3 parts) in absolute alcohol (5 parts) with concentrated sulphuric acid (3 parts acid, Sp. Gr. 1.84). After heating for four hours on the water bath, the mixture was allowed to cool, precipitated with water, and the ether washed with a dilute solution of sodic carbonate. The crude ether was then dried by exposure to the air and distilled. The yield of pure distilled ether which is thus obtained amounts to about 85 per cent of the weight of the acid taken. This is somewhat less than that which may be obtained by means of hydrochloric acid, but the method is much more expeditious and convenient.

When dry chlorine is passed over ethyl pyromucate we found that the ether was rapidly liquefied with the evolution of heat, and that the formation of the addition product proceeds as described by Malaguti until the ether has increased in weight very nearly the amount required by the addition of four atoms of chlorine. We soon found, however, that, no matter how carefully the chlorine was dried, hydrochloric acid escaped, showing the formation of a substitution product, and that the amount of hydrochloric acid formed depended largely upon the rapidity of the stream of chlorine and the consequent elevation of temperature. Even when the ether was carefully cooled to 0° during the whole of the treatment with chlorine, the formation of hydrochloric acid could not wholly be avoided. In this respect our experience agrees with that of Hill and Sanger,* who were unable to form the ethyl pyromucic tetrabromide without the simultaneous formation of substitution products. While the statements of Malaguti seemed to leave no room for doubt that the ethyl pyromucic tetrachloride was completely carbonized by heat, experiments made with bromine in this laboratory had shown that substitution products could readily be formed from the ethyl pyromucic tetrabromide by heat,

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* These Proceedings, xxi. 155.

and it seemed to us hardly conceivable that complete carbonization should ensue. A preliminary trial showed so much less charring under ordinary pressure than we had anticipated, that we were encouraged to hope that the ethyl pyromucic tetrachloride itself might be distilled under diminished pressure without essential decomposition. Ethyl pyromucate was therefore carefully treated with chlorine at 0° until it ceased to gain in weight. Hydrochloric acid was given off in small quantity, and the total gain in weight was 94 per cent of the weight of ethyl pyromucate taken, instead of the theoretical gain of 101 per cent. The product was then fractionally distilled under a pressure of 15 mm. and showed its complex nature by the wide range of its boiling point, 104–160°. Above 160° there remained a residue which even under 15 mm. pressure could not be distilled without decomposition.

None of the fractions showed any tendency to solidify in a freezing mixture. After several distillations, it became evident that the greater portion boiled without essential decomposition between 150–160°, and that a smaller portion boiled below 110°.

In order to determine the nature of the several products, the following analyses were made. Each fraction was collected under 15 mm. pressure.

A. Boiling point 104–110°; weight = 2.6 grm.

0.2235 grm. substance gave 0.2139 grm. AgCl.

	Calculated for $C_5H_2ClO_3C_2H_5$.	Found.
Cl	20.34	23.63

B. Boiling point 145–150°; weight = 3.2 grm.

0.2334 grm. substance gave 0.4418 grm. Ag. Cl.

C. Boiling point 152–153°; weight = 7.7 grm.

I. 0.1678 grm. substance gave 0.3431 grm. AgCl.

II. 0.1415 grm. substance gave 0.2889 grm. AgCl.

D. Boiling point 153–157°; weight = 12.0 grm.

0.1502 grm. substance gave 0.3094 grm. AgCl.

	Calculated for $C_5H_3O_3C_2H_5Cl_4$.	Found.			
		B.	C.		D.
			I.	II.	
Cl	50.36	46.77	50.55	50.49	50.97

From these analyses it was evident that the fraction C consisted of pure ethyl pyromucic tetrachloride; the fraction D contained a slight admixture of a product containing a higher percentage of chlorine; the fraction A approached in composition the ethyl chlorpyromucate; while the fraction B was a mixture. In order to be quite sure of the correctness of our conclusions, we treated these successive fractions with an alcoholic solution of sodic hydrate, and obtained acids in each case confirming the results of our analyses. From fraction A we obtained an acid crystallizing from hot water in irregular leafy plates which melted at 176–177°. The physical properties and melting point were sufficient to identify this acid as the δ chlorpyromucic acid later described, and to prove that the lower boiling fraction consisted chiefly of ethyl δ chlorpyromucate. Fraction C yielded us without difficulty, and in nearly theoretical quantity, an acid which when recrystallized twice from benzol melted sharply at 168–169°, and in other respects proved to be identical with the βγ dichlorpyromucic acid which we shall hereafter fully describe. The formation of this acid in nearly theoretical quantity and without recognizable admixture proves that the fraction C consisted of pure ethyl pyromucic tetrachloride. Fraction D yielded us a somewhat less pure βγ dichlorpyromucic acid, as did also fraction B. In the latter case, however, we were able to isolate a small quantity of a sparingly soluble acid, crystallizing from water in minute needles which closely resembled trichlorpyromucic acid. It was therefore evident that the main product formed by the action of chlorine at 0° upon ethyl pyromucate was the tetrachloride and this might be distilled under diminished pressure without essential decomposition. At the same time, it was shown that substitution was effected even in the cold, and that the product contained ethyl δ chlorpyromucate and very possibly its tetrachloride.

δ Chlorpyromucic Acid.

Since substitution had taken place at low temperatures, it seemed not unlikely that at 100° the substitution might be so rapid as to offer a convenient mode for the preparation of chlorpyromucic acids. Ethyl pyromucate when treated with bromine at 100° yields δ brompyromucic and βδ brompyromucic acids still more readily than pyromucic acid itself. We accordingly passed dry chlorine through ethyl pyromucate heated to 100°, but found that a higher temperature was necessary in order that substitution might promptly be effected. At 145° the action was sufficiently rapid, and the chlorine was passed through the melted ether at this temperature until a gain in weight was noted which corresponded to the substitution of one hydrogen atom by chlorine. The viscous liquid which was thus obtained was then slowly added to an excess of a concentrated alcoholic solution of sodic hydrate, care being taken to avoid any great elevation of temperature. When the action was completed the sparingly soluble sodium salt was removed by filtration and dried. The alcoholic filtrate contained small quantities of this sodium salt in solution, and contained further a small amount of some volatile furfuran compound. We converted the excess of sodic hydrate into carbonate with carbonic dioxide, removed the sodic carbonate by filtration, and distilled the alcoholic filtrate. The distillate when mixed with water threw down a minute quantity of a colorless oil of peculiar aromatic odor, which we have as yet been unable to identify through lack of material. The small amount of sodium salt obtained from the alcoholic mother liquors was then added to the main portion. The sodium salt when dissolved in water and acidified with hydrochloric acid then yielded the crude δ chlorpyromucic acid, which not infrequently needed no other purification than recrystallization from benzol. If, however, the treatment with chlorine had been too long continued, or the action had taken place at too low a temperature, the product contained dichlorpyromucic and trichlorpyromucic acids which could not be removed by simple recrystallization. Whenever the crude acid failed on trial to crystallize from hot water in shining irregular plates, it was necessary to resort to chemical means for its purification. The acid was suspended in twenty times its weight of cold water, ammonia added in slight excess, and then baric chloride in quantity sufficient to precipitate the sparingly soluble barium salts of the admixed acids. After the separation of these salts is complete, the filtered solution gives on acidification an acid which crystallizes from water in leafy plates, and which may further be purified by recrystallization from benzol. The yield of chlorpyromucic acid thus obtained amounts to about 40 per cent of the weight of ether taken, or 38 per cent of the theoretical amount.

I. 0.2761 grm. substance gave 0.4145 grm. CO_2 and 0.0494 grm. H_2O.
II. 0.2667 grm. substance gave 0.2642 grm. AgCl.
III. 0.2990 grm. substance gave 0.2950 grm. AgCl.

	Calculated for	Found.		
	$C_5H_3ClO_3$.	I.	II.	III.
C	40.96	40.94		
H	2.05	1.99		
Cl	24.23		24.49	24.39

The δ chlorpyromucic acid is readily soluble in hot water, sparingly in cold water, and crystallizes in large irregular leafy plates, which closely resemble the corresponding bromine derivative. It dissolves readily in alcohol, ether, or hot benzol, but sparingly in cold benzol. The acid recrystallized from benzol melted at 176–177°, and a preparation made from the pure ethyl ether melted at the same point. Its solubility in cold water was determined according to the method of V. Meyer. A weighed portion of the solution saturated at 19°.5 was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 37.8458 grm. solution saturated at 19°.5 gave 0.0833 grm. $BaSO_4$.
II. 33.5216 grm. solution saturated at 19°.5 gave 0.0742 grm. $BaSO_4$.

According to these determinations, the solution saturated at 19°.5 contained the following percentages of acid.

I.	II.
0.28	0.28

Baric δ Chlorpyromucate, $Ba(C_5H_2ClO_3)_2 . H_2O$. — The barium salt was prepared by boiling the acid with an excess of baric carbonate. The salt is quite readily soluble even in cold water, still more readily soluble in hot water, and separates from a hot concentrated solution in thin leafy plates, usually aggregated in globular form. The air-dried salt contains one molecule of water, which it loses rapidly at 100°.

I. 1.2193 grm. air-dried salt lost at 100° 0.0491 grm. H_2O.
II. 0.5932 grm. air-dried salt gave 0.3094 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_2ClO_3)_2 . H_2O$.	Found. I.	Found. II.
H_2O	4.04	4.04	
Ba	30.72		30.67

0.6909 grm. salt dried at 100° gave 0.3763 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_2ClO_3)_2$.	Found.
Ba	32.01	32.02

The solubility of the salt in cold water was determined according to the method of V. Meyer.

I. 9.3523 grm. solution saturated at 19°.5 gave 0.2932 grm. $BaSO_4$.
II. 8.3395 grm. solution saturated at 19°.5 gave 0.2534 grm. $BaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt.

I.	II.
5.76	5.58

Calcic δ Chlorpyromucate, $Ca(C_5H_2ClO_3)_2 . 3 H_2O$. — The calcium salt was prepared by boiling the acid with an excess of calcic carbonate. It is readily soluble in hot water, rather sparingly soluble in cold water, and separates from a hot concentrated solution in clustered prisms with rectangular terminations. The air-dried salt contains three molecules of water. It effloresces slowly over sulphuric acid, and loses all its water readily at 100°.

I. 1.0814 grm. air-dried salt lost at 100° 0.1480 grm. H_2O.
II. 1.2247 grm. air-dried salt lost at 100° 0.1689 grm. H_2O.

	Calculated for $Ca(C_5H_2ClO_3)_2 . 3 H_2O$.	Found. I.	Found. II.
H_2O	14.03	13.70	13.79

I. 0.6236 grm. salt dried at 100° gave 0.2564 grm. $CaSO_4$.
II. 0.5509 grm. salt dried at 100° gave 0.2244 grm. $CaSO_4$.

	Calculated for $Ca(C_5H_2ClO_3)_2$.	Found. I.	Found. II.
Ca	12.09	12.09	11.98

The solubility of the salt in cold water was determined according to the method of V. Meyer. The calcium was precipitated as oxalate, and the oxalate ignited with sulphuric acid.

I. 21.6494 grm. solution saturated at 19°.5 gave 0.1002 grm. $CaSO_4$.
II. 17.7467 grm. solution saturated at 19°.5 gave 0.0809 grm. $CaSO_4$.

The solution saturated at 19°.5 contained therefore the following percentages of anhydrous salt.

I.	II.
1.13	1.11

Potassic δ Chlorpyromucate, $KC_5H_2ClO_3$. — The potassium salt is readily soluble even in cold water, and separates from a hot concentrated solution on rapid cooling in fine branching needles; on slower cooling, in small thin oblique plates. The salt lost nothing in weight when dried at 120°, and analysis showed it to be anhydrous.

I. 0.6543 grm. salt dried at 120° gave 0.3100 grm. K_2SO_4.
II. 0.6390 grm. salt dried at 120° gave 0.3018 grm. K_2SO_4.

	Calculated for $KC_5H_2ClO_3$.	Found. I.	Found. II.
K	21.18	21.27	21.20

Argentic δ Chlorpyromucate, $AgC_5H_2ClO_3$. — The silver salt may best be prepared by precipitating a solution of the barium salt with argentic nitrate.

For analysis the precipitated salt was well washed, recrystallized from hot water, and dried *in vacuo* over sulphuric acid. It is sparingly soluble even in hot water, and separates from a hot concentrated solution in irregularly branching flattened needles.

I. 0.4843 grm. substance gave 0.2730 grm. AgCl.
II. 0.3948 grm. substance gave 0.2220 grm. AgCl.

	Calculated for $AgC_5H_2ClO_3$.	Found. I.	II.
Ag	42.60	42.44	42.34

Ethyl δ Chlorpyromucate, $C_5H_2ClO_3C_2H_5$. — The ethyl ether was prepared by heating at 100° a solution of 5 parts of δ chlorpyromucic acid in 10 parts of absolute alcohol, with the addition of 5 parts of concentrated sulphuric acid (Sp. Gr. 1.84).

After heating for three hours, the ether was precipitated by the addition of water, washed first with dilute sodic carbonate, then with water, and finally dried with calcic chloride. The ether is a colorless heavy oil boiling at 216–218° (column completely in vapor) under a pressure of 76.8 mm., solidifying at 1–2°, and melting at the same point.

I. 0.2740 grm. substance gave 0.2219 grm. AgCl.
II. 0.2918 grm. substance gave 0.2402 grm. AgCl.

	Calculated for $C_5H_2ClO_3C_2H_5$.	Found. I.	II.
Cl	20.34	20.02	20.35

δ *Chlorpyromucamide*, $C_5H_2ClO_2NH_2$. — δ chlorpyromucic ether is but slowly attacked by concentrated ammonia in the cold, and the amide may more readily be prepared from the acid chloride by means of solid ammonic carbonate. The amide is readily soluble in hot water, sparingly soluble in cold water and separates from a hot concentrated solution in fine branching needles, which melt at 154–155°.

For analysis, the amide was dried over sulphuric acid.

I. 0.1696 grm. substance gave 0.1677 grm. AgCl.
II. 0.2933 grm. substance gave 25.7 c.c. moist N at 25° and under a pressure of 764 mm.

	Calculated for $C_5H_2ClO_2NH_2$.	Found. I.	II.
Cl	24.40	24.44	
N	9.62		9.82

Preparation I. was made from the ether, and II. from the acid chloride.

There seemed no room for doubt that the chlorpyromucic acid thus formed by the direct replacement of hydrogen by chlorine, like the δ brompyromucic acid obtained in a similar way, contained its chlorine in the δ position. We considered it necessary, however, to establish this point by direct experiment.

Action of Bromine and Water.

Although the action of bromine on δ brompyromucic acid suspended in water varied greatly with the conditions, Hill and Sanger* found that, when the oxidation was carefully conducted, fumaric acid alone was formed. We therefore suspended the δ chlorpyromucic acid in about twenty-five times its weight of water, and passed in bromine vapor slowly with a current of air. The acid gradually dissolved, and but little more than two molecules of bromine were needed to complete the oxidation. After standing for some time in the cold, the solution was evaporated to a small volume, and the crystalline acid which appeared as the solution cooled recrystallized from hot water. In this way we obtained a white crystalline acid which contained neither chlorine nor bromine, which was sparingly soluble in cold water, more readily in hot water, and which remained unchanged when heated to 200°. Although the acid was thus sufficiently characterized as fumaric acid, we further analyzed its silver salt.

0.4943 grm. substance dried at 120° gave 0.5591 grm. AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found.
Ag	65.46	64.97

In the oxidation of the δ chlorpyromucic acid by bromine water, fumaric acid had therefore been formed according to the equation:

$$C_5H_3ClO_3 + 2\,Br_2 + 3\,H_2O = C_4H_4O_4 + CO_2 + 4\,HBr + HCl.$$

Action of Nitric Acid.

δ chlorpyromucic acid is not as readily attacked by nitric acid as the δ brompyromucic acid, and for its complete oxidation we found it necessary to heat one part of the acid with three parts of strong nitric acid (Sp. Gr. 1.42) diluted with twice its weight of water. After heating for three hours the oxidation was completed, and on evaporation fumaric acid was obtained, which was recognized by its sufficiently characteristic physical properties.

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* These Proceedings, xxi. 141.

β Chlorpyromucic Acid.

Hill and Sanger* found no difficulty in preparing β brompyromucic acid by the reduction of either of the two dibrompyromucic acids described by them. The corresponding dichlorpyromucic acids we found to be much more refractory, and we succeeded in preparing the β chlorpyromucic acid only after many unsuccessful attempts. The βγ dichlorpyromucic acid, which was the more accessible, proved to be the more difficult of reduction, so that almost the whole of the material for this investigation was made from the βδ dichlorpyromucic acid. When zinc dust is added to a cold ammoniacal solution of this acid, no perceptible reaction takes place, and even after long standing no essential change can be detected. Even when the ammoniacal solution is boiled with a large excess of zinc dust the reduction is but slowly effected, and long continued heating is necessary to complete the reaction. We have found it advantageous to dissolve the acid in about twenty times its weight of dilute ammonic hydrate, to add an equal weight of zinc dust, and to boil for eight or ten hours, taking care to keep the solution strongly ammoniacal. The filtered solution is then cooled and acidified with dilute sulphuric acid, the acid which separates removed by filtration, the filtrate extracted with ether, and the residue left upon the evaporation of the ether added to the main product. The crude acid thus obtained melted at about 130°, and evidently contained unaltered βδ dichlorpyromucic acid. We therefore dissolved it in dilute ammonic hydrate, and added to the ammoniacal solution calcic chloride as long as a sparingly soluble calcium salt was promptly precipitated. The filtered solution then gave, when acidified with hydrochloric acid, a crystalline acid, which after recrystallization from hot water melted at 145–146°, and proved upon analysis to be a chlorpyromucic acid. From the sparingly soluble calcium salt, which had been removed by filtration, we obtained only unaltered βδ dichlorpyromucic acid, which in its turn was treated with zinc dust. In this way we found it possible to obtain from the βδ dichlorpyromucic acid at least 80 per cent of the theoretical amount of pure β chlorpyromucic acid. Zinc dust, even after long boiling, seems to have but little action upon βγ dichlorpyromucic acid in ammoniacal solution, but sodium amalgam slowly reduces it at 100°. In order to effect complete reduction, it proved to be necessary to use a large excess of sodium in the form of a one per cent amalgam, and the reaction was then completed after heating for three hours on the water bath.

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* These Proceedings, xxi. 147.

The acid obtained by acidification melted at 145–146°, contained the percentage of chlorine required by a chlorpyromucic acid, and appeared to be in all respects identical with the acid obtained from the $\beta\delta$ dichlorpyromucic acid. While the yield of pure acid was in this case but 50 per cent of the theoretical amount, it is possible that it might be somewhat increased by further experiments. From the third isomeric dichlorpyromucic acid, subsequently described, we have as yet been able to obtain no definite reduction product.

The β chlorpyromucic acid dried over sulphuric acid gave on analysis the following results: —

I. 0.2710 grm. substance gave 0.4073 grm. CO_2 and 0.0513 grm. H_2O.
II. 0.1385 grm. substance gave 0.1355 grm. AgCl.
III. 0.1736 grm. substance gave 0.1692 grm. AgCl.

	Calculated for $C_5H_3ClO_3$.	Found. I.	II.	III.
C	40.96	40.99		
H	2.05	2.10		
Cl	24.23		24.18	24.10

Analysis III. was made with material prepared from the $\beta\gamma$ dichlorpyromucic acid.

β chlorpyromucic acid is readily soluble in hot water, sparingly soluble in cold water, and crystallizes from hot aqueous solution in thin irregular striated plates or flattened prisms. It is readily soluble in alcohol, ether, hot benzol or hot chloroform, and is but sparingly soluble in cold benzol or cold chloroform. When repeatedly crystallized from hot water it melted at 145–146°, and recrystallization from other solvents failed to raise this melting point.

In order to determine the solubility of the acid in cold water, a weighed quantity of a solution of the acid saturated at 19°.8 was boiled with baric carbonate, and the barium taken into solution precipitated as sulphate.

I. 31.6300 grm. solution saturated at 19°.8 gave 0.2019 grm. $BaSO_4$.
II. 34.0328 grm. solution saturated at 19.°8 gave 0.2176 grm. $BaSO_4$.

The solution saturated at 19°.8 therefore contained the following percentages of the acid: —

I.	II.
0.80	0.80

For the further characterization of the acid we prepared certain of its salts.

Baric β Chlorpyromucate, $Ba(C_5H_2ClO_3)_2 . H_2O$. — The barium salt was prepared by boiling a solution of the acid with an excess of baric carbonate. The filtered solution was evaporated, and the salt which separated on cooling recrystallized from hot water. It proved to be readily soluble in hot water, more sparingly soluble in cold water, and crystallized in long obliquely terminated prisms, which contained one molecule of water. The salt is permanent in the air or over sulphuric acid, but loses its water readily at 100°.

I. 0.6092 grm. of the air-dried salt gave 0.3180 grm. $BaSO_4$.
II. 1.3540 grm. of the air-dried salt lost at 100° 0.0576 grm. H_2O.

	Calculated for $Ba(C_5H_2ClO_3)_2 . H_2O$.	Found. I.	Found. II.
Ba	30.72	30.69	
H_2O	4.04		4.25

0.4749 grm. of the salt dried at 100° gave 0.2587 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_2ClO_3)_2$.	Found.
Ba	32.01	32.03

The solubility of the salt in cold water was determined in the usual way.

I. 10.2683 grm. solution saturated at 19°.1 gave 0.1149 grm. $BaSO_4$.
II. 6.8737 grm. solution saturated at 19°.1 gave 0.0747 grm. $BaSO_4$.

According to these determinations, the aqueous solution saturated at 19°.1 contained the following percentages of the anhydrous salt: —

I.	II.
2.06	2.00

Calcic β Chlorpyromucate, $Ca(C_5H_2ClO_3)_2 . 3\,H_2O$. — This salt was prepared by neutralizing with calcic carbonate a boiling solution of the acid. If the solution thus obtained is evaporated upon the water bath clustered, pointed prisms of an anhydrous salt are formed when the solution becomes highly concentrated. By evaporation *in vacuo* over sulphuric acid at ordinary temperatures, tufts of fine branching prisms are obtained which contain three molecules of water. The latter salt is permanent in the air, effloresces over sulphuric acid, and loses its water readily at 105°.

I. 0.4226 grm. of the air-dried salt gave 0.1490 grm. $CaSO_4$.
II. 1.3627 grm. of the air-dried salt lost at 105° 0.1902 grm. H_2O.

	Calculated for $Ca(C_5H_2ClO_3)_2 . 3\,H_2O$.	Found. I.	Found. II.
Ca	10.39	10.37	
H_2O	14.03		13.95

0.5160 grm. of the salt dried at 105° gave 0.2111 grm. $CaSO_4$.

	Calculated for $Ca(C_5H_2ClO_3)_2$.	Found.
Ca	12.09	12.03

The pointed prisms obtained by evaporating the solution at 100° gave the following results.

0.4433 grm. of the air-dried salt gave 0.1796 grm. $CaSO_4$.

	Calculated for $Ca(C_5H_2ClO_3)_2$.	Found.
Ca	12.09	11.92

The solubility of the calcium salt in cold water was determined in the usual manner. The calcium was precipitated as oxalate, and converted into the sulphate before weighing.

I. 5.0960 grm. solution saturated at 19°.5 gave 0.0653 grm. $CaSO_4$.
II. 5.8981 grm. solution saturated at 19°.5 gave 0.0752 grm. $CaSO_4$.

According to these determinations, the aqueous solution saturated at 19°.5 contained the following percentages of the anhydrous salt: —

I.	II.
3.12	3.10

Ethyl β Chlorpyromucate, $C_5H_2ClO_3 . C_2H_5$. — The ethyl ether was prepared by heating at 100° for four hours a mixture of 2 parts of the acid, 3 parts of absolute alcohol, and 2 parts of sulphuric acid (Sp. Gr. 1.84). On dilution with water the ether separated as an oil, which was thoroughly washed and dried over calcic chloride. It then distilled without essential decomposition at 217° (mercury column completely in vapor) under a pressure of 764 mm. The liquid distillate solidified on cooling, with the formation of concentrically grouped prisms, which, after repeated recrystallization by cooling the melted ether, showed the constant melting point of 29–30°.

0.1864 grm. of substance gave 0.1523 grm. AgCl.

	Calculated for $C_5H_2ClO_3 . C_2H_5$.	Found.
Cl	20.34	20.19

Action of Nitric Acid.

β chlorpyromucic acid is readily attacked by dilute nitric acid, but the oxidation is not smoothly effected, and the yield of chlorfumaric acid is comparatively small. The best results were obtained when the acid was boiled with 2 parts of nitric acid (Sp. Gr. 1.42) diluted with

5 parts of water. After the lapse of two hours, the action appeared to be completed, although a few drops of oil were still suspended in the clear solution. The products of the reaction were then extracted from the diluted solution with ether, the residue obtained by the evaporation of the ether pressed thoroughly with filter-paper and dried at 100°. The dry residue was then repeatedly washed with benzol in which chlorfumaric acid is but sparingly soluble. The product thus obtained was readily soluble in water, almost insoluble in benzol, melted at 188°, and contained the percentage of chlorine required by chlorfumaric acid.*

0.1089 grm. substance dried over H_2SO_4 gave 0.1027 grm. AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.31

The reaction may therefore be represented, in part at least, by the equation

$$C_5H_3ClO_3 + 3\,O = C_4H_3ClO_4 + CO_2.$$

Action of Bromine and Water.

Since β brompyromucic acid in aqueous solution is readily converted by an excess of bromine into mucobromic acid,† it seemed to us of interest to study the behavior of the β chlorpyromucic acid under the same conditions, since a product containing bromine and chlorine might then be formed. The acid was therefore suspended in five times its weight of water, and an excess of bromine at once added. After heating for a short time a clear nearly colorless solution was obtained, which was concentrated by evaporation on the water bath. On cooling, the solution deposited a crystalline acid which was readily soluble in hot water or hot benzol, and but sparingly soluble in these solvents in the cold. The acid recrystallized from water formed thin rhombic plates which melted at 120–121°, but this melting point could easily be raised to 121–122° by recrystallization from benzol.

An analysis of the substance dried over sulphuric acid showed that it was the mucochlorbromic acid whose formation we had been led to expect.

0.2871 grm. substance gave 0.4486 grm. AgCl + AgBr.

	Calculated for $C_4H_2BrClO_3$.	Found.
Br + Cl	54.11	54.45

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* Kauder (Journ. f. prakt. Chem., [2], xxxi. 28) gives the melting point of chlorfumaric acid as 191°.

† These Proceedings, xxi. 152.

The reaction was then precisely analogous to that by means of which mucobromic acid was formed from β brompyromucic acid:

$$C_5H_3ClO_3 + 3\ Br_2 + 2\ H_2O = C_4H_2BrClO_3 + Co_2 + 5\ HBr.$$

With the material which for the moment was at our disposal, we were unable to study the decomposition of the mucochlorbromic acid by alkalies. We shall hope in the future to prepare in this way a chlorbromacrylic acid, and compare it with the acid of the same composition already described by Mabery and Loyd.*

$\beta\gamma$ DICHLORPYROMUCIC ACID.

Hill and Sanger † had shown that in the decomposition of pyromucic tetrabromide or of ethyl pyromucic tetrabromide by alcoholic sodic hydrate, two isomeric dibrompyromucic acids are formed in not widely unequal quantities. There was, therefore, every reason to expect that two isomeric dichlorpyromucic acids could be found in the product formed in a similar way from ethyl pyromucic tetrachloride. Since we had found that a low temperature was essential to the preparation of a pure product, we allowed the ethyl pyromucate to absorb chlorine at 0° until a constant weight was reached, expelled the excess of chlorine by a current of dry air, and decomposed the product at once with an excess of an alcoholic solution of sodic hydrate. The best results were obtained when the tetrachloride was slowly added to a concentrated sodic hydrate solution, taking care to keep the mixture cold.

The sodium salts formed are sparingly soluble in alcohol, and after a short time can be removed by filtration. The alcoholic solution was freed from the excess of sodic hydrate by means of carbonic dioxide, and, after removing the sodic carbonate by filtration, distilled. The sodium salts left on distillation appeared to be identical with those already obtained and were therefore added to the main portion. The alcoholic distillate grew turbid when mixed with water, and gradually deposited a small quantity of a colorless oil which had a peculiar aromatic odor. The quantity of this oil was so small that no investigation of it has as yet been made.

The sodium salt which was obtained from the tetrachloride was dried, dissolved in hot water, and acidified with hydrochloric acid. In this way an acid was obtained which crystallized in finely felted needles which usually melted at 155°. After two recrystallizations from benzol the acid melted at 168–169°, and further recrystalliza-

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* These Proceedings, xvi. 238.

† These Proceedings, xxi. 156.

tions failed to raise this melting point. Analysis showed this acid to be a dichlorpyromucic acid.

I. 0.4235 grm. substance gave 0.5135 grm. CO_2 and 0.0455 grm. H_2O.
II. 0.2332 grm. substance gave 0.3695 grm. AgCl.
III. 0.2195 grm. substance gave 0.3490 grm. AgCl.

	Calculated for $C_5H_2Cl_2O_3$.	Found. I.	II.	III.
C	33.15	33.07		
H	1.10	1.19		
Cl	39.22		39.16	39.31

The acid, which proved on subsequent investigation to be the $\beta\gamma$ dichlorpyromucic acid, is sparingly soluble in cold water, readily in hot, and crystallizes as the solution cools in finely felted needles. It is readily soluble in alcohol, ether, or in hot benzol; in cold benzol it is sparingly soluble and crystallizes from it in short prisms. In hot chloroform it is also readily soluble, sparingly soluble in the cold. The ready purification of this acid by recrystallization rendered it improbable that any sensible amount of an isomeric acid was formed with it. The most patient search has failed to show the formation of such a product in appreciable quantity, and from pure ethyl pyromucic tetrachloride almost pure $\beta\gamma$ dichlorpyromucic acid is obtained at once. The yield of pure acid ordinarily obtained from pyromucic ether is not wholly satisfactory, since it amounts to about 50 per cent of the weight of ether taken, or about 39 per cent of the theoretical amount.

The solubility of the acid in cold water we determined as usual. A weighed quantity of a solution of the acid saturated at 19.5° was boiled with baric carbonate and the barium dissolved precipitated by sulphuric acid.

I. 36.2505 grm. solution saturated at 19°.5 gave 0.0619 grm. $BaSO_4$.
II. 35.6546 grm. solution saturated at 19°.5 gave 0.0615 grm. $BaSO_4$.

According to these determinations, the solution saturated at 19°.5 contains the following percentages of acid: —

I.	II.
0.27	0.27

Baric $\beta\gamma$ Dichlorpyromucate, $Ba(C_5HCl_2O_3) . 3 H_2O$.* — The barium salt may be most conveniently prepared by precipitating a solution of the

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* We have already referred to the brief description of the $\beta\gamma$ dichlorpyromucic acid published by Denaro in the Gazzetta Chimica (xvi. 333), and have asserted that the analyses of the two salts which he describes are not worthy of confidence. In support of our assertion we append his results in full, together

ammonium salt with baric chloride. It is rather sparingly soluble even in hot water, and still less soluble in cold water. It separates from a hot concentrated solution in fine clustered needles which contain three molecules of water. The crystals are permanent in the air, but lose their water readily at 100°.

I. 1.2048 grm. air-dried salt lost at 100° 0.1170 grm. H_2O.
II. 1.2118 grm. air-dried salt lost at 100° 0.1132 grm. H_2O.
III. 0.5694 grm. air-dried salt gave 0.2393 grm. $BaSO_4$.
IV. 0.3783 grm. air-dried salt gave 0.1593 grm. $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2 . 3 H_2O$.	Found. I.	II.	III.	IV.
H_2O	9.80	9.71	9.34		
Ba	24.86			24.71	24.76

I. 0.4828 grm. salt dried at 100° gave 0.2250 grm. $BaSO_4$.
II. 0.5540 grm. salt dried at 100° gave 0.2579 grm. $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2$.	Found. I.	II.
Ba	27.56	27.40	27.36

The solubility of the salt in water at 19°.5 was determined according to the method of V. Meyer.

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with the analytical data upon which they depend. The errors in the calculated percentages are corrected in parenthesis.

Barium salt:

0.4480 grm. of the salt lost at 110° 0.00204 grm. H_2O.

	Calculated for $Ba(C_5HCl_2O_3)_2 . 3 H_2O$.	Found.
H_2O	9.80	8.30 (0.445)

0.1939 grm. of the dry salt gave 0.0769 grm. $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2$.	Found
Ba	23.54 (27.56)	23.32

Calcium salt:

0.6942 grm. of the salt lost at 110° 0.0300 grm. H_2O.

	Calculated for $Ca(C_5HCl_2O_3)_2 . 3\frac{1}{2} H_2O$.	Found.
H_2O	13.60	14.45 (4.32)

0.3024 grm. of the salt gave 0.1072 grm. $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2$.	Found.
Ca	10.00	10.42

These results can hardly be explained unless it is assumed that they contain both typographical and arithmetical errors. The two remaining analyses contained in Denaro's paper, two chlorine determinations in the free acid are correctly calculated, and agree well with the theory.

I. 23.0222 grm. solution saturated at 19°.5 gave 0.0503 grm. $BaSO_4$.
II. 22.4890 grm. solution saturated at 19°.5 gave 0.0487 grm. $BaSO_4$.

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt.

I.	II.
0.46	0.46

Calcic βγ Dichlorpyromucate, $Ca(C_5HCl_2O_3)_2 . 4 H_2O$. — The calcium salt was prepared by boiling a solution of the acid with an excess of calcic carbonate. It is readily soluble in hot water, less soluble in cold, and crystallizes from a hot concentrated solution in long clustered needles which contain four molecules of water.

The crystallized salt is permanent in the air, effloresces slowly over sulphuric acid, and loses all its water readily at 110°.

I. 2.7640 grm. air-dried salt lost at 110° 0.4160 grm. H_2O.
II. 3.1275 grm. air-dried salt lost at 113° 0.4707 grm. H_2O.

	Calculated for $Ca(C_5HCl_2O_3)_2 . 4 H_2O$.	Found.	
		I.	II.
H_2O	15.26	15.05	15.05

I. 0.6595 grm. salt dried at 110° gave 0.2227 grm. $CaSO_4$.
II. 0.7004 grm. salt dried at 113° gave 0.2366 grm. $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2$.	Found.	
		I.	II.
Ca	10.00	9.93	9.94

The solubility of the salt in water at 19.5° was determined as usual. The calcium was precipitated as oxalate and the oxalate ignited with sulphuric acid.

I. 22.8797 grm. solution saturated at 19°.5 gave 0.0944 grm. $CaSO_4$.
II. 21.5915 grm. solution saturated at 19°.5 gave 0.0891 grm. $CaSO_4$.

The solution saturated at 19°.5 therefore contained the following percentages of anhydrous salt:

I.	II.
1.21	1.21

Potassic βγ Dichlorpyromucate, $KC_5HCl_2O_3$. — The potassium salt is readily soluble in hot water, but rather sparingly soluble in cold water, and separates from a hot concentrated solution in small prisms which are anhydrous.

I. 0.6130 grm. substance dried at 120° gave 0.2435 grm. K_2SO_4.
II. 0.8200 grm. substance dried at 120° gave 0.3265 grm. K_2SO_4.

	Calculated for $KC_5HCl_2O_3$.	Found.	
		I.	II.
K	17.84	17.83	17.87

Argentic βγ Dichlorpyromucate, $AgC_5HCl_2O_3$. — If argentic nitrate is added to a cold aqueous solution of the acid, the silver salt is precipitated in the form of fine needles. For analysis we prepared the salt by precipitating a dilute neutral solution of the ammonium salt with argentic nitrate, and recrystallizing the precipitated salt from hot water. It is sparingly soluble even in hot water, and separates on cooling the hot saturated solution in fine needles.

I. 0.3230 grm. substance dried over H_2SO_4 gave 0.1612 grm. AgCl.
II. 0.2580 grm. substance dried over H_2SO_4 gave 0.1282 grm. AgCl.

	Calculated for $AgC_5HCl_2O_3$.	Found. I.	Found. II.
Ag	37.50	37.57	37.41

Ethyl βγ Dichlorpyromucate, $C_5HCl_2O_3C_2H_5$. — The ethyl ether was prepared by heating at 100° for three hours a mixture of 5 parts of acid, 8 parts of absolute alcohol, and 5 parts of concentrated sulphuric acid (Sp. Gr. 1.84). It was precipitated with water, washed with dilute sodic carbonate, and then with water. It is readily soluble in hot alcohol, more sparingly in cold, and crystallizes in large needles which melt at 63–64°.

I. 0.2645 grm. substance dried over H_2SO_4 gave 0.3640 grm. AgCl.
II. 0.1933 grm. substance dried over H_2SO_4 gave 0.2673 grm. AgCl.

	Calculated for $C_5HCl_2O_3C_2H_5$.	Found. I.	Found. II.
Cl	33.98	34.02	34.18

βγ Dichlorpyrmucamide, $C_5HCl_2O_2NH_2$. — The ethyl ether of βγ dichlorpyromucic acid is readily attacked by strong aqueous ammonia even in the cold, and in a short time is converted into the amide. The amide is sparingly soluble even in hot water, and crystallizes in long slender needles which melt at 176–177°.

0.4015 grm. substance dried over H_2SO_4 gave 28.5 c.c. moist N at 23° under a pressure of 767 mm.

	Calculated for $C_5HCl_2O_2NH_2$.	Found.
N	7.78	8.03

The formation of but one dichlorpyromucic acid in the decomposition of the ethyl pyromucic tetrachloride by alkalies, while two isomeric acids are always obtained under the same circumstances from the corresponding bromine compound, made it impossible to predict its constitution from the method of formation. Still, its comparatively high melting point, its physical properties, and the ready solubility of its calcium salt, in which it closely resembled the $\beta\gamma$ dibrompyromucic acid, gave fair ground for the conjecture that it had a similar structure. A study of its oxidation products showed that such was the case, since we easily obtained from it mucochloric and dichlormaleic acids.

Action of Bromine and Water.

If bromine is added to $\beta\gamma$ dichlorpyromucic acid suspended in six or eight times its weight of cold water, oxidation rapidly ensues, with the escape of carbonic dioxide. A slight excess of bromine was added, and the reaction completed by the aid of heat. On cooling, the solution solidified with the separation of colorless crystals, which when recrystallized from water and finally from benzol melted at 124–125°, and had the characteristic form of mucochloric acid. Analysis also gave the proper percentage of chlorine.

I. 0.2015 grm. substance dried over H_2SO_4 gave 0.3408 grm. AgCl.
II. 0.2320 grm. substance dried over H_2SO_4 gave 0.3922 grm. AgCl.

	Calculated for $C_4H_2Cl_2O_3$.	Found.	
		I.	II.
Cl	42.01	41.81	41.79

In this case the reaction may be represented by the equation

$$C_5H_2Cl_2O_3 + 2Br_2 + 2\,H_2O = C_4H_2Cl_2O_3 + CO_2 + 4\,HBr.$$

Action of Nitric Acid.

Nitric acid acts but slowly upon the $\beta\gamma$ dichlorpyromucic acid, and for its complete oxidation we have found it necessary to take for one part of the acid 3 parts of concentrated nitric acid (Sp. Gr. 1.42) diluted with twice its weight of water. After boiling for five hours the action appeared to be complete, and as the clear solution deposited nothing on cooling we extracted it with ether. The ether left upon evaporation a colorless crystalline mass, which proved to be a mixture of two substances, one readily soluble, the other but sparingly soluble in cold water. The sparingly soluble substance when recrystallized from hot water was recognized by its crystalline form and by its melting point, 124–125°, as mucochloric acid. The acid, which was readily soluble in cold water, was neutralized with baric carbonate, the barium salt precipitated from its aqueous solution by alcohol, and the acid liberated from this purified barium salt again extracted with ether. The crystalline acid left by the evaporation of the ether was then dissolved in a small amount of water, and on standing well formed rhombic plates separated which were dried over sulphuric acid for analysis.

0.2233 grm. substance gave 0.3433 grm. AgCl.

	Calculated for $C_4H_2Cl_2O_4$.	Found.
Cl	38.38	38.01

The identity of this acid with dichlormaleic acid was further determined by the melting point of the anhydride prepared by sublimation, which we found to be 119–120°, in agreement with the statement of Ciamician and Silber.*

The oxidation therefore took place in accordance with the following reactions,

$$C_5H_2Cl_2O_3 + 2\,O = C_4H_2Cl_2O_3 + CO_2,$$
$$C_5H_2Cl_2O_3 + 3\,O = C_4H_2Cl_2O_4 + CO_2,$$

and the dichlorpyromucic acid in question is thus conclusively shown to have its chlorine atoms in the β and γ positions.

Preparation of Isomeric Dichlorpyromucic Acids.

Although we had been unable to find the $\beta\delta$ dichlorpyromucic acid among the products formed by the action of alkalies upon ethyl pyromucic tetrachloride, it seemed to us probable that it might be formed under the proper conditions by the direct action of chlorine upon ethyl pyromucate, or by the decomposition of its tetrachloride by heat alone.

Tönnies † had already shown that δ brompyromucic acid could be formed by heating pyromucic tetrabromide, and Hill and Sanger ‡ had further shown that δ brompyromucic acid and $\beta\delta$ dibrompyromucic acid could conveniently be made by the action of bromine upon pyromucic acid at high temperature. As subsequent experiments in this laboratory had shown that these two acids could more advantageously be made by substituting the ethyl ether for the acid, and our own experiments had shown that the δ chlorpyromucic acid could readily be made in this way, we proceeded to study the action of chlorine upon ethyl pyromucate at high temperature. It seems hardly necessary to describe in detail the numerous experiments which we made under widely varying conditions, each one of which yielded us purely negative results. Ethyl pyromucate was treated with chlorine at

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* Berichte d. deutsch. chem. Gesellsch., xvi. 2396.

† Ibid., xi. 1088.

‡ These Proceedings, xxi. 136, 160.

temperatures ranging from 145° to its boiling point, both by itself and after the addition of iodine or aluminic chloride, but in no case was the desired product obtained. Pyromucic acid and δ chlorpyromucic acid also failed to give such a product when treated at high temperatures with chlorine, and we were equally unsuccessful when we used the chloranhydrides of these acids either with or without an excess of phosphoric pentachloride. We then studied the action of heat upon the tetrachloride of pyromucic acid itself, of its chloranhydride and ethyl ether, and of the ethyl ether of δ chlorpyromucic acid, and found in each case that small quantities of a dichlorpyromucic acid were formed which closely resembled the βδ dibrompyromucic. A more careful investigation further proved that in the decomposition of the ethyl pyromucic tetrachloride a second new dichlorpyromucic acid was formed concerning whose constitution we are not yet able to speak definitely. This acid we propose to call the χ dichlorpyromucic acid until its structure is established. The amount of the dichlorpyromucic acids which we have been able to obtain is but small, and we have made many unsuccessful attempts to increase the yield by varying the temperature or the mode of heating, or by adding iodine, or aluminic or ferric chloride, before heating.

We first obtained the βδ dichlorpyromucic acid by distilling under ordinary pressure the product formed by treating pyromucic acid with chlorine at 100°. Hydrochloric acid is given off in quantity, and, although a large carbonaceous residue is left in the retort, a liquid distillate is obtained which, after repeated distillation through a Hempel's column, amounts to about 85 per cent of the weight of the pyromucic acid taken and then distils leaving but an insignificant carbonaceous residue. This distillate is extremely complex in its nature and we have as yet made no thorough study of its constituents. We found, however, that the portions which boiled between 196° and 220° gave considerable quantities of βδ dichlorpyromucic acid when treated with cold water. They therefore contained the corresponding chloranhydride of the acid. The yield thus obtained amounted to but about 4 per cent of the pyromucic acid taken. From ethyl pyromucic tetrachloride we succeeded in obtaining a somewhat better yield. We found it advantageous to purify the tetrachloride by one distillation *in vacuo,* and to distil the product thus obtained under ordinary pressure. More or less carbonization ensued, and on fractional distillation *in vacuo* through a Hempel's column * the distillate

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* For fractional distillation under diminished pressure we used the extremely convenient apparatus of Anschütz. We found that the ease of separation could

was found to contain considerable unaltered tetrachloride. That portion which boiled above 140° under 16 mm. pressure was therefore redistilled under ordinary pressure and the distillate again fractioned *in vacuo*. After repeated distillations we found that the portion which boiled between 118° and 123° under 16 mm. pressure partially solidified on cooling, and that a few crystals were also formed in the next lower fraction. These fractions were therefore strongly cooled and the crystalline solid removed by filtration and the liquid portions further distilled. The solid thus obtained proved to be the ethyl ether of the new χ dichlorpyromucic acid melting at 197–198°, which we shall presently describe. When no more of this crystalline ether could be obtained by cooling, the liquid fractions were saponified by alcoholic sodic hydrate, the acids liberated by hydrochloric acid and separated through their calcium and barium salts. From the fraction boiling below 110° (16 mm.) we obtained chiefly δ chlorpyromucic acid melting at 176–177°, although it yielded also a small quantity of $\beta\delta$ dichlorpyromucic acid, which was readily isolated by means of its sparingly soluble barium salt. The fractions 110–118° and 118–123° apparently consisted chiefly of the ethyl ether of $\beta\delta$ dichlorpyromucic acid, but the latter necessarily contained also a small amount of the crystalline ethyl χ dichlorpyromucate held in solution. The two dichlorpyromucic acids could readily be separated through the different solubilities of their calcium salts, the calcic $\beta\delta$ dichlorpyromucate like the calcium salt of the corresponding bromine derivative being very sparingly soluble in water. From 123° to 130° but an insignificant fraction was collected and the fraction 130°–153° consisted in part at least of unaltered ethyl pyromucic tetrachloride, from which $\beta\gamma$ dichlorpyromucic acid was obtained.

100 grm. of ethyl pyromucate yielded us 197 grm. of the tetrachloride and from this we obtained the following weights of pure products:

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be materially increased by filling a few inches of the stem of the distilling flask with glass beads, and thus combining the Hempel's column with the vacuum distillation. The beads were supported upon a perforated disk of platinum foil slipped over the capillary air tube and held in place by a slight enlargement of the tube. The thermometer was then raised to the proper line by a short bit of small glass tubing dropped into the air tube. Hantzsch (Ann. Chem. u. Pharm., ccxlix. 57) has used with advantage for distillation under ordinary pressure a long necked boiling flask whose stem is partially filled with beads supported upon a platinum foil forced into the neck. We have for a long time used such a Hempel's column, but have supported the beads conveniently upon a glass bulb which nearly fills the stem and whose sealed neck is long enough to rest upon the bottom of the flask.

5.0 grm. δ chlorpyromucic acid.
12.2 grm. βδ dichlorpyromucic acid.
2.7 grm. χ dichlorpyromucic acid.
16.1 grm. ethyl χ dichlorpyromucate.

If pyromucyl chloride is treated with chlorine at 0°, the chlorine is absorbed very slowly, but the gain in weight finally approximately corresponds with that required for the formation of a tetrachloride. If the tetrachloride is distilled under ordinary pressure, only an inconsiderable carbonaceous residue is left in the retort, and after repeated distillations through a Hempel's column under ordinary pressure a product is obtained which, when treated with water, yields the βδ dichlorpyromucic acid and the χ dichlorpyromucic acid. While the yield of the βδ dichlorpyromucic acid thus obtained is somewhat greater than that obtained from the ethyl pyromucic tetrachloride, the yield of the χ dichlorpyromucic acid is much smaller.

By treating ethyl δ chlorpyromucate in the cold with chlorine, and distilling the addition product thus formed under ordinary pressure, we also obtained the βδ dichlorpyromucic acid. While the yield was somewhat larger than that obtained from the ethyl pyromucic tetrachloride, it did not repay us for the loss of time and material involved in making the δ chlorpyromucic acid. Moreover, to our surprise, we could obtain in this way none of the crystalline ethyl χ dichlorpyromucate.

βδ DICHLORPYROMUCIC ACID.

The acid whose preparation has just been described can most readily be purified by repeated precipitation from ammoniacal solution with calcic chloride, and recrystallization from chloroform. The acid thus purified gave on analysis the following results:

I. 0.2577 grm. substance gave 0.3129 grm. CO_2 and 0.0259 grm. H_2O.
II. 0.1933 grm. substance gave 0.3053 grm. AgCl.

	Calculated for $C_5H_2ClO_3$.	Found. I.	II.
C	33.15	33.11	
H	1.10	1.12	
Cl	39.22		39.04

βδ dichlorpyromucic acid is readily soluble in ether or alcohol. It dissolves readily in hot water, benzol, or chloroform, and the greater part of the acid is in each case deposited on cooling in oblique prisms, which are frequently twinned in forms which can hardly be distinguished from those of the $\beta\delta$ dibrompyromucic acid. The acid melts sharply at 155–156°, and sublimes unaltered at a higher temperature.

The solubility of the acid in water at 19°.5 was determined in the usual manner. A weighed quantity of a solution of the acid saturated at 19°.5 was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid:

I. 42.8007 grm. solution saturated at 19°.5 gave 0.0724 grm. $BaSO_4$.
II. 51.4109 grm. solution saturated at 19°.5 gave 0.0907 grm. $BaSO_4$.

According to these determinations, the solution saturated at 19°.5 contained the following percentages of acid:

I.	II.
0.26	0.27

Baric $\beta\delta$ Dichlorpyromucate, $Ba(C_5HCl_2O_3)_2 . 4 H_2O$. — The barium salt was prepared by precipitating a dilute solution of the ammonium salt with baric chloride, and recrystallizing the product thus obtained from water. The salt is sparingly soluble in hot water, still less soluble in cold water, and crystallizes from a hot concentrated solution in long irregular flat prisms which contain four molecules of water.

The salt is permanent in the air, effloresces over sulphuric acid, and loses its water readily at 100°.

I. 1.4513 grm. air-dried salt lost at 100° 0.1795 grm. H_2O.
II. 0.4908 grm. air-dried salt gave 0.1981 grm. $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2 . 4 H_2O$.	Found.	
		I.	II.
H_2O	12.66	12.37	
Ba	24.07		23.73

0.4751 grm. salt dried at 100° gave 0.2205 grm. $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2$.	Found.
Ba	27.56	27.29

The solubility of the salt in water at 19.5° was determined in the usual manner.

I. 28.4671 grm. solution saturated at 19°.5 gave 0.0561 grm. $BaSO_4$.
II. 28.6844 grm. solution saturated at 19°.5 gave 0.0573 grm. $BaSO_4$.

The solution saturated at 19°.5 therefore contained the following percentages of anhydrous salt:

I.	II.
0.42	0.43

Calcic βδ Dichlorpyromucate, $Ca(C_5HCl_2O_3)_2 . 3 H_2O$. — The calcium salt was prepared by precipitating a dilute solution of the ammonium salt with calcic chloride, and recrystallizing the product from hot water. It is but sparingly soluble in hot water, still less soluble in cold water, and separates from a hot concentrated solution in flattened prisms with rectangular terminations. The crystallized salt is permanent in the air, effloresces slowly over sulphuric acid and loses all its water at 125°.

I. 1.5490 grm. air-dried salt lost at 125° 0.1820 grm. H_2O.
II. 0.4067 grm. air-dried salt gave 0.1219 grm. $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2 . 3 H_2O$.	Found.	
		I.	II.
H_2O	11.90	11.75	
Ca	8.81		8.81

0.6899 grm. salt dried at 125° gave 0.2332 grm. $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2$.	Found.
Ca	10.00	9.94

The solubility of the salt in water at 19°.5 was determined in the usual manner. The calcium was precipitated as oxalate and ignited with sulphuric acid.

I. 32.1733 grm. solution saturated at 19°.5 gave 0.0244 grm. $CaSO_4$.
II. 36.7555 grm. solution saturated at 19°.5 gave 0.0289 grm. $CaSO_4$.

The solution saturated at 19°.5 therefore contained the following percentages of anhydrous salt:

I.	II.
0.22	0.23

Ethyl βδ Dichlorpyromucate, $C_5HCl_2O_3C_2H_5$. — The ethyl ether was prepared by the action of ethyl iodide on the silver salt, and is a heavy liquid of pleasant odor. It melts at 2–3° and distils at 116–118° under a pressure of 16 mm., the oil bath being at 165–175°. An analysis of the distilled ether gave the following result.

0.2157 grm. substance gave 0.2957 grm. AgCl.

	Calculated for $C_5HCl_2O_3C_2H_5$.	Found.
Cl	33.98	33.89

βδ Dichlorpyromucamide, $C_5HCl_2O_2NH_2$. — The ethyl ether is but slowly attacked by concentrated ammonia in the cold, but at 100° it is readily converted to the amide. The amide is sparingly soluble in cold water, more readily in hot, and separates from a hot concentrated solution in long needles which on standing are converted into oblique prisms which melt at 153–154°.

0.2781 grm. substance dried over H_2SO_4 gave 20.0 c.c. moist N at 25.5° under a pressure of 766 m.m.

	Calculated for $C_5HCl_2O_2NH_2$.	Found.
N	7.78	8.06

Although the melting point, the crystalline form, and the insolubility of its calcium salt showed that this acid closely resembled the $\beta\delta$ dibrompyromucic acid, it was evidently necessary to establish the position of the chlorine atoms by means of its oxidation products.

Action of Bromine and Water.

Hill and Sanger* found that the $\beta\delta$ dibrompyromucic acid was readily attacked by aqueous bromine in the cold with the formation of monobrommaleyl bromide. The $\beta\delta$ dichlorpyromucic acid is but slowly attacked by aqueous bromine in the cold, and we therefore suspended it in five times its weight of water, added at once somewhat more than four atoms of bromine, heated until the oil which was first formed had almost all disappeared, and evaporated the solution at a gentle heat. The crystalline mass thus obtained was readily soluble even in cold water, and very sparingly soluble even in hot chloroform or benzol. The product was dissolved in cold water, filtered, and evaporated nearly to dryness. The crystals which separated were pressed dry with filter paper, washed carefully with hot benzol, and recrystallized from a little hot water. The acid thus prepared crystallized in microscopic crystals, which melted at 189–190°,† and proved on analysis to contain the percentage of chlorine required by monochlorfumaric acid.

0.1288 grm. substance dried over H_2SO_4 gave 0.1227 grm. AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.55

The oxidation with bromine and water therefore takes place in accordance with the following equation:

$$C_5H_2Cl_2O_3 + 2Br_2 + 3H_2O = C_4H_3ClO_4 + CO_2 + HCl + 4\,HBr.$$

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* These Proceedings, xxi. 165.

† Kauder (Journal für prakt. Chemie, [2], xxxi. 28) gives the melting point as 191°.

Since the $\beta\delta$ dichlorpyromucic is but slowly attacked even by concentrated nitric acid, it was not thought worth while to study the reaction in detail.

χ Dichlorpyromucic Acid.

The formation of the ethyl ether of this acid by the decomposition of ethyl pyromucic tetrachloride has already been described. The ether was recrystallized from hot alcohol, and saponified by alcoholic sodic hydrate. On the addition of hydrochloric acid to the aqueous solution of the sodium salt, a sparingly soluble acid separates, which may easily be purified by recrystallization from hot water.

The acid dried over sulphuric acid gave on analysis the following results: —

I. 0.2196 grm. substance gave 0.2672 grm. CO_2 and 0.0237 grm. H_2O.
II. 0.2212 grm. substance gave 0.3492 grm. AgCl.

	Calculated for $C_5H_2Cl_2O_3$.	Found. I.	Found. II.
C	33.15	33.18	
H	1.10	1.20	
Cl	39.22		39.03

χ dichlorpyromucic acid is readily soluble in ether or alcohol, and but sparingly soluble in cold water. In hot water it is freely soluble, and crystallizes as the solution cools in long needles which melt at 197–198°. The acid readily sublimes unchanged below its melting point. Sodium amalgam slowly reduces it to pyromucic acid melting at 129–130°.

The solubility of the acid in water at 19°.5 was determined in the usual manner. A solution of the acid saturated at 19°.5 was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 38.2670 grm. solution saturated at 19°.5 gave 0.0322 grm. $BaSO_4$.
II. 37.5125 grm. solution saturated at 19°.5 gave 0.0301 grm. $BaSO_4$.

The solution saturated at 19°.5 therefore contained the following percentages of acid: —

I.	II.
0.13	0.12

Baric χ Dichlorpyromucate, $Ba(C_5HCl_2O_3)_2 . 4 H_2O$. — The barium salt may most readily be prepared by boiling the acid with baric carbonate. The salt is quite readily soluble in cold water, more soluble in hot water, and crystallizes in columnar aggregations of prisms which contain four molecules of water. The crystallized salt is stable in the air, effloresces over sulphuric acid, and loses all its water at 100°.

I. 1.0471 grm. air-dried salt lost at 100° 0.1285 grm. H_2O.
II. 0.5464 grm. air-dried salt gave 0.2235 grm. $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2 . 4 H_2O$.	Found. I.	Found. II.
H_2O	12.66	12.27	
Ba	24.07		24.05

0.4495 grm. salt dried at 100° gave 0.2091 grm. $BaSO_4$.

	Calculated for $Ba(C_5HCl_2O_3)_2$.	Found.
Ba	27.56	27.35

The solubility of the salt in water at 19°.5 was determined in the usual manner.

I. 11.1910 grm. solution saturated at 19°.5 gave 0.0820 grm. $BaSO_4$.
II. 8.6544 grm. solution saturated at 19°.5 gave 0.0644 grm. $BaSO_4$.

According to these determinations, the solution saturated at 20° contained the following percentages of anhydrous salt:—

I.	II.
1.56	1.59

Calcic χ Dichlorpyromucate, $Ca(C_5HCl_2O_3)_2 . 4 H_2O$. — The calcium salt was prepared by boiling the acid with calcic carbonate. The filtered solution was then concentrated on the water bath to a small volume, and the salt which separated was filtered out and washed with a little water. Since the salt appeared to be about as soluble in cold water as in hot, it was dissolved in water and the solution concentrated *in vacuo* over sulphuric acid. The salt which separated was then pressed dry with filter paper. It is quite readily soluble in water, and crystallizes in prisms which contain four molecules of water. The crystallized salt is permanent in the air, effloresces slowly over sulphuric acid, and loses all its water at 117°.

I. 0.9075 grm. air-dried salt lost at 117° 0.1380 grm. H_2O.
II. 0.6080 grm. air-dried salt gave 0.1746 grm. $CaSO_4$.

	Calculated for $Ca(C_5HCl_2O_3)_2 . 4 H_2O$.	Found. I.	Found. II.
H_2O	15.25	15.21	
Ca	8.48		8.44

0.3377 grm. salt dried at 117° gave 0.1152 grm. $CaSO_4$.

	Calculated for $Ca (C_5HCl_2O_3)_2$.	Found
Ca	10.00	10.02

The solubility of the salt in water at 19°.5 was determined in the usual manner. The calcium was precipitated as oxalate and ignited with sulphuric acid.

I. 6.5743 grm. solution saturated at 19°.5 gave 0.1522 grm. $CaSO_4$.
II. 7.2115 grm. solution saturated at 19°.5 gave 0.1689 grm. $CaSO_4$.

The solution saturated at 19°.5 therefore contained the following percentages of anhydrous salt:

I.	II.
6.81	6.89

Ethyl χ Dichlorpyromucate, $C_5HCl_2O_3C_2H_5$. — The process by which the ethyl ether was obtained has already been described. It is readily soluble in hot alcohol, sparingly soluble in cold alcohol, and crystallizes in clustered prisms with rectangular truncations which melt at 72–73°. A sample of the ether melting at 72–73° was distilled under a pressure of 16 mm. and boiled constant at 122°.5, temperature of bath 170–175°. For analysis the ether was dried over sulphuric acid.

I. 0.2034 grm. substance gave 0.2790 grm. AgCl.
II. 0.2302 grm. substance gave 0.3160 grm. AgCl.

	Calculated for $C_5HCl_2O_3C_2H_5$.	Found.	
		I.	II.
Cl	33.98	33.91	33.94

In order to determine the constitution of this dichlorpyromucic acid we studied its oxidation products with aqueous bromine.

Action of Bromine and Water.

As it was desirable to compare the oxidation product obtained from this acid with that obtained from the βδ dichlorpyromucic acid under the same conditions, the acid was suspended in five times its weight of water, somewhat more than four atoms of bromine added as rapidly as possible, and the solution boiled until the oil which was at first formed had nearly disappeared. The filtered solution was evaporated to dryness at a gentle heat, the crystalline residue dissolved in a little cold water, filtered, and again evaporated nearly to dryness. The acid which separated was readily soluble even in cold water, almost insoluble in hot chloroform or benzol. It was therefore pressed dry with filter paper and carefully extracted with hot benzol. The acid as thus prepared crystallized in microscopic crystals which melted at 188–189°, and moreover gave on analysis the percentage of chlorine required by monochlorfumaric acid.*

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* Kauder, *loc. cit.*

0.1441 grm. substance dried over H_2SO_4 gave 0.1377 grm. AgCl.

	Calculated for $C_4H_3ClO_4$.	Found.
Cl	23.59	23.62

The χ dichlorpyromucic acid, like the βδ dichlorpyromucic acid, therefore gives with aqueous bromine as the chief product chlorfumaric acid according to the equation

$$C_5H_2Cl_2O_3 + 2\,Br_2 + 3\,H_2O = C_4H_3ClO_4 + CO_2 + HCl + 4\,HBr.$$

Since the oxidation with bromine had shown with sufficient precision that one of the chlorine atoms of the χ dichlorpyromucic acid occupied the δ position, we thought it unnecessary for our purposes to study also the action of nitric acid.

Action of Fuming Sulphuric Acid.

The two isomeric dibrompyromucic acids had shown marked differences in their behavior toward fuming sulphuric acid.* While the βγ acid had rapidly been converted into the corresponding sulphonic acid, brommaleic acid in nearly theoretical quantity had been formed from the βδ dibrompyromucic acid, and no trace of a sulphonic acid could be detected. Preliminary experiments proved that the βγ and βδ dichlorpyromucic acids showed a similar difference in their behavior toward fuming sulphuric acid. While the formation of chlormaleic acid in the latter case could not definitely be proved, certainly no sulphonic had been formed, and it seemed to us of interest to study also the behavior of the third isomeric dichlorpyromucic acid under the same conditions. χ dichlorpyromucic acid dissolves readily in fuming sulphuric acid, and if care be taken to prevent any marked elevation of temperature no very essential decomposition ensues, although a slight effervescence is noticeable. After the solution of the acid in four times its weight of fuming sulphuric acid had stood for thirty-six hours, it was poured into a large amount of cold water, the solution cooled, and thoroughly extracted with ether. The ethereal extract left on evaporation a small quantity of a colorless oil which reduced silver oxide, and whose vapor vigorously attacked the eyes and nose. The amount of oil thus obtained was wholly insufficient for further study. On standing, it deposited a few clustered needles, which probably were unaltered acid, although they may possibly have been the decomposition product subsequently described. From the aqueous solution the barium salt was prepared in the usual way, and,

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* These Proceedings, xxiii. 218.

since the properties of the neutral salt were unfavorable to purification, it was converted into the acid salt, and this recrystallized from hot water. The acid salt was readily soluble in hot water, more sparingly soluble in cold water and crystallized in triclinic (?) prisms which effloresced on exposure to the air. It gave an excellent qualitative reaction for sulphur, and when dried over sulphuric acid * gave the percentage of barium required by the formula $Ba(C_5HCl_2SO_6)_2$.

0.3886 grm. of the salt dried over sulphuric acid gave 0.1338 grm. $BaSO_4$.

	Calculated for $Ba(C_5HCl_2SO_6)_2$.	Found.
Ba	20.84	20.24

Baric χ Dichlorsulphopyromucate, $BaC_5Cl_2SO_6 \cdot 2\,H_2O$. — From the acid barium salt we prepared the neutral salt by neutralizing its aqueous solution with baric carbonate. Since the hot saturated solution deposited little or nothing on cooling, it was evaporated *in vacuo* over sulphuric acid. The salt then crystallized in sheaves of prisms which appeared to be triclinic. It was permanent in the air, effloresced over sulphuric acid, and lost its water completely at 160°.

1.4159 grm. of the air-dried salt lost at 160° 0.1277 grm. H_2O.

	Calculated for $BaC_5Cl_2SO_6 \cdot 2\,H_2O$.	Found.
H_2O	8.33	9.02

0.5296 grm. of the salt dried at 160° gave 0.3126 grm. $BaSO_4$.

	Calculated for $BaC_5Cl_2SO_6$.	Found.
Ba	34.59	34.69

The formation of a dichlorsulphopyromucic acid by the action of fuming sulphuric acid upon the χ dichlorpyromucic acid is thus sufficiently established. The bromsulphopyromucic acids are so readily reduced in alkaline solution that we hoped to be able to prepare from this dichlorsulphopyromucic acid the corresponding sulphopyromucic acid, and thus establish the position of the two chlorine atoms. We soon found, however, that the chlorine was held with unusual persistence, and with the material at our disposal we have as yet been unable to reach decisive results.

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* The single determination of the water of crystallization was unfortunately defective. It gave 13.34 per cent of water in the salt dried by short exposure to the air, while a salt crystallizing with 2½ molecules of water should contain 13.70 per cent.

Decomposition by Hydrochloric Acid.

If the χ dichlorpyromucic acid is heated with water in a sealed tube to 170°, no change is effected, but a reaction which we had in no way anticipated takes place if it is heated upon the water bath in an open flask with concentrated hydrochloric acid. Carbonic acid is evolved, and in a short time the acid is completely decomposed with the formation of a neutral body which volatilizes when the solution is boiled, and which can be extracted, although with difficulty, from the distillate, or from the original solution with ether. The ethereal solution left on evaporation a white crystalline solid which was sparingly soluble in water, readily soluble in cold chloroform or benzol, and but sparingly soluble in ligroin. When recrystallized from ligroin it formed long slender lustrous prisms, which melted at 52–53°, and sublimed rapidly at ordinary temperatures. It reduced argentic oxide on warming, and dissolved in aqueous alkalies, forming a yellow solution. The physical properties and the behavior of this substance at once recalled to our minds the crystalline body melting at 77° which Hill and Sanger* had obtained in small quantity from the by-products of the decomposition of pyromucic tetrabromide by alcoholic sodic hydrate. The formula of this body had been shown to be $C_4H_3BrO_2$ and an analysis of the new substance left no doubt of its similar composition.

0.1045 grm. substance gave 0.1261 grm. AgCl.

	Calculated for $C_4H_3ClO_2$.	Found.
Cl	29.95	29.84

This interesting body is probably formed according to the reaction

$$C_5H_2Cl_2O_3 + H_2O = C_4H_3ClO_2 + CO_2 + HCl.$$

And since we found little difficulty in obtaining 40 per cent of the yield which this equation demands, it will be possible to study it more in detail. Unfortunately, it was discovered so late in our work as to make it impossible to present the results of such a study in this paper. While it would be easy for us to venture a conjecture as to its structure, we prefer to await the results of a future investigation.

TRICHLORPYROMUCIC ACID.

For the preparation of the trichlorpyromucic acid it was evidently most convenient to decompose with alkalies the tetrachloride of the δ chlorpyromucic acid. It did not seem necessary, however, to pre-

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* These Proceedings, xxi. 158.

pare this tetrachloride in a pure condition, and indeed we first obtained the trichlorpyromucic acid from one of the earlier preparations of the ethyl pyromucic tetrachloride in which an unusually great spontaneous elevation of temperature had taken place through the rapid absorption of chlorine. For its preparation we heated the ethyl pyromucate to 145°, and passed in chlorine at this temperature until the gain in weight showed that one atom of hydrogen had been replaced by chlorine. We then allowed the temperature to fall to about 120°, and continued the chlorination to saturation. The total gain in weight then corresponded approximately to that required by the formation of the tetrachloride of the ethyl chlorpyromucate. On decomposing this product as usual with a cold concentrated alcoholic solution of sodic hydrate, the alcoholic solution filtered from the insoluble sodium salts contained, as in the previous cases, small quantities of liquid furfuran derivatives, but the amount was so minute that no separate study of them was made. The sodium salts dissolved in hot water gave with hydrochloric acid an impure trichlorpyromucic acid as a more or less colored oil, which solidified as the solution cooled. For the purification of the acid we have found it convenient to take advantage of the slight solubility of the ammonium salt in cold water. The crude acid was suspended in about thirty times its weight of water, ammonic hydrate added in excess, and the hot solution treated with bone-black. The filtered solution deposits on cooling the greater part of the trichlorpyromucic acid as the ammonium salt from which the pure acid can readily be obtained. The small amount of trichlorpyromucic acid remaining in the ammoniacal solution may be recovered. although at the expense of considerable trouble, by precipitation with calcic chloride and repeated recrystallization from water and dilute alcohol of the acid obtained from the insoluble calcium salt.

The yield of pure trichlorpyromucic acid was far from satisfactory, as we could obtain only 30 per cent of the weight of the ethyl pyromucate taken, but 15 per cent of the theoretical amount.

For analysis the acid was dried over sulphuric acid.

I. 0.3214 grm. substance gave 0.3248 grm. CO_2 and 0.0211 grm. H_2O.
II. 0.2107 grm. substance gave 0.4192 grm. AgCl.
III. 0.2135 grm. substance gave 0.4255 grm. AgCl.

	Calculated for $C_5HCl_3O_3$.	Found		
		I.	II.	III.
C	27.85	27.56		
H	0.46	0.73		
Cl	49.43		49.19	49.27

Trichlorpyromucic acid is readily soluble in alcohol or ether, quite readily soluble in boiling benzol, and but sparingly soluble in cold benzol. Hot water dissolves it but sparingly, and as the solution cools most of the acid is deposited in microscopic needles which melt at 172–173°. This melting point was so much below that which we had been led to expect from analogy to the known acid containing bromine that we felt some doubt of its correctness, more especially since the crude acid was so far from pure. A sample of the acid melting at 172–173° was therefore recrystallized twice from water and then three times from benzol without perceptibly changing the melting point. The acid was then converted into the calcium salt, and this separated by crystallization into three successive fractions. The acid from these three fractions melted simultaneously and sharply at 172–173°. Finally, the ethyl ether was made, and the acid prepared from the repeatedly recrystallized pure ether melted at the same point.

The solubility of the acid in water at 19°.5 was determined by boiling with baric carbonate a weighed quantity of a solution of the acid saturated at that temperature, and determining the barium dissolved as sulphate.

I. 49.1742 grm. solution saturated at 19°.5 gave 0.0344 grm. $BaSO_4$.
II. 47.0228 grm. solution saturated at 19°.5 gave 0.0331 grm. $BaSo_4$.

The solution saturated at 19.5° therefore contained the following percentages of acid:

I.	II.
0.13	0.13

Baric Trichlorpyromucate, $Ba(C_5Cl_3O_3)_2 . 4 H_2O$. — The barium salt was prepared by precipitating a dilute solution of the ammonium salt with baric chloride, and recrystallizing the sparingly soluble salt thus thrown down from hot water. The salt proved to be but sparingly soluble even in hot water, and still less soluble in cold water. It separates from a hot concentrated solution in needles which apparently contain four molecules of water. The salt is permanent in the air, but loses three molecules of its crystal water over sulphuric acid. When dried at 120°, it still retains a half-molecule of water which cannot be expelled without essential decomposition.

I. 0.6847 grm. air-dried salt gave 0.2511 grm. $BaSO_4$.
II. 0.6205 grm. air-dried salt gave 0.2273 grm. $BaSO_4$.
III. 0.5672 grm. air-dried salt gave 0.2076 grm. $BaSO_4$.
IV. 1.3625 grm. air-dried salt lost over H_2SO_4 0.1148 grm. H_2O and at 120° 0.1338 grm. H_2O.

V. 1.1645 grm. air-dried salt lost over H_2SO_4 0.1003 grm. H_2O and at 100° 0.1124 grm. H_2O.

VI. 1.3000 grm. air-dried salt lost over H_2SO_4 0.1124 grm. H_2O and at 100° 0.1256 grm. H_2O.

	Calculated for $Ba(C_5Cl_3O_3)_2 \cdot 4\,H_2O$.	Found. I.	II.	III.	IV.	V.	VI.
Ba	21.47	21.56	21.54	21.52			
3 H_2O	8.46				8.43	8.61	8.65
3½ H_2O	9.87				9.83	9.65	9.66

I. 0.7484 grm. substance dried at 120° gave 0.3038 grm. $BaSO_4$.

II. 0.6247 grm. substance dried at 100° gave 0.2521 grm. $BaSO_4$.

III. 0.6497 grm. substance dried at 100° gave 0.2634 grm. $BaSO_4$.

	Calculated for $Ba(C_5Cl_3O_3)_2 \cdot \frac{1}{2}\,H_2O$.	Found. I.	II.	III.
Ba	23.83	23.86	23.72	23.84

The solubility of the salt in water at 19°.5 was determined in the usual way.

I. 41.4499 grm. solution saturated at 19°.5 gave 0.0470 grm. $BaSO_4$.

II. 44.9822 grm. solution saturated at 19°.5 gave 0.0500 grm. $BaSO_4$.

The solution saturated at 19°.5 therefore contained the following percentages of anhydrous salt: —

I.	II.
0.27	0.27

Calcic Trichlorpyromucate, $Ca(C_5Cl_3O_3)_2 \cdot 4\,H_2O$. — The calcium salt was prepared by precipitating a dilute solution of the ammonium salt with calcic chloride. The precipitated salt was then crystallized from hot water, and proved to be sparingly soluble in hot water, still less soluble in cold water, and separated from a hot solution in irregular aggregations of small leafy plates.

The salt is permanent in the air, effloresces over sulphuric acid, and loses all its water at 110°.

I. 1.3008 grm. air-dried salt lost at 110° 0.1697 grm. H_2O.

II. 1.8389 grm. air-dried salt lost at 110° 0.2417 grm. H_2O.

	Calculated for $(C_5Cl_3O_3)_2Ca \cdot 4\,H_2O$.	Found. I.	II.
H_2O	13.30	13.05	13.14

I. 0.6399 grm. salt dried at 110° gave 0.1855 grm. $CaSO_4$.

II. 0.6974 grm. salt dried at 110° gave 0.2019 grm. $CaSO_4$.

	Calculated for $Ca(C_5Cl_3O_3)_2$.	Found. I.	II.
Ca	8.53	8.53	8.51

The solubility of the salt in water at 19°.5 was determined in the usual manner. The calcium was precipitated as oxalate, and the oxalate ignited with sulphuric acid.

I. 18.1457 grm. solution saturated at 19°.5 gave 0.0342 grm. $CaSO_4$.
II. 14.6806 grm. solution saturated at 19°.5 gave 0.0265 grm. $CaSO_4$.

The solution saturated at 19°.5 therefore contained the following percentages of anhydrous salt: —

I.	II.
0.65	0.62

Potassic Trichlorpyromucate, $KC_5Cl_3O_3$. — The potassium salt was prepared by boiling the acid with a slight excess of potassic carbonate. The solution was then concentrated until the salt began to separate, and on cooling it solidified to a mass of crystals, which were filtered off on the pump and pressed dry with filter paper. The salt is readily soluble even in cold water, and separates from a hot concentrated solution in sheaves of fine needles, which lose nothing in weight when heated to 120°. Analyses of the salt dried at this temperature proved it to be anhydrous.

I. 0.5338 grm. salt dried at 120° gave 0.1851 grm. K_2SO_4.
II. 4425 grm. salt dried at 120° gave 0.1532 grm. K_2SO_4.

	Calculated for $KC_5Cl_3O_3$.	Found.	
		I.	II.
K	15.42	15.57	15.54

Argentic Trichlorpyromucate, $AgC_5Cl_3O_3$. — The silver salt may best be prepared by precipitating a hot solution of the calcium salt with argentic nitrate. For analysis the precipitated salt was well washed, and then recrystallized from hot water. It is sparingly soluble even in hot water, less soluble in cold water, and crystallizes from a hot concentrated solution in moss-like aggregations of fine needles.

The air-dried salt gave on analysis much too low a percentage of silver, and although the sample analyzed was free from calcium salt and free acid, it failed to give perfectly satisfactory results even when dried *in vacuo* over sulphuric acid or at 100°.

I. 0.5142 grm. salt dried *in vacuo* over H_2SO_4 gave 0.2254 grm. AgCl.
II. 0.4545 grm. salt dried at 100° gave 0.1998 grm. AgCl.

	Calculated for $C_5Cl_3O_3Ag$.	Found.	
		I.	II
Ag	33.48	33.00	33.10

Ethyl Trichlorpyromucate, $C_5Cl_3O_3C_2H_5$. — The ethyl ether was prepared in the usual manner, by warming an alcoholic solution of the acid with concentrated sulphuric acid. 5 parts of the acid, 10 parts of absolute alcohol, and 5 parts of concentrated sulphuric acid (Sp. Gr. 1.84) were heated together for three hours at 100°. The ether was then precipitated with water, washed with warm dilute sodic carbonate, and finally with water. The ether is readily soluble in hot alcohol, more sparingly in cold alcohol, and crystallizes in flat prisms which melt at 62–63°.

I. 0.2142 grm. substance dried over H_2SO_4 gave 0.3793 grm. AgCl.
II. 0.2536 grm. substance dried over H_2SO_4 gave 0.4476 grm. AgCl.

	Calculated for $C_5Cl_3O_3C_2H_5$.	Found. I.	Found. II.
Cl	43.74	43.77	43.64

Trichlorpyromucamide, $C_5Cl_3O_2NH_2$. — Concentrated aqueous ammonia attacks the trichlorpyromucic ether but slightly at ordinary temperatures. Even after three hours' heating in a sealed tube at 100° most of the ether was found to be unaltered, and we were obliged to prepare the amide from the acid chloride by the action of solid ammonic carbonate. The amide is but sparingly soluble even in hot water and crystallizes in long slender needles, which melt at 160–161°.

0.3804 grm. substance dried over H_2SO_4 gave 23.2 c.c. moist N at 21° under a pressure of 765 mm.

	Calculated for $C_5Cl_3O_2NH_2$.	Found.
N	6.53	6.95

Although there could be no doubt as to the constitution of the trichlorpyromucic acid it seemed better for the sake of completeness to study its behavior with oxidizing agents.

Action of Bromine and Water.

Trichlorpyromucic acid was suspended in ten times its weight of cold water, and a little more than one molecule of bromine was added. Carbonic dioxide was evolved and the color of the bromine rapidly disappeared. When the reaction had been completed, a white insoluble substance remained, which was removed by filtration and washed with a dilute solution of sodic carbonate. The alkaline solution gave on acidification a copious precipitate of unaltered trichlorpyromucic acid, whose identity was established by the melting point 172–173°. The substance which remained undissolved by the alkaline solution had the characteristic odor of the tetrabromfurfuran, and crystallized from hot alcohol in irregular plates, which melted at 75–76°. Analysis showed this substance to be a trichlorbromfurfuran.

I. 0.1749 grm. substance dried over H_2SO_4 gave 0.4269 grm. AgCl and AgBr.

II. 0.1411 grm. substance dried over H_2SO_4 gave 0.3447 grm. AgCl and AgBr.

	Calculated for C_4Cl_3BrO.	Found.	
		I.	II.
$Cl_3 + Br$	74.45	73.60	73.67

The strongly acid filtrate from the trichlorbromfurfuran and unaltered trichlorpyromucic acid yielded on extraction with ether a crystalline acid which was readily soluble in water. The amount of this acid was too small for analysis, but it was easily identified as dichlormaleic acid by the melting point of its anhydride, 119–120°.*

The reaction had therefore taken place in accordance with the following equations:

$$C_5HCl_3O_3 + Br_2 = C_4Cl_3BrO + CO_2 + HBr.$$

$$C_5HCl_3O_3 + 2\,Br_2 + 3\,H_2O = C_4H_2Cl_2O_4 + CO_2 + HCl + 4\,HBr.$$

Action of Nitric Acid.

Trichlorpyromucic acid is but slowly attacked by nitric acid, and prolonged heating with moderately strong nitric acid is needed for complete oxidation. Even after heating the acid for six hours with six times its weight of nitric acid (Sp. Gr. 1.42) diluted with an equal weight of water, a portion of the trichlorpyromucic acid escaped oxidation. Carbonic dioxide was slowly given off, and a small quantity of an insoluble oil was formed, which had a peculiar penetrating odor not unlike that of substituted furfuran derivatives. Its quantity was too small to admit of its identification. In solution we were able to find nothing but dichlormaleic acid, which we purified through the barium salt and identified by the melting point of its anhydride and by analysis.

0.1997 grm. substance dried over H_2SO_4 gave 0.3086 grm. AgCl.

	Calculated for $C_4H_2Cl_2O_4$.	Found.
Cl	38.38	38.20

The reaction had therefore taken place in accordance with the following equation:

$$C_5HCl_3O_3 + 2\,O + H_2O = C_4H_2Cl_2O_4 + CO_2 + HCl.$$

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* Ciamician and Silber, *loc. cit.*

We have also prepared several other trisubstituted pyromucic acids, which may conveniently be described here.

βγ-Dichlor-δ-Brompyromucic Acid.

Hill and Sanger[*] found that βγ dibrompyromucic acid was easily converted into tribrompyromucic acid by the action of bromine at ordinary temperatures.

If βγ dichlorpyromucic acid is exposed to the vapors of bromine at ordinary temperatures, bromine is rapidly absorbed, hydrobromic acid is evolved, and the gain in weight approaches that required by the displacement of hydrogen by bromine. The product was treated with small quantities of boiling water to remove unaltered dichlorpyromucic acid, and then recrystallized from dilute alcohol, and finally from water. The acid is readily soluble in alcohol or ether, dissolves freely in boiling benzol, more sparingly in cold benzol. Even in boiling water it is very sparingly soluble. It crystallizes in short clustered prisms, which melt at 185–186°.

0.3189 grm. substance dried over H_2SO_4 gave 0.5817 grm. AgCl and AgBr.

	Calculated for $C_5HCl_2BrO_3$.	Found.
$Cl_2 + Br$	58.08	57.99

βγ-Dibrom-δ-Chlorpyromucic Acid.

This acid we made by treating the ethyl βγ dibrompyromucate with chlorine and decomposing the product with alcoholic sodic hydrate. On acidifying the aqueous solution of the sodium salts thus obtained, a crystalline acid was precipitated, which after one recrystallization from dilute alcohol melted at 192–193°. After recrystallization from benzol the melting point rose to 193–194°. The acid was readily soluble in alcohol, ether, or hot benzol; sparingly soluble in cold benzol, or even in boiling water.

0.2315 grm. substance dried over H_2SO_4 gave 0.3960 grm. AgCl and AgBr.

	Calculated for $C_5HClBr_2O_3$.	Found.
$Cl + Br_2$	64.19	64.37

We have attempted to prepare these acids also by the decomposition with alcoholic sodic hydrate of products formed by the addition of

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[*] These Proceedings, xxi. 172.

bromine to δ chlorpyromucic acid and of chlorine to ethyl δ brompyromucate. Although we readily prepared in this way trisubstituted acids, the products in neither case were homogeneous, tribrom- or trichlorpyromucic acids being formed together with the acid containing both halogens.

βγ-Dichlor-δ-Nitropyromucic Acid.

Hill and Palmer* have shown that βγ dibrompyromucic acid is easily converted into a sulphonic acid by means of sulphuric acid, and that the sulpho group in this acid may readily be replaced by the nitro group. βγ dichlorpyromucic acid was dissolved in fuming sulphuric acid, and the barium salt of the sulphonic acid isolated in the usual way. Since a more complete study of the salt did not fall within the plan of our work, we precipitated the barium exactly with sulphuric acid, and evaporated the dilute solution of the acid first at 100° and afterwards *in vacuo* over sulphuric acid. The crystalline somewhat deliquescent acid thus obtained was dissolved in several times its weight of fuming nitric acid, to which half its volume of concentrated sulphuric acid had been added. After the action was finished, the nitric acid was partially expelled, the residue diluted with water, and extracted with ether. The ether was then shaken with a dilute solution of sodic carbonate, and the acid precipitated from this alkaline solution by the addition of hydrochloric acid. The ethereal solution proved to contain no substance which invited further investigation.

The βγ-dichlor-δ-nitropyromucic acid is readily soluble in alcohol, ether, or hot benzol. Hot water dissolves it freely, and on cooling the greater part of the acid is deposited in flattened leafy prisms which melt at 189–190°.

0.2168 grm. substance dried over H_2SO_4 gave 0.2756 grm. Ag. Cl.

	Calculated for $C_5HCl_2NO_5$.	Found.
Cl	31.42	31.42

We have as yet made no further study of this acid.

Theoretical Considerations.

The acids melting at 168–169° and 155–156°, which in the preceding pages we have called the βγ and βδ dichlorpyromucic acids, are without doubt identical in structure with the two dibrompyromucic acids described by Hill and Sanger.† Their physical properties and

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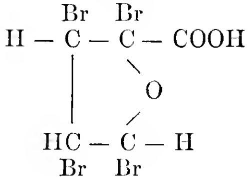
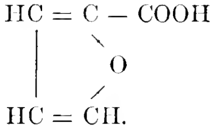
* These Proceedings, xxiii. 201, 205.

† These Proceedings, xxi. 137.

the solubility of their salts show their close relationship to these bromine derivatives, while the products formed from them by oxidation conclusively prove that they are structurally isomeric, and that the chlorine atoms occupy the same relative position that the bromine atoms hold in the dibrompyromucic acids. On reduction these two acids both yield the same chlorpyromucic acid, which in its turn closely resembles the β brompyromucic acid in its physical properties, although its melting point, 145–146°, is comparatively high. It is to be noted, however, that the βγ dichlorpyromucic acid alone is formed by the action of alkalies upon the ethyl pyromucic tetrachloride, while the two isomeric dibrompyromucic acids are simultaneously formed under similar conditions. This simultaneous formation of the two structurally isomeric acids from pyromucic tetrabromide to which the formula



may be assigned led Hill and Sanger[*] to the conclusion that these acids must have their bromine atoms in the βγ and βδ positions respectively, and that pyromucic acid itself probably had the formula



The structure of the βγ and βδ dichlorpyromucic acids seems to us to be thus sufficiently established.

As to the third isomeric form, which for the present we have called the χ dichlorpyromucic acid, since it gives chlorfumaric acid by oxidation, it is evident that it must either have its chlorine atoms in the γ and δ position, or that it must be a geometrically isomeric form of the βδ acid. Unfortunately, we have been able to obtain as yet no evidence which conclusively proves either view to be correct. A dichlorpyromucic acid having its chlorine atoms in the γ and δ positions could not well be formed from ethyl pyromucic tetrachloride by the simple loss of hydrochloric acid. Tönnies[†] had shown that δ brom-

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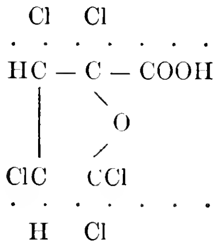
[*] These Proceedings, xxi. 182.

[†] Berichte de deutsch. chem. Gesellsch.

pyromucic acid could be formed by the action of heat upon pyromucic tetrabromide, when bromine must be eliminated as well as hydrobromic acid. Since we had noticed that hydrochloric acid invariably was evolved in the preparation of ethyl pyromucic tetrachloride, it seemed to us not improbable that the χ dichlorpyromucic acid was in fact the γδ acid which had been formed in a similar way from the tetrachloride of the δ chlorpyromucic ether necessarily contained in the crude product.



We found, however, that no χ dichlorpyromucic acid was formed on heating ethyl δ chlorpyromucic tetrachloride, and that our product in this case contained the βδ acid alone, so that the molecule of chlorine, which had been eliminated in the reaction, had taken its chlorine atoms from the γ and δ positions. We hoped also to get further evidence as to the structure of the χ dichlorpyromucic acid by reducing it to a chlorpyromucic acid, or by substituting the chlorine of the χ dichlorsulphopyromucic acid by hydrogen; but in neither case have we yet succeeded in obtaining well characterized products.

While it seems to us probable that the χ dichlor pyromucic acid is geometrically isomeric with the βδ acid, we have as yet been unable to convert one acid into the other. Both acids volatilize unchanged when heated, and the ordinary reagents which usually effect conversion in such cases have failed to bring about any perceptible isomerization. While lack of material has to a great degree limited our work with the χ acid, we have studied the behavior of the βδ acid under a variety of conditions with purely negative results. If the two acids are in fact geometrically isomeric, the simultaneous appearance of both forms in the distillation of ethyl pyromucic tetrachloride with the escape of large quantities of hydrochloric acid shows that the conversion of one acid into the other is effected with difficulty, while the formation of the βδ acid alone from the ethyl δ chlorpyromucic tetrachloride under similar conditions is especially worthy of note. Since pyromucic acid apparently contained two pairs of carbon atoms doubly tied, the existence of geometrically isomeric forms of its derivatives seemed at the outset more than probable, and during the progress of the investigations which for many years have been carried on in this laboratory careful search had been made for such bodies, but hitherto only the two isomeric dibromfurfuran tetrabromides of Hill and Hartshorn * had been discovered. Since the discovery of the χ dichlorpyromucic acid, which we made toward the close of our work, we have attempted to prepare the corresponding bromine derivative, but as yet without success. The isolation of the body $C_4H_3BrO_2$, which Hill and Sanger † found among the products of the decomposition of pyromucic tetrabromide by alkalies, certainly is an indication of the previous existence of such an acid, although it is by no means clear in what stage of the process the decomposition of the acid was effected, nor how the decomposition product itself escaped further alteration. Any detailed consideration of the geometrical structure of pyromucic acid we feel obliged to postpone until more facts bearing upon the question are at our disposal.

II. — ON CERTAIN DERIVATIVES OF FURFURACRYLIC ACID.

By H. B. Gibson and C. F. Kahnweiler.

Presented May 28, 1889.

The preparation of furfuracrylic acid was described by v. Baeyer ‡ 1877. At that time, however, the investigation of the acid was pushed in but one direction, and the successive steps by which it could be converted into α pimelic acid were alone described in detail. It seemed that a further study of the acid in other directions also could hardly fail to yield interesting results.

The ready decomposition of furfuracrylic acid by mineral acids compelled us to relinquish the line of work we originally had proposed to follow, and we consequently began an investigation into the nature of this decomposition. The study of the action of hydrochloric acid upon an alcoholic solution of furfuracrylic acid was just beginning

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* Berichte der deutsch. chem. Gesellsch., xviii. 450.

† These Proceedings, xxi. 158.

‡ Ber. d. deutsch. chem. Gesellsch., x. 355.

to yield us results when the paper of Markwald[*] upon the same subject reached us, and we were therefore obliged to abandon our work in this direction, and turned our attention to the products formed by the action of bromine, which promised to repay investigation. We felt ourselves quite at liberty to continue our study of furfuracrylic acid in this direction, since Markwald had declared himself unable to obtain well defined crystalline products in this way.

Furfuracrylic Acid.

In the preparation of furfuracrylic acid we have found it to our advantage to modify slightly the proportions given by v. Baeyer, and in this respect our experience agrees more closely with that of Markwald. We have heated 2 parts of furfurol with 3 parts of fused sodic acetate and 3 parts of acetic anhydride with reverse cooler at 160–170° for about ten hours, extracted the acid with a dilute solution of sodic carbonate, precipitated with hydrochloric acid, and recrystallized the product thus obtained from boiling water. Although the yield varied somewhat in successive preparations, we frequently obtained an amount equal to the weight of furfurol employed. The melting point of the pure acid we found to be 140°, in agreement with the observations of Jaffe and Cohn,[†] instead of 136° as given by v. Baeyer. From the acid we made the methyl ether and the amide, which we may describe a little more in detail, since no description of them has yet been published.

Methyl Furfuracrylate, $C_7H_5O_3 . CH_3$. — By precipitating with argentic nitrate a solution of ammonic furfuracrylate the silver salt was obtained as a heavy curdy precipitate. This was carefully dried and treated with an excess of methyl iodide. When the decomposition was complete the product of the reaction was extracted with ether, and purified by distillation under diminished pressure. Under a pressure of 15 mm. the methyl furfuracrylate distils unchanged at 112°, and the distillate solidifies in beautiful rhombic crystals which melt at 27°. Under a pressure of 774 mm. we found that the ether distilled without apparent decomposition at 227–228°. It possessed an agreeable characteristic odor, and dissolved readily in alcohol, ether, ligroin, or benzol. An analysis gave the following results : —

0.2224 grm. substance gave 0.5157 grm. CO_2 and 0.1084 grm. H_2O.

	Calculated for $C_8H_8O_3$.	Found.
C	63.17	63.23
H	5.26	5.42

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[*] Ber. d. deutsch. chem. Gesellsch., xx. 2811.

[†] Ibid., xx. 2315.

Furfuracrylamide, $C_7H_5O_2 . NH_2$. — Concentrated aqueous ammonic hydrate acted but slowly upon methyl furfuracrylate in the cold, but at 100° in sealed tube the decomposition was readily effected. The amide was sparingly soluble in cold water, more readily in hot water, and crystallized in pearly scales which melted at 168–169°.

I. 0.4076 grm. substance gave 35.5 c.c. moist nitrogen at 21°.4 and under a pressure of 766 mm.

II. 0.4590 grm. substance gave 41.9 c.c. moist nitrogen at 21°.7 and under a pressure of 767 mm.

	Calculated for $C_7H_7NO_2$.	Found. I.	Found. II.
N	10.22	9.98	10.45

Action of Bromine.

It had already been observed by v. Baeyer that furfuracrylic acid was readily attacked by aqueous bromine, but he had made no careful study of the products formed. Since the product formed in this way was uninviting, and the reaction undoubtedly complicated, it seemed advisable to study instead the action of dry bromine, which might yield well characterized addition products. We soon found, however, that with dry bromine even in the cold substitution was readily effected, so that the simplest well defined product contained three atoms of bromine. Subsequent study showed that this product was a saturated compound in which one atom of bromine had taken its place in the furfuran ring.

Bromfurfurdibrompropionic Acid, $C_7H_5Br_3O_3$. — If furfuracrylic acid is suspended in ten times its weight of carbonic disulphide and two molecules of dry bromine added, a clear deep red solution is at once obtained, from which hydrobromic acid is soon evolved in quantity. Although the reaction progresses steadily at ordinary temperatures, it may be greatly hastened by heat, and we usually have heated the mixture upon the water bath soon after the addition of the bromine. When the evolution of the hydrobromic acid slackens, and a crystalline substance has separated in quantity, the solution is well cooled, filtered, and the crystalline solid well washed with cold carbonic disulphide. The substance then gives on analysis percentages which closely agree with those required by the formula $C_7H_5Br_3O_3$; but it may still further be recrystallized from hot benzol or carbonic disulphide.

I. 0.2080 grm. substance gave 0.3117 grm. AgBr.

II. 0.3798 grm. of substance recrystallized from carbonic disulphide gave 0.3099 grm. CO_2 and 0.0502 grm. H_2O.

III. 0.2005 grm. substance recrystallized from benzol gave 0.2998 grm. AgBr.
IV. 0.2003 grm. substance recrystallized from benzol gave 0.2993 grm. AgBr.

	Calculated for $C_7H_5Br_3O_3$.	Found I.	II.	III.	IV.
C	22.28		22.26		
H	1.33		1.47		
Br	63.66	63.78		63.65	63.60

Bromfurfurdibrompropionic acid crystallizes in small flat oblique prisms, which are sparingly soluble in cold benzol or carbonic disulphide, more readily in hot. It is readily soluble in alcohol or ether, insoluble in water, although slowly decomposed by it. On heating, the acid is gradually decomposed, with the evolution of hydrobromic acid and slight carbonization. As might be expected, we found it impossible to prepare salts, or even ethers, of the acid.

The action of cold water upon the acid was so well marked, that we proceeded to determine the products formed. When bromfurfurdibrompropionic acid is suspended in water, carbonic dioxide soon begins to escape, and after long standing the crystalline solid is completely converted into a colorless oil. The aqueous solution then contains hydrobromic acid in abundance. As the decomposition was greatly facilitated by gentle heat, we usually have allowed the reaction to proceed at about 40°. When the decomposition was complete, we distilled with steam, and dried the heavy colorless oil thus obtained with calcic chloride. On distilllation under diminished pressure, we found that this oil began to boil at 108° under a pressure of 14 mm., and that the thermometer gradually rose to 112° the pressure remaining constant. The distillate was at first nearly colorless, and of high refractive power, but on standing it quite rapidly became dark-colored. Analyses of the freshly distilled substance showed it to be a bromfurfurbromethylen.

I. 0.3173 grm. substance gave 0.3350 grm. CO_2 and 0.0476 grm. H_2O.
II. 0.1928 grm. substance gave 0.2883 grm. AgBr.
III. 0.2045 grm. substance gave 0.3056 grm. AgBr.

	Calculated for $C_6H_4Br_2O$.	Found. I.	II.	III.
C	28.57	28.79		
H	1.59	1.67		
Br	63.49		63.65	63.60

The reaction is then strictly analogous to that by which β bromstyrol may be made from phenyldibrompropionic acid:

$$C_7H_5Br_3O_3 = C_6H_4Br_2O + CO_2 + HBr.$$

The aqueous solution left in the retort after distillation with steam deposited on long standing a small quantity of a crystalline acid. The quantity of this acid was so insignificant that we were able to identify it only after uniting the products obtained in many successive preparations. Two determinations of the percentage of bromine showed the acid to be the bromfurfuracrylic acid subsequently described. Lack of material made it impossible to prove with precision the identity of the two acids, and we can therefore only assert their close resemblance.

I. 0.1262 grm. substance gave 0.1091 grm. AgBr.
II. 0.1956 grm. substance gave 0.1700 grm. AgBr.

	Calculated for $C_7H_5BrO_3$.	Found. I.	Found. II.
Br	36.86	36.79	36.99

We have hitherto been unable to find other definite products of the reaction.

By the action of bromine upon bromfurfurbromethylen we could obtain no products which invited further study. On the other hand, alcoholic potassic hydrate gave us the corresponding acetylen derivative, although we have not yet isolated it in a pure condition. The oil obtained as the direct product of the reaction contained much too large a percentage of bromine, and prolonged action at a higher temperature gave no more satisfactory results. That the oil contained the acetylen derivative was readily shown by its behavior with an ammoniacal solution of silver or copper. The silver compound was white, the copper compound a greenish yellow. The latter was made in larger quantity, carefully washed by decantation, and dried over sulphuric acid. It then exploded violently by heat or on contact with fuming nitric acid, and contained the required percentage of copper.

I. 0.6479 grm. substance gave by electrolysis 0.1748 grm. Cu.
II. 0.6178 grm. substance gave 0.1681 grm. Cu.

	Calculated for $[C_6H_2BrO]_2Cu_2$.	Found. I.	Found. II.
Cu	27.16	26.98	27.20

From the copper compound we attempted to prepare the bromfurfuracetylen in a pure condition. By decomposing with acid, extracting with ether, and distilling the well dried extract under diminished pressure, we obtained a colorless oil which boiled at 65–68° under a pressure of 19 mm. This oil contained a percentage of bromine, which left no doubt as to its identity, but showed at the same time that it was still impure. We have as yet made no further attempt at its complete purification.

It seemed to us of interest to prepare by oxidation the diacetylen derivative also, analogous to the diacetenylphenyl of Gläser,* which was afterward more fully studied by v. Baeyer and Landsberg.† In its preparation we followed closely the method of v. Baeyer. To the copper compound was added one molecule of potassic ferricyanide in aqueous solution. When the oxidation was complete, the precipitate formed was collected on a filter, dried, and extracted with hot alcohol. On cooling the alcohol deposited the new compound in small iridescent plates which melted at 126°. It was readily soluble in hot alcohol, sparingly in cold alcohol, and dissolved freely in ether, chloroform, benzol, or ligroin. Analysis showed the substance to be dibromdifurfurdiacetylen (diacetenylbromfurfuryl):

$$C_4H_2BrO - C \equiv C - C \equiv C - C_4H_2BrO.$$

I. 0.2476 grm. substance gave 0.3888 grm CO_2 and 0.0383 grm. H_2O.
II. 0.1538 grm. substance gave 0.1696 grm. AgBr.
III. 0.1548 grm. substance gave 0.1702 grm. AgBr.

	Calculated for $C_{12}H_4Br_2O_2$.	Found. I.	II.	III.
C	42.36	42.82		
H	1.18	1.72		
Br	47.06		46.93	46.79

Bromfurfuracrylic Acid.

The behavior of the acid containing three atoms of bromine which was obtained by the direct action of bromine upon furfuracrylic acid left little doubt that it was a bromfurfurdibrompropionic acid. If this view were correct, it seemed not improbable that the bromine attached to the the side-chain might be removed without disturbing the bromine in the furfuran ring, and that a bromfurfuracrylic acid would thus be formed. After a few preliminary experiments it was found that zinc dust added to an alcoholic solution of the bromfurfurdibrompropionic acid brought about the desired result. The reaction is vig-

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* Ann. Chem. u. Pharm., cliv. 159.

† Ber. d. deutsch. chem. Gesellsch., xv. 57.

orous, and the boiling point of the alcohol soon reached. When the reaction is over, water is added to the filtered solution, and the acid which is thus precipitated is purified by conversion into its sodium salt, reprecipitation with hydrochloric acid, and recrystallization from dilute alcohol or boiling water. The yield of the new acid thus obtained was between 80 and 90 per cent of the theoretical amount, and analysis showed that it had the desired composition.

I. 0.2645 grm. substance gave 0.3768 grm. CO_2 and 0.0566 grm. H_2O.
II. 0.2511 grm. substance gave 0.2161 grm. AgBr.
III. 0.2223 grm. substance gave 0.1920 grm. AgBr.
IV. 0.1490 grm. substance gave 0.1288 grm. AgBr.

	Calculated for $C_7H_5BrO_3$.	Found. I.	II.	III.	IV.
C	38.71	38.86			
H	2.30	2.38			
Br	36.86		36.63	36.76	36.80

Bromfurfuracrylic acid crystallizes in long slender prisms, which are sparingly soluble in cold water, more readily in hot water. The acid dissolves readily in alcohol, ether, hot benzol, or hot chloroform, in cold benzol or cold chloroform it is but sparingly soluble, and it is nearly insoluble in ligroin. It melts sharply at 176–177°, but since it is somewhat decomposed and blackened by long continued heating above 150°, the bath must first be heated to within a few degrees of the melting point. Small quantities of the acid may readily be sublimed between watch-glasses. The sublimed product also melts at 176–177°, and darkens upon long heating. With bromine the acid unites readily, and forms the original substituted propionic acid. We have made many attempts to convert the acid into the corresponding substituted pyromucic acid, or to obtain from it by oxidation a product which should enable us to fix the position of the bromine atom, but hitherto without success. We can, therefore, at present only conjecture that the bromine in this case, as with the pyromucic acid, enters first the δ position. For the further characterization of the acid we have prepared a few of its salts.

Baric Bromfurfuracrylate, $Ba(C_7H_4BrO_3)_2 . H_2O$.—The barium salt is sparingly soluble in cold water, somewhat more readily in hot water, and crystallizes in clustered needles. When air-dried it loses nothing over sulphuric acid, gives up one molecule of water slowly at 100°, and is decomposed at a somewhat higher temperature.

I. 1.1830 grm. of the air-dried salt lost at 100° 0.0380 grm. H_2O.

II. 0.7064 grm. of the air-dried salt lost at 100° 0.0227 grm. H_2O.
III. 0.4898 grm. of the air-dried salt gave 0.1951 grm. $BaSO_4$.

	Calculated for $Ba(C_7H_4BrO_3)_2 . H_2O$.	Found.		
		I.	II.	III.
H_2O	3.07	3.21	3.21	
Ba	23.34			23.42

I. 0.5258 grm. of the salt dried at 100° gave 0.2149 grm. $BaSO_4$.
II. 0.4787 grm. of the salt dried at 100° gave 0.1955 grm. $BaSO_4$.

	Calculated for $Ba(C_7H_4BrO_3)_2$.	Found.	
		I.	II.
Ba	24.07	24.02	24.01

Calcic Bromfurfuracrylate, $Ca(C_7H_4BrO_3)_2 . 3\,H_2O$. — This salt crystallizes in columnar aggregations of plates, and is sparingly soluble in cold water, more readily in hot water. The air-dried salt effloresces over sulphuric acid, and is gradually decomposed at 100°, but may be dried without difficulty at 80–85°.

I. 1.1639 grm. of the air-dried salt lost at 82° 0.1184 grm. H_2O.
II. 0.7362 grm. of the air-dried salt lost at 83–85° 0.0740 grm. H_2O.
III. 0.6331 grm. of the air-dried salt gave 0.1648 grm. $CaSO_4$.
IV. 0.5287 grm. of the air-dried salt gave 0.1375 grm. $CaSO_4$.

	Calculated for $Ca(C_7H_4BrO_3)_2 . 3\,H_2O$.	Found.			
		I.	II.	III.	IV.
H_2O	10.07	10.17	10.05		
Ca	7.61			7.65	7.65

0.6123 grm. of the salt dried at 82° gave 0.1774 grm. $CaSO_4$.

	Calculated for $Ca(C_7H_4BrO_3)_2$.	Found.
Ca	8.47	8.52

Sodic Bromfurfuracrylate, $NaC_7H_4BrO_3$. — This salt is readily soluble even in cold water, and crystallizes in anhydrous nodular aggregations.

I. 0.7612 grm. of the salt gave 0.2228 grm. Na_2SO_4.
II. 0.7589 grm. of the salt gave 0.2206 grm. Na_2SO_4.

	Calculated for $NaC_7H_4BrO_3$.	Found.	
		I.	II.
Na	9.62	9.48	9.42

Argentic Bromfurfuracrylate, $AgC_7H_4BrO_3$. — The silver salt, formed by the addition of argentic nitrate to a neutral solution of the ammonium salt, proved to be nearly insoluble in water, and was apparently amorphous.

I. 0.3919 grm. of the salt gave 0.2261 grm. AgBr.
II. 0.4065 grm. of the salt gave 0.2347 grm. AgBr.

	Calculated for $AgC_7H_4BrO_3$.	Found. I.	II.
Ag	33.34	33.13	33.16

Ethyl Bromfurfuracrylate, $C_7H_4BrO_3 . C_2H_5$. — To a solution of the acid (5 parts) in somewhat more than its own weight of absolute alcohol (6.5 parts) was added concentrated sulphuric acid (3 parts), and the mixture heated upon the water bath for two or three hours. We found that too long heating should be avoided since decomposition then ensued, and a product was formed which undoubtedly was analogous to that obtained by Markwald.* We have, however, made no careful study of it. As soon as the etherification appeared to be complete, the ether was precipitated with water, dried with calcic chloride, and distilled under diminished pressure. The greater part of the product distilled at 151–152° under a pressure of 14 mm., and on cooling this distillate completely solidified. From ligroin the ether could be obtained in large flat prisms, which melted at 42°. It was readily soluble in alcohol, ether, chloroform, benzol, or ligroin and had a faint aromatic odor.

I. 0.1968 grm. substance gave 0.3168 grm. CO_2 and 0.0673 grm. H_2O.
II. 0.2251 grm. substance gave 0.1722 grm. AgBr.
III. 0.2545 grm. substance gave 0.1943 grm. AgBr.

	Calculated for $C_9H_9BrO_3$.	Found. I.	II.	III.
C	44.08	43.88		
H	3.67	3.80		
Br	32.65		32.55	32.49

We further attempted to make the amide, but found that the ether was hardly attacked by concentrated ammonic hydrate at 100°, and that at a much higher temperature (215°) most of the ether employed also remained unchanged.

BROMFURFURBROMACRYLIC ACID.

It already has been mentioned that bromfurfurdibrompropionic acid is decomposed by heat with the evolution of hydrobromic acid, and the simultaneous formation of a disubstituted furfuracrylic acid might be inferred. We have made many attempts to bring about this loss of one molecule of hydrobromic acid by more convenient and more economical methods, but without success. In alcoholic solution potassic hydrate gave chiefly the ethylen derivative and potassic carbonate.

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* *Loc. cit.*

no matter how the conditions of the reaction were varied. A number of high boiling neutral solvents gave no better results than those obtained by heating the acid by itself. The bromfurfurdibrompropionic acid was therefore carefully heated in shallow crystallizing dishes immersed in a sulphuric acid bath. The hydrobromic acid thus escaped without blackening the product to any great extent. The temperature was slowly raised to 130°, and when at this point the formation of hydrobromic acid was no longer noticeable the residue was boiled with dilute ammonic hydrate filtered, heated with bone-black, and the filtered solution concentrated by evaporation. In this way sparingly soluble finely felted needles of ammonic bromfurfurbromacrylate were obtained, which yielded the acid in a state of purity.

I. 0.2246 grm. substance gave 0.2328 grm. CO_2 and 0.0317 grm. H_2O.
II. 0.2290 grm. substance gave 0.2373 grm. CO_2 and 0.0314 grm. H_2O.
III. 0.2059 grm. substance gave 0.2615 grm. AgBr.
IV. 0.2025 grm. substance gave 0.2571 grm. AgBr.

	Calculated for $C_7H_4Br_2O_3$.	Found. I.	II.	III.	IV.
C	28.38	28.27	28.26		
H	1.35	1.57	1.53		
Br	54.05			54.04	54.03

Bromfurfurbromacrylic acid is almost insoluble even in hot water. It dissolves freely in ether or alcohol, and when precipitated by water from a hot alcoholic solution is obtained in fine clustered needles. At ordinary temperatures it is very sparingly soluble in chloroform or carbonic disulphide, but dissolves somewhat more freely on heating. The acid melts at 178–179° and small quantities of it may easily be sublimed without essential decomposition.

In spite of many attempts, we have been unable to obtain experimental evidence as to the position of the bromine atoms. We have also been unable to prepare definite products by the addition of bromine to the acid, or to form from it bromfurfurpropiolic by the elimination of hydrobromic acid. The following salts may serve for the better characterization of the acid.

Baric Bromfurfurbromacrylate, $Ba(C_7H_3Br_2O_3)_2 \cdot 2\ H_2O$. — This salt was prepared by adding baric chloride to a solution of the ammonium salt. It is very sparingly soluble even in boiling water, and crystallizes in lustrous scales. The air-dried salt contains two molecules of water, which it does not lose over sulphuric acid.

I. 1.4911 grm. of the air-dried salt lost at 120° 0.0674 grm. H_2O.
II. 0.8824 grm. of the air-dried salt lost at 120° 0.0399 grm. H_2O.

	Calculated for	Found.	
	$Ba(C_7H_3Br_2O_3)_2 . 2 H_2O$.	I.	II.
H_2O	4.72	4.52	4.52

I. 0.2130 grm. of the anhydrous salt gave 0.0684 grm. $BaSO_4$.
II. 0.2229 grm. of the anhydrous salt gave 0.0712 grm. $BaSO_4$.
III. 0.4376 grm. of the anhydrous salt gave 0.1398 grm. $BaSO_4$.

	Calculated for		Found.	
	$Ba(C_7H_3Br_2O_3)_2$.	I.	II.	III.
Ba	18.85	18.88	18.78	18.78

Argentic Bromfurfurbromacrylate, $AgC_7H_3Br_2O_3$. — The silver salt made by precipitation is very sparingly soluble even in boiling water, and is apparently amorphous.

I. 0.2052 grm. of the salt dried over sulphuric acid gave 0.0951 grm. AgBr.
II. 0.2101 grm. of the salt dried over sulphuric acid gave 0.0977 grm. AgBr.

	Calculated for	Found.	
	$AgC_7H_3Br_2O_3$.	I.	II.
Ag	26.80	26.62	26.71

Potassic Bromfurfurbromacrylate, $KC_7H_3Br_2O_3$.—The potassium salt is sparingly soluble in cold water, more readily soluble in hot water, and crystallizes in slender clustered needles which are anhydrous.

I. 0.2275 grm. of the salt gave 0.0589 grm. K_2SO_4.
II. 0.5386 grm. of the salt gave 0.1407 grm. K_2SO_4.

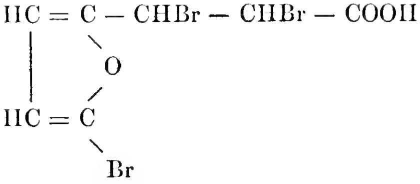
	Calculated for	Found.	
	$KC_7H_3Br_2O_3$.	I.	II.
K	11.70	11.62	11.72

Ethyl Bromfurfurbromacrylate, $C_7H_3Br_2O_3 . C_2H_3$. — The ethyl ether was made by heating for three hours on the water bath a solution of the acid (4 parts) in absolute alcohol (40 parts), with the addition of a small amount (3 parts) of concentrated sulphuric acid. The ether was then precipitated with water, washed with a dilute solution of sodic carbonate, and recrystallized from ligroin. It crystallized easily in radiated needles which melted at 55–56° and dissolved readily in alcohol, ether, chloroform, benzol, ligroin, or carbonic disulphide.

I. 0.3774 grm. of substance gave 0.4592 grm. CO_2 and 0.0849 grm. H_2O.
II. 0.2125 grm. substance gave 0.2464 grm. AgBr.
III. 0.2179 grm. substance gave 0.2525 grm. AgBr.

	Calculated for $C_9H_8Br_2O_3$.	Found.		
		I.	II.	III.
C	33.34	33.19		
H	2.47	2.50		
Br	49.39		49.35	49.32

While we have been unable to establish with precision the constitution of the foregoing derivatives of furfuracrylic acid, the analogies offered by the derivatives of pyromucic and cinnamic acids naturally suggest the following formulæ for the substances in question: —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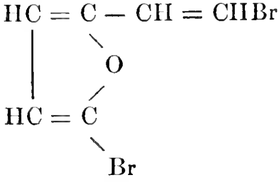
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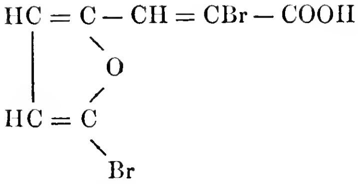
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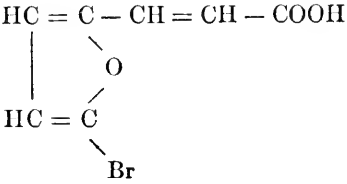
Bromfurfuracrylic Acid.

III. ON THE SO CALLED DIOXYMALEIC ACID.

By W. S. Hendrixson.

Presented May 28, 1889.

Several years ago Bourgoin[*] announced the discovery of two new acids which he had obtained by replacing the bromine of brommaleic and dibrommaleic acid by hydroxyl, and which he therefore called oxymaleic and dioxymaleic acid. Although the experimental evidence as to the existence of these acids was very slight, and their assumed structure wholly anomalous, they soon found place in many text-books.

In 1886, at the suggestion of Fittig, the work of Bourgoin upon oxymaleic acid was repeated by Scherks,[†] who found that his statements were without foundation, and that brommaleic acid in aqueous solution was not in the least attacked by argentic oxide, even at 100°. Scherks further concluded that Bourgoin's statements concerning his dioxymaleic acid must also be incorrect, because the dibrommaleic acid which he used he claimed to have made from his tribromsuccinic acid, an acid which could not be formed under the given conditions, as shown by Fittig and Petri,[‡] or if formed would at once be decomposed into dibromacrylic acid and carbonic dioxide. This conclusion of Scherks seems hardly justified by Bourgoin's statements. The dibrommaleic acid which he used undoubtedly was made by the action of aqueous bromine upon succinic acid, and, while his material may have been far from pure, the question of its identity is in no way affected by his erroneous assumption that it had been formed by the decomposition of tribromsuccinic acid. In any case the subject seemed to demand a more careful investigation. At the suggestion of Prof. H. B. Hill, I have, therefore, repeated Bourgoin's work upon dioxymaleic acid, and find that decomposition is in this case readily effected, but that the product formed is not dioxymaleic acid.

The dibrommaleic acid needed for this investigation was made by the oxidation of mucobromic acid with cold fuming nitric acid, a method which had already been found in this laboratory to be much more advantageous than the methods previously described. Muco-

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[*] Bull. de la Soc. Chim., xix. 482; xxii. 443.

[†] Ann. d. Chem. u. Pharm., ccvii. 223.

[‡] Ibid., cxcv. 70.

bromic acid was dissolved in cold fuming nitric acid, and the nearly saturated solution allowed to stand for several days at ordinary temperatures. When the mixture had completely solidified, the nitric acid was expelled by gentle heat, and the dry residue distilled from a small retort. In order to obtain a perfectly pure product, the distillate was dissolved in water, neutralized with baric carbonate, and the baric dibrommaleate precipitated by the addition of alcohol. The barium salt was then converted into the sodium salt, and from this the silver salt was made by precipitation with argentic nitrate.

According to Bourgoin, dioxymaleic acid is formed by heating argentic dibrommaleate with water to 150°. On opening the tubes after heating for five hours he found that carbonic dioxide escaped, that argentic bromide had been formed, and that the liquid in the tubes was distinctly acid. On the addition of argentic nitrate to this acid solution carefully neutralized with ammonic hydrate he obtained a white insoluble silver salt, which gave on ignition a residue closely agreeing with the weight of metallic silver required by the formula $Ag_2C_4H_2O_6$. He found the acid to be a white crystalline solid, which was readily soluble in water and alcohol, and barely soluble in ether. With the alkalies and alkaline earths it formed readily soluble salts, and showed itself to be non-saturated in that it was capable of fixing hydrogen and bromine. Bourgoin gives, however, no analytical results whatsoever except the one already mentioned.

On following closely the directions of Bourgoin, I found that the argentic dibrommaleate had been almost completely decomposed, and that at least 95 per cent of the theoretical amount of argentic bromide had been formed. The liquid in the tubes was strongly acid, but the carbonic dioxide which escaped was by no means insignificant in quantity. Although the aqueous solution gave a crystalline precipitate with argentic nitrate after careful neutralization with ammonic hydrate, it was thought advisable to distil the liquid with steam before preparing salts for analysis, since it was found that the acid volatilized readily under these conditions. The acid distillate was neutralized with calcic carbonate, the silver salt precipitated by the addition of argentic nitrate to the concentrated solution, and recrystallized from hot water. The silver salt thus obtained closely resembled argentic acetate, and its identity was established by analysis.

I. 0.4677 grm. of the air-dried salt gave 0.5249 grm. AgBr.

II. 0.2263 grm. of the air-dried salt gave 0.1465 grm. Ag.

III. 0.2056 grm. of the salt dried over sulphuric acid gave 0.1082 grm. CO_2, 0.0330 grm. H_2O, and 0.1327 grm. Ag.

	Calculated for $AgC_2H_3O_2$.	Found. I.	II.	III.
Ag	64.67	64.46	64.73	64.54
C	14.37			14.35
H	1.80			1.78

The barium salt was also made by neutralizing the acid distillate with baric carbonate. The salt obtained on evaporation was either recrystallized from water, or precipitated from a concentrated aqueous solution by alcohol. I failed to find any definite statements as to the composition of the salt thus precipitated by alcohol, but experiments of my own showed that it contained one molecule of water like the salt crystallized from water.

I. 1.1456 grm. of the air-dried salt lost at 150° 0.0780 grm. H_2O.
II. 0.9187 grm. of the air-dried salt lost at 125° 0.0609 grm. H_2O.
III. 0.4561 grm. of the air-dried salt gave 0.3899 grm. $BaSO_4$.
IV. 0.6868 grm. of the air-dried salt gave 0.5841 grm. $BaSO_4$.

	Calculated for $Ba(C_2H_3O_2)_2 . H_2O$.	Found. I.	II.	III.	IV.
H_2O	6.59	6.80	6.62		
Ba	50.18			50.25	50.02

0.8554 grm. of the salt dried at 125° gave 0.7811 grm. $BaSO_4$.

	Calculated for $Ba(C_2H_3O_2)_2$.	Found.
Ba	53.73	53.69

It thus appears that acetic acid is formed in the decomposition of argentic dibrommaleate by water at 150° and the reaction may be expressed by the equation :

$$Ag_2C_4Br_2O_4 + 2\,H_2O = 2\,AgBr + CO_2 + C_2H_4O_2.$$

The weight of baric acetate which was obtained from the distilled liquid amounted to about 60 per cent of the theoretical yield required by this equation, while 85 per cent of the theoretical amount of free acid, calculated as acetic acid, was found by direct titration of the contents of the tubes. The higher result in the latter case may in part have been due to incomplete expulsion of the carbonic dioxide, but the most careful search failed to show that any well defined organic acid except acetic acid had been formed in the reaction. Dibrommaleic acid therefore yields, under the conditions prescribed by Bourgoin for its conversion into dioxymaleic acid, carbonic dioxide and acetic acid. The facts observed give no certain information as to the mechanism of the reaction. If it is assumed that the body

$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{OH}} \\ \| \\ \mathrm{C}^{\mathrm{OH}}_{\mathrm{H}} \end{array}$$

is first formed, it would pass at once into the aldehyde alcohol

$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{C}^{\mathrm{H_2}}_{\mathrm{OH}} \end{array}$$

from which acetic acid would then be formed, precisely in the same way that tartronic acid is formed from dibrompyruric acid,* or from dioxytartaric acid.† It is more probable, however, that the ketone acid

$$\begin{array}{l} \mathrm{COOH} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{C}^{\mathrm{H}}_{\mathrm{OH}} \\ | \\ \mathrm{COOH} \end{array}$$

is the first product, and that this passes into acetic acid in a similar way through the loss of carbonic dioxide.

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* Grimaux, Bull. de la Soc. Chim., xxvii. 440.

† Kékulè, Ann. Chem. u. Pharm., ccxxi. 230.

XXVII.

AN ADDRESS

DELIVERED AT THE MEETING OF APRIL 10, WHEN THE RUMFORD MEDALS WERE PRESENTED TO PROFESSOR A. A. MICHELSON.

BY JOSEPH LOVERING.

FOR many generations it was assumed that no sensible time was taken by light in moving over the largest distances. The velocity of sound was found by noting the time which elapsed between seeing the flash and hearing the report of an explosion. It was only in the vast spaces of astronomy that distances existed large enough to unmask the finite velocity of light, and, in extreme cases, to make it seem even to loiter on its way.

The satellites of Jupiter were discovered by Galileo in 1610; and the eclipses of these satellites by the shadow of Jupiter became an interesting subject of observation. It was soon noticed that the interval between successive eclipses of the same satellite was shorter when the earth was approaching Jupiter, and longer when the earth was receding from Jupiter. The change of pitch in the whistle of a locomotive, under similar motions, would suggest to the modern mind an easy explanation. A Danish astronomer, Römer, without the help of this analogy, deciphered the problem in astronomy. The eclipse was telegraphed to the observer by a ray of light, and the news was hastened or delayed in proportion to the distance from which it came. In this way it was discovered that light took about 18 minutes to run over the diameter of the earth's orbit. This discovery was published by Römer in the Memoirs of the French Academy in 1675. The mathematical astronomer Delambre, from a discussion of one thousand of these eclipses observed between 1662 and 1802, found for the velocity of light 193,350 miles a second.

Meanwhile Römer's method, after fifty years of waiting, had been substantially confirmed in an unexpected quarter. Dr. Bradley of the Greenwich Observatory, the greatest astronomical observer of his day, was perplexed by certain periodical fluctuations, of small amount, in the position of the stars. Suddenly the explanation was flashed upon him by something he observed while yachting on the River Thames. He noticed that, whenever the boat turned about, the direction of the vane altered. He asked the sailors, Why? All they could say was, that it always did. Reflecting upon the matter, Bradley concluded that the motion of the boat was compounded with the velocity of the wind, and that the vane represented the resultant direction. He was not slow in seeing the application of this homely illustration of the parallelogram of motion to his astronomical puzzle. The velocity of light was compounded with the velocity of the earth in its orbit, so that its apparent direction differed by a small angle from its true direction, and the difference was called aberration. In spearing a fish or shooting a bird, the sportsman does not aim *at* them, but *ahead* of them. This inclination from the true direction is similar, in angular measure, to what the astronomer calls aberration. Struve's measurement of aberration combined with the velocity of the earth in its orbit gave for the velocity of light 191,513 miles a second. Both of the two methods described for obtaining the velocity of light depend for their accuracy upon the assumed distance of the earth from the sun. The distance adopted was the one found by the transits of Venus in 1761 and 1769, viz. 95,360,000 miles.

During the last forty years, the opinion has been gaining ground among astronomers that the distance of the sun, as deduced from the transits of Venus in 1761 and 1769, was too large by three per cent. Expeditions have been sent to remote parts of the earth for observing the planet Mars in opposition. The ablest mathematical astronomers, as Laplace, Pontecoulant, Leverrier, Hansen, Lubbock, Airy, and Delaunay, have applied profound mathematical analysis to the numerous perturbations in the planetary motions, and proved that the sun's distance must be diminished about 2,000,000 miles in order to reconcile observations with the law of gravitation. Airy reduced the distance of the sun by more than 2,000,000 miles, to satisfy the observations on the transit of Venus in 1874. Glasenapp derived from observed eclipses of Jupiter's satellites a distance for the sun of only 92,500,000 miles. From these and similar data, Delaunay concluded that the velocity of light is about 186,420 miles a second.

These triumphs of astronomical theory recall the witty remark of Fontenelle, that Newton, without getting out of his armchair, calculated the figure of the earth more accurately than others had done by travelling and measuring to the ends of it. And Laplace, in contemplation of similar mathematical achievements, says: "It is wonderful that an astronomer, without going out of his observatory, should be able to determine exactly the size and figure of the earth, and its distance from the sun and moon, simply by comparing his observations with analysis; the knowledge of which formerly demanded long and laborious voyages into both hemispheres."

The ancients supposed that light came instantaneously from the stars; a consolation for those who believed that the heavens revolved around the earth in twenty-four hours. Galileo and the academicians of Florence obtained even negative results.

While the number of physical sciences has received numerous additions during the last half-century, new affiliations and a more intimate correlation have been manifested. In this mutual helpfulness light has played an important part. The optical method of studying sound, and the many varieties of flame apparatus, have made acoustics as intelligible through the eye as through the ear.

Velocity being expressed by space divided by time, it is evident that, in measuring an immense velocity, we must have at our command an enormous distance, such as we find only in astronomy, or else possess the means of measuring fractions of time as small as one millionth of a second. The first successful attempt to measure such a velocity was made by Wheatstone in 1834. Discharges from a Leyden jar were sent through a wire, having two breaks in it, $\frac{1}{4}$ of a mile apart. The wire was in the form of a loop, so as to bring the breaks into the same vertical line. The sparks, seen at these breaks, were reflected by a mirror, at the distance of 10 feet, and revolving 800 times per second. The images of the two sparks were relatively displaced in a horizontal direction. As the displacement did not exceed one half of an inch, the time taken by electricity to go from one break to the other was less than a millionth of a second. Since the distance was one quarter of a mile, the electricity travelled, *in that case,* at the rate of 288,000 miles a second. If this experiment is interpreted to mean that electricity would go over 288,000 miles of similar wire in one second, as it probably often was at that time, the conclusion is fallacious. The velocity of electricity, unlike that of sound or light, diminishes when the length of wire increases.

In 1838, Wheatstone suggested a method for measuring the velocity of light, which he thought was adequate for giving, not only the absolute velocity, but the difference of velocity in different media.

In that year Arago communicated to the French Academy the details of an experiment which he thought would give the velocity of light in air or a vacuum. As his own health was broken down (he died in 1853) he appealed to two young French physicists to undertake the experiment. On July 23, 1849, Fizeau, by a method wholly his own, made a successful experiment. A disk, cut at its circumference into 720 teeth and intervals, and made by Breguet, was rapidly rotated by a train of wheels and weights. A concentrated beam of light was sent out through one of the intervals between two teeth of the disk, which was mounted in a house in Suresne, near Paris, and was sent back by a mirror placed on Montmartre at a distance of about five miles. The light, on its return, was cut off from the eye or entered it, according as it encountered a tooth or an interval of the disk. If the disk turned 12.6 times in a second, the light encountered the tooth adjacent to the interval through which the light went out. With twice as many rotations in the disk, the light could enter the eye through the adjacent interval. With three times the original velocity, it was cut off by the next tooth but one, and so on. From the number of teeth and the number of rotations in a second, the time taken by the light in going and returning was easily calculated. In this way the velocity of light was found to be 195,741 miles per second. In 1856 the Institute of France awarded to Fizeau the Imperial Prize of 30,000 francs in recognition of this capital experiment.

In 1862, Foucault succeeded in measuring the velocity of light by a wholly different method, all parts of the apparatus for it being embraced within the limits of his laboratory. The light emanated from a fine reticule, ruled on glass and strongly illuminated by the sun. It then fell upon a plane mirror revolving 400 times a second, by which it was reflected successively to five other mirrors, the last of which was plane, and returned it back, by the same path. to the revolving mirror and reticule. The total distance travelled was only about 66 feet. As the revolving mirror had moved while the light was making this short journey, the image of the reticule was displaced in reference to the reticule itself; and this displacement was the subject of measurement. Although the time involved was only about one 15,000,000th of a second, this brief interval was translated by the method of the experiment into a measurable space, and gave 185,177 miles per second for the velocity of light, differing from the best results of astronomical methods by only 1,243 miles. Foucault was prompted to this experiment by Leverrier, Director of the Observatory. Arago was the first to propose the experiment. To obtain greater accuracy, he placed the moving mirror in a vacuum, but without any advantage: he said, "Le mieux est l'ennemi du bien." His modest claim was that he had suggested to Foucault the problem. and indicated certain means of resolving it. Babinet thought that the experiment admitted of ten times greater accuracy. With three times only it might correct Struve's value of aberration.

In 1873, Cornu, another French physicist, repeated the experiments of Fizeau with a toothed wheel, the work extending over three years. The observer was stationed at the École Polytechnique. The reflecting mirror and collimating telescope were placed on Mont Valerian, at a distance of about 33,816 feet. Three different wheels were tried, having 104, 116, and 140 teeth respectively, and rotating between 700 and 800 times a second, the velocity being registered by electricity. Cornu used at times all the eclipses from the first to the seventh order. Calcium and petroleum light were tried, as well as sunlight. A chronograph with three pens recorded automatically seconds, the rotations of the toothed wheel, and the time of the eclipse. More than a thousand experiments were made, 600 of which were reduced. The velocity of light as published by Cornu in 1873 was 185,425.6 miles per second. The probable error was one per cent. In 1874, Cornu gave the result of a new set of experiments made by him in conjunction with Fizeau, over a distance of more than 14 miles between the Observatory and Montlhéry. The experiments were repeated more than five hundred times, mostly at night with the lime light. The light was sent through a 12 inch telescope and returned through a 7 inch telescope. The toothed wheel which produced the eclipse was capable of rotating 1,600 times a second. From these experiments the velocity of light was placed at 186,618 miles. The probable error did not exceed 187 miles. The time was recorded accurately within a thousandth of a second.

I come now to that which most interests us to-night, viz. the part taken in this country for the measurement of these great velocities. About 1854, Dr. Bache, chief of the U. S. Coast Survey, appropriated $1,000 for the construction of apparatus to be used in repeating Wheatstone's experiment on the velocity of electricity. But those who were expected to take part in the investigation were called to other duties, and the money was never drawn.

In 1867, Professor Newcomb recommended a repetition of Foucault's experiment, in the interest of astronomy, to confirm or correct the received value of the solar parallax. In August, 1879, Mr. Albert A. Michelson, then a Master in the United States Navy, presented a paper to the meeting of the American Association for the Advancement of Science, on the measurement of the velocity of light. This paper attracted great attention. Mr. Michelson adopted Foucault's method with important modifications. In Foucault's experiment, the deflection of the light produced by the revolving mirror was too small for the most accurate measurement. Mr. Michelson placed the revolving mirror 500 feet from the slit (which was 10 times the distance in Foucault's experiment) and obtained a deflection 20 times as great, although the mirror made only 128 turns in a second. With apparatus comparatively crude, he obtained for the velocity of light 186,500, with a probable error of 300 miles. This preliminary experiment, made in the laboratory of the Naval Academy in May, 1878, indicated the directions in which improvements must be made in order to insure greater accuracy. The distance from the slit to the revolving mirror must be increased, the mirror must revolve at least 250 times a second, and the lens for economizing the light must have a large surface and a focal length of about 150 feet. With the aid of $2,000 from a private source, Mr. Michelson was able to carry out his ideas on a liberal scale.

His new experiments were made in the summer of 1879. The revolving mirror, made by Alvan Clark and Sons, was moved by a turbine wheel. Its rapidity of revolution was measured by optical comparison with an electric fork which made about 128 vibrations a second, the precise value being accurately measured by reference to one of König's standard forks. The velocity generally given to the mirror was about 256 turns a second. The distance between the revolving and the fixed mirror was 1,986.26 feet. The light from the moving mirror was concentrated on the fixed mirror by a lens 8 inches in diameter, with a focal length of 150 feet. These improvements on Foucault's arrangement were so advantageous that Mr. Michelson obtained, even with a smaller speed in the revolving mirror, an angle of separation between the outgoing and returning rays of light so great that the inclined plate of glass in front of the micrometer was not necessary; the head of the observer not shutting off the light. The mean result of 100 observations taken on 18 different days made the velocity of light 186,313 miles per second; with a probable error of 30 miles.

In 1882, at the request of Professor Newcomb, Mr. Michelson made a redetermination of the velocity of light at the Case Institute, in Cleveland, Ohio, by the method already described, with some modifications. The space traversed by the light in going and returning between the two mirrors was 4,099 feet. Two slight errors in the reduction of his former work were corrected in this. The velocity deduced from 563 new observations was 186,278 miles, with a probable error of 37 miles.

In March, 1879, Congress had voted an appropriation of $5,000 for experiments on the velocity of light, to be made under the direction of Professor Newcomb. All the delicacy of instrumental construction, all the skill of scientific observation, and all the resources of mathematical discussion, were enlisted in this service. The method adopted was that of the revolving mirror. The movable mirror was mounted at Fort Myer. Two different locations were selected for the fixed mirror, viz. the Naval Observatory, and the Washington Monument. In one case the distance was 2,550.95 meters, or about 8,367.12 feet; in the second case, 3,721.21 meters, or about 12,205.57 feet. Mr. Michelson assisted in the observations until his removal to Cleveland, in the autumn of 1880. The observations began in the summer of 1880, and were continued into the autumn of 1882, the most favorable days in spring, summer, and autumn being selected. In all 504 sets of measurements were made; viz. 276 by Professor Newcomb, 140 by Professor Michelson, and 88 by Mr. Holcombe. After a full discussion of all the observations and the possible sources of error, Professor Newcomb decided to rest the final result on the 132 sets of observations made in 1882 over the long distance between Fort Myer and the Washington Monument. The velocity then obtained was 186,282 miles. The velocity deduced from the three sets of observations was 186,251 miles. The probable error of the first result was about 19 miles.

For some future attack upon this problem Professor Newcomb suggested a prism for the reflector with a pentagonal section, and placed at such a distance that it could revolve through an arc of 36° while the light was going and returning: 500 turns a second and a distance of 19 miles would fulfil this condition. In the Rocky Mountains, or the Sierra Nevada, stations from 20 to 30 miles distant could be found, and with no greater loss of light from absorption than is produced by 2 or 3 miles of common air.

The first experiments made in Great Britain for the measurement of the velocity of light were published by James Young and Professor G. Forbes in the Philosophical Transactions of 1882. They adopted the method of Fizeau. In 1878, between 600 and 700 observations were made; but the number of teeth in the rotating wheel was insufficient. New experiments were made in 1880–81 across the river Clyde. Two reflectors were used at unequal distances, and the time was noted when an electric light after the two reflections was at its maximum. The corrected distances for the two mirrors were 18,212.2 and 16,835 feet. After an elaborate mathematical discussion of the theory of this method, the velocity of light was placed at 187,221 miles. This value exceeded those obtained by Cornu or Michelson; but this might be explained by the color of the light used in the different experiments. Mr. Young and Professor Forbes made some experiments with lights of different colors, in confirmation of this view. But Professor Michelson compared his 318 observations with sunlight and 267 observations with electric light, and found that the difference was in the opposite direction; and in a differential experiment, when half the slit was covered with red glass, he found no displacement. Young and Forbes were attracted to their experiments on the velocity of light by Maxwell's speculations on the electromagnetic theory of light, and also as promising the most accurate method of obtaining the parallax and distance of the sun. Their velocity of light combined with Struve's constant of aberration made the sun's parallax $20''.445$, and its distance 93,223,000 miles.

When Arago, in 1838, suggested to the French Academy an experiment on the velocity of light, and explained his method of making it, which was essentially the one afterwards adopted by Foucault, he had in view the settlement of the long controversy between the advocates of the corpuscular and undulatory theories. Almost all of the different classes of phenomena in geometrical optics can be explained by either one of these theories, though even here the undulatory has the advantage of greater simplicity. But in one respect the two theories are antagonistic. According to the corpuscular theory, light should move faster in glass or water than in air, for example. The undulatory theory reversed this proposition. Here was an *experimentum crucis.* In 1850, Fizeau and Foucault made the experiment, each in his own way, and in both experiments the result was in favor of the theory of undulations. It has been shown that in the case of air alone lengths of many thousand feet are practicable. But the absorbing power of water prevents the use of greater lengths than about 10 feet. Light would pass through 10 feet of air in less time than $\frac{1}{18000}$ of a second; and the difference of time for air and water would be only a fraction of that small fraction. Hence the exceeding delicacy of the experiment.

In 1883, Mr. Michelson, at the request of Professor Newcomb, repeated Foucault's experiments for finding the difference of the velocity of light in air and water. Foucault did not aspire to quantitative precision in his results. The experiments of Michelson proved that the ratio of the velocities was inversely as the indices of refraction. The velocity with sunlight was a little greater than with the electric light;

which opposes the conclusion of Young and Forbes. When Mr. Michelson covered half of the slit with red glass, the two halves of the image were exactly in line. Experiments were also made on the velocity of light in carbon disulphide, which led to the inference that its index of refraction was 1.77, and that orange-red light travelled from one to two per cent faster than greenish blue light. Mr. Michelson was enabled to make this investigation by a grant from the trustees of the Bache Fund.

Various other methods of measuring the velocity of light have been proposed. About 1850, Laborde suggested, in a letter to Arago, a mechanical method of measuring the velocity of light. He supposes two disks, with many holes at the outside, connected by a very long axis and rotating rapidly. The light which was sent out through a hole in one wheel would be transmitted or arrested by the second wheel, behind which an observer was stationed. The distance between the wheels, the time of rotation, and the order of the eclipse, would be sufficient for calculating the velocity of light. Laborde imagined an enormous axis more than 200,000 miles long. Moigno recommended the substitution of a mirror for the observer and the second wheel, which would double the distance travelled by the light. A distance of 1,640 feet, a disk 25 feet in radius, with 1,000 holes, and turning 360 times a second, would be more than sufficient to surprise the reflected ray and stop it.

In 1874, Burgue suggested a new way of finding the velocity of light by experiment. If a white disk, with a black radius, is rotated rapidly, and at each turn is illuminated by an instantaneous flash, this radius will appear immovable. If this flash is reflected on the disk from a distant mirror, the black radius will be displaced. No details of the arrangement of apparatus and no experiments were published.

In 1885, Wolf proposed the following arrangement. Two mirrors were placed five meters apart and facing each other. The radius of curvature of each mirror was five meters. The first mirror was 0.20 of a meter in diameter: the other, 0.05 m., revolved rapidly (200 turns a second). A slit was made in the centre of the large mirror through which light was sent to the small mirror, forming an image on the surface of the large mirror: this image became an object for the small mirror, forming another image on the large mirror, at a distance from the first mirror depending on the velocity of rotation. These images could be sent out laterally by an inclined plate of thin glass, and their distances measured by a micrometer. Wolf expected advantages from the proximity of the two mirrors which would more than balance those of the long distances used by Foucault and Michelson.

The greatest difficulty which the undulatory theory of light has encountered is found in the attempted reconciliation between the requirements of the refraction of light and the aberration of light. To explain refraction, the density of the luminiferous ether must be greater when the index of refraction is greater. If a body moves, it must carry its enclosed ether with it, as its refractive power does not change. On the other hand, to explain the aberration of light, it must be supposed that the ether in the telescope does not move with the telescope; that the ether sifts through the telescope, the ether in front taking the place of the ether left behind; or, as Young expressed it, that the ether flows through the air and solid earth as easily as the wind blows through the trees of a forest.

The difficulty can be eluded by supposing that a refracting body carries along with it as much of the ether as it possesses in excess of what would exist in a vacuum of the same bulk. This, added to what is always sifting through it, would maintain its ether at a constant density. What this fraction is which must travel with the body was calculated by Fresnel. But while the refracting power has been protected, how is it with aberration? That would be increased to a small extent. But as the aberration is very small, only about 20½″ at its maximum, the required change in its value might be masked by ordinary errors of observation. Boscovich suggested to Lalande, in 1766, that a telescope filled with water instead of air would test the theory; but he made no experiment. Wilson of Glasgow also proposed a water telescope in 1782. In the course of time it appeared that not only was the effect of the earth's motion on refraction and aberration under trial, but also the solar parallax, the motion of the solar system, and that of other stars.

The case is clearly stated by Lodge in this way. Sound travels quicker with the wind than against it. Is it the same with light? Does light travel quicker with the wind? Well, that depends altogether on whether the ether is blowing along as well as the air. If it is, then its motion must help the light on a little; but if the ether is at rest, no motion of the air, or of matter of any kind, can make any difference. According to Fresnel, the free is at rest, the bound is in motion. Therefore the speed of light will be changed by the motion of the medium; but only by a fraction, depending on its index of refraction, — infinitesimal for air, but sensible for water.

At an early day Arago investigated the effect which a change in the velocity of light would produce on aberration and refraction. He saw that a change of five per cent in the velocity of light would alter the aberration by only one second, whereas the refraction in a prism of 45° would be affected to the extent of two minutes. He observed the zenith distances of stars with and without the prism; and also the deviation of stars which passed the meridian at 6 A. M. and 6 P. M. The observations were made with a mural circle and a repeating circle. Arago expected to find a difference of 10 or 15 seconds, but found none. He thought that a difference no greater than one ten-thousandth would have been manifested by his observations had it existed. Arago attempted to explain his negative results by assumptions based upon the corpuscular theory of light. But Lloyd thought that the change in the length of the wave would balance the change in the direction of the ray. Arago's observations were communicated to the Institute on December 10, 1816, and excited great interest. They were quoted by Laplace and Biot. But the manuscript was mislaid and not found until 1853, when it was published. Mascart thinks that this experiment of Arago owes its reputation to Fresnel's explanation of it by his fraction.

In regard to the wave-motion involved in the transmission of light, Maxwell says: "It may be a displacement, or a rotation, or an electrical disturbance, or indeed any physical quantity which is capable of assuming negative as well as positive values. But the ether is loosely connected with the particles of gross matter: otherwise they would reflect more light." Then he asks the question, "Does the ether pass through bodies as water through the meshes of a net which is towed by a boat?" It is difficult to obtain the relative motion of the earth and ether by experiment, as the light must move forward and then back again. One way is to compare the velocities of light obtained from the eclipses of Jupiter's satellites when Jupiter is in opposite points of the ecliptic. Cornu referred, in 1883, to the difficulty of observing these eclipses, especially when Jupiter is in conjunction with the sun. On account of this difficulty observations have been neglected for the last fifty years. Observations must be made near quadratures. Cornu suggests a proper arrangement for this purpose.

At various times between 1864 and 1868 Maxwell repeated Arago's experiment in a more perfect form. A spectroscope was used, having three prisms of 60° each. A plane mirror was substituted for the slit of the collimator. The cross-wires of the observing telescope were illuminated by light reflected by a plate of thin glass placed at an angle of 45°. Light went to the mirror and was sent back to the wires from which it started after passing through six prisms. The experiment was tried when the light started in the direction of the earth's motion, and when in the opposite; also, at different seasons of the year. In all cases the image of the wires coalesced with the wires.

Lodge states the case clearly thus: "If all the ether were free, there would have been a displacement of the image of the wires. If all the ether were bound to the glass, there would have been a difference on the other side. But, according to Fresnel's hypothesis, there should be no difference either way. According to his hypothesis, the free ether, which is the portion in relative motion, has nothing to do with the refraction. It is the addition of the bound ether which causes the refraction, and this part is stationary relatively to the glass, and is not streaming through it at all. Hence the refraction is the same whether the prism be at rest or in motion through space." Maxwell is more guarded in his own statement of the case. He says: "We cannot conclude certainly that the ether moves with the earth. For Stokes has shown from Fresnel's hypothesis that the relative velocities of the ether in the prism and that outside are inversely as the square of the index of refraction, and the deviation in this case would not be sensibly altered; the velocity of the earth being only one ten-thousandth of the velocity of light."

In 1879, Maxwell wrote to Professor D. P. Todd, then at the Nautical Almanac Office in Washington, asking him if he had observed an apparent retardation of the eclipses of Jupiter's satellites depending on the geocentric position of the planet. Such observations, he thought, would furnish the only method he knew of finding the direction and velocity of the sun's motion through the surrounding medium. In terrestrial methods of measuring the velocity of light, it returns on its path, and the velocity of the earth in relation to the ether would alter the whole time of passage by a quantity depending on the square of the ratio of the velocities of the earth and light, and this is quite too small to be observed.

In 1839, Babinet made a very delicate experiment on the relation of the luminiferous ether to the motion of the earth. He found that when two pieces of glass of equal thickness were placed across two beams of light which interfered so as to produce fringes, one of them moving in the direction of the earth's motion and the other contrary to it, the fringes were not displaced. The experiment was made three times by Babinet, with new apparatus each time. He concludes that here is a new condition to be fulfilled by all theories in regard to the propagation of light in refracting media. According to all the theories admitted or proposed, the displacement of the fringes should have been equal to many lengths of a fringe, that is, many millimeters, while by observation it was nothing. Stokes has calculated the result according to Fresnel's theory, or his own modification of it, and found that the retardation expressed in time was the same as if the earth were at rest. Fizeau has pointed out a compensation in the effect of Babinet's experiment. He says: "When two rays have a certain difference of march, this difference is altered by the reflexion from the turning mirror." By calculating the two effects in Babinet's experiment, Fizeau finds that they have sensibly equal values, and of opposite sign.

In 1860, Angström communicated to the Royal Society of Upsala a method of determining the motion of the solar system by observations on the bands of interference produced by a glass grating. In 1863 he published the results which he had obtained. After allowing for Babinet's correction on account of the motion of the grating, Angström finds that a difference in the direction of the observing telescope with reference to the earth's motion might produce a displacement of the fringes amounting to $49''.8$. Selecting the line D in the fourth spectrum, he thought that the influence of the earth's annual motion was verified, but that of the motion of the solar system was less decided. The observations were more consistent with the assumption that the solar system moved with a velocity equal to one third of that in its orbit, than with an equal velocity, or none at all. In 1862–63, Babinet presented to the Academy of Paris a paper on the influence of the motion of the earth on the phenomena produced by gratings, which depend not on reflection, refraction, or diffraction, but on interference. His principal object was a study of the motion of the solar system. He calculated the effects to be expected, but published no observations. In 1867, Van der Willigen measured the length of waves of light by means of a grating. When a slit was used, no effect was produced by the motion of the earth, the slit partaking of that motion. With a star, a movement of the earth in the direction of the light had an effect. This is the theoretical result, and agrees with Babinet's experiment, but is not applicable to solar light when reflected by a mirror. That behaves as light from a terrestrial source. In 1873, he rejects the proposition that the refraction of light is modified by the motion of its source or of the prism. In 1874, he seems to doubt the reality of the effect produced on diffraction.

In 1867, Klinkerfues used a transit instrument having a focal length of eighteen inches. In the tube was a column of water eight inches long, and a prism. He observed transits of the sun and of certain stars whose north polar distance was equal to the sun's, and which passed the meridian at midnight. The difference of right ascension is affected by double the coefficient of aberration. He computed that the column of water and the prism would increase the aberration by 8″. The amount observed was 7″.1. In 1868–69, Hoek of Amsterdam discussed the influence of the earth's motion on aberration. Delambre had calculated from the eclipses of Jupiter's satellites that light must take 493″.2 in coming from the sun. Hence the aberration must be 20″.255. Struve's observed aberration made the time 497″.8. Hoek decided in favor of Struve; but he thought that it was desirable that a new set of observations should be made on the eclipses. Klinkerfues espoused the side of Delambre. Hoek said that, if the earth's motion was taken into account, according to Fresnel's fraction, different results would be harmonized. In 1868 he made experiments on a divided beam of light, the two parts going in opposite directions through tubes filled with water. There was no interference attributable to the effect of the earth's motion. As to any influence to be expected from the motion of the solar system, he thinks that motion must be insignificant compared with the initial motion of the comets, and with the cometary orbits, which are parabolas with few hyperbolas.

In 1872, and on several previous occasions, one of the grand prizes of the Academy of Paris was offered for an investigation of the effect produced by the motion of the luminary or of the observer. This prize, consisting of a gold medal or three thousand francs, was awarded in 1874 to Mascart. He maintained that in Arago's experiment the change in refraction produced by the fraction of the earth's motion was compensated by the displacement of the observing telescope. Mascart repeated Babinet's experiment with gratings, where the effects of the motion of the telescope and of the grating would be additive, and found the sum small compared with Babinet's calculation. He thinks that the change in the length of the wave caused by the motion is compensated by the displacement of the measuring apparatus. He concludes that reflection, diffraction, double refraction, and circular polarization are powerless to show the motion of the earth, either with solar light or that from a terrestrial source.

In 1871, Airy used a vertical telescope, and measured the meridional zenith distance of γ Draconis, the star by which Bradley discovered aberration. It is about 100″ north of the zenith. The tube of the telescope, which was 35.3 inches long, was filled with water. The days of observation included the seasons of the equinoxes, when the star is most affected in opposite directions by aberration. The observations were repeated in the spring and autumn of 1872. No increase was produced in the aberration by the water in the telescope.

In 1873, Ketteler, in the Preface to the "Laws of the Aberration of Light," enumerates thirty-nine persons who have investigated the effect of motion on the phenomena of sound and light. From his own analysis he concludes: 1. that a motion of the prism and telescope perpendicular to the direction of a star produces no effect on the refraction; 2. that when the motion is in the direction of the star, the velocity of the light is changed according to Fresnel's fraction of that motion; and 3. that for any intermediate direction it is changed to the extent of that fractional part of the motion multiplied by the cosine of the angle between the direction of the motion and the direction of the star.

In 1859, Fizeau proposed an experiment for ascertaining if the azimuth of the plane of polarization of a refracted ray is influenced by the motion of the refracting medium. When a ray of polarized light passes through an inclined plate of glass, the plane of polarization is changed, according to certain laws investigated by Malus, Biot, and Brewster. The degree of change depends upon the inclination of the ray, the azimuth of the plane of primitive polarization, and the index of refraction of the glass. The incidence and azimuth being constant, this rotation of the plane of polarization increases with the index of refraction. This index being inversely as the velocity of light, the rotation is smaller the greater this velocity. Fizeau used two bundles of glass, four plates in each, and slightly prismatic, inclined to one another. One bundle was made of common glass; the other of flint glass. The angle of incidence for the ray was 58° 49′. When the azimuth of the primitive plane of polarization was 20°, the rotation of the plane of polarization was 18° 40′ and 24° 58′ for the two bundles. By Fresnel's hypothesis the change in the velocity of light from the motion of the medium is $\pm\left(\frac{\mu^2-1}{\mu^2}\right)v$. The greatest available velocity for the medium is that of the earth in its orbit, viz. 101,708 feet per second (31,000 meters). At the time of the solstices this motion is horizontal, and from east to west at noon. If the incident light comes from the west, the velocity of light is diminished by Fresnel's fraction of the velocity of the earth. If the light comes from the east, its velocity is increased by the same amount. The change in the index of refraction $\left(\text{or } \frac{\delta\mu}{\mu}\right)$ is equal to $\frac{v'}{v}(\mu^2 - 1)$; this for an index of 1.513 amounts to $\frac{1}{11740}$. Measurements show that in glass, the index increasing by a certain fraction, the rotation increases by a fraction $4\frac{1}{2}$ times greater, and the consequent change in the plane of polarization would be $\frac{1}{2500}$. The total change on reversing the direction from which the light came would be $\frac{1}{1250}$. If the incidence is 70°, and allowance is made for the change of direction inside of the glass, the fraction becomes $\frac{1}{1500}$. When a ray of light falls on a single plate of glass at an angle of 70°, if its plane of primitive polarization makes an angle of 20° with the plane of refraction, this plane is changed by 6° 40′. This multiplied by $\frac{1}{1500}$ gives 16 seconds for the probable effect of the earth's motion. With 40 such plates the effect would be increased to $10\frac{2}{3}$ minutes. Two mirrors were used, one to the east and the other to the west, and light could be sent by a heliostat upon either one. The apparatus was easily turned through 180° so as to receive successively the light which travelled with or against the earth's motion.

With a single pile of plates, highly inclined, and a second pile, less inclined, of more highly tempered glass and in the opposite azimuth, a rotation of 50° could be produced while the tendencies to elliptical polarization were exactly balanced. The motion of the earth could modify this result to the extent of only 2 minutes; which is too small for accurate observation. Fizeau then resorted to a device already indicated by Botzenhart for amplifying this effect. A small variation in the primitive plane of polarization produces a greater effect the smaller the azimuth of this plane. If the original azimuth is only 5°, a small change in the azimuth trebles the value of the rotation. A large rotation is first produced on a ray whose azimuth is large, and then this rotation is largely changed by another pile so placed that the ray enters it under a small azimuth. More than 2,000 measurements were made under various conditions. For noon observations at the time of solstice the rotation was always greater when the light came from the west, and was less at other times of day. The excess in the value of the rotation when the light came from the west varied between 30′ and 155′, according to the different ways in which the piles of plates were combined. The difference in the values of the rotation according as the light came from the west or east was consistent with a change in the index of refraction corresponding to Fresnel's hypothesis. Fizeau indicated his intention of renewing the research with improved apparatus, but no further publication on the subject by him can be found.

Faye has criticised this investigation of Fizeau, on the ground that he has taken no account of the motion of the solar system towards the constellation Hercules. This motion, recognized by astronomers on substantial evidence, amounts to 25,889 feet per second (7,894 meters) at its maximum. Its influence is almost zero at noon of the solstices. But it increases after noonday. Faye examines Fizeau's observations at 4 P. M., and finds discrepances of 12′ or 15′ between the results of theory and observation. By neglecting the term which corresponds to the motion of the solar system, Fizeau's observations accord better at all hours of the day. Must the inference be, Faye asks, that the solar system does not move? Tessan, in reply to Faye, says that the sun, from which Fizeau derived the light used in his experiments, moves with the rest of the solar system; and that therefore Fizeau was justified in neglecting the term which expresses this motion, as of no effect on his calculations. Fizeau's theory depends only on the relative velocity between the source of light and the body which receives it; that is, the velocity of revolution and rotation of the earth.

In 1881, Professor Michelson published the results of his investigation on this delicate problem. He first calculates the probable difference of time taken by the light in going and returning over a given distance, according as that distance lies in the direction of the earth's motion or at right angles to it. If the distance were 1200 millimeters, the difference of time translated into space would be equal to $\frac{1}{25}$ of a wave-length of yellow light. The apparatus was ingeniously devised, so as to bring about fringes of interference between the two rays which have travelled on rectangular paths. The whole apparatus was then turned round bodily through 90°, so as to exchange the conditions of the two interfering rays. Special apparatus was made for this experiment by Schmidt and Haensch of Berlin, and was mounted on a stone pier at the Physical Institute of Berlin. It was so sensitive to accidental vibrations that it could not be used in the daytime, nor indeed earlier than midnight. To secure greater stability the apparatus was moved to the Astrophysikalisches Observatorium in Potsdam, in charge of Professor Vogel. But even here the stone piers did not give sufficient protection against vibration. The apparatus was then placed in the cellar, the walls of which formed the foundation for an equatorial. But stamping with the feet, though at a distance of 100 meters, made the fringes disappear.

The experiments were made in April, 1881. At this time of the year, the earth's motion in its orbit coincides roughly with the motion of the solar system, viz. towards the constellation Hercules. This direction is inclined about 26° to the plane of the earth's equator, and a tangent to the earth's motion in its orbit makes an angle of 23½° with the plane of the equator. The resultant would be within 25° from the equator. The nearer the components are in magnitude, the more nearly would the resultant coincide with the equator. If the apparatus is placed so that the arms point north and east *at noon*, the eastern arm would coincide with the resultant motion of the earth, and the northern arm would be at a right angle to it. The displacement produced by revolving the whole apparatus through 90° should amount to $\frac{1}{25}$ of the interval between two fringes. If the proper motion of the solar system is small compared with the velocity of the earth in its orbit, the displacement would be less. Mr. Michelson drew from these experiments the conclusion that there was not a sufficient displacement of the fringes to support the theory of aberration, which supposes the ether to move with a certain fraction of the earth's velocity. The displacement, however, was so small that it easily might have been masked by errors of experiment. Mr. A. Graham Bell supplied Mr. Michelson with the money required for this investigation.

In 1886, Mr. Michelson and Mr. Morley published a paper on the influence of the motion of the medium traversed by the light on its velocity. Fizeau had made similar experiments. In both cases the interfering rays were changed in velocity in opposite ways by flowing air or water through which they were transmitted. With air having a velocity of about 82 feet (25 meters) a second, the effect was so small that it might easily be covered up by errors of experiment; but with water it was measurable, and the result corresponded with the assumption of Fresnel, that the ether in a moving body is stationary, except the portions which are condensed around its particles. In this sense, it may be said that the ether is not affected by the motion of the medium which it permeates. For this investigation, which was made possible by a grant from the Bache Fund of the National Academy, Mr. Michelson and Mr. Morley devised a new instrument, called the Refractometer. Cornu writes of Michelson's experiments on moving media: "Leur travail conçu dans l'esprit le plus élevé exécuté avec ces puissant moyens d'action que les savants des États-Unis aimant à déployer dans les grandes questions scientifiques fait le plus grand honneur à leurs auteurs."

In 1887, Professor Michelson published another investigation of the question whether the motion of the earth in its orbit carried its ether with it. In his previous experiment his apparatus was sensitive to the smallest jars, and it was difficult to revolve it without producing distortion of the fringes, and an effect amounting to only $\frac{1}{20}$ of the distance between the fringes might easily be hidden by accidental errors of experiment. In the new experiment the apparatus was placed on a massive rock, which rested on a wooden base, which floated upon mercury. The stone was 1.5 meters square and 0.3 of a meter thick. At each corner four mirrors were placed, by reflection from which the length of path traversed by the light was increased to ten times its former value. The width of the fringes of interference, which were the subject of observation, measured from 40 to 60 divisions of the observing micrometer. The light came from an Argand burner sent through a lens. To prevent jars from stopping and starting, the float was kept constantly in slow circulation, revolving once in six minutes. Sixteen equidistant marks were made on the stationary framework within which the float moved. Observations were taken on the fringes whenever any one of these marks came in the range of the micrometer. The observations were made near noon, and at 6 P. M. The noon and evening observations were plotted on separate curves. One division of the micrometer measured $\frac{1}{50}$ of a wave-length. Mr. Michelson was confident that there was no displacement of the fringes exceeding $\frac{1}{100}$ of a wave-length. It should have been from twenty to forty times greater than this. Mr. Michelson concludes that this result is in opposition to Fresnel's theory of aberration.

As late as 1872, Leverrier thought that a new measurement of the velocity of light by Fizeau very important in the interest of astronomy; and in 1871 Cornu wrote that the parallax of the sun, and hence the size of the earth's orbit, were not yet known with the desirable precision. In 1875, Villarceau made a communication to the Paris Academy on the theory of aberration. He says that the parallax of the sun by astronomical measurement is 8″.86. Foucault's velocity of light combined with Struve's aberration makes the sun's parallax 8″.86. Cornu's velocity of light gives the same result only when it is combined with Bradley's aberration, which differs from that of Struve by 0″.20. Villarceau thinks that there is an uncertainty about the value of aberration on account of the motion of the solar system. In 1883, M. O. Struve discussed seven series of observations made by his father, Nyrén, and others, with various instruments and by different methods, at the Observatory of Pulkowa. He was certain that the mean result for the value of aberration was 20″.492, with a probable error of less than $\frac{1}{100}$ of a second. This aberration, combined with the velocity of light as deduced from the experiments of Cornu and Michelson, made the parallax of the sun 8″.784; differing from the most exact results of the geometric method by only a few hundredths of a second. Villarceau proposed to get the solar motion by aberration; selecting two places on the earth in latitude 35° 16′ north and south, and, after the example of Struve, observing the zenith distances of stars near the zenith. The tangents of these latitudes are $\pm \frac{1}{\sqrt{2}}$; so that they contain the best stations for obtaining the constant of aberration, and the three components of the motion of translation of the solar system. In 1887, Ubaghs, a Belgian astronomer, published his results on the determination of the direction and velocity of the movement of the solar system through space. For finding the direction, he used the method of Folie. For calculating the velocity, he combined the observations on three groups of stars, the brightest belonging probably to the solar nebula. The resulting velocity was only about ten million miles a year. Homann, working on the spectroscopic observations at Greenwich, had obtained a velocity of 527 millions of miles. As late as 1887, Fizeau studied the nature of the phenomena when light was reflected from a mirror moving with a great velocity, and inferred that aberration was the same in this case as when the light was taken directly from a star.

The solar parallax, calculated from Cornu's last experiment on the velocity of light and Delambre's equation of light (493″.2 being the time for passing over the radius of the earth's orbit)	= 8″.878
From Struve's observed aberration,	8″.797
From Bradley's observed aberration,	8″.881
From Foucault's velocity with Struve's aberration,	8″.860
From Leverrier's latitudes of Venus by transits,	8″.853
From meridian observations of Venus during 106 years,	8″.859
From occultations of χ Aquarius in 1672,	8″.866

Glasenapp calculated the time taken by the light in travelling the mean distance of the earth's orbit as equal to 500″.85 ± 1.02. This time combined with Michelson's velocity of light makes the solar parallax 8″.76. Struve's constant of aberration with Michelson's velocity gives a parallax of 8″.81. From Gill's mean of the nine best modern determinations of aberration (= 20″.496) the parallax comes out equal to 8″.78. If we regard the solar parallax as known, the eclipses give nearly the same velocity as aberration, though the former is a group-velocity and the latter a wave-velocity. Gill's parallax from observations of Mars ($8''.78$) agrees with Michelson's velocity of light and the mean constant of aberration.

In 1877–78, Lord Rayleigh, in his profound treatise on the Theory of Sound, discussed the distinction between wave-velocity and group-velocity. In 1881, he recognized the same difference in the case of luminous waves. In the experiments of Young and Forbes, the wave-velocity might be nearly three per cent less than the group-velocity. With toothed wheels and the revolving mirror, group-velocity was the subject of observation. Aberration gave wave-velocity; Jupiter's satellites, group-velocity; experiment, however, showed but little difference. Lord Rayleigh found formulæ for the relation between these two kinds of velocity, which involved the wave-length and the index of refraction, and J. Willard Gibbs has compared them, and other formulæ proposed by Schuster and Gouy, with the experimental velocities of light. Michelson's experiment on the index of refraction of carbon disulphide agrees with the assumption that he was dealing with the group-velocity.

Although there is not a complete accordance between the results of different methods of investigation, astronomers and physicists will be slow to abandon the theory of undulations, and take up again the corpuscular theory of light. The latter theory has received fatal blows from which it cannot recover. The undulatory theory, which started with Huyghens more than two hundred years ago, and was elaborated by Fresnel sixty years ago has survived many crises in its history, and is supported by a wonderful array of experiments. Some of the experiments of Mr. Michelson may require a modification in Fresnel's interpretation. Stokes and Challis have worked for many years upon it, and established it on mathematical principles differing from Fresnel's and from each other. Ketteler in his *Theoretische Optik*, published in 1885, builds upon the Sellmeier hypothesis, that ponderable particles are excited by the ethereal vibrations and then react upon them. There remains Maxwell's electromagnetic theory of light, which has been elaborated by Glazebrook and Fitzgerald, and is supported, to say the least of it, by remarkable numerical coincidences.

Discrepancies between theory and experiment are always to be welcomed, as they contain the germs of future discoveries. We have learned in astronomy not to be alarmed by them. More than once the law of gravitation has been put again on trial, resulting in a new discovery or in improved mathematical analysis. We may not expect in light such a brilliant discovery as that of the planet Neptune. The luminiferous ether is a mysterious substance, enough of a fluid for the planets to pass easily through it, but at the same time enough of a solid to admit of transverse vibrations. Stokes suggests water with a little glue dissolved in it as a coarse representation of what is required of the ether.

Mr. G. A. Hirn has written recently on the constitution of celestial space. He decides against the existence of an all-pervading medium. He thinks that matter exists in space only in the condition of distinct bodies, such as stars, planets, satellites, and meteorites. In nebulæ it is in a state of extreme diffusion; but elsewhere space is empty. But how would it be after the correction is applied for the equation of light? Humboldt said that the light of distant stars reaches us as a voice from the past. The astronomer is not seeing for the most part contemporaneous events. He is reading history; and often ancient history, and of very different dates. Stellar photography reveals millions of stars which cannot be seen in the largest telescopes, and new harvests of these blossoms of heaven (as they have been called) spring up like the grass in the night. Numbers fail to express their probable distances and the time taken by their light in coming to the earth. In the theogony of Hesiod, the brazen anvil took only nine days in falling from heaven to earth. On the other hand, the reduction of the sun's distance by three per cent not only affects its mass and heat, but it changes the unit of measure for the universe. Such are the remote results of any change in the estimated velocity of light.

We may thank Professor Michelson not only for what he has established, but also for what he has unsettled. In his various researches, which I have hastily sketched, but which require diagrams or models to be clearly understood, he has displayed high intelligence, great experimental skill and ingenuity, and unflagging perseverance. With a high appreciation of his work, the Rumford Committee recommended, and the Academy voted, that the Rumford Premium be awarded to him.

PROCEEDINGS.

Eight hundred and thirteenth Meeting.

May 29, 1888. — ANNUAL MEETING.

The PRESIDENT in the chair.

In the absence of the Recording Secretary, Mr. Henry W. Haynes was appointed Recording Secretary *pro tempore.*

The report of the Council was read by the Corresponding Secretary.

The Treasurer's report was read by Mr. Augustus Lowell, accepted, and placed on file.

The Librarian's report was read by Mr. Henry W. Haynes, accepted, and placed on file.

The report of the Rumford Committee was read by the President as follows.

The Rumford Committee present the following report for the year ending May 29, 1888: —

An appropriation of $250 was recommended by the Committee, and voted by the Academy, to assist Professor Trowbridge in his investigations on metallic spectra. The committee have approved of bills amounting to $219.72 for printing in the Memoirs or Proceedings of the Academy papers on the subjects of Light or Heat.

After mature deliberation, the Committee have voted unanimously to recommend to the Academy the award of the Rumford Medals to Professor Albert A. Michelson for his determination of the velocity of light, for his researches upon the motion of the luminiferous ether, and for his work on the absolute determination of the wave-lengths of light; and the annexed vote is offered for the consummation of this award.

For the Committee,

JOSEPH LOVERING, *Chairman.*

The report was accepted, and it was

Voted, That the Rumford Premium be awarded to Professor Albert A. Michelson, as recommended by the Rumford Committee, and that the Treasurer be authorized to pay from the income of the Rumford Fund the amount required for the preparation of the Rumford Medals.

On the motion of the Corresponding Secretary it was

Voted, To meet on adjournment on the second Wednesday in June.

On the motion of Professor Jackson, it was

Voted, To amend No. 9 of the standing votes by changing the hour for the Annual Meeting from half-past three o'clock, P. M., to half-past seven o'clock, P. M.

Dr. William Everett read a biographical notice of the late Hugh A. J. Munro.

Professor Arthur Searle read a notice of the late Alvan Clark.

The annual election resulted in the choice of the following officers: —

JOSEPH LOVERING, *President.*
ANDREW P. PEABODY, *Vice-President.*
JOSIAH P. COOKE, *Corresponding Secretary.*
WILLIAM WATSON, *Recording Secretary.*
ELIOT C. CLARKE, *Treasurer.*
HENRY W. HAYNES, *Librarian.*

Council.

C. LORING JACKSON,
CHARLES R. CROSS, } of Class I.
AMOS E. DOLBEAR,

HENRY W. WILLIAMS, WILLIAM G. FARLOW, ALEXANDER AGASSIZ,	of Class II.

JOHN C. ROPES, FREDERICK W. PUTNAM, WILLIAM EVERETT,	of Class III.

Rumford Committee.

WOLCOTT GIBBS, JOSIAH P. COOKE,
EDWARD C. PICKERING, JOSEPH LOVERING,
JOHN TROWBRIDGE, GEORGE B. CLARK,
ERASMUS D. LEAVITT.

Member of the Committee of Finance.

THOMAS T. BOUVÉ.

The President appointed the following standing committees: —

Committee of Publication.

JOSIAH P. COOKE, ALEXANDER AGASSIZ,
JOHN C. ROPES.

Committee on the Library.

HENRY P. BOWDITCH, AMOS E. DOLBEAR,
EDWARD J. LOWELL.

Auditing Committee.

HENRY G. DENNY, THOMAS T. BOUVÉ.

The President reported that he had requested Mr. W. W. Story, of Rome, Associate Fellow, to represent the Academy at the celebration of the eighth hundredth anniversary of the University of Bologna, and this action was ratified by the Academy.

Eight hundred and fourteenth Meeting.

June 13, 1888. — ADJOURNED ANNUAL MEETING.

The PRESIDENT in the chair.

The President announced the deaths of Charles S. Bradley and John Dean, Resident Fellows; of Spencer F. Baird, Associate Fellow; and of Matthew Arnold, Foreign Honorary Member.

The meeting was devoted to a commemoration of the late Asa Gray. The President opened the proceedings in the following words: —

The death of Dr. ASA GRAY has already been announced to the Academy in the usual simple manner, and the Council has discharged its duty in providing for an appropriate notice of his life and scientific work. Before calling for the reading of this paper, I desire to say a few words, and present some resolutions.

Nowhere else, except in his home, will Dr. Gray be so much missed as in this hall, and from these meetings. He was elected into the Academy on November 10, 1841, — a year before he took up his residence in Cambridge as Professor of Natural History in Harvard University. From the first, he was devoted to the scientific interests of the Academy, and active in its administration.

He was the Corresponding Secretary for seventeen years, viz. from 1844 to 1850, and again from 1852 to 1863. He was highly qualified for this office, as he had a large personal acquaintance with the scientific men of Europe. He was Chairman of the Committee of Publication for four years, viz. from 1846 to 1850, and in this capacity inaugurated the publication of the Proceedings of the Academy in octavo form, to supplement the ponderous volumes of Memoirs. He was President for ten years, viz. from 1863 to 1873. As Corresponding Secretary and President, he was an *ex officio* member of the Council, and for six years, at other times, by election, — in all for seventeen years. But all these official duties are only the means to an end: this end is the advancement and diffusion of science. The richness of Dr. Gray's contribution to the Memoirs and Proceedings of the Academy admits of no comparison; though it was only the overflow from his abundant learning, which was circulating at the same time in numerous other channels.

In view of Dr. Gray's many and varied services to the Academy, of his devotion to his chosen science, his exalted character, and his inspiring example, I propose to the Academy to put on record the following resolutions: —

Resolved, That, as Fellows of the Academy, we are deeply sensible of the loss it has suffered by the death of one who has been associated with it for forty-seven years, who has served it zealously in many relations, and who has done much to maintain its usefulness and the honor of its name at home, and to make it respected throughout the world of science.

Resolved, That, as members of the community, we realize that it also sustains a bereavement in the death of our lamented associate which is not fully measured by his scientific work and reputation, great as these were. By his unselfish devotion to his favorite studies, by his wide sympathies, which condescended to the youngest and least knowing lover of nature, by his joyous spirit and his simple Christian life, he has shown that complete devotion to science can be reconciled with the highest interests of humanity.

Resolved, That a copy of these resolutions be sent to Mrs. Gray, his helpful companion in his life's work, with the respectful sympathies of the Fellows of the Academy.

The resolutions offered by the President were seconded by Mr. Augustus Lowell.

Mr. President, — I have been asked to second the resolutions presented, and to offer a few thoughts suggested by the affectionate reverence with which we dwell upon the memory of our dear friend, Dr. Gray.

In recalling him, we naturally think first of the affection he inspired. We remember the charming smile, the ready grasp, the strong expressions of interest, with which he greeted us. We remember his readiness to help, his patience, his sympathy. None ever sought his aid without being impressed, first, by the certainty of his knowledge, and then by the great kindness with which he gave it. The affection of all who have ever benefited by his teaching is the highest tribute that can be paid to that side of his character.

Dr. Gray was a man of singular simplicity. That consciousness of power he had which is essential to high achievement, but so easily and almost from the start did he assume the place that he was to fill in science, that he bore about him none of the signs of conflict, but held it as a birthright. Ranking with the highest botanists of the age, he did more than perhaps any American to raise the appreciation of our scholarship abroad, while the same simple, lovable qualities which endeared him to us charmed and fascinated his co-laborers there.

But perhaps the most remarkable trait in Dr. Gray was the steadfastness of his religious convictions under a strain to which so many other minds succumbed. Early captivated with the theory of Darwin, which ended by making its author an Agnostic, and has driven into the ranks of unbelief nearly every one of its most earnest disciples, Dr. Gray preserved his religious faith, and strove to reconcile the truths of nature to what he knew to be the truth of God. Unlike Darwin, he could not be dazzled by his own processes of thought, nor could he suffer the ingenuity of any human theory to undermine his convictions of fundamental truth. We all know with what earnestness he argued to reconcile the two, and even those of us who cannot quite follow him in both directions bear witness to the nobleness of his aim, and to the essential service he performed for each.

Others better qualified than I will speak of his professional triumphs. Mine is a simple tribute to the character of one whom I honored, reverenced, and loved.

I ask leave, Mr. President, to second the resolutions you have offered.

After Mr. Lowell, President Eliot of Harvard University addressed the Academy.

The life of Asa Gray always seemed to me a singularly happy one. His disposition was eminently cheerful, and his circumstances and occupations gave fortunate play to his natural disposition and capacity for enjoyment. From opening manhood he studied with keenest interest in a department of natural history which abounds in beauty, fragrance, and exquisite adaptation of means to ends, and opens inexhaustible opportunities for original observing, experimenting, and philosophizing. For sixty years he enjoyed to the full this elevating and rewarding pursuit. These years fell at a most fortunate period; for the continent was just being thoroughly explored, and its botanical treasures brought to light. Dr. Gray's labors therefore cover the principal period of discovery and of accurate classification in American botany. Merely to have one's intellectual life-work make part of a structure so fair and lasting, is in itself a substantial happiness.

His pursuit was one which took him out of doors, and made him intimate with Nature in all her moods. It required him to travel often, and so enabled him to see with delight different lands, skies, and peoples; it gave him intellectual contact with many scholars of various nationalities, whose pursuits were akin to his own. Intellectual sympathy and co-operation led to strong friendships founded securely upon common tastes and mutual services. All these are elements of happiness, — love of nature, acquaintance with the wide earth, congenial intercourse with superior minds, and abiding friendships.

Although Dr. Gray had no children, his domestic experience was one of rare felicity. His life illustrated a remark of his friend Darwin, that with natural history and the domestic affections a man can be perfectly happy. His way of living was that most agreeable to a philosopher; for it was independent, comfortable, and free alike from the restrictions of poverty and the incumbrances of luxury. With simplicity and regularity of life went health and a remarkable capacity for labor.

All appropriate honors came in due course to Dr. Gray from academies, scientific associations, and universities, at home and abroad. The stream began to flow as early as 1844, and continued to the end of his life. With these honors came the respect and affection of hundreds of persons who were devoted to the pursuit in which he was a leader. His reputation was larger than that of a specialist; he was recognized as a clear thinker on philosophical and religious themes, a just and sagacious critic, and a skilful and vigorous writer. It is the greatest of human rewards to be thus enfolded, as years advance, in an atmosphere of honor, gratitude, and love.

Finally, Dr. Gray enjoyed the conscious satisfaction of having rendered during his long and industrious life a great and lasting service to his kind. For many years past he could not but know that he had made the largest and most durable contribution to American botanical science which had ever been made, and that he had done more than any other man to diffuse among his countrymen a knowledge of botany and a love for it. He knew, moreover, that by his own work, and by the interest which his labors inspired in others, he had placed on a firm foundation the botanical department of the University which he served for forty-six years, and that the collections he had created there would have for generations a great historical importance. To have rendered such services was solid foundation indeed for heartfelt content.

Professor G. L. Goodale, the successor of Dr. Gray as Fisher Professor of Natural History in Harvard University, next spoke.

Mr. President, — You have touchingly and truly said that this was one of the scientific homes of him whom we commemorate. Here, almost as distinctly as in the Herbarium which he founded, and which was the principal seat of his ceaseless activities, we can feel his presence. Under the influence of that presence, those who knew the simplicity and modesty of Asa Gray, as the members of this Academy were permitted to know him, realize how completely out of place and taste would be any formal eulogium. Therefore these tributes of affection which are brought to-night do not partake of the nature of formal eulogies; they are merely the presentation of certain phases of what has been so often called a beautiful, fruitful, and well-rounded life.

Not long since, it fell to my lot, as an officer of another scientific organization, to present a sketch of some of the leading events in Dr. Gray's career. During the preparation of the outlines, two things kept pressing themselves constantly upon my attention: first, the singleness of purpose with which Professor Gray devoted himself to the establishment of an Herbarium for the elucidation of the North American Flora; secondly, the zeal with which he engaged in the consideration of every question touching the educational interests of Botany.

This evening you are to hear from one of his successors a biographical notice, in which these two features must be presented as parts of the whole; from another successor, to whom has been wisely intrusted the care of the Herbarium and the completion of the monumental work, you will learn of the devotedness and self-sacrifice by which Professor Gray placed his collection among herbaria of the very first rank. There would therefore appear to be occasion for a special, though very brief, consideration of the second point, namely, some of the relations of Professor Gray to botanical education. On this subject, the Corresponding Secretary has invited me to speak.

Concerning Dr. Gray as a college instructor, I am permitted to quote a few words from a letter by a leading jurist. He says: —

> "I was in college when Dr. Gray was appointed to his professorship at Harvard, and was, I think, the first, or one of the first, to whom he lectured. I remember his lectures well, they were so full of knowledge and of enthusiasm, and so calculated to impress the young mind. I suppose he had not lectured much of late years, and in his many other successes his powers as a lecturer may have been overlooked by those who have written of him."

Even early in his connection with the College, Dr. Gray was accustomed to open his library and herbarium to those who expressed any inclination to carry their botanical studies farther than the very narrow limits of the prescribed course. This generosity was accepted by many, and most highly appreciated by them. It may be said that Dr. Gray always maintained a deep interest in those who had availed themselves of these special opportunities.

It was, however, by his educational works that Dr. Gray was able to exert a wider influence on botanical education than if he had confined himself to the formal college instruction. The works of his educational series are of three grades: 1st, for very young children; 2d, for our grammar schools; 3d, for high schools and colleges. All of these treatises are characterized by the perspicuous style with which you are all familiar in his general writings. The style is never involved: it is essentially French in its clearness. This is as true of his first work, published when he was barely twenty-six, as of his last.

Careful examination of all these many works shows that Dr. Gray's constant endeavor was to lead the student to examine the plant, and not the book, and thus to become self-reliant.

It is worthy of note, that in his books prepared for children Dr. Gray never writes *down* to them; there is no air of condescension. The subject is developed under his charmed hand as naturally as foliage and flowers unfold from buds. The same may be said of his books for the higher grades. There is never any straining after a certain pedagogic effect. Hence his works have an attraction even for those who have little or no interest in Botany itself. Even Mr. Ruskin, in that pleasing, and yet withal provoking, sketch entitled "Proserpina," has a kind word to say for Asa Gray's Text-Book.

One of the most remarkable things connected with Dr. Gray's series is the fact that his Text-Book, now in its plan expanded into a four-volume work, is laid down on substantially the same lines as his earliest treatise, the "Elements." His earliest work is on the whole, however, rather more dogmatic than the last.

Perhaps no single subject treated of in these earliest and latest works is of greater general interest than his presentation of the doctrine of species. One realizes, as he compares the first book with the last, how difficult it must have been to detect relationship, when one felt at heart that there was no more real relationship between different species than exists between the different sorts of trinkets in a toy-shop; those of the same kind being reckoned of one kind because of their shapes, size, substance, and the fact that they have been perhaps turned out by the same machine. In his last treatise, relationship among plants is recognized as true kinship; allied plants are of common blood. And yet the transition from one view to the other is made so naturally, that no shock is felt at the profound change in statement.

Although Dr. Gray welcomed new methods of botanical instruction, there was one which never met his approval; namely, that which attempts to introduce the student first to the lowest and microscopic organisms, and passes thence to the higher plants. He held it to be wrong in theory and vicious in practice to lead a student from the unseen to the seen, — to investigate the unknown before taking up the known. He naturally preferred to have examinations of flowering plants precede a study of microscopic forms. It is of interest to observe that the writers against whom some of his strictures were directed have seen fit in a recent treatise to reverse their earlier sequence.

Professor Gray manifested a sincere interest in public and private schools, especially those designed to prepare boys for college. He watched with attention the attempt to introduce elementary botany as one of the requirements for admission to our College, and he was one of the first to realize that, under existing conditions, the requisition was likely to do more harm than good to botanical education.

In 1872, after almost thirty years of college service, he relinquished it to other hands. But he by no means gave up his care over the department. He remained to the last its judicious counsellor, patiently answering questions and aiding in every way the happy solution of difficult problems of policy. Mr. President, I dare not trust myself to dwell upon this phase of the subject which has been assigned me. The memories of those hours of conference in which the learned teacher gave advice to his younger colleague are yet too fresh to permit of any other than the most general allusion. To the affection which every member of this Academy felt for him was added, in the case of his colleagues, associated in the work of teaching, and brought into daily contact with him, a feeling almost of reverence for a patience which never overstepped its bounds. Hence you will pardon me if reference is made only to the general subjects which appeared to command his interest in the curriculum of his University.

Professor Gray viewed with pleasure the enlargement of facilities for laboratory instruction in Botany. Twice in the fifteen years after he laid down the charge of the department, he had the gratification of seeing the natural development of his well-matured plans demand larger and larger rooms for work. He watched with keen interest attempts to secure accommodations for the accumulating illustrations of Economic

Botany, — collections which he had done everything to divert into the channels marked out by himself. He was particularly attracted to the important adjunct for instruction and research, and for popular education, the Arnold Arboretum. He devised plan after plan to bring back into the course of medical study its traditions of Botany, and he was never wholly reconciled to give this science up to the schools of Pharmacy. He urged his colleagues to overcome their prejudice against having at least one large general elective in Botany, which might serve as a possible attraction to those intending to study the profession of medicine, and he was fond of noting the success attending a smaller elective termed Biology, specially designed for them. Believing that the study of Botany might be made of great use as a discipline in a far different field, he suggested establishing at the Bussey Institution an exceedingly general elective, open to college students, under the title of "Rural Affairs." This elective, comprising a modicum of Botany, was to be arranged for the increasing number of those on whom sooner or later might devolve the care of estates. In short, every phase of botanical study was carefully examined by him with reference to the needs of his University, and of sound learning in general.

His visits to St. Louis, to consult with the venerable founder of the Shaw School of Botany in regard to the establishment, attest the fact that his interests in education were not local in their character. The wisdom with which that great enterprise was planned shows how far-reaching was his good judgment. It may with truth be said, that the Shaw School of Botany is at once a memorial of Henry Shaw, and of his friends George Engelmann and Asa Gray. It may well be numbered among Professor Gray's most enduring distinctions, that he assisted in shaping the future of two working schools of Botany.

Besides his educational works, his critical reviews have exerted a profound influence on the direction and scope of botanical education in this country. These reviews were judicial and impartial, — discriminating rather than laudatory. His censure was given in a kindly spirit, frequently with a light touch of humor, which was never suggestive of cynicism. He could find faults, but not as a fault-finder; his aim was always to secure improvement. When, as in one memorable instance, the errors pointed out by him were perpetuated in a second edition, he could bring to bear a severity of criticism which was promptly remedial. His command over written speech, by which sometimes words long unused by others were brought out of the armory for a single thrust, make many of his reviews instructive studies in style.

If the present speaker were to refer to Dr. Gray's contributions to education in general, instead of his influence on botanical education in particular, it would be necessary to bring to your notice also his treatment of Darwinism, and his popular expositions of scientific subjects. Of the effect which these have had in shaping educational methods in this country, in stimulating interest in natural history, and in promoting research, others will perhaps speak.

And others must allude to the incalculable influence of his dignified simplicity and noble character. But you will permit me, in closing these remarks, to emphasize that Professor Gray was directly and indirectly a teacher. Whoever examines the subject carefully will find that Harvard University and this Academy account among the highest services of the three naturalists whom we associate together their direct and indirect influence as teachers, — Louis Agassiz, Jeffries Wyman, and Asa Gray.

Professor Goodale was followed by Mr. Sereno Watson, the Curator of the Herbarium which Dr. Gray founded.

It is an interesting coincidence that the life of Asa Gray was closely parallel in this century to that of Linnæus in the last, — the one born in 1707, and dying in January, 1788; the other born in 1810, and dying in January, 1888. Linnæus was easily the master of all that was known in his day through the entire round of the natural sciences. Now, the ablest man finds ample scope for all his energies in any single branch of science. It is no longer derogatory to a man's fame that the field of his work has been circumscribed; it is rather a necessary condition to success.

The life-work of Asa Gray was thus in a great measure limited; and it is as a systematic botanist that he stands forth as especially eminent. The qualities of his mind fitted him remarkably for success in this department, — his accuracy of observation, not only seeing but knowing what it was that he saw, his power of recognizing the resemblances and affinities of plants as well as their differences, his clear judgment of the weight to be given to characters in any given case, and not least his wonderful memory, by virtue of which a plant once examined was never forgotten, and anything once read or heard was ever at command. His keen eye, his sound, quick, and critical judgment, his own confidence in that judgment, and his power of expressing his opinions in clear and concise language, gave him that weight of authority which has been acknowledged by all contemporary botanists.

Mr. Bentham, than whom there could be no one more competent to express a just opinion, said of him in 1866: —

> "No botanists in America are more actively at work than Asa Gray, whose well known accuracy of detail, connected with great correctness of general views, a thorough knowledge of general botany in all its branches, and a philosophical mind, has given him so high a rank among the votaries of the science."

And again in 1873: —

> "Of all the modern contributions to the study of Compositæ none are more important for the accuracy of observation and the due appreciation of characters and affinities than those of Asa Gray. His views may always be implicitly followed without any danger of being led into error, although sometimes a difference of opinion may exist upon such minor points as the generic or subgeneric value to be given to a group."

It was the study of the flora of North America to which he devoted these abilities, — the critical mastery of its orders, genera, and species in their relations to each other as forming one great flora, and as related more or less closely to the floras of other regions and other times. Everything that was done by him had a more or less direct reference to this main object, or was subordinate to it, whether it was giving instruction to his classes, preparing text-books and manuals, or writing articles and notices for the journals. It may even be said that it was only incidentally that he became a participant in the discussions on Darwinism, for which his previous study of species had eminently fitted him.

His early botanical work was done under difficulties. The prime requisites to the work of any systematic botanist are an herbarium and a library. Of these there were then none worthy the name in America. The best to be found were those belonging to the Academy of Natural Sciences at Philadelphia, and what Dr. Torrey had gathered about him in New York, and it was here that Dr. Gray made all his early researches. But type specimens of species for comparison were almost wholly wanting, as none of the collections which contained them were in this country. The collections of Clayton, Kalm, and Catesby; of Walter, Bartram, and Michaux; of Bradbury and Pursh, and even of our own Government explorers, Lewis and Clark; of Menzies and Douglas, and of all the arctic explorers, — upon which collections a very large part of the species then known had been founded, — were scattered through different European herbaria. Many of these were consulted by Dr. Gray on his first visit to Europe, and this fact gave to the published volumes of Torrey and Gray's Flora their great value.

With his settlement in Cambridge began in earnest an endeavor to gather together the herbarium and library that were absolutely necessary to the continuation of his work. He had already plants which he had himself collected in New York, New Jersey, and the Alleghanies, specimens received from many correspondents throughout the country, and some very valuable contributions from European botanists with whom he was now in intimate and most friendly relationship. In the preface to the early Flora acknowledgments are made of such gifts of plants, illustrative of the American flora, from Sir William Hooker, Dr. Richardson, Bentham, Lindley, Arnott, Spach, the elder De Candolle, Schlechtendal, Trinius, Bongard, and Lehmann. By a continuance of similar liberality on the part of both foreign and home friends, and by purchase from his own limited means (it is impossible now to say in what relative proportions), both herbarium and library gradually grew year by year, until after twenty-two years the house which he occupied became too strait to hold the accumulations. The whole, books and plants together, were then presented to Harvard University, in the building which had been erected for them by Nathaniel Thayer, and a small fund was raised by private subscription affording an income barely sufficing for the most necessary expenses of their care.

Twenty-four years more have passed, and herbarium and library have more than doubled in extent. Cases for plants have been added once and again, and a large room has been built for the library, in which the shelf-room is already too small. These later accretions have also been for the greater part the gift of Dr. Gray. Through his membership in numerous foreign societies, his position as botanical editor of the Journal of Science, and especially his eminence as the great botanist of America, whose acceptance and approval of a work were an honor, many more additions have been made to the library than by purchase with the small amount of money that could be spared for that purpose. And thus the library has grown to be by far the best working botanical library in the United States, though not indeed complete, nor what it needs to be. In like manner the herbarium has from many sources become very general in its character, and there is scarcely an accessible region on the globe whose flora is not to some extent, and often very largely, represented in it, and the number of known genera of phenogamous plants of which it does not possess specimens is remarkably small. This has been due mainly to Dr. Gray's wide acquaintance with the botanists of the world, and especially to the close intimacy that has always existed between him and the directors of the Royal Gardens at Kew, Sir William J. Hooker, Sir Joseph D. Hooker, and the present director, Mr. W. T. Thistleton Dyer, and to their generous sharing of the wealth of specimens continually coming in to them from all parts of the British Empire and from elsewhere, and to his like friendly relations with Russian botanists, from whom have come large collections from Central and Eastern Asia. But it is in the richness of its American collections that the great value of the Gray Herbarium to the American botanist lies. In the possession of typical specimens it stands unrivalled, including as it does the fullest sets of the collections of Fendler, Lindheimer, Wright, Hall, Parry, Bolander, Brewer, Palmer, Pringle, and others, the basis of many of Dr. Gray's classical papers, and procured often by a costly outlay of time and labor in their determination. It has also large sets of the collections made upon the Government Pacific Railroad Surveys, the Mexican Boundary Survey, and Geological Surveys, and very many specimens from collectors in British America and the Canadian Government Surveys, and from Greenland, Arctic America, and Alaska from various sources. It is enriched, moreover, with his determinations and notes, and with his memoranda upon the types of early species and the specimens of early collectors which have been examined by himself at various times in the herbaria at Kew, London, Paris, Madrid, Geneva, Berlin. Munich, Vienna, and elsewhere. In short, the Herbarium has become what Dr. Gray endeavored to make it, a mass of material fit to form the basis for a Flora of North America.

That Flora he labored upon for years, but left incomplete. *Finis coronat opus.* The crown of a finished life-work it was not permitted him to wear. But his monument is the Gray Herbarium, that makes completion still possible. The care of this Herbarium and its Library Harvard University has assumed; and Harvard University may be trusted, in honor of the man who has been its high honor, to maintain their integrity and pre-eminence, and to perpetuate, so far as possible, that high grade of botanical work and research of which they have hitherto been the main centre in America, and for which alone they have been created.

The resolutions were adopted by a unanimous vote.

Professor William G. Farlow then read a biographical notice of Dr. Gray, which had been prepared at the request of the Council, and is printed with the Report of the Council in Vol. XXIII. of these Proceedings.

The following papers were presented by title: —

On Sodic Zincates. By C. Loring Jackson and Arthur M. Comey.

Action of Sodium Malonic Ester on Tribromdinitrobenzol. By C. Loring Jackson and W. S. Robinson.

Contributions from the Physical Laboratory of Harvard University: 1. Limits of the Ultra Violet Spectra of Metals. By John Trowbridge and W. C. Sabine. 2. Photography of the Infra Red Spectra. By John Trowbridge and J. C. B. Burbank. 3. On a new Method of Measuring the Efficiency of Electrical Transformers. By John Trowbridge. 4. Experiments on the Electromagnetic Theory of Light. By John Trowbridge.

Eight hundred and fifteenth Meeting.

October 10, 1888. — STATED MEETING.

The PRESIDENT in the chair.

The President announced the death of Rudolph Julius Emmanuel Clausius, Foreign Honorary Member, and of Samuel Kneeland, Resident Fellow.

The Corresponding Secretary read a letter from the Secretary of the Franklin Institute, announcing that the Institute is empowered to award certain medals for meritorious discoveries and inventions which tend to the progress of the arts and sciences.

The following gentlemen were elected members of the Academy: —

John William Strutt, Lord Rayleigh, of Witham, to be a Foreign Honorary Member in Class I., Section 3, in place of the late Balfour Stewart.

Friherre Adolf Erik Nordenskiöld, of Stockholm, to be a Foreign Honorary Member, in Class II., Section 1, in place of the late Bernhard Studer.

Carl Johann Maximowicz, of St. Petersburg, to be a Foreign Honorary Member in Class II., Section 2, in place of the late August Wilhelm Eichler.

Henry Sidgwick, of Cambridge, to be a Foreign Honorary Member in Class III., Section 1, in place of the late Sir Henry James Sumner Maine.

John Evans, of Hemel Hempstead, to be a Foreign Honorary Member in Class III., Section 2, in place of the late Hugh Andrew Johnstone Munro.

Johann Wilhelm Adolf Kirchhoff, of Berlin, to be a Foreign Honorary Member in Class III., Section 2, in place of the late Georg Curtius.

Charles Jacques Victor Albert, Duc de Broglie, of Paris, to be a Foreign Honorary Member in Class III., Section 3, in place of the late Leopold von Ranke.

Leslie Stephen, of London, to be a Foreign Honorary Member in Class III., Section 4, in place of the late Matthew Arnold.

George Brown Goode, of Washington, to be an Associate Fellow in Class II., Section 3, in place of the late Spencer Fullerton Baird.

On the recommendation of the Rumford Committee, it was

Voted, That an appropriation of five hundred dollars ($500) be made from the income of the Rumford Fund to assist Professor Trowbridge in his work on the metallic spectra.

Voted, That an appropriation of five hundred dollars ($500) be made from the income of the Rumford Fund to enable Mr. W. H. Pickering to observe the solar corona during the eclipse of January 1, 1889, which is visible in California.

On the motion of the Corresponding Secretary, it was

Voted, To meet, on adjournment, on the second Wednesday in November.

The following papers were read: —

Atmospheric Economy of Solar Radiation. By Arthur Searle.

Further Study of the Structure of Iron Meteorites. By Oliver W. Huntington.

Some Defects in Physical Terminology. By Amos E. Dolbear.

The following papers were presented by title: —

Studies from the Newport Marine Laboratory, communicated by Alexander Agassiz. A Preliminary Account of the Development and Histology of the Eyes in the Lobster. By G. H. Parker.

List of Plants collected by Dr. Edward Palmer, in 1887, at Guaymas, Sonora, and at Los Angeles Bay and adjacent Localities in Lower California. By Sereno Watson.

Eight hundred and sixteenth Meeting.

November 14, 1888. — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

Letters were read from John Evans and Henry Sidgwick, acknowledging their election as Foreign Honorary Members; also, a letter from George Brown Goode, acknowledging his election as Associate Fellow.

The following papers were presented: —

A New Galvanic Cell. By Amos E. Dolbear.

The Strength of the Microphone Current as influenced by Variations in Normal Pressure and Mass of the Electrodes. By Annie W. Sabine.

Researches on Microphone Currents. By Charles R. Cross and Annie W. Sabine.

The Strength of the Current of the Magneto Telephone as influenced by Variations in the Strength of the Magnet. By Charles R. Cross and Arthur S. Williams.

Eight hundred and seventeenth Meeting.

December 12, 1888. — MONTHLY MEETING.

The PRESIDENT in the chair.

Dr. Charles S. Minot presented a paper entitled "Researches on the Problem of Growth and Death."

Eight hundred and eighteenth Meeting.

January 9, 1889. — STATED MEETING.

In the absence of the President, Dr. Henry W. Williams took the chair.

The Corresponding Secretary read letters from the Duc de Broglie, A. Kirchhoff, A. E. Nordenskiöld, and Lord Rayleigh, acknowledging their election as Foreign Honorary Members; from the Royal Bohemian Society of Sciences, announcing the death of its president, Josef Jireček; and from Mr. W. W. Story, the Delegate of the Academy appointed to attend the celebration of the eight hundredth anniversary of the University of Bologna.

PROFESSOR JOSEPH LOVERING: —

Dear Sir, — I have to apologize for having so long delayed to report to you, as President of the Academy of Arts and Sciences, the proceedings and ceremonies which took place at Bologna on the celebration of the eight hundredth anniversary of its famous University; but I rely on your kindness to find an excuse for me, without my going into the reasons for my delay.

In conformity with the mandate of the Academy, I proceeded to Bologna on the 10th of June, and there was received most kindly by the Rector and the Syndic, who furnished me with a most pleasant apartment in a private house, where your representative had no possible cause of complaint, but, on the contrary, everything to be grateful for personally. I make this statement because I have heard that much complaint was made by others on the manner of their accommodation, and this naturally grew out of the fact of the numerous concourse of representatives from every quarter of the world, and of the confusion naturally incident to such a state of things.

On the 11th, at nine in the morning, there was a formal presentation of all the delegates from the various universities, academies, and scientific institutes to the Syndic. At noon the inauguration of the equestrian monument to Victor Emanuel took place, at which all the various delegates were present. At half-past eight in the evening there was an artistic torchlight procession in honor of the King and Queen, which was eminently imposing and picturesque.

On the 12th, all the professors and delegates met at the University at nine o'clock, and there formed in procession, proceeding through the main street of the city to the building of the Archiginnasio. Nothing could be more picturesque and interesting than this procession. By special request of the authorities, the greater portion of the delegates were dressed in their academical and official robes, the effect of which was most striking. Every variety of costume was there to be seen, from all the quarters of the world. Mr. James Russell Lowell and myself appeared in Oxford gowns as Doctors of Law. The streets through which we passed were thronged with a dense crowd. Every window and balcony was filled, and as the procession passed along each delegation was saluted with hearty cheers, while from the windows and balconies showers of roses and bay and laurel leaves were rained upon it. The great Cortile of the Archiginnasio, which is a noble old structure, was covered with a striped awning of blue and red. The upper porticos were thronged by invited guests, the intermediary columns and arches being decorated with wreaths and flowers, while the floor was occupied by the students and professors of the University and the delegates. In the central arch, facing the entrance, a lofty canopy was erected, with a dais on which were seated the King, Queen, and Prince Royal, attended by the officials of the court, all in uniform and court dress. When the company had assembled, a Cantica, the words of which were composed by Professor Panzacchi and set to music by Baron Alberto Franchetti, was sung by a grand chorus, and after this Professor Giosue Carducci, the distinguished writer and poet, delivered an interesting discourse, the subject of which was "Lo Studio Bolognese."

On the same day, at six P. M., all the representatives of the various foreign universities and academies were invited to a great banquet given by the government of His Majesty, the King of Italy, which was largely attended, all present being in full dress, with their decorations, by particular request.

On the 13th, all the delegates were again brought together in the Cortile of the Archiginnasio, all in their academic or official robes and with their decorations. The scene was similar to that of the previous day, and equally imposing. On this occasion degrees of honor were conferred by the Rector, one being given to each delegation. The degree conferred on the American delegation was given to Mr. Lowell, in accordance with the general wish of all the representatives from America.

As each degree was given by the Rector, the whole delegation of which the recipient of the honor was a member was called, and accompanied him to the foot of the canopy under which the royal family was seated. The Rector then made a short address, placed on his finger the large ring of the University, and then, withdrawing it, presented him with his diploma. To this the Laureate replied in an address, either in Latin or Italian, to the King and Queen, as well as to the Rector and Professors.

In accordance with the request of the American Legation, the duty of making this address in their behalf and that of the Laureate was performed by me in Italian, and I am happy to say that it was well received by the royal family, as well as the Rector and Professors and the audience in general, so that I hope I did not do discredit to the distinguished Academy which I had the honor to represent.

All the delegates were furnished with tickets to the Exhibition, which was extremely interesting, and to the various concerts and ceremonies and entertainments given by the authorities. Among these I have omitted to speak of the interesting discourse by Professor Enrico Panzacchi, to which we were all invited by a committee of the students.

A grand reception was also given by the King and Queen at the Palace of the Prefettura, at which all the delegates were personally presented to their Majesties and received with the greatest courtesy and kindness.

The ceremonies and receptions having come to an end on the evening of the 13th, I left Bologna, and have nothing further to report.

With high regard, I have the honor to be

Yours most faithfully,

W. W. STORY.

LONDON, July 10, 1888.

On the motion of the Corresponding Secretary it was

Voted, To meet, on adjournment, on the second Wednesday in February.

The following paper was read: —

Comparison of Right Ascensions of Polar Stars in Recent Catalogues. By Truman H. Safford.

The following papers were presented by title: —

Determination of Chromium in Chrome Iron Ore. By Leonard P. Kinnicutt and George W. Patterson.

Measurements of Specific Inductive Capacity. By William W. Jacques.

Eight hundred and nineteenth Meeting.

February 13, 1889. — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

The President announced the death of John Call Dalton, of New York, Associate Fellow.

The Corresponding Secretary read letters from the New York Academy of Sciences, requesting aid in erecting a monument to Audubon; from the United States Commissioner to the Paris Exhibition, requesting information in reference to the library of the Academy; and from the Royal Academy of Sciences of Turin, announcing the conditions of competition for the seventh Bressa Prize.

The following papers were presented: —

The Application of the Stroboscopic Method to the Study of the Excursion of the Electrode of a Microphone Transmitter. By Charles R. Cross.

On the Rotation resulting from the Vibration of a Chladni Plate. By Amos E. Dolbear.

On Pentamidobenzol. By C. Loring Jackson and A. W. Palmer.

On Reversible Chemical Reactions. By P. C. Freer.

Eight hundred and twentieth Meeting.

March 13, 1889. — STATED MEETING.

The PRESIDENT in the chair.

The following gentlemen were elected members of the Academy: —

Cecil Hobart Peabody, of Boston, to be a Resident Fellow in Class I., Section 4.

Peter Schwamb, of Boston, to be a Resident Fellow in Class I., Section 4.

Henry Willey, of New Bedford, to be a Resident Fellow in Class II., Section 2.

Harold Clarence Ernst, of Boston, to be a Resident Fellow in Class II., Section 3.

Samuel Henshaw, of Cambridge, to be a Resident Fellow in Class II., Section 3.

Edward Hickling Bradford, of Boston, to be a Resident Fellow in Class II., Section 4.

Arthur Tracy Cabot, of Boston, to be a Resident Fellow in Class II., Section 4.

David Williams Cheever, of Boston, to be a Resident Fellow in Class II., Section 4.

Reginald Heber Fitz, of Boston, to be a Resident Fellow in Class II., Section 4.

John Homans, of Boston, to be a Resident Fellow in Class II., Section 4.

Frederick Irving Knight, of Boston, to be a Resident Fellow in Class II., Section 4.

George Hinckley Lyman, of Boston, to be a Resident Fellow in Class II., Section 4.

Henry Pickering Walcott, of Cambridge, to be a Resident Fellow in Class II., Section 4.

Franklin Carter, of Williamstown, to be a Resident Fellow in Class III., Section 2.

Franklin Bache Stephenson, of Boston to be a Resident Fellow in Class III., Section 2.

Frank William Taussig, of Cambridge, to be a Resident Fellow in Class III., Section 3.

Barrett Wendell, of Boston, to be a Resident Fellow in Class III., Section 4.

John Nelson Stockwell, of Cleveland, Ohio, to be an Associate Fellow in Class I., Section 1, in place of the late Ezekiel Brown Elliott.

Alexander Johnston, of Princeton, New Jersey, to be an Associate Fellow in Class III., Section 3, in place of the late Samuel Gilman Brown.

Dmitri Ivanowitsh Mendeleeff, of St. Petersburg, to be a Foreign Honorary Member in Class I., Section 3.

Wilhelm Edward Weber, of Göttingen, to be a Foreign Honorary Member in Class I., Section 3, in place of the late Gustav Robert Kirchhoff.

Anatole François Hüe, Marquis de Caligny, of Versailles, to be a Foreign Honorary Member in Class I., Section 4, in place of the late Rudolph Julius Emmanuel Clausius.

The Rumford Committee, through its chairman, Professor Lovering, submitted the following report: —

The Rumford Committee recommend to the Academy an appropriation of $100 to Professor E. Hall to enable him to make certain investigations as to the fluctuations of temperature which occur at the inner surface of the cylinder of a steam-engine in operation.

They also recommend an appropriation of $250 from the same fund to Professor C. C. Hutchins, of Bowdoin College, for the purchase of a large parabolic mirror of glass and its mounting to be used for the completion of his investigation on Lunar Radiation.

The report of the committee was adopted, and the appropriations voted.

The following papers were read: —

Experimental Proof of Newton's Law of Cooling as applied to Thermometers and to Rectangular Bars of Metal. By William A. Rogers.

Experimental Proof that the Relative Coefficient of Expansion between Brass and Steel is Constant between the Limits of —5° Fahr. and +100° Fahr. By William A. Rogers.

Professor Charles R. Cross read a paper entitled "On the Relation of the Candle-Power of Incandescent Electric Lamps to Current, Potential Difference, and Energy consumed in them." By L. A. Ferguson and D. A. Center.

Professor Benjamin O. Peirce presented the following papers by title: —

On Lunar Radiation. By C. C. Hutchins.

On the Charging of Condensers by Galvanic Batteries. By B. O. Peirce and R. W. Wilson.

Eight hundred and twenty-first Meeting.

April 10, 1889. — MONTHLY MEETING.

THE PRESIDENT in the chair.

Letters were read from Messrs. Bradford, Cheever, Ernst, Fitz, Knight, Lyman, Peabody, Schwamb, Stephenson, and Wendell, accepting Fellowship in the Academy; also, from Messrs. Johnston and Stockwell, acknowledging their election as Associate Fellows.

The President, having stated that the special business of the meeting was the presentation of the Rumford Medals, made the address printed among the papers of this volume, on the numerous investigations which had been made on the velocity of light, and their relation to the theories of optics and delicate questions in astronomy. He then addressed Professor Michelson in these words: —

PROFESSOR MICHELSON, — It is now my duty and privilege to present to you, in the name of the Academy and in the presence of these members, here assembled to administer Count Rumford's Trust, the gold and silver medals which together constitute the Rumford Premium. Be pleased to receive with these medals my congratulations, and those of all the other members of the Academy, for the intelligence, ingenuity, and perseverance with which you have labored towards the solution of problems of the greatest concern to more than one of the physical sciences.

Professor Michelson, having received the medals, made the following reply: —

MR. PRESIDENT AND GENTLEMEN OF THE ACADEMY, — I wish to thank you sincerely, and to express my appreciation of the high honor you have just conferred upon me. These medals I shall always regard as a token of your encouragement and approval; but in addition they will, I trust, be a strong incentive for the future to do the best that is in me to justify this expression of your kind appreciation.

The following paper was presented by title: —

Classification of the Atomic Weights in two Ascending Series, corresponding to the Groups of Artiads and Perissads. By W. R. Livermore.

Eight hundred and twenty-second Meeting.

May 8, 1889. — MONTHLY MEETING.

THE PRESIDENT in the chair.

The President announced the death of Jonathan Ingersoll Bowditch, senior Resident Fellow, elected on November 12, 1834, who died on February 19, 1889. He served as Treasurer from 1842 to 1852, and was a member of the Council from 1854 to 1856, and from 1858 to 1863.

WRITERS OF NOTICES IN REPORT OF THE COUNCIL.

GEORGE RUMFORD BALDWIN, by Rev. George E. Ellis.
JONATHAN INGERSOLL BOWDITCH, by Rev. A. P. Peabody.
SAMUEL KNEELAND, by Prof. J. D. Runkle.
E. B. ELLIOTT, by Gen. F. A. Walker.
F. A. P. BARNARD, by Prof. J. Lovering.
JOHN C. DALTON, by Dr. H. P. Walcott.
M. E. CHEVREUL, by Prof. F. H. Storer.
R. J. E. CLAUSIUS, by Prof. J. Willard Gibbs.
F. C. DONDERS, by Dr. H. W. Williams.

REPORT OF THE COUNCIL.

MAY 28, 1889.

Since the last Annual Meeting, on May 23, 1888, the Academy has lost by death nine of its members; — viz. three Resident Fellows, George Rumford Baldwin, Jonathan Ingersoll Bowditch, and Samuel Kneeland; three Associate Fellows, Frederick A. P. Barnard, John C. Dalton, and Rowland G. Hazard;* and three Foreign Honorary Members, Michel Eugène Chevreul, Rudolph Julius Emanuel Clausius, and Franciscus Cornelius Donders.

RESIDENT FELLOWS.

GEORGE RUMFORD BALDWIN.

George Rumford Baldwin was elected a Fellow of the Academy on December 12, 1871, in Class I., Section 4, Technology and Engineering. He was born on January 26, 1798, in the Baldwin mansion, North Woburn, Mass., and died there on October 11, 1888, having devoted his lengthened life, with the full possession of his faculties till its close, to the pursuits of practical science, as a surveyor, a civil engineer, and a constructor.

The "Baldwin mansion," as an edifice, the estate connected with it, and the generations and individuals successively owning and occupying it in the performance of many valuable and distinguished public services, justify a special notice here. The first of the family line of the Baldwins in this Colony was Henry Baldwin, an emigrant from Devonshire, England, coming with the earliest settlers. He was one of the first founders of the town of Woburn, in 1640, took up lands there, still held by his descendants, now including between five and six hundred acres of farm and woodland, and was one of the selectmen of the town and deacon of the church.

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* A notice of Rowland G. Hazard could not be prepared for this volume; but the notice of Ezekiel Brown Elliott, necessarily omitted last year, is now given.

The old mansion, dating, as marked on one of its massive oak timbers, from 1662, with successive additions and improvements, is one of the noteworthy survivals of our earliest times, in size, arrangement, adornment, and in its well-preserved relics. A history and description of it might engage the zeal of the relic-hunters of the day. In it are to be found implements, household utensils, paintings, ornaments, and sundry furnishings, with luxurious appliances, gathered by the generations which have occupied it from birth to death. Piles of trunks and boxes contain their private papers and settlements of estates. Most interesting among its contents is a large, select, and valuable library of many thousand volumes, collected principally by the father and brothers of our associate, and by himself, giving evidence of their scientific and literary tastes. Learned tomes in many languages, costly illustrated works, series of scientific publications on construction and engineering, and sumptuous editions of the best writers in various departments of literature, are among its treasures. It may be that, sooner or later, the collection will find its deposit in the noble Public Library of the city of Woburn, as a memorial of one of the oldest and most distinguished families of its citizens.

Of the fourth generation from the original colonist was that distinguished military officer in our Revolutionary war, honored with the high esteem of Washington, and afterwards eminent as the earliest civil engineer in this State, Colonel Loammi Baldwin. He was born in 1744, and died in 1807. Of his relations with his fellow townsman, playfellow, schoolmate, and life-long friend, the farmer's son, Benjamin Thompson, afterward Count Rumford, mention will be made further on. Baldwin manifested from his earliest years an ardent passion for acquiring knowledge, with skill in practical works, and inventive ingenuity. He sought and obtained permission to attend the lectures of Professor Winthrop at Harvard, walking to Cambridge for that purpose with young Thompson, whose tastes and genius were similar. After his patriotic service in the war, Colonel Baldwin devoted himself to public offices in the town and in the Legislature, and was the first High Sheriff of the County of Middlesex, never intermitting his scientific pursuits. On the projection of the first of our public enterprises for more extended internal communication, the connection of the waters of the Merrimac with those of the harbor by the Middlesex Canal, chartered in 1793, he was one of its leading promoters. Its course lay through his own estate. It was completed in 1803. Of this then signal enterprise, Colonel Baldwin, as surveyor, engineer, and constructor, was the efficient aid of Mr.

Weston, the English surveyor from Philadelphia. The canal served its uses till superseded by the Lowell Railroad. Colonel Baldwin was a Fellow of the Academy, and received the honorary degree of A. M. from Harvard College in 1785.

The fourth child of the Colonel was the equally eminent Loammi Baldwin, Esq., born in 1780, graduated at Harvard in 1800, and a Fellow of the Academy. The father, this son, and his two brothers, yet to be mentioned, by their inheritance of scientific proclivities and skill, furnish a marked illustration of transmission by heredity. The second Loammi was employed in many public works by the government, and was the constructor of the Naval Dry Docks in Charlestown and Norfolk. His brother, James Fowler Baldwin, was eminent as a Boston merchant and a State Senator, and, as one of the Commissioners for the introduction of the Cochituate water into Boston, found opportunity for the exercise of the family ingenuity, and for engaging the professional services in his chosen work of his younger brother, the subject of this sketch.

Our late associate was a son of Colonel Loammi Baldwin by a second wife. His middle name of Rumford recalls the relations just referred to, which existed between his father and the distinguished Count. The farmer boy Thompson early developed the ingenuity, the inventive and philosophical genius, and the skill in practical science, especially in utilitarian directions, which won him advancement and distinction. As the close companion of young Baldwin, they engaged together in the tentative trial of their experiments, and walked to the lectures in Cambridge. After Thompson left his country in early manhood, under a cloud which obscured his patriotism, the intercourse of the friends was suspended.* When Thompson had attained rank and title at Munich, a correspondence began between the easily reconciled friends, which is of great personal and historical interest. In a letter following the birth of our present subject, the Colonel writes to the Count, "I have had a son born to me to whom I have given your name." The father wished this boy, as he grew up, to succeed his brother Loammi at College; but the son was disinclined to the pursuit of general scholarship in that institution. From his earliest years his bent was for mathematical and scientific studies pursued by himself, and for practical out of door work in waterways, surveying and engineering, in the examination of mills and water-power, dams and raceways. As has been noticed, he had marked facilities for practice of this sort — after preliminary training

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* See Memoir of Count Rumford, by the present writer, published by the Academy.

in a school kept by Dr. Stearns, in Medford — by accompanying his father and brother in field and office work. I find among his papers some "Sketches" of proposed works made by him when employed by his brother Loammi on the fortifications of Boston harbor in the war of 1812, he being then in his fourteenth year.

I have in my hands the series of his diaries for more than fifty years, with the daily entries upon them of his employments and occupations. They contain most miscellaneous and comprehensive notes of a life of marvellous industry, of wide travel and of useful service. Only the most conspicuous and important of the enterprises and undertakings in which he had the chief part and responsibility in planning and supervising mechanical scientific and industrial schemes for public improvements, can be noted here. We find him called upon in all directions, on a large variety of occasions, as expert, witness, referee, or examiner of wharves and docks, in making surveys, drawing maps and plans, exploring state and city archives, tracing estates, estimating damages, assessing costs, consulting lawyers, instructing legislative committees, and alone or with associates disposing of a vast number of trivial or serious interests at a period when the development of our railroad and manufacturing enterprises made a demand for talent and skill not then easily obtained. He was instrumental in forming the first associated company of engineers. It should be noted here, that the varied and constant demand for his presence and services, especially when called upon for any utterance in public before many persons, was a serious strain upon one of his peculiar temperament. He was naturally shy, modest, diffident, and reticent, of most retiring and undemonstrative ways. His social intercourse was very limited, but his domestic ties and habits drew out from him very engaging and tender qualities. Under no stress of circumstances could he have made in public a speech of advocacy or argument. His delicacy and refinement made him personally attractive to his intimates.

His brother Loammi, living in Charlestown in a spacious house with garden and open grounds, had married the widow of Mr. Beckford, who had been the partner of Mr. Joshua Bates, afterward the London banker, when the firm had done business in Boston. Mrs. Beckford had two daughters by her first marriage, but no child by the second. One of these daughters, Catherine Richardson, became the wife of George Rumford Baldwin, thus bringing the brothers into a peculiar relationship. The younger brother had his first home in Boston; but in 1842, after the death of Loammi in 1838, he moved with his family to the Beckford house. Here, with occasional sojourn at Woburn, he made his home, till his important work at Quebec — soon to be referred to — occupied him there so many years, that he became a householder and resident there. It was on an autumn visit to the family mansion at Woburn that his life of ninety years closed where it began.

On a fragment among his papers is the following brief mention of some of his early engagements: "1821. Built P. C. Brooks' Stone Bridge [over the Mystic, in Medford]. 1822, Sept. 16, to 1823, Jan. 13, in Pennsylvania, with Loammi Baldwin. 1823, May 1, to 1825, June 25, at Factories in Lowell. 1826. Surveyed Navy Yard, Charlestown. Executed Marine Railway, Boston. 1831, Nov. 25, to 1833, Jan. 5, in England. 1833, Feb. or March, to 1834, Nov. 18, on Lowell Railroad. 1834, Nov., to 1836, April, in Nova Scotia. 1837, in Georgia on Brunswick Canal."

On November 6, 1845, he left Boston on an appointment as chief engineer to make a survey for the route of the Buffalo and Mississippi Railroad. His report, with specifications and estimates, was rendered in 1847. In 1846 he was employed in the examination of water power in Augusta, Georgia, and by the national government on the Board of Commissioners for Dry Docks, in Washington and Brooklyn.

It was in July, 1847, that he was summoned to Quebec by a letter from the Mayor, engaging him on a professional task which was to occupy him diligently and laboriously till he completed it, in 1856, though many years afterwards he was employed in further perfecting some details and improvements in it. The enterprise resulted in the introduction of water into the city from the Indian village of Lorette. From August to October he was engaged in his survey. His field-books and journals give full evidence of the general and some special difficulties of the undertaking, in a region exposed to extreme changes of temperature, to ice and freshets, with marshes, streams, and hard rocky cliffs. He brought home with him his Profiles and Estimates, on which he worked, presenting his report in print in the following June. A contract for pipes was to be made in Scotland. He was put in full superintendence of the work, under the Mayor and a Water Board, in November, 1850, and in February, 1851, he had made a survey of the city. After a short visit home, he sailed with his family for Europe, in November, to superintend at a foundry in Glasgow the casting of pipes, gates, etc., and to make arrangements for their shipment. The water-jet flowed in the city in 1852, and at the end of 1853 he returned temporarily to Boston. His resignation as Chief Engineer took effect in 1856.

From April, 1857, to July, 1858, he spent with his family in Europe, principally in Paris and London, with many excursions. He was a most intelligent and inquisitive traveller. With accomplished skill in draughting and etching, his pencil was ever busy in sketching all the objects of special interest to him. His descriptions of such objects in his journals are illustrated by a mass of drawings, more or less perfected, preserved in his numerous collections. On October 25, 1848, he witnessed the introduction of the Cochituate water into Boston. His papers show that his services in this undertaking had been frequently engaged by his brother James, already mentioned as one of the Water Commissioners. He mentions that on this occasion he had in charge Sarah Countess Rumford. She had been permitted by the Elector of Bavaria to take this title after the death of her father in France. She spent her closing years in her fine family home in Concord, N. H., the children of her father's friend having the oversight of her interests.

Mr. Baldwin was Assistant Consulting Engineer of the Mystic Water Works in Charlestown. He notes that his photograph as such an official was deposited in the copper box under the engine-house in 1860. In February, 1861, he was appointed by the Legislature as Engineer for the proposed Ship Canal at Cape Cod. His report is among the State archives. Under date of Boston, June 6, 1864, he made his report on the survey for the Boston, Hartford, and Erie Railroad.

In 1867 he was commissioned by Governor Bullock as State Engineer of Improvements in Boston Harbor.

In this brief sketch, as already intimated, only the more important of the great undertakings of a professional character which occupied Mr. Baldwin's long life have been mentioned. His journals show how fully every interval between these public works, and every moment of leisure, was employed in a vast variety of occasions in which he was called upon as an expert. But he always found time to indulge himself as an amateur in many congenial pursuits. He was skilled in all farming, horticultural, and agricultural labors. He had his work-bench, with the best of tools and scientific instruments. His pen was ever busy in his own affairs, or for the service of friends.

It may be that his voluminous and carefully arranged and filed papers may yet need to be consulted for the facts and information contained in them.

Mr. Baldwin had but one child, a daughter, now married and residing mainly in Quebec.

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JONATHAN INGERSOLL BOWDITCH.

Jonathan Ingersoll Bowditch, the second son of Nathaniel and Mary (Ingersoll) Bowditch, was born in Salem, October 15, 1806. He inherited more amply than any other member of the singularly gifted family his father's love and aptness for mathematical science, and had opportunity served he would have attained distinguished eminence, as he won no little reputation, in that department. But after his school days were over he entered upon a mercantile career, which for many years left him scanty leisure for scientific pursuits, except when at sea, and then, of course, with limited access to books and none to teachers. He commenced business in Boston as a clerk in the office of Messrs. Ropes and Ward, East India merchants, and in their service made several voyages as supercargo. At that time a passage to or from the East Indies round the Cape of Good Hope occupied seldom less than four, and often five months. During these voyages Mr. Bowditch made diligent use of his father's "Practical Navigator," taking observations, and keeping the ship's reckoning. At the same time, by well chosen books and well directed courses of reading he supplied in no small measure what in his earlier culture fell short of a liberal education. In 1836 he became President of the American Insurance Company in Boston, and held that office till 1861, retaining his place on the Board of Directors till 1884. As a business man he was distinguished not only by integrity of the most rigid type, but equally by promptness, energy, efficiency, and a practical wisdom closely akin to intuition. For these qualities his services were sought as a director in institutions of all kinds, financial, industrial, and charitable, and, numerous as were the trusts thus devolved upon him, he never suffered one of them to be a sinecure, though very many of them involved the gratuitous bestowal of large amounts of time and labor. Indeed, he sustained for many years two characters not often united in a superlative degree; in business circles being regarded as of exceptionally sound and safe judgment and superior executive capacity, while the outside world looked upon him as a public benefactor.

Mr. Bowditch shared, and no one who knew him can doubt that he shared with his whole heart and soul, the honor that rests upon all his father's children in determining unselfishly the question whether he should devote a full third part of what would be their patrimony to the publication of his great astronomical work, or should accept the subsidies that might be offered by the American Academy and the friends of science. After his father's death in 1838, Mr. Bowditch assumed the editorship of frequent successive editions of "The Practical Navigator," making such corrections and new calculations as were needed, until the copyright was purchased by the United States government, and so became public property.

Mr. Bowditch erected a private astronomical observatory in connection with his summer residence at Canton, and for many years made there observations of celestial phenomena, while he kept at the same time a full meteorological register. He early interested himself in the Observatory of Harvard College. He was the fellow townsman and the early and lifelong friend of Benjamin Peirce, the first Professor of Astronomy in the University, and was in intimate association with both the Bonds and with Professor Winlock. Professor Pickering is of his near kindred; but Mr. Bowditch, though fully aware of his scientific talents and attainments, hesitated to recommend him for his present office, on the ground that he had never made a specialty of astronomy, and withdrew his objections only when persuaded that the training of an accomplished physicist implies an ability in the invention, improvement, and direction of instruments and methods of observation which the mere scientific knowledge of astronomy cannot furnish, — a proposition which, if it needs proof, is abundantly demonstrated in the recent history and present condition of the Harvard Observatory. Mr. Bowditch was for many years a member of the committee appointed by the Overseers of the College for visiting the Observatory, and rendered important aid to its administration, especially in the investment and increase of its funds, to which he was himself a generous contributor, and for which he secured in many instances donations and annual subscriptions. He took an equally active and beneficent interest in various other departments and enterprises of the University, — in the erection of Memorial Hall, in the establishment of the Scientific Museum, and in the various improvements that have been made in the Medical and in the Divinity School. He was among the efficient promoters of the plan of furnishing cheap board for poor students, which resulted in the erection and furnishing of a large and commodious dining hall by the munificence of the late Nathaniel Thayer, and was superseded only by the ample provision of board at cost for several hundred students in Memorial Hall. The University recognized at once Mr. Bowditch's long and varied services, and his claim to high regard for scholarly and scientific attainments, by conferring on him the degree of Master of Arts in 1849, and that of Doctor of Laws on its two hundred and fiftieth anniversary, in 1887.

Mr. Bowditch was also a benefactor of the Massachusetts Institute of Technology, and a member of its Corporation and of its Financial Committee.

In addition to all these public interests Mr. Bowditch for many years had the management of large and important private trusts, especially of estates of widows and orphans, — a charge in which equal reliance was placed, and never misplaced, in his painstaking fidelity, his far-seeing prudence, and his financial skill. It is impossible to overestimate the benefit conferred on dependent families by the administration of trusts of this class in the hands of men who, like Mr. Bowditch, employ the treasured experience and wisdom of a lifetime for the security and well-being of those who cannot take due thought for themselves.

It would be difficult to name any public charity, or any enterprise for the welfare of the community, which has not had aid and furtherance from Mr. Bowditch. He was a liberal giver, and in a good cause he knew how to elicit gifts, even from those whose sympathies are not easily moved. He could, almost in a literal sense, command resources where others might plead in vain. His private character gave weight to his influence. Truth, honor, purity, and benignity, while they were manifested in his relations with society and the outside world, made him unspeakably precious in the more intimate circle of home, kindred, and friends. Impulsive, but with only generous impulses; free-spoken, but with the freedom of one who has nothing to hide; with quick indignation, but only for meanness and depravity, — he has left the memory of a truly noble life, and a void place in the community, larger and more diversified than it is often the lot of any one man to fill. He retained much of his working power and active usefulness till he had passed his eightieth year, though the last few months of his life were a season of decline and infirmity.

Mr. Bowditch was happy in his domestic life and relations. He married, in 1836, Lucy Orne Nichols, daughter of Benjamin R. and Mary (Pickering) Nichols, and granddaughter of Timothy Pickering. She died several years ago. Of their eight children, six, three sons and three daughters, reached years of maturity, and are all still living.

SAMUEL KNEELAND.

Dr. Samuel Kneeland was born in Boston, August 1st, 1821. He was a thoughtful boy, early developed a taste for reading and study, and entered the Boston Latin School in 1831.

A classmate for five years at the Latin School, and afterwards at Harvard College, says: —

"My acquaintance with Kneeland dates from August 31, 1831. On the morning of that day we met in front of the old Latin School-house in School Street. Here a friendship sprang up between us which lasted till the day of his death.

"At school he was industrious and studious, stood well with his teachers, took a high rank in his class, and at the end of the five years' course was awarded a Franklin medal. He left the Latin School a fine classical scholar, but says himself that he knew next to nothing of mathematics. He was, however, admitted to college without conditions even in mathematics, and sustained a creditable rank in that study. Without being especially popular, he kept up friendly relations with all of the class. He was an inveterate reader of miscellaneous books, but did not allow this habit to interfere with his studies. He took a respectable rank at graduation, and was a member of the Phi Beta Kappa Society."

Another classmate says: "Kneeland and I were excellent friends all through our college course, without a break; and yet it was hard to get at his inner life on account of a certain reserve which kept even near friends somewhat at a distance. He had no liking for mathematics, but developed an interest in and fondness for natural history and the practical sciences."

Still another classmate says: —

"My recollections of Dr. Kneeland are very agreeable. I recall him as one eminently self-poised, one who had come to feel

'My mind to me a kingdom is.'

Hence he was restrained from mingling in any boisterous carousals, and kept also from courting the companionships of his classmates. We could have pardoned his being a little more demonstrative, or his taking a little more pains to hunt us up. When, however, we were thrown into company with him, I, for one, can testify to his inspiring by his pure life and manly bearing, and by his genial greeting, a hearty respect.

"It was always a pleasure to meet him. He was one of the few persons who have a decidedly handsomer and more impressive aspect at sixty than at twenty. As I met him in recent years, I never thought, 'How I wish I could make you young again!' He had matured without losing the vivacity or the energy of youth. Indeed, from his love of nature and his researches into things of lofty import there had come a charm and an elevation into his face which led me to rejoice that there was such a classmate so near at hand, and caused me to deplore his sudden death."

I have given these extracts from the letters so kindly furnished me because they show us Dr. Kneeland during his early manhood, and foreshadow so plainly what those who knew him well in his later years found him to be. After graduating from Harvard College, in 1840, he studied medicine under Doctors D. H. Storer, O. W. Holmes, Jacob Bigelow, and Edward Reynolds, and at the Medical School, then situated in Mason Street, from which he graduated in 1843. From 1843 to 1845 he studied medicine and surgery in Paris. Returning home after fourteen years of continuous study since his entrance into the Latin School, we may suppose him particularly well prepared to enter upon the practice of his profession, which he continued in Boston till failing health in the early part of 1848 led him to make a voyage to Brazil. After an absence of about six months, he returned in good health, was married, and resumed the practice of his profession. But a love of the study of natural history and a desire to travel led him to relinquish the practice of his profession. He soon found congenial employment as the Secretary of the Boston Society of Natural History, a post which he filled with dignity and ability for five years. In 1856 he went to Portage Lake, the copper district of Lake Superior, as physician and surgeon to several copper mining companies, where he remained one year. On his return he accepted the position of contributor to Appleton's New American Cyclopædia, then in course of publication. The medical and zoological articles were assigned to him, of which he prepared over one thousand, beginning with Volume III.

For two years he served as Secretary of the American Academy of Arts and Sciences. He took an active part in those measures which finally led to the grant by the State of the land on which the buildings of the Society of Natural History and Institute of Technology now stand.

In 1861 he entered the service of the United States government as surgeon, and served until February, 1866, when he was mustered out with the rank of Brevet Lieutenant-Colonel of Volunteers.

In August, 1866, he was chosen Secretary of the Massachusetts Institute of Technology, and here my personal acquaintance with Dr. Kneeland begins. From this time till his resignation, December 31, 1878, twelve years, our official and personal relations were constant and intimate. He was the secretary of the Faculty and of the Society of Arts, as well as of the Corporation, and also for some years the Professor of Zoölogy and Physiology. He performed the duties of these various positions with ability and with signal fidelity.

But few ever really knew Dr. Kneeland. Outside of his immediate family he had but few intimate friends who were permitted to see and know his inner self. His manner was cold, and to casual acquaintance seemed somewhat forbidding, if not morose. He had little or no desire or power to conciliate, and to those who were indifferent to him, or as he thought disliked him, he was literally a sealed book. But for those who had gained his entire confidence, and with whom he was in full sympathy, no man was ever more transparent. He had a large and loving heart, and when he gave his friendship it was in full measure. He hated deceit and all forms of indirection, and would never countenance such practice either in word or manner. But he had a large power of self-control, seldom lost or even exhibited temper, and usually when he could not speak favorably and kindly was absolutely silent.

He was not in the usual sense a popular man, but at the Institute teachers and students alike soon became accustomed to his manner, and held him in high regard. The qualities of his character which most deeply impressed me were strength, depth, and purity, and during the more than twenty years of my intimate acquaintance with him he lived a life of almost Spartan simplicity. His long vacations at the Institute, and the period between his resignation, at the end of 1878, and his death, on September 28, 1888, were spent in travel and literary work, but the results in books, miscellaneous papers, and in Lowell Institute lectures, it is not needful here to enumerate.

In the latter part of March, 1888, he sailed from New York for Hamburg, on what proved to be his last voyage across the Atlantic, to meet a friend who was on his way home from the Philippine Islands, and also to visit old friends, residents of that city. He had also the pleasure during the summer of visiting several of the most interesting cities and places in Germany, accompanied by his daughter and her husband, to whom he bade a last good-by at Cologne.

He died very suddenly at Hamburg on the morning of September 28, 1888. The previous evening he spent with his friends, expecting to leave the next day for London, where he intended to remain a few days, and then go on to Liverpool, where his passage for the homeward voyage had already been engaged.

Soon after an early breakfast taken in his room, he was heard to fall, and was found with his overcoat on prepared to go out. By his side lay a letter addressed to his son-in-law, evidently just written, and stamped but not sealed, which he was on the point of mailing. It was written in excellent spirits, detailing his preparations for the homeward voyage, and the pleasure he should experience in again seeing his daughter and her family. Such a termination of his life had been anticipated for some years by Dr. Kneeland. He knew and had informed some intimate friends of a chronic trouble of the heart, which would in all probability suddenly end his days.

His remains were tenderly cared for by his friends, and laid by loving hands in the cemetery at Ohlsdorf, near Hamburg. They have also placed over his grave, for themselves and for his family and friends on this side of the Atlantic, a monumental stone in affectionate remembrance.

ASSOCIATE FELLOWS.

FREDERICK AUGUSTUS PORTER BARNARD.

Frederick Augustus Porter Barnard was born in Sheffield, Massachusetts, on May 5, 1809. He died in New York on April 27, 1889. He was descended on his father's side from Francis Barnard of Coventry, Warwickshire, England; and on his mother's side from John Porter of Warwickshire, who emigrated to Massachusetts in 1628. In 1886 he furnished to a magazine an interesting article on "How I was educated." After receiving some elementary instruction from his mother, he was sent, with a sister two years older, to the village school in Sheffield. At six years of age, he had read from Shakespeare, Cowper, Burns, Addison, etc., and began the study of Latin. When nine years old, he lived for a time at Saratoga Springs with his grandfather, General B. P. Porter, afterwards Secretary of War under John Quincy Adams. At his leisure, he learned the art of printing so effectually that he might have supported himself by it had circumstances compelled him. From Saratoga Springs he went to Stockbridge, Mass., and became interested in scientific studies. He entered Yale College in 1824, and graduated honorably in 1828.

Thirty years after his graduation he delivered the annual oration before the society of the Yale Alumni. After some experience in teaching at the Hartford Grammar School, he served as Tutor at Yale in 1830. In those days young graduates of the College were broken in for tutors at Hartford. Having an apprehension of deafness, which was in the family and which had begun to reveal itself in his own case, he connected himself, in 1831, as instructor with the Asylum for Deaf and Dumb at Hartford, and a year later with a similar institution in New York. He originated a system still used in institutions for the deaf and dumb, and published an analytic grammar with symbolic illustrations. His leisure he devoted to the study of theology, and to writing for the Hartford Review, which the poet Whittier was editing. The friendship which he then formed with Whittier lasted for sixty years, and was recognized by the poet in 1870 by dedicating to him his "Miriam." It was a graceful and generous compliment which the great poet paid to the President of Columbia College when he wrote that in those old days of their early acquaintance Dr. Barnard had a greater chance of distinction even in literature and poetry than himself.

In 1837 Dr. Barnard accepted an appointment as Professor of Mathematics and Natural Philosophy in the University of Alabama; in 1848 he became Professor of Chemistry. Meanwhile resuming his theological studies, he took orders in the Episcopal Church. In 1854 he went to Oxford University in Mississippi as Professor of Mathematics and Astronomy. In 1856 he was elected President; a title changed in 1858 to Chancellor. While in the South, he urged the claims of science to a higher place in a liberal education. In the agitation between Northern and Southern views in regard to California, and other burning questions of the day, he spoke boldly for the Union. On July 4, 1851, he delivered an address at Tuscaloosa, and wrote a patriotic ode. At the outbreak of the civil war he found himself in a delicate position; he resigned his place in the University in 1861, and sought to return North, but was refused a passport by Jefferson Davis. For a time he was not permitted to leave the Confederate States, but finally was allowed to go to Europe. On his journey, by the way of Fortress Monroe, he was stopped at Norfolk, where he remained until the city came into the hands of the Union army. Going then to Washington, he found friends and employment. In 1862 he was engaged on the reduction of Gilliss's observations on southern stars, under the Director of the Naval Observatory. In 1863 he was placed in charge of chart-printing and lithography for war maps in the office of the U. S. Coast Survey. In 1864, Mr. McCulloch, Professor of Physics in Columbia College, N. Y., resigned, and linked his fortunes with the Southern Confederacy. Professor Barnard applied for the vacant office; but the Trustees made him President.

President Barnard for many years had been interested in the improvement of education of every grade, and had claimed for science its proper place in the curriculum. At his accession to the presidency, the managers of Columbia College were induced by him to enlarge the sphere of collegiate education by the establishment of the School of Mines with an independent faculty. The friendly rivalry between this department and the classical has invigorated both, and brought greater numbers and more funds to the College. The centennial celebration of the revival and confirmation by the Legislature of the State of New York of the Royal Charter granted in 1754, which occurred on April 13, 1887, took place under circumstances of great present prosperity, and of rich promises for the future.

The labors of Dr. Barnard were never limited by his professional duties. When the American Astronomical Expedition was organized by the Superintendent of the U. S. Coast Survey, under the authority of Congress, for the purpose of observing the solar eclipse of July 17, 1860, Professor Stephen Alexander was chief, and President Barnard one of a large corps of able assistants. Mr. Alexander made the report on the observations taken on Cape Chadleigh in Labrador, and Mr. Barnard furnished an account of them for the American Journal of Science. In 1867 Dr. Barnard was appointed one of the U. S. Commissioners to the Universal Exposition in Paris, and his report was printed by Congress. He was also Assistant Commissioner General to the Exposition of 1878. He received the Cross of Officer of Legion of Honor from the French Ministry, and a gold medal for his work as editor in chief of Johnson's Cyclopaedia.

Dr. Barnard joined the American Association for the Advancement of Science at the seventh meeting, held at New York in 1846. He was elected President of the fifteenth meeting, which was expected to convene at Nashville, Tenn., on April 15, 1861. But that meeting was prevented by the impending civil war. In 1866 Dr. Barnard thought that the time had come for renewing the meetings, and, in co-operation with Joseph Lovering, the Permanent Secretary, he arranged for a meeting in Buffalo, beginning on August 15, over which he presided. Absence in Europe prevented him from giving his valedictory address as retiring President at the next meeting, in Burlington, Vt., but it was delivered at the meeting in Chicago in

1868. In this address, after a comprehensive survey of recent advances in the science of all the physical forces, in the widest meaning of that phrase, culminating in the doctrine of the conservation and correlation of force, he strenuously opposed the philosophy which confuses mental or moral power with physical force. His last words were: "In conclusion, gentlemen, thanking you for the kind attention with which you have listened to me, permit me to congratulate you on the cheering auspices under which you are once more assembled. You are here in a strength which recalls the happy days when your Association was in the zenith of its prosperity and its usefulness, and which justifies the hope that a fresh career of still more fruitful labors and of higher services to humanity is before it." When, at a later day, the American Metrical Society was instituted, Dr. Barnard was its President.

Although Dr. Barnard made no great discovery in science, his acquaintance with it was accurate and of wide range. Besides many articles in the Cyclopædia, he published eleven papers in the American Journal of Science, and four in the Proceedings of the American Association for the Advancement of Science. In 1859, as chairman of a committee of twenty, he made an elaborate report to this Association on the History, Methods, and Results of the U. S. Coast Survey. In 1860, he gave an interesting course of lectures in the Smithsonian Institution, which were published in the Report of 1862. In 1869, he published "Recent Progress in Science," and in 1871, a volume on the Metric System. Dr. Barnard was no specialist; his love of knowledge included all the sciences, mathematical, physical, and social; and with it was blended a love of poetry and art. But above all and through all he was an educator. For sixty years education was the great subject of his thoughts and his professional activity. In early life he published text-books on arithmetic and grammar for schools and colleges. At a later period, he wrote a book upon Art-Culture. He was a frequent contributor to Dr. Henry Barnard's Journal of Commerce and Education. His essays and reports on collegiate and university education, and his letters on college government, attracted attention throughout the country. Books and the periodical and daily press equally served him for the dissemination of his independent views. His pamphlet on University Education, addressed to the Trustees of the University of Mississippi, was a plea for building up a university in this country; an idea afterwards realized in more than one college, though at the time a voice crying in the wilderness.

The value of Dr. Barnard's many services to science and education were recognized by academies and seats of learning. He was elected an Associate Fellow of the American Academy of Arts and Sciences in 1860. He was included among those named in the act of incorporation of the National Academy of Science by Congress, in 1863, was chairman of an important committee on weights, measures, and coinage, and Foreign Secretary for a time. In 1871 he was chosen a member of the Philosophical Society of Philadelphia. He was also a corresponding member of the Royal Society of Liege. He received the degree of LL. D. from Jefferson College in 1855, and from Yale in 1859; and the degree of S. T. D. from the University of Mississippi in 1861. The Regents of the University of New York made him a Doctor of Letters in 1872.

It is understood that Dr. Barnard, devoted to the end to the cause of education, and faithful to the College which had adopted and honored him, and to which he had given twenty years of his ripened thought, has left his whole property (about 80,000 dollars) to Columbia College, to be available after the death of Mrs. Barnard.

JOHN CALL DALTON.

John Call Dalton was born in Chelmsford, Mass., on February 2, 1825. He was the son of John Call Dalton, a practitioner of medicine of unusual attainments and great success in his profession.

The subject of this notice was a graduate of Harvard College, of the class of 1844, and received his degree in medicine from the same institution in 1847. He at once devoted himself to the study of experimental physiology and comparative pathology. After a short residence in Boston, he was appointed to the Professorship of Physiology in the medical department of the University of Buffalo. He subsequently occupied the same position in the Vermont Medical College, and in the Long Island College Hospital. In 1861 he became assistant surgeon of the New York Seventh Regiment, and, later, Brigade Surgeon U. S. Volunteers, serving in many important medical duties till February 14, 1864.

In 1864 he began his active work in New York and was until his death, on February 12, 1889, connected with the College of Physicians and Surgeons, at first as Professor of Physiology, and from 1883 as its President.

Dr. Dalton was distinctly a teacher. To a thorough knowledge of his subject he added the skill of a successful experimenter, and a command of simple, exact, and attractive language, and in consequence never failed to attract and retain the attention of listener and reader. His great merit was this, that he made a place here for the study of experimental physiology. He had been preceded by Magendie and Claude Bernard in Europe, but in this country he was incontestably the leader.

His first published work of importance was an essay on the "Corpus Luteum of Pregnancy." This received a prize offered by the American Medical Association, and was at once recognized as the work of an independent and careful investigator.

In 1859 appeared the first edition of the "Treatise on Human Physiology." This work was soon found to be better adapted to the uses of students of medicine than any other then in existence, and it has been the text-book of the majority of the physicians of this country. It was one of the few text-books in which a teacher of physiology had ventured to discard the well-worn commonplaces, which seem to have a meaning, but are, in fact, nothing but abstract ideas, and scarcely recognize a connection between the laws that govern the universe and those that affect the human body. Vital force was a phrase much used; and so long as the student was taught that this mysterious something was the only explanation of the functional activities, investigation was necessarily at a standstill.

Dalton brilliantly asserted the claims of original investigation upon the living subject to the chief place in the study of physiology. Both the merits and the defects of this book were eminently characteristic of the man. The subjects not sufficiently elaborated in this work — and they are few in number — were those which had not been experimentally studied by himself. That this text-book after the lapse of thirty years is still in general use, is conclusive evidence of the careful revisions and additions which the author was constantly making.

His pronounced position brought upon him the reproaches and threats of those who oppose vivisection under all circumstances. Before legislative bodies, as well as at the bar of public opinion, he maintained most convincingly the position he had early assumed, — that vivisection, as he practised and taught it, was essentially humane.

In 1885 he published his "Topographical Anatomy of the Brain." In this, his last contribution to science, as in his earliest essay, the same good qualities are manifest. He sought to display the structure of the brain, — so far at least as the unaided eye can study it. Fortunately he brought his great work to a conclusion, and has built by it a permanent monument to his skilful, well-trained eye, powers of patient investigation and exact observation, and that felicity of statement in which he never failed.

Upon this and upon the Treatise on Physiology his reputation hereafter will rest; but they represent by no means all his useful activities. In all the higher relations of medical teaching he was constantly busied. A large number of instructive, original, and attractive addresses are proofs of the eagerness with which men listened to him.

He became an Associate Fellow of the Academy in 1855, and was an early member of the National Academy of Sciences.

EZEKIEL BROWN ELLIOTT.

Ezekiel Brown Elliott was born in Sweden, near Brockport, Monroe County, New York, on July 16, 1823. His father, John B. Elliott, was a doctor of medicine. In 1845 the family moved to Waterloo, Seneca County, New York. Ezekiel Elliott attended the High School in that place, and later, the Academy at Geneva, New York, where he was prepared for admission to Hamilton College which he entered in 1840. He graduated in 1844, having been a diligent student, displaying marked capacity for mathematics, astronomy, and physics.

Subsequent to graduation from college, Mr. Elliott pursued the vocation of teacher, until 1849, having charge of schools in Grand Rapids, Michigan, Lyons and Macedon, New York, and Eastport, Maine. In the last named year Mr. Elliott went to Boston and opened an office as "Actuary and Electrician." It was to work in the latter capacity that, during the first succeeding years, he devoted the greater part of his time. I find, in Mr. Elliott's handwriting, the following account of his connection with the extension of the telegraph service in the Eastern States: "Just before the latter half of the year 1849, I aided in opening the House Printing Telegraph line between Boston and New York, taking charge of the office in Boston, having previously spent a few weeks in Providence, R. I., making myself familiar with the operations necessary. Subsequently I became, for a short time, joint proprietor of the line with Mr. W. O. Lewis, of Hartford, Connecticut; and still subsequently Mr. Lewis and myself were joint superintendents. Later, I accepted the superintendency of the Boston, Troy, and Albany Printing [House] line of telegraph. I relinquished my relation with the telegraph, I think, in 1854." Mr. Elliott, however, industriously kept up his work in physics. I find that in 1853 he was awarded a medal by the Massachusetts Charitable Mechanics' Association for "white flint telegraphic insulators." Among his subsequent inventions were a portable dynamo; an electric motor; a "storer" for electricity; and an "auroral telephone or phono-flash."

From 1855 onward, Mr. Elliott was increasingly engaged in actuarial work. In that and the following year he prepared for the New England Mutual Life Insurance Company tables of Two-Life Survivorships, comprising about 18,000 logarithmic values, computed on the basis of the London Actuary's life table, at four per cent interest. He had, in 1851, been employed by Mr. Amasa Walker, Secretary of State, in actuarial work upon the pension lists of Massachusetts; and in 1860 he prepared, at the instance of Mr. Oliver Warner, Secretary of State, a pamphlet, to be issued to city and town officials, containing Instructions concerning the Registration of Births, Marriages and Deaths in Massachusetts (pp. 56, octavo). In all his actuarial work, whether done for private employers or for the Commonwealth, he won a high reputation for accuracy of computation, ingenuity in method, and wide range of knowledge.

In 1856 Mr. Elliott read before the Association for the Advancement of Science, at its Buffalo meeting, the following papers: —

A. Tables of Prussian Mortality, interpolated for annual intervals of age; accompanied with formula and process for construction.

B. Discussion of certain methods for converting ratios of deaths to population, within given intervals of age, into the logarithm of the probability that one living at the earlier of two ages will attain the later; with illustrations from English and Prussian data.

C. Process for deducing accurate average duration of life, present value of life annuities, and other useful tables involving life-contingencies, from returns of population and deaths, without intervention of general interpolation.

At the meeting of the Association in Montreal, in 1857, Mr. Elliott presented a paper on the Law of Mortality in Massachusetts, with practical tables.

At the outbreak of the War of Secession, Mr. Elliott was called to join in the work of the United States Sanitary Commission, into which he entered with intense zeal and unflagging industry. In 1862 he made a Preliminary Report on the Mortality and Sickness of the Volunteer Forces of the United States Government during the Present War. This report led to his being elected a Fellow of the American Academy of Arts and Sciences, and to his appointment as

Actuary to the Sanitary Commission. In the same year he made a Statistical Report to the United States Sanitary Commission on the Mortality and Sickness of the United States Volunteers. He also contributed to the Republic Magazine of July, 1863, a paper on Mutual Relations, as to Price, of Gold, Greenbacks, Silver Bullion, and Silver Coin.

In 1863 he was sent as a delegate from the American Statistical Association to the International Statistical Congress at Berlin, September 6th to 12th, where he presented a paper on the Military Statistics of the United States of America, which was published, in English, by the Royal Printer of Prussia (44 pages, 4to), with appended charts.

In 1864 Mr. Elliott was sent by the Sanitary Commission to inspect the hospital and ambulance services of the armies engaged in the Danish war. In the discharge of this duty, Mr. Elliott visited the hospitals of the contending forces on both sides. The results of his observations were submitted to the Sanitary Commission, but have not, so far as I am advised, been published. During his tour Mr. Elliott prepared a report on Prussian Mortality, which was published in the Zeitschrift of the Royal Statistical Bureau of Prussia.

At the close of the War of Secession, Mr. Elliott was appointed Secretary of the United States Revenue Commission, under the chairmanship of Mr. David A. Wells, to which had been assigned the almost hopeless task of bringing order out of the weltering chaos of customs duties and internal revenue taxes which had been imposed, in defiance of all recognized laws of finance, by an uninstructed Congress urged on by the continually recurring exigencies of a war of unexampled proportions. Mr. Elliott's services in this capacity were of incalculable value to the country, although they did not appear in a form distinct from the general work of the Commission. After the Commission was dissolved, and Mr. Wells became sole Special Commissioner of the Revenue, Mr. Elliott continued his work upon the revenue system.* On the discontinuance of Mr. Wells's office, in 1869,† Mr. Elliott was assigned to duty in the Bureau of Statistics, Treasury

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* At the Chicago meeting of the American Association, in 1868, Mr. Elliott presented a paper on "Redemption Periods of Monetary Values involving Life-Contingencies." Also, a paper on the "Metrical Unification of International Coinage," suggested by the International Monetary Conference of that year in Paris.

† In this year Mr. Elliott prepared the extended section (60 pages, 4to) on the Moneys, Weights, and Measures of different Countries, embraced in Webster's Counting-House Dictionary.

Department, under the present writer. On the accession of Mr. Edward Young to the charge of the Bureau, Mr. Elliott became its chief clerk, although his time continued to be devoted chiefly to the preparation of reports and tables for the use of the Secretary of the Treasury, and to answering special calls for information coming from Congress, where financial questions were resuming the importance they had lost during the periods of war and reconstruction.

In 1879 Mr. Elliott was appointed as the representative of the Treasury Department upon the commission, under the chairmanship of Mr. George William Curtis, constituted by President Grant to frame rules and regulations to govern the admission of persons into the civil service of the United States. He was chosen Secretary, and occupied that position until the discontinuance of the work of the Commission, which was, in fact, never legally dissolved, but ceased to act through the failure of appropriation on the part of Congress, owing to the hostility of the advocates of the Spoils System.

During this period Mr. Elliott continued to carry on his actuarial duties in the Treasury Department. On December 1, 1871, he published a letter on the Credit of the United States Government, with comparative tables, addressed to the Secretary of the Treasury. In 1872, at the request of the Superintendent of the Census, he prepared two papers, which are contained in the volume on Vital Statistics of the Ninth Census, as follows: —

A. On the Table of Births, — correcting manifest incongruities in the distribution, as to age, of the population under five years (pp. 517–531, inclusive).

B. Upon the Statistics of Mortality, — their reduction to the practical form of life tables (pp. x–xv. inclusive).

In 1879 he was joined with Mr. Thomas L. James, afterwards Postmaster General, in a commission to report upon trials of the electric light in the post-office building of New York City, and to compare the relative economy of illuminating gas and of electricity in lighting. The report of the commission is on file in the Treasury Department.

In January, 1880, he prepared a series of Tables on the Credit of the United States Government, giving the prices of the several classes of the securities of the United States, together with the corresponding rates of interest realized to investors therein. These tables were published in the letter of the Secretary of the Treasury to the Chairman of the Finance Committee of the Senate, bearing date January 30, 1880.

Meanwhile he had continued his contributions to the meetings of the American Association. In 1874, he presented, at the Hartford meeting, a paper on the Future Population of the United States. In 1875, he presented to the Detroit meeting a paper on the Subsidiary Principle applied to Coinage and Money of Account.* At the Buffalo meeting of 1876, he presented a paper on the Relative Market Prices of Gold and Silver, and their influence on the Metallic Monetary Standard of the United States, accompanied by a diagram showing for thirty-four years the relative values of gold and silver; also the mint ratios adopted by the government with regard to the gold and silver coinage, and their successive changes. At the Nashville meeting of 1877, he presented two papers, one on the Monetary Standard, the other on Standard Time. The last-named subject had strongly attracted Mr. Elliott's attention,† and he continued to work in this line until the adoption of the principle throughout the United States.

In 1881, Congress passed an act creating the office of Government Actuary; and on the 1st of July Mr. Elliott was appointed to that office, which he held during the remainder of his life. The reports prepared by him, in this capacity, are too numerous and various to be individually noticed. Among the questions presented to him for investigation and discussion were the apportionment of representation in Congress under the Tenth Census; the condition of the United States Sinking Fund; the probable population of the country, at successive dates; the interest borne by various species of United States Government securities; and the effect of innumerable schemes for refunding the debt of the United States.‡ The calls upon Mr. Elliott as Government Actuary came from all the executive departments, from the Smithsonian Institution, from both Houses of Congress, and from many individual members and committees of Congress.

From the date of his appointment as Government Actuary, his

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* In this year he wrote the article on Coinage in Johnson's Cyclopædia.

† In 1881, he joined with Professor Cleveland Abbe in forming a Universal Time Table, and in a report on Standard Time, made to the Metrological Society, of which he was an active member.

‡ Senator Hawley relates an amusing incident concerning a scheme which had passed the House, and was being very indulgently considered by the Finance Committee of the Senate, when Mr. Elliott appeared before the Committee and in a few minutes showed conclusively that the measure, if adopted, would cost the government in excess of thirty-three millions of dollars. The bill was thereupon incontinently dropped, and no one could afterwards be found who had ever been in favor of it.

official duties, and perhaps also his advancing years, restricted somewhat his contributions to the American Association. In 1881 he presented papers to the Association at its Cincinnati meeting; in 1882 he was President of Section I., and delivered an address upon Economic Science and Statistics; and in 1886 he made the last of his many contributions, at the Buffalo meeting, in a paper dealing with the rate of interest realized to investors in government securities, and offering formulas for determining the United States gold value of silver bullion, when the London price per ounce of standard silver and the price of Sterling Exchange between New York and London are known.

His last scientific work was in connection with the Metrological Society, in 1887. The second volume of the Proceedings of that Society contains several communications from his pen.

Mr. Elliott reached the close of his busy and useful life, at Washington, on May 24, 1888, in his sixty-third year. He was never married.

This brief review of his numerous and varied works fully justifies the conclusion that he was among the most meritorious of American statisticians and actuaries. Personally, Mr. Elliott was one of the most amiable of men, with a childlike simplicity of character and utterly incapable of offence or of guile.

FOREIGN HONORARY MEMBERS.

MICHEL EUGÈNE CHEVREUL.

Michel Eugène Chevreul died in Paris, April 9, 1889. He was born at Angers, on a branch of the Loire, August 31, 1786. The mere fact that any one prominent in the world of science should have lived to the extraordinary age of almost one hundred and three years is in itself so surprising and unprecedented that our thoughts tend to dwell upon it unduly. A moment's reflection is needed to bring into clear light the deeds of merit which made the man illustrious. It is to be remembered that Chevreul was the contemporary of chemists who died when most of us here present were children or not yet born. The friends of his youth were Ampère and Gay-Lussac, D'Arcet, Davy, Oersted, Wollaston, and Berzelius. Proust was his townsman, Vauquelin was his teacher, and it is evident that Fourcroy also had no little influence upon his scientific life.

With Cuvier and with Ampère, as he tells us, he was accustomed to hold unending friendly debates upon plans of classification and upon the aims and methods of scientific research. Years after Chevreul had been left the sole survivor of the chemists of his time, he was accustomed, in his lectures at the Gobelins, to make fond allusion to the works of these men, almost as if they had been still alive. Chenevix, also, as he assured us, "was a very conscientious man, with immense encyclopedic knowledge."

It is said that Chevreul's early education was carefully looked to by his father, who was a distinguished physician. Between the ages of eleven and seventeen the boy studied at the École Centrale of Angers. He then went to Paris, where he immediately attracted the attention of his teachers. When twenty years old he was assistant in charge of Vauquelin's laboratory, and teacher in a scientific school which Fourcroy had founded. In this same year, 1806, he began to publish scientific papers, and before ten more years had passed it was recognized by every one that he had gained a place in the foremost rank of chemists. In 1810 he was appointed assistant naturalist at the Garden of Plants, and he subsequently succeeded to the Chair of Chemistry at the Garden, which had been occupied, successively, by Geoffroy, the Brothers Rouelle, Lemery, Macquer, Fourcroy, and Vauquelin. It is noticeable that no small part of Chevreul's work related to subjects in the domain of natural history, and that he published many papers in the Annales and Mémoires of the Museum. In 1816 he was appointed Professor of Chemistry at the Gobelins, and director of its dye-houses. In 1826 he became a member of the French Academy of Sciences and a foreign honorary member of the Royal Society of London.

As a chemist, Chevreul investigated a great variety of substances, ranging from the sugar of diabetes and the oxidation products of cork, on the one hand, to compounds of tungsten, uranium, and zirconium, on the other. He edited several scientific journals also, and contributed articles to encyclopædias and dictionaries of science and of technology. As an example of work of this kind may be cited a review written by him, in 1822, of a French translation of Sir Humphry Davy's Lectures on Agricultural Chemistry. This review is well worth reading to-day, and it has a certain historic interest, since it marks better even than the Lectures themselves the very considerable progress which had been made at that early period by chemists who sought to classify and explain the phenomena of vegetable growth by referring them to scientific principles.

At the very first, Chevreul devoted much attention to the investigation of the coloring matters in dye-woods, not because the subject was at that time in the line of his duty, but, apparently, because of the facility with which the materials could be procured. It has long been a maxim of the French chemists, that it is well for beginners in research to work upon some technical product, such as can readily be obtained at a manufactory, since by so doing much of the trouble and cost of procuring materials fit for investigation may be avoided. The results of several of these early investigations were valuable additions to scientific knowledge. It was Chevreul who discovered brazilin, white-indigo, and hæmatoxylin, — also creatin. But by far the most noteworthy of his works at this period was the classical research on the composition of fats, which was published in book form in 1823. He had been actively engaged in studying this subject during the years 1811 to 1820. Of this research chemists have always held one opinion, namely, that it was masterly. Hermann Kopp says of it, in his Geschichte der Chemie, "Chevreul's work on the fats is a model of a complete and exhaustive research in organic chemistry." It may well be said of it, that it gave to the world a new source of power, akin to those gained by the investigation of the properties of steam and of electricity. A great flood of light was thrown upon a matter of extreme darkness. By mere force of its clearness, the publication of this work led directly to numberless improvements in the arts and in household economy. At a time when methods of investigating organic substances were little known, this research brought out, as by a touch, complete, accurate, and enduring knowledge of the composition and properties of a large and important class of chemical substances, the study of which had previously been supposed to be peculiarly difficult. The research itself was thoroughly and purely scientific. As Kopp has set forth, it disclosed the proximate and ultimate composition of the fats, both in general and in particular, qualitatively and quantitatively, as well as the composition of the products of the decomposition of fats; it developed a rational theory as to the chemical structure of the fats, and displayed the relations which the fats bear to other chemical substances. Meanwhile, the processes of organic analysis which Chevreul used were decided improvements on those of his predecessors.

It is because of the purity and fulness of this particular fountain, so to say, of scientific knowledge, that so many useful technical applications have flowed from it. Even up to the present time it has exerted an enormous influence upon all that relates to the manufacture and use of soaps, oils, glycerine, and candles. Such familiar words as cholesterin, stearin, margarin, oleic acid, butyric acid, and the like, have come down to us from Chevreul's work. It is safe to say that, if the man had died in his fortieth year, his name and fame would still have been familiar to us.

Subsequently to his work upon the fats, Chevreul occupied himself with a great variety of chemical studies, and gave special attention to matters relating to dyeing and painting. It was at this epoch that he began his investigations of the laws of the harmony of colors. His book upon this subject, published in 1839, has been widely read, with no little interest, by several generations of men.

In studying the question of the harmony of colors, Chevreul was impressed with the importance of having a definite standard with which all colors could be compared, and by means of which all colors could be accurately named. He argued that in the technical application of colors, either for painting or dyeing, it is impossible to lay down definite rules for obtaining a desired result unless each of the colors to be employed can be accurately described. In order to do this, he devised his so called chromatic circle, which was manifestly a great improvement both upon the common practice of comparing colors with natural objects, and upon the ideas of several scientific men who have urged that definite standards of comparison might be chosen among colored minerals, or birds, or flowers. This chromatic circle well illustrates one peculiarity of Chevreul which was not a little conspicuous; namely, his leaning towards the methods of naturalists. He sought always to classify ideas and substances into families, genera, and species. He insisted on carefully distinguishing the chemical properties of bodies from their physical and organoleptic properties. To him the characteristic peculiarities of the "immediate principles" (proximate constituents) in a compound were of deeper interest than the question of their ultimate composition.

For the fundamental points of comparison in his circle of colors he chose from the solar spectrum definite rays of red, yellow, and blue, the position of each of which was marked by that of certain stated lines of Fraunhofer. These three colors were placed at equidistant points on the circle, and between each pair of them were intercalated twenty-three mixtures, so that the complete circle comprised seventy-two colors in all. For example, half-way between yellow and blue came green, and half-way between yellow and green came "yellow-green." But between yellow and yellow-green were five different tints, named yellow with green 1, or 2, or 3, or 4, or 5, respectively;

and so between blue and red, and between red and yellow. In addition to this "normal" circle, he had eight others, the colors of which were toned down, respectively, with one tenth, two tenths, three tenths, and so on, of black. In order to compare shades of colors, he prepared standard rows, or columns, by mixing his normal colors with one tenth, two tenths, and so on, of black in one direction, and with one tenth, etc. of white in the other. Chevreul's idea was that standard circles of color should be kept in the custody of public officers, just as standards of weights and measures are kept. But in seeking to carry out this scheme a grave difficulty is encountered in that most colors speedily fade. Moreover, while it is comparatively easy to compare colored threads with the colors of a circle made in silk or woollen, it would not be easy to compare colored woollen stuffs with the colors of a circle made of porcelain; that is to say, the varying lustres of colors, according as they have been put upon one or another kind of material, hinders very decidedly the accurate comparing of them. It is in fact difficult to compare the colors of metals or alloys with those of dyes fixed upon wool, or of pigments printed on paper. In the course of his lectures, Chevreul was accustomed to construct with skeins of worsted upon the floor of the great exhibition hall at the Gobelins a mammoth circle, which was an object of great beauty. It carried conviction to his audience that the device would be one of great practical utility, if it were but possible to obtain permanent colors with which to construct the circle.

It was in 1832 that Chevreul printed his first paper on the harmony of colors, and his book upon the subject was published seven years later, when he was fifty-three years old. He continued to write about the contrast of colors as long as he lived; but not with his old-time sagacity. It must be said, indeed, that, in spite of his very long life, the term of Chevreul's useful working years was practically no longer than that of many another scientific man whose life was shorter than his by a quarter of a century. Even in Chevreul's seventieth year it was very evident that he was already "a savant somewhat past his faculties."

During his declining years he had much to say, both by way of reclamation and of explanation, in favor of the views and labors of earlier investigators, and there can be no question that he held in mind many matters of historic interest; but, sad to say, in his enfeebled condition the task of putting these things in order was beyond his powers. Worst of all, perhaps, the ways of thinking of the new generations had become so unlike his ways that hardly any one could find time to give heed to what he had to say. Indeed, it is by no means easy, even if it be possible, to apprehend justly the import of some of his later views and statements. It may well be questioned whether the somewhat painful impression which must have been made upon his grandchildren and great-grandchildren by many of the utterances of Chevreul's last years does not explain the singular request made by them to the French Academy, that no eulogy should be pronounced upon their ancestor.

In many notices which have been printed since Chevreul's death stress has been laid, justly enough, upon the great influence which he exerted in the field of industrial chemistry. All this is true. Few men have had a wider influence than he for good in this department. On the approach of his hundredth birthday, it was suggested that there should be displayed to the public at the Garden of Plants specimens of the various products of industry which had been made better by means of his thoughts and studies. But this idea had to be given up, because not even the large new hall of the Zoölogical Museum could heve held all the materials which were offered for exhibition. In point of fact, on his hundredth birthday there came marching with banners into the great hall of the Museum, to do him honor, two thousand and more delegates from the learned societies, the schools, the museums, and the workshops in whose behoof he had labored so faithfully during many useful years. It should be borne in mind, none the less, that Chevreul was not an industrial chemist, in the modern acceptation of the term. It was not for money prizes that he lived and labored. But the brilliant technical results which followed the publication of his researches showed to all men what stores of wealth may be gained by the judicious application of scientific knowledge for the correcting of rules of art. In recent days there has been no lack of workers in this alluring field.

It is a matter of history that the influences of the Revolution, and of the succeeding long struggle between France and the rest of Europe, gave more or less of a practical or economic bias to the minds of most French teachers and scientific men of the period in which Chevreul's youth was passed. With his fellows, he felt the influence of the wars of the Revolution, and of the public feeling which found expression in the École Normale and the École Polytechnique. In this sense, it is true that he worked by preference upon subjects intimately connected with the ordinary affairs of life; but it should be remembered of him that he was not only an accomplished chemist, but always, from first to last, a thoroughly scientific man of an admirable type.

RUDOLF JULIUS EMANUEL CLAUSIUS.

Rudolf Julius Emanuel Clausius was born at Cöslin in Pomerania, January 2, 1822. His studies, after 1840, were pursued at Berlin, where he became Privat-docent in the University, and Instructor in Physics in the School of Artillery. He was Professor of Physics at Zürich in the Polytechnicum (1855–67) and in the University (1857–67), at Würzburg (1867–69), and finally at Bonn (1869–88), where he died on the 24th of August, 1888.

His literary activity commenced in 1847, with the publication of a memoir in Crelle's Journal, "Ueber die Lichtzerstreuung in der Atmosphäre, und über die Intensität des durch die Atmosphäre reflectirten Sonnenlichts." * This was immediately followed by other writings relating to the same subject, two of which were subsequently translated from Poggendorff's Annalen † for Taylor's Scientific Memoirs. A treatise entitled "Die Lichterscheinungen der Atmosphäre" formed part of Grunert's "Beiträge zur meteorologischen Optik."

An entirely different subject, the elasticity of solids, was discussed in his paper, (1849,) "Ueber die Veränderungen, welche in den bisher gebräuchlichen Formeln für das Gleichgewicht und die Bewegung fester Körper durch neuere Beobachtungen nothwendig geworden sind." ‡

But it was with questions of quite another order of magnitude that his name was destined to be associated. The fundamental questions concerning the relation of heat to mechanical effect, which had been raised by Rumford, Carnot, and others, to meet with little response, were now everywhere pressing to the front.

"For more than twelve years," said Regnault in 1853, "I have been engaged in collecting the materials for the solution of this question: — Given a certain quantity of heat, what is, theoretically, the amount of mechanical effect which can be obtained by applying the heat to evaporation, or the expansion of elastic fluids, in the various circumstances which can be realized in practice?" § The twenty-first volume of the Memoirs of the Academy of Paris, describing the first part of the magnificent series of researches which the liberality of the French government enabled him to carry out for the solution of this

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* Vol. xxxiv. p. 122, and vol. xxxvi. p. 185.

† Vol. lxxvi. pp. 161 and 188.

‡ Pogg. Ann., vol. lxxvi. p. 46 (1849).

§ Comptes Rendus, vol. xxxvi. p. 676.

question, was published in 1847. In the same year appeared Helmholtz's celebrated memoir, "Ueber die Erhaltung der Kraft." For some years Joule had been making those experiments which were to associate his name with one of the fundamental laws of thermodynamics and one of the principal constants of nature. In 1849 he made that determination of the mechanical equivalent of heat by the stirring of water which for nearly thirty years remained the unquestioned standard. In 1848 and 1849 Sir William Thomson was engaged in developing the consequences of Carnot's theory of the motive power of heat, while Professor James Thomson in demonstrating the effect of pressure on the freezing point of water by a Carnot's cycle, showed the flexibility and the fruitfulness of a mode of demonstration which was to become canonical in thermodynamics. Meantime Rankine was attacking the problem in his own way, with one of those marvellous creations of the imagination of which it is so difficult to estimate the precise value.

Such was the state of the question when Clausius published his first memoir on thermodynamics: "Ueber die bewegende Kraft der Wärme, und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen." *

This memoir marks an epoch in the history of physics. If we say, in the words used by Maxwell some years ago, that thermodynamics is "a science with secure foundations, clear definitions, and distinct boundaries," † and ask when those foundations were laid, those definitions fixed, and those boundaries traced, there can be but one answer. Certainly not before the publication of that memoir. The materials indeed existed for such a science, as Clausius showed by constructing it from such materials, substantially, as had for years been the common property of physicists. But truth and error were in a confusing state of mixture. Neither in France, nor in Germany, nor in Great Britain, can we find the answer to the question quoted from Regnault. The case was worse than this, for wrong answers were confidently urged by the highest authorities. That question was completely answered, on its theoretical side, in the memoir of Clausius, and the science of thermodynamics came into existence. And as Maxwell said in 1878, so it might have been said at any time since the publication of that memoir, that the foundations of the science were secure, its definitions clear, and its boundaries distinct.

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* Read in the Berlin Academy, February 18, 1850, and published in the March and April numbers of Poggendorff's Annalen.

† Nature, vol. xvii. p. 257.

The constructive power thus exhibited, this ability to bring order out of confusion, this breadth of view which could apprehend one truth without losing sight of another, this nice discrimination to separate truth from error, — these are qualities which place the possessor in the first rank of scientific men.

In the development of the various consequences of the fundamental propositions of thermodynamics, as applied to all kinds of physical phenomena, Clausius was rivalled, perhaps surpassed, in activity and versatility by Sir William Thomson. His attention, indeed, seems to have been less directed toward the development of the subject in extension, than toward the nature of the molecular phenomena of which the laws of thermodynamics are the sensible expression. He seems to have very early felt the conviction, that behind the second law of thermodynamics, which relates to the heat absorbed or given out by a body, and therefore capable of direct measurement, there was another law of similar form, but relating to the quantities of heat (i. e. molecular *vis viva*) absorbed in the performance of work, external or internal.

This may be made more definite, if we express the second law in a mathematical form, as may be done by saying that in any reversible cyclic process which a body may undergo

$$\int \frac{dQ}{t} = 0,$$

where dQ is an elementary portion of the heat imparted to the body, and t the absolute temperature of the body, or the portion of it which receives the heat. Or, without limitation to cyclic processes, we may say that for any reversible infinitesimal change,

$$dQ = t\, dS,$$

where S denotes a certain function of the state of the body, called by Clausius the *entropy*. The element of heat may evidently be divided into two parts, of which one represents the increase of molecular *vis viva* in the body, and the other the work done against forces, either external or internal. If we call these parts dH and $d\,Q_w$, we have

$$dQ = dH + d\,Q_w.$$

Now the proposition of which Clausius felt so strong a conviction was that for reversible cyclic processes

$$\int \frac{dQ_w}{dt} = 0,$$

and that for any reversible infinitesimal change

$$d\,Q_w = t\,d\,Z,$$

where Z is another function of the state of the body, which he called the *disgregation*, and regarded as determined by the positions of the elementary parts of the body without reference to their velocities. In this respect it differed from the entropy. An immediate consequence of these relations is that for any reversible cyclic process

$$\int \frac{dH}{t} = 0,$$

and therefore that H, the molecular *vis viva* of the body, must be a function of the temperature alone. This important result was expressed by Clausius in the following words: "Die Menge der in einem Körper wirklich vorhandenen Wärme ist nur von seiner Temperatur und nicht von der Anordnung seiner Bestandtheile abhängig."

To return to the equation

$$d\,Q_w = t\,d\,Z.$$

This expresses that heat tends to increase the disgregation, and that the intensity of this tendency is proportional to the absolute temperature. In the words of Clausius: "Die mechanische Arbeit, welche die Wärme bei irgend einer Anordnungsänderung eines Körpers thun kann, ist proportional der absoluten Temperatur, bei welcher die Aenderung geschieht."

Such in brief and in part were the views advanced by Clausius in 1862, in his memoir, "Ueber die Anwendung des Satzes von der Aequivalenz der Verwandlungen auf die innere Arbeit." * Although they were advanced rather as a hypothesis than as anything for which he could give a formal proof, he seems to have little doubt of their correctness, and his confidence seems to have increased with the course of time.

The substantial correctness of these views cannot now be called in question. The researches especially of Maxwell and Boltzmann have shown that the molecular *vis viva* is proportional to the absolute temperature, and Boltzmann has even been able to determine the precise nature of the functions which Clausius called entropy and disgregation.† But the anticipation, to a certain extent, at so early a

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* Pogg. Ann., vol. cxvi. p. 73. See also vol. cxxvii. p. 477 (1866).

† Sitzungsberichte Wien. Akad., vol. lxiii. p. 728 (1871).

period in the history of the subject, of the ultimate form which the theory was to take, shows a remarkable insight, which is by no means to be lightly esteemed on account of the acknowledged want of a rigorous demonstration. The propositions, indeed, as relating to quantities which escape direct measurement, belong to molecular science, and seem to require for their complete and satisfactory demonstration a considerable development of that science. This development naturally commenced with the simplest case involving the characteristic problems of the subject, — the case, namely, of gases.

The origin of the kinetic theory of gases is lost in remote antiquity, and its completion the most sanguine cannot hope to see. But a single generation has seen it advance from the stage of vague surmises to an extensive and well established body of doctrine. This is mainly the work of three men, Clausius, Maxwell, and Boltzmann, of which Clausius was the earliest in the field, and has been called by Maxwell the principal founder of the science.* We may regard his paper, (1857,) "Ueber die Art der Bewegung, welche wir Wärme nennen," † as marking his definite entrance into this field, although many points were incidentally discussed in earlier papers.

This was soon followed by his papers, "Ueber die mittlere Länge der Wege, welche bei der Molecularbewegung gasförmiger Körper von den einzelnen Molecülen zurückgelegt werden," ‡ and "Ueber die Wärmeleitung gasförmiger Körper." §

A very valuable contribution to molecular science is the conception of the *virial*, defined in his paper, (1870,) "Ueber einen auf die Wärme anwendbaren Satz," ‖ where he shows that in any case of stationary motion the mean *vis viva* of the system is equal to its virial.

In the mean time, Maxwell and Boltzmann had entered the field. Maxwell's first paper, "On the Motions and Collisions of perfectly elastic Spheres," ¶ was characterized by a new manner of proposing the problems of molecular science. Clausius was concerned with the mean values of various quantities which vary enormously in the smallest time or space which we can appreciate. Maxwell occupied himself with the relative frequency of the various values which these quantities have. In this he was followed by Boltzmann. In reading

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* Nature, vol. xvii. p. 278.

† Ibid., vol. c. p. 353 (1857).

‡ Ibid., vol. cv. p. 239 (1858). See also Wied. Ann., vol. x. p. 92.

§ Ibid., vol. cxv. p. 1 (1862).

‖ Ibid., vol. clxi. p. 124. See also Jubelband, p. 411.

¶ Phil. Mag., vol. xix. p. 19 (1860).

Clausius, we seem to be reading mechanics; in reading Maxwell, and in much of Boltzmann's most valuable work, we seem rather to be reading in the theory of probabilities. There is no doubt that the larger manner in which Maxwell and Boltzmann proposed the problems of molecular science enabled them in some cases to get a more satisfactory and complete answer, even for those questions which do not at first sight seem to require so broad a treatment.

Boltzmann's first work, however, (1866,) "Ueber die mechanische Bedeutung des zweiten Hauptsatzes der Wärmetheorie,"* was in a line in which no one had preceded him, although he was followed by some of the most distinguished names among his contemporaries. Somewhat later (1870) Clausius, whose attention had not been called to Boltzmann's work, wrote his paper, "Ueber die Zurückführung des zweiten Hauptsatzes der mechanischen Wärmetheorie auf allgemeine mechanische Principien." †

The point of departure of these investigations, and others to which they gave rise, is the consideration of the mean values of the force-function and of the *vis viva* of a system in which the motions are periodic, and of the variations of these mean values when the external influences are changed. The theorems developed belong to the same general category as the principle of least action, and the principle or principles known as Hamilton's, which have to do, explicitly or implicitly, with the variations of these mean values.

Among other papers of Clausius on this subject, we may mention the two following: "Ueber einen neuen mechanischen Satz in Bezug auf stationäre Bewegung," ‡ (1873,) and "Ueber den Satz vom mittleren Ergal und seine Anwendung auf die Molecularbewegungen der Gase" § (1874).

The first problem of molecular science is to derive from the observed properties of bodies as accurate a notion as possible of their molecular constitution. The knowledge we may gain of their molecular constitution may then be utilized in the search for formulas to represent their observable properties. A most notable achievement in this direction is that of van der Waals, in his celebrated memoir "On the Continuity of the Gaseous and Liquid States." To this part of the subject belong the following papers of Clausius: "Ueber das Verhalten der Kohlensäure in Bezug auf Druck, Volumen und Tem-

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* Sitzungsberichte Wien. Akad., vol. liii. p. 195.

† Pogg. Ann., vol. cxlii. p. 433.

‡ Ibid., vol. cl. p. 106.

§ Ibid., Ergänzungsband vii. p. 215.

peratur,"* and "Ueber die theoretische Bestimmung des Dampfdruckes und der Volumina des Dampfes und der Flüssigkeit" (two papers).†

Another matter in which Clausius showed his originality and power was the vexed subject of electrodynamics, as treated in his memoir, "Ueber die Ableitung eines neuen electrodynamischen Grundgesetzes."‡ Various points in the theory of electricity in which the principles of thermodynamics or of molecular science were involved, had previously been treated in different papers, of which the earliest appeared in 1852,§ while the doctrine of the potential (electrical and gravitational) was treated in a separate book, which appeared in 1859, with the title, "Die Potentialfunction und das Potential, ein Beitrag zur mathematischen Physik." This subsequently went through several editions, in which it was revised and enlarged. All these subjects, with others, were brought together in a single volume, "Die mechanische Behandlung der Electricität," which appeared in 1879, forming the second volume of his "Mechanische Wärmetheorie."‖ Later papers on electricity related to the principles of electrodynamics,¶ electrical and magnetic units,** and dynamo-electric machines.††

The Royal Society's catalogue of scientific papers, and the excellent indices to the Annalen der Physik und Chemie, in which Clausius's work usually appeared, render it unnecessary to enumerate in detail his scientific papers. The list, indeed, would be a long one. The

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* Wied. Ann., vol. ix. p. 337 (1880).

† Ibid., vol. xiv. p. 279 and p. 692 (1881).

‡ Crelle's Journal, vol. lxxxii. p. 85 (1877).

§ "Ueber das mechanische Aequivalent einer electrischen Entladung und die dabei stattfindende Erwärmung des Leitungsdrahtes." Pogg. Ann., vol. lxxxvi. p. 337. "Ueber die bei einem stationären electrischen Strome in dem Leiter gethane Arbeit und erzeugte Wärme." Pogg. Ann., vol. lxxxvii. p. 415 (1852). "Ueber die Anwendung der mechanischen Wärmetheorie auf die thermoelectrischen Erscheinungen." Pogg. Ann., vol. xc. p. 513 (1853). "Ueber die Electricitätsleitung in Electrolyten." Pogg. Ann., vol. ci. p. 338 (1857).

‖ The first volume of this work appeared in 1876, and contained the general theory with the more immediate consequences of the two fundamental laws. The third volume has not yet appeared, but it is expected very soon, edited by Professor Planck and Dr. Pulfrich. In a certain sense this work may be regarded as a second edition of an earlier one (1864 and 1867), which consisted of a reprint of papers and had the title "Abhandlungen über die mechanische Wärmetheorie."

¶ Wied. Ann., vol. x. p. 608; vol. xi. p. 604.

** Ibid., vol. xvi. p. 529; vol. xvii. p. 713.

†† Ibid., vol. xx. p. 353; vol. xxi. p. 385.

Royal Society's catalogue gives seventy-seven titles for the years 1847–1873. Subsequently twenty-five papers have appeared in the Annalen alone, and about half as many others elsewhere.

But such work as that of Clausius is not measured by counting titles or pages. His true monument lies not on the shelves of libraries, but in the thoughts of men, and in the history of more than one science.

FRANCISCUS CORNELIUS DONDERS.

In assuming the honorable duty of preparing a biographical notice of Professor Donders, the writer must acknowledge indebtedness, for many details, to accounts of his life and work by his coadjutors and friends, Moleschott, Snellen, Nuel, and Landolt, and to his own speech at the festival in his honor on his seventieth birthday.

Franciscus Cornelius Donders was born at Tilbury, in Holland, on the 17th of May, 1818; the tenth child and only son of parents in very moderate circumstances. His father's death occurred about a year later. From his seventh to his thirteenth year he was at school in Duizel, where he learned to write his own language, something of French, mathematics, and music. From eleven to thirteen years he served as submaster at the school, thus defraying his expenses. His studies were continued at Liege, in pursuance of his mother's wish that he should become a priest; but this plan being defeated by the occurrence of the Belgian revolution, he returned to the French school at Tilbury. Becoming fond of study, he was sent to Boxmeer, where he learned to write and speak Latin with great fluency, and a little Greek, but where mathematics, for which he seems to have had special aptitude, was neglected. At the age of seventeen he entered the School of Military Medicine at Utrecht, where he became enthusiastic in the experimental study of chemistry, the natural sciences, and physiology. After four years of study, desiring to obtain his diploma, he applied for examination; but a technical objection being made by the Faculty, he was advised to present himself at the University of Leyden. Here, through the merits of his dissertation and an address in Latin in which he convinced the Faculty that he was worthy to receive the degree of Doctor, he made such an impression of his capacity that in three days he returned to Utrecht as M. D. Of his "Dissertatio Inauguralis sistens Observationes Anatomico-pathologicas," Professor Moleschott says. "In this trial test I could well discern the future master."

Before he was twenty-two years of age, Donders was sent as junior military surgeon to the garrison at Vlissingen. Here, and especially at The Hague, the seat of government, where he was stationed a year later, he had the advantage of polite society, and of contact with distinguished men, — with opportunities for culture in art and literature, as well as in science and general and professional knowledge. He amply profited by these advantages, and perfected his acquaintance with French, English, and German, so that he wrote and spoke these as if they had been his native tongue; acquiring also a grace and urbanity of manner for which he was distinguished in all his social and professional life. The attention of his superiors being attracted by some of his published scientific papers, he was sent again to Utrecht, in 1842, to reorganize the Military Medical School; and was appointed Professor of Anatomy and of Physiology at the institution where so recently he had been a pupil.

Here began Donders's real scientific life. Convinced that book knowledge, especially in the natural sciences, has little value in contributing to further advancement, unless completed by careful personal experimental investigation, he accepted the offered position without a moment's hesitation, although he thus gave up the pleasures and advantages of the capital, and accepted a smaller income: "For I felt," he says, "that to teach was my vocation."

Thus he established himself for life, as it proved, in a small city of Holland. Quickened into still greater activity by the labors he assumed, and animated by the example of Professor Mulder, — whose laboratory became, as Donders expressed it, the cradle of physiological chemistry, — and in co-operation with his venerated teacher, Professor Schroeder, he devoted himself with ardor to explorations in every part of anatomy and physiology, verifying each observation with his own eyes, and accepting nothing as proved which his own experience had not confirmed; but showing marvellous lucidity in directing researches, in forming conclusions, and in appreciating the values of results gained and the means of utilizing them. "There is no domain in the vast science of Physiology," says Landolt, "in which Donders did not leave traces of his labors. The vitality of tissues, the circulation of the blood, digestion, secretions, movements, language, the organs of sense, the secrets of the nervous system, have all in turn been investigated by this indefatigable explorer." He founded, with Ellermann and Jansen, the "Nederlandsch Lancet," that they might have an organ for the announcement of new discoveries; and he largely augmented his own labors by frequent contributions to its pages. Rousing emulation in others, he disarmed jealousy by his candid and cordial recognition of their meritorious work. Hoarding none of his own acquisitions, he added to the joys of discovery the pleasures of disclosure. As a teacher, he was radiant; he seemed superb in the lucidity, conciseness, elegance, and adaptiveness of his style of explanations, — which he often made, in several vernaculars, where he saw that he was not understood by an intelligent disciple. Donders himself says: "To teach is as great a joy as to learn. Acquired knowledge is as a hidden treasure, which slumbers useless until it is disclosed in teaching." His instruction was most suggestive, for himself as well as for his hearers, — opening as it were new horizons of thought. Nuel says of his manner of teaching, "Few have equalled, none surpassed him." And Moleschott, in his address of greeting on his seventieth birthday, says of him, "Donders has remained at Utrecht, but all the world has come to him."

We find him, at the age of twenty-four, giving, as Professor, eighteen lectures weekly for forty-six weeks of the year, on anatomy, histology, and physiology, and yet finding time for a vast amount of original investigations. In his modest address on the occasion of his jubilee, last year, he thus expresses his appreciation of the favorable circumstances by which he had been surrounded: "No other period has been comparable with this for great discoveries in so many fields of biological science. Von Baer had discovered the ovule of the mammifers; Bischoff had demonstrated that the embryo is built up exclusively by means of segmentation of cells; Schwann found in the cell the origin of all the fundamental forms of life; Henle had created, in his "Anatomie Generale," an organon of histology. At the same epoch appeared the Physiology of Jean Muller. It was in such a world I had the good fortune to have place; every circumstance seemed to be adapted to render my life and my work prolific."

In 1847 Donders became Professor Extraordinarius at the University of Utrecht, giving courses on Legal Medicine, Hygiene, Anthropology, and Ophthalmology. "After a time," he says, "my teaching of Ophthalmology gave a new direction to my life." Two distinguished men from Edinburgh were one day among his auditors, and urged him to visit the great eye hospitals of England at the time of the International Exhibition in 1851. At London he saw Bowman, equally renowned as physiologist and ophthalmologist, and also Von Jaeger of Vienna and Von Graefe of Berlin. These friends became to him "the most precious treasure of my whole career." He could announce to them the recent discovery, by his compatriot Cramer of Haarlem, of the *modus operandi* by which was effected the accommodation in the human eye, hitherto unexplained; and he learned from them of the invention of the Ophthalmoscope by Helmholtz; by means of which all the secrets of the before unexplored interior of the eye could be revealed to the wondering observer. Before returning to Holland he went to Paris in company with Von Graefe; there visiting the large Cliniques for diseases of the eye, and comparing their methods of diagnosis and practice with those seen at London. Thenceforth, without abandoning general physiology, Donders worked especially in physiological optics as applied to eye affections, in so doing largely enhancing his already great renown. Impatient to await the arrival of an ophthalmoscope which Helmholtz was to send to him, he constructed one for himself; not of superimposed glass plates, as contrived by Helmholtz, but of a silvered mirror with a central perforation, as now generally used; — and was enthusiastic in his instant perception of the value of its disclosures.

In 1864 appeared Donders's monumental work on the Refraction and Accommodation of the Eye, published by the Sydenham Society at London, and soon translated into many other languages. It came to the world of Ophthalmology as a revelation, — a complete and finished creation, involving infinite labor and research, — from which nothing could be retrenched without loss, and to which nothing could be added without superfluity. It created scientific Ophthalmology. His discovery of Hypermetropia, his explanation of Astigmatism, his indication of the relations between different forms of Strabismus and the hypermetropic or myopic conditions of refraction of the eye, were and must remain masterpieces of absolute demonstration.

It would be almost impossible to give even a catalogue of Donders's published works. His friend Nuel, in the "Annales d'Oculistique," cites two hundred and eight of these, and adds, "This list is by no means complete." Already, in 1846, he had translated into Dutch a German work on Ophthalmology by Ruete, which seems unquestionably to have inclined his spirit of investigation towards the eye. He says, "Thanks to the progress of the histology and physiology of the eye, its diseases are those which best admit of a physiological explanation." To elucidate some questions which had suggested themselves in this translation, Donders published within about a year, in the Nederlandsch Lancet, three notable papers on Physiological Optics, — among these a monograph on "The Relations between the Convergence and the State of Accommodation of the Eyes."

After his return from England, in 1851, Donders obtained endowments for the Netherlands Hospital for Diseases of the Eyes, which, with the co-operation of Snellen, he established and conducted at Utrecht; — thus entering a field where the large opportunities for direct and skilled personal service towards his suffering fellow men afforded a new satisfaction to his sympathetic nature. The means thus offered for continuing scientific observation were also most advantageous, and afforded ample fruition in the hands of such a man, — who loved accurate research, not only for its own sake, but for the delight of imparting and applying the knowledge thus gained for the relief of humanity.

So great a man cannot be wholly unconscious of his worth; but Donders's modesty was sometimes almost diffidence. We rejoice that in his later years he was allowed the gratification of knowing that he had been eminently useful, not only by his own labors, which had advanced Ophthalmology a century, but largely also by rendering applicable the results of the labors of others. The invention of Von Helmholtz, which indeed opened a new world to Ophthalmology, might have rested in the laboratory of the renowned physicist who devised it, but perhaps little suspected its practical value, as a mere bit of apparatus for experiment, because he lacked opportunities for its clinical use. Moreover, as an apostle of Ophthalmology, Donders became the exemplar and teacher of disciples from near and far countries.

When, in 1862, upon the decease of Schroeder, the Professorship of Physiology at the University was tendered to Donders, he once more obtained subscriptions of large sums for the building and equipment of a new physiological laboratory, so supplied with all modern means of research that it should be a model institution. But his enormous labors in so many departments made it imperative that he should divide his responsibilities with worthy assistants, — Snellen assuming the management of the Ophthalmic Hospital, and Englemann the charge of the laboratory and of the courses in Microscopic Anatomy and Physiological Chemistry, — Donders reserving to himself the instruction in General Physiology and Physiological Optics, and the time for original investigations. At the Festsitzung der Ophthalmologischen Gesellschaft, in 1886, in the great hall of the University of Heidelberg, for the presentation to Von Helmholtz of the Graefe Medal, which, according to the statutes of its founder, should be given once in ten years to him of any nationality who had done most for the promotion of Ophthalmology, Donders, as the most distinguished member of the society, was selected as the orator. After a feeling eulogy of the founder, Von Graefe, he spoke of Von Helmholtz, who, as the inventor of the Ophthalmoscope, had marked the dawn of a new era in our knowledge of diseases of the eye; and of the gratitude due to him for having thus endowed the profession and humanity, taking away the reproach of our former utter ignorance of the pathology of the deep-seated parts of the eye, and well deserving the high award then for the first time made.

In May, 1888, Donders attained his seventieth birthday; at which time, according to the laws of the University of Utrecht, its Professors retire from office. This event was made the occasion of a festal homage, rendered by the King of Holland, the most distinguished of his fellow countrymen, his fellow citizens, his coadjutors, and by representatives of his disciples and of Ophthalmology from every part of the world. It was an apotheosis. There he gave a most simple and unostentatious narration of his life and work, with grateful acknowledgment of the friendships by which he had been encouraged, and of the circumstances by which he had been favored.

Once again, in August, 1888, he assumed the place of honor at the Heidelberg annual convocation of Ophthalmologists. Now, alas! we shall see him no more. Since March the 24th, Ophthalmology mourns its chief, — the world of science one of its brightest ornaments.

Since the last Report, the Academy has received an accession of twenty-four members, — fifteen Resident Fellows, two Associate Fellows, and seven Foreign Honorary Members. One Resident Fellow has resigned. The list of the Academy, corrected to November 30, 1889, includes 190 Resident Fellows, 89 Associate Fellows, and 71 Foreign Honorary Members.

To this volume are added the Statutes and Standing Votes of the Academy, which have been out of print for several years.

LIST

OF THE FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to November 30, 1889.)

RESIDENT FELLOWS. — 190.

(Number limited to two hundred.)

Class I. — *Mathematical and Physical Sciences.* — 77.

Section I. — 7.

Mathematics.

Gustavus Hay,	Boston.
Benjamin O. Peirce,	Cambridge.
James M. Peirce,	Cambridge.
John D. Runkle,	Brookline.
T. H. Safford,	Williamstown.
Edwin P. Seaver,	Newton.
William E. Story,	Worcester.

Section II. — 11.

Practical Astronomy and Geodesy.

Seth C. Chandler,	Cambridge.
Alvan G. Clark,	Cambridgeport.
George B. Clark,	Cambridgeport.
J. Rayner Edmands,	Cambridge.
Henry Mitchell,	Boston.
Edward C. Pickering,	Cambridge.
John Ritchie, Jr.,	Boston.
William A. Rogers,	Waterville, Me.
Edwin F. Sawyer,	Brighton.
Arthur Searle,	Cambridge.
O. C. Wendell,	Cambridge.

Section III. — 43.

Physics and Chemistry.

A. Graham Bell,	Washington.
Clarence J. Blake,	Boston.
Francis Blake,	Weston.
John H. Blake,	Boston.
Josiah P. Cooke,	Cambridge.
James M. Crafts,	Boston.
Charles R. Cross,	Boston.
William P. Dexter,	Roxbury.
Amos E. Dolbear,	Somerville.
Thos. M. Drown,	Boston.
Charles W. Eliot,	Cambridge.
Moses G. Farmer,	Eliot, Me.
Thomas Gaffield,	Boston.
Wolcott Gibbs,	Newport, R. I.
Frank A. Gooch,	New Haven.
Edwin H. Hall,	Cambridge.
Henry B. Hill,	Boston.
N. D. C. Hodges,	New York.
Silas W. Holman,	Boston.
William L. Hooper,	Somerville.
Eben N. Horsford,	Cambridge.
T. Sterry Hunt,	New York.
Charles L. Jackson,	Cambridge.
William W. Jacques,	Newton.
Alonzo S. Kimball,	Worcester.
Leonard P. Kinnicutt,	Worcester.
Joseph Lovering,	Cambridge.
Charles F. Mabery,	Cleveland.
Arthur Michael,	Worcester.
A. A. Michelson,	Worcester.
Lewis M. Norton,	Newton.
William H. Pickering,	Cambridge.
Robert H. Richards,	Boston.
Edward S. Ritchie,	Brookline.
A. Lawrence Rotch,	Boston.
Stephen P. Sharples,	Cambridge.
Francis H. Storer,	Boston.
Elihu Thomson,	Lynn.
John Trowbridge,	Cambridge.
Cyrus M. Warren,	Brookline.
Harold Whiting,	Cambridge.
Charles H. Wing,	Boston.
Edward S. Wood,	Cambridge.

SECTION IV. — 16.

Technology and Engineering.

John M. Batchelder,	Cambridge.
Chas. O. Boutelle,	Washington.
Winfield S. Chaplin,	Cambridge.
Eliot C. Clarke,	Boston.
James B. Francis,	Lowell.
Gaetano Lanza,	Boston.
E. D. Leavitt, Jr.,	Cambridgeport.
William R. Lee,	Roxbury.
Hiram F. Mills,	Lawrence.
Cecil H. Peabody,	Boston.
Alfred P. Rockwell,	Boston.
Peter Schwamb,	Boston.
Charles S. Storrow,	Boston.
George F. Swain,	Boston.
William Watson,	Boston.
Morrill Wyman,	Cambridge.

CLASS II. — *Natural and Physiological Sciences.* — 58.

SECTION I. — 8.

Geology, Mineralogy, and Physics of the Globe.

Thomas T. Bouvé,	Boston.
Algernon Coolidge,	Boston.
William O. Crosby,	Boston.
William M. Davis,	Cambridge.
O. W. Huntington,	Cambridge.
Jules Marcou,	Cambridge.
William H. Niles,	Cambridge.
Nathaniel S. Shaler,	Cambridge.

SECTION II. — 7.

Botany.

William G. Farlow,	Cambridge.
George L. Goodale,	Cambridge.
H. H. Hunnewell,	Wellesley.
Charles S. Sargent,	Brookline.
Charles J. Sprague,	Boston.
Sereno Watson,	Cambridge.
Henry Willey,	New Bedford.

SECTION III. — 20.

Zoölogy and Physiology.

Alex. E. R. Agassiz,	Cambridge.
Robert Amory,	Boston.
James M. Barnard,	Milton.
Henry P. Bowditch,	Boston.
Edward Burgess,	Boston.
Harold C. Ernst,	Boston.
J. Walter Fewkes.	Boston.
Hermann A. Hagen,	Cambridge.
Samuel Henshaw,	Cambridge.
Alpheus Hyatt,	Cambridge.
Theodore Lyman,	Brookline.
Edward L. Mark,	Cambridge.
Charles S. Minot,	Boston.
Edward S. Morse,	Salem.
James J. Putnam.	Boston.
Samuel H. Scudder,	Cambridge.
William T. Sedgwick.	Boston.
D. Humphreys Storer.	Boston.
Henry Wheatland,	Salem.
James C. White,	Boston.

SECTION IV. — 23.

Medicine and Surgery.

Samuel L. Abbot,	Boston.
Henry J. Bigelow,	Boston.
Henry I. Bowditch,	Boston.
Edward H. Bradford,	Boston.
Arthur T. Cabot,	Boston.
David W. Cheever.	Boston.
Benjamin E. Cotting.	Roxbury.
Frank W. Draper,	Boston.
Thomas Dwight,	Boston.
Reginald H. Fitz,	Boston.
Charles F. Folsom,	Boston.
Richard M. Hodges,	Boston.
Oliver W. Holmes,	Boston.
John Homans,	Boston.

Alfred Hosmer,	Watertown.
Frederick I. Knight,	Boston.
George H. Lyman,	Boston.
Francis Minot,	Boston.
Wm. L. Richardson,	Boston.
George C. Shattuck,	Boston.
Henry P. Walcott,	Cambridge.
John C. Warren,	Boston.
Henry W. Williams,	Boston.

CLASS III. — *Moral and Political Sciences.* — 55.

SECTION I. — 9.

Philosophy and Jurisprudence.

James B. Ames,	Cambridge.
Phillips Brooks,	Boston.
Charles C. Everett,	Cambridge.
Horace Gray,	Boston.
John C. Gray,	Boston.
Nathaniel Holmes,	Cambridge.
John Lowell,	Newton.
Henry W. Paine,	Cambridge.
James B. Thayer,	Cambridge.

SECTION II. — 19.

Philology and Archæology.

William S. Appleton,	Boston.
William P. Atkinson,	Boston.
Lucien Carr,	Boston.
Franklin Carter,	Williamstown.
Joseph T. Clarke,	Boston.
William C. Collar,	Boston.
Henry G. Denny,	Boston.
Epes S. Dixwell,	Cambridge.
William Everett,	Quincy.
William W. Goodwin,	Cambridge.
Henry W. Haynes,	Boston.
Bennett H. Nash,	Boston.
Frederick W. Putnam,	Cambridge.
F. B. Stephenson,	Boston.
Joseph H. Thayer,	Cambridge.
Crawford H. Toy,	Cambridge.
John W. White,	Cambridge.
Justin Winsor,	Cambridge.
Edward J. Young,	Waltham.

SECTION III. — 17.

Political Economy and History.

Chas. F. Adams,	Quincy.
Edward Atkinson,	Boston.
John Cummings,	Woburn.
Charles F. Dunbar,	Cambridge.
Samuel Eliot,	Boston.
George E. Ellis,	Boston.
Henry C. Lodge,	Boston.
Augustus Lowell,	Boston.
Edward J. Lowell,	Boston.
Francis Parkman,	Boston.
Andrew P. Peabody,	Cambridge.
John C. Ropes,	Boston.
Denman W. Ross,	Cambridge.
F. W. Taussig,	Cambridge.
Henry W. Torrey,	Cambridge.
Francis A. Walker,	Boston.
Robert C. Winthrop,	Boston.

SECTION IV. — 10.

Literature and the Fine Arts.

George S. Boutwell,	Groton.
Martin Brimmer,	Boston.
J. Elliot Cabot,	Brookline.
Francis J. Child,	Cambridge.
Charles G. Loring,	Boston.
James Russell Lowell,	Cambridge.
Charles Eliot Norton,	Cambridge.
Horace E. Scudder,	Cambridge.
Barrett Wendell,	Boston.
John G. Whittier,	Amesbury.

ASSOCIATE FELLOWS. — 89.

(Number limited to one hundred.)

Class I. — *Mathematical and Physical Sciences.* — 34.

Section I. — 6.

Mathematics.

William Ferrel,	Kansas City, Mo.
Thomas Hill,	Portland, Me.
Simon Newcomb,	Washington.
H. A. Newton,	New Haven.
James E. Oliver,	Ithaca, N.Y.
J. N. Stockwell,	Cleveland.

Section II. — 12.

Practical Astronomy and Geodesy.

W. H. C. Bartlett,	Yonkers, N.Y.
J. H. C. Coffin,	Washington.
Geo. Davidson,	San Francisco.
Wm. H. Emory,	Washington.
Asaph Hall,	Washington.
J. E. Hilgard,	Washington.
George W. Hill,	Washington.
E. S. Holden,	San José, Cal.
Sam. P. Langley,	Washington.
C. H. F. Peters,	Clinton, N.Y.
George M. Searle,	New York.
Chas. A. Young,	Princeton, N.J.

Section III. — 10.

Physics and Chemistry.

J. Willard Gibbs,	New Haven.
S. W. Johnson,	New Haven.
M. C. Lea,	Philadelphia.
John Le Conte,	Berkeley, Cal.
J. W. Mallet,	Charlottesville, Va.
A. M. Mayer,	Hoboken, N. J.
Ira Remsen,	Baltimore.
Ogden N. Rood,	New York.
H. A. Rowland,	Baltimore.
L. M. Rutherfurd,	New York.

Section IV. — 6.

Technology and Engineering.

Henry L. Abbot,	New York.
Geo. W. Cullum,	New York.
Geo. S. Morison,	New York.
John Newton,	New York.
William Sellers,	Philadelphia.
W. P. Trowbridge,	New Haven.

Class II. — *Natural and Physiological Sciences.* — 30.

Section I. — 15.

Geology, Mineralogy, and Physics of the Globe.

Cleveland Abbe,	Washington.
George J. Brush,	New Haven.
James D. Dana,	New Haven.
Sir J. W. Dawson,	Montreal.
J. C. Fremont,	New York.
F. A. Genth,	Philadelphia.
James Hall,	Albany, N.Y.
F. S. Holmes,	Charleston, S.C.
Clarence King,	New York.
Joseph Le Conte,	Berkeley, Cal.
J. Peter Lesley,	Philadelphia.
J. S. Newberry,	New York.
J. W. Powell,	Washington.
R. Pumpelly,	Newport, R.I.
Geo. C. Swallow,	Columbia, Mo.

SECTION II. — 2.

Botany.

A. W. Chapman,	Apalachicola, Fla.
D. C. Eaton,	New Haven.

SECTION III. — 7.

Zoölogy and Physiology.

Joel A. Allen,	New York.
G. B. Goode,	Washington.
Joseph Leidy,	Philadelphia.
O. C. Marsh,	New Haven.
S. Weir Mitchell,	Philadelphia.
A. S. Packard,	Providence.
A. E. Verrill,	New Haven.

SECTION IV. — 6.

Medicine and Surgery.

Fordyce Barker,	New York.
John S. Billings,	Washington.
Jacob M. Da Costa,	Philadelphia.
W. A. Hammond,	New York.
Alfred Stillé,	Philadelphia.
H. C. Wood,	Philadelphia.

CLASS III. — *Moral and Political Sciences.* — 25.

SECTION I. — 7.

Philosophy and Jurisprudence.

D. R. Goodwin,	Philadelphia.
A. G. Haygood,	Oxford, Ga.
James McCosh,	Princeton, N.J.
Charles S. Peirce,	New York.
Noah Porter,	New Haven.
E. G. Robinson,	Providence.
Jeremiah Smith,	Dover, N.H.

SECTION II. — 6.

Philology and Archæology.

A. N. Arnold,	Pawtuxet, R.I.
D. C. Gilman,	Baltimore.
A. C. Kendrick,	Rochester, N.Y.
E. E. Salisbury,	New Haven.
A. D. White,	Ithaca, N.Y.
W. D. Whitney,	New Haven.

SECTION III. — 6.

Political Economy and History.

Henry Adams,	Washington.
George Bancroft,	Washington.
M. F. Force,	Cincinnati.
Henry C. Lea,	Philadelphia.
W. G. Sumner,	New Haven.
J. H. Trumbull,	Hartford.

SECTION IV. — 6.

Literature and the Fine Arts.

James B. Angell,	Ann Arbor, Mich
L. P. di Cesnola,	New York.
F. E. Church,	New York.
R. S. Greenough,	Florence.
William W. Story,	Rome.
Wm. R. Ware,	New York.

FOREIGN HONORARY MEMBERS.—71.

(Elected as vacancies occur.)

Class I.—*Mathematical and Physical Sciences.*—24.

Section I.—6.

Mathematics.

John C. Adams,	Cambridge.
Sir George B. Airy,	London.
Francesco Brioschi,	Milan.
Arthur Cayley,	Cambridge.
Charles Hermite,	Paris.
J. J. Sylvester,	Oxford.

Section II.—5.

Practical Astronomy and Geodesy.

Arthur Auwers,	Berlin.
J. H. W. Döllen,	Pulkowa.
H. A. E. A. Faye,	Paris.
Eduard Schönfeld,	Bonn.
Otto Struve,	Pulkowa.

Section III.—10.

Physics and Chemistry.

Adolf Baeyer,	Munich.
Marcellin Berthelot,	Paris.
R. Bunsen,	Heidelberg.
H. L. F. Helmholtz,	Berlin.
A. W. Hofmann,	Berlin.
Mendeleeff,	St. Petersburg.
Lord Rayleigh,	Witham.
G. G. Stokes,	Cambridge.
Julius Thomsen,	Copenhagen.
W. E. Weber,	Göttingen.

Section IV.—3.

Technology and Engineering.

Marquis de Caligny,	Versailles.
F. M. de Lesseps,	Paris.
Sir Wm. Thomson,	Glasgow.

Class II.—*Natural and Physiological Sciences.*—26.

Section I.—6.

Geology, Mineralogy, and Physics of the Globe.

H. Ernst Beyrich,	Berlin.
Alfred Des Cloizeaux,	Paris.
A. E. Nordenskiöld,	Stockholm.
C. F. Rammelsberg,	Berlin.
Sir A. C. Ramsay,	Beaumaris.
Heinrich Wild,	St. Petersburg.

Section II.—7.

Botany.

J. G. Agardh,	Lund.
Alphonse de Candolle,	Geneva.
Sir Joseph D. Hooker,	London.
C. J. Maximowicz,	St. Petersburg.
Carl Nägeli,	Munich.
Julius Sachs,	Würzburg.
Marquis de Saporta,	Aix.

Section III. — 10.

Zoölogy and Physiology.

P. J. Van Beneden,	Louvain.
Du Bois-Reymond,	Berlin.
Thomas H. Huxley,	London.
Albrecht Kölliker,	Würzburg.
Lacaze-Duthiers,	Paris.
Rudolph Leuckart,	Leipsic.
C. F. W. Ludwig,	Leipsic.
Sir Richard Owen,	London.
Louis Pasteur,	Paris.
J. J. S. Steenstrup,	Copenhagen.

Section IV. — 3.

Medicine and Surgery.

C. E. Brown-Séquard,	Paris.
Sir James Paget,	London.
Rudolph Virchow,	Berlin.

Class III. — *Moral and Political Sciences.* — 21.

Section I. — 3.

Philosophy and Jurisprudence.

James Martineau,	London.
Henry Sidgwick,	Cambridge.
Sir James F. Stephen,	London.

Section II. — 7.

Philology and Archæology.

John Evans,	Hemel Hempstead.
Pascual de Gayangos,	Madrid.
Benjamin Jowett,	Oxford.
J. W. A. Kirchhoff,	Berlin.
G. C. C. Maspero,	Paris ?
Max Müller,	Oxford.
Sir H. C. Rawlinson,	London.

Section III. — 7.

Political Economy and History.

Duc de Broglie,	Paris.
Ernst Curtius,	Berlin.
W. Ewart Gladstone,	London.
Charles Merivale,	Ely.
Theodor Mommsen,	Berlin.
Jules Simon,	Paris.
William Stubbs,	Chester.

Section IV. — 4.

Literature and the Fine Arts.

Jean Léon Gérôme,	Paris.
John Ruskin,	Coniston.
Leslie Stephen,	London.
Lord Tennyson,	Isle of Wight.

STATUTES AND STANDING VOTES

OF THE

AMERICAN ACADEMY OF ARTS AND SCIENCES.

(*Adopted May* 30, 1854: *amended September* 8, 1857, *November* 12, 1862, *May* 24, 1864, *November* 9, 1870, *May* 27, 1873, *January* 26, 1876, *and June* 16, 1886.)

CHAPTER I.

Of Fellows and Foreign Honorary Members.

1. The Academy consists of *Fellows* and *Foreign Honorary Members*. They are arranged in three Classes, according to the Arts and Sciences in which they are severally proficient, viz.: Class I. The Mathematical and Physical Sciences; — Class II. The Natural and Physiological Sciences; — Class III. The Moral and Political Sciences. Each Class is divided into four Sections, viz.: Class I., Section 1. Mathematics; — Section 2. Practical Astronomy and Geodesy; — Section 3. Physics and Chemistry; — Section 4. Technology and Engineering. Class II., Section 1. Geology, Mineralogy, and Physics of the Globe; — Section 2. Botany; — Section 3. Zoölogy and Physiology; — Section 4. Medicine and Surgery. Class III., Section 1. Philosophy and Jurisprudence; — Section 2. Philology and Archæology; — Section 3. Political Economy and History; — Section 4. Literature and the Fine Arts.

2. Fellows resident in the State of Massachusetts can alone vote at the meetings of the Academy.* They shall each pay to the Treasurer the sum of ten dollars on admission, and an annual assessment of ten dollars, with such additional sum, not exceeding five dollars, as the Academy shall, by a standing vote, from time to time determine.

3. Fellows residing out of the State of Massachusetts shall be known and distinguished as Associate Fellows. They shall not be liable to the payment of any fees or annual dues, but on removing

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* The number of Resident Fellows is limited by the Charter to 200.

within the State shall be admitted to the privileges,* and be subject to the obligations, of Resident Fellows. The number of Associate Fellows shall not exceed *one hundred*, of whom there shall not be more than *forty* in either of the three Classes of the Academy.

4. The number of Foreign Honorary Members shall not exceed *seventy-five;* and they shall be chosen from among persons most eminent in foreign countries for their discoveries and attainments in either of the three departments of knowledge above enumerated. And there shall not be more than *thirty* Foreign Members in either of these departments.

CHAPTER II.

OF OFFICERS.

1. There shall be a President, a Vice-President, a Corresponding Secretary, a Recording Secretary, a Treasurer, and a Librarian, which officers shall be annually elected, by written votes, at the Annual Meeting, on the day next preceding the last Wednesday in May.

2. At the same time and in the same manner, nine Councillors shall be elected, three from each Class of the Academy, but the same Fellows shall not be eligible on more than three successive years. These nine Councillors, with the President, Vice-President, the two Secretaries, the Treasurer, and the Librarian, shall constitute the Council. It shall be the duty of this Council to exercise a discreet supervision over all nominations and elections. With the consent of the Fellow interested, they shall have power to make transfers between the several Sections of the same Class, reporting their action to the Academy.

3. If any office shall become vacant during the year, the vacancy shall be filled by a new election, and at the next stated meeting.

CHAPTER III.

OF THE PRESIDENT.

1. It shall be the duty of the President, and, in his absence, of the Vice-President, or next officer in order as above enumerated, to preside at the meetings of the Academy; to summon extraordinary

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* Associate Fellows may attend, but cannot vote, at meetings of the Academy. See Chapter I., 2.

meetings, upon any urgent occasion; and to execute or see to the execution of the Statutes of the Academy.

2. The President, or, in his absence, the next officer as above enumerated, is empowered to draw upon the Treasurer for such sums of money as the Academy shall direct. Bills presented on account of the Library, or the Publications of the Academy, must be previously approved by the respective committees on these departments.

3. The President, or, in his absence, the next officer as above enumerated, shall nominate members to serve on the different committees of the Academy which are not chosen by ballot.

4. Any deed or writing to which the common seal is to be affixed, shall be signed and sealed by the President, when thereto authorized by the Academy.

CHAPTER IV.

OF STANDING COMMITTEES.

1. At the Annual Meeting there shall be chosen the following Standing Committees, to serve for the year ensuing, viz.: —

2. The Committee of Finance, to consist of the President, Treasurer, and one Fellow chosen by ballot, who shall have charge of the investment and management of the funds and trusts of the Academy. The general appropriations for the expenditures of the Academy shall be moved by this Committee at the Annual Meeting, and all special appropriations from the general and publication funds shall be referred to or proposed by this Committee.

3. The Rumford Committee, of seven Fellows, to be chosen by ballot, who shall consider and report on all applications and claims for the Rumford Premium, also on all appropriations from the income of the Rumford Fund, and generally see to the due and proper execution of this trust.

4. The Committee of Publication, of three Fellows, to whom all memoirs submitted to the Academy shall be referred, and to whom the printing of memoirs accepted for publication shall be intrusted.

5. The Committee on the Library, of three Fellows, who shall examine the Library, and make an annual report on its condition and management.

6. An Auditing Committee, of two Fellows, for auditing the accounts of the Treasurer.

CHAPTER V.

OF THE SECRETARIES.

1. The Corresponding Secretary shall conduct the correspondence of the Academy, recording or making an entry of all letters written in its name, and preserving on file all letters which are received; and at each meeting he shall present the letters which have been addressed to the Academy since the last meeting. With the advice and consent of the President, he may effect exchanges with other scientific associations, and also distribute copies of the publications of the Academy among the Associate Fellows and Foreign Honorary Members, as shall be deemed expedient; making a report of his proceedings at the Annual Meeting. Under the direction of the Council for Nomination, he shall keep a list of the Fellows, Associate Fellows, and Foreign Honorary Members, arranged in their Classes and in Sections in respect to the special sciences in which they are severally proficient: and he shall act as secretary to the Council.

2. The Recording Secretary shall have charge of the Charter and Statute-book, journals, and all literary papers belonging to the Academy. He shall record the proceedings of the Academy at its meetings; and after each meeting is duly opened, he shall read the record of the preceding meeting. He shall notify the meetings of the Academy, and apprise committees of their appointment. He shall post up in the Hall a list of the persons nominated for election into the Academy; and when any individual is chosen, he shall insert in the record the names of the Fellows by whom he was nominated.

3. The two Secretaries, with the Chairman of the Committee of Publication, shall have authority to publish such of the proceedings of the Academy as may seem to them calculated to promote the interests of science.

CHAPTER VI.

OF THE TREASURER.

1. The Treasurer shall give such security for the trust reposed in him as the Academy shall require.

2. He shall receive officially all moneys due or payable, and all bequests or donations made to the Academy, and by order of the

President or presiding officer shall pay such sums as the Academy may direct. He shall keep an account of all receipts and expenditures; shall submit his accounts to the Auditing Committee; and shall report the same at the expiration of his term of office.

3. The Treasurer shall keep a separate account of the income and appropriation of the Rumford Fund, and report the same annually.

4. All moneys which there shall not be present occasion to expend shall be invested by the Treasurer, under the direction of the Finance Committee, on such securities as the Academy shall direct.

CHAPTER VII.

OF THE LIBRARIAN AND LIBRARY.

1. It shall be the duty of the Librarian to take charge of the books, to keep a correct catalogue of the same, and to provide for the delivery of books from the Library. He shall also have the custody of the publications of the Academy.

2. The Librarian, in conjunction with the Committee on the Library, shall have authority to expend, as they may deem expedient. such sums as may be appropriated, either from the Rumford or the General Fund of the Academy, for the purchase of books, and for defraying other necessary expenses connected with the Library. They shall have authority to propose rules and regulations concerning the circulation, return, and safe-keeping of books; and to appoint such agents for these purposes as they may think necessary.

3. To all books in the Library procured from the income of the Rumford Fund, the Librarian shall cause a stamp or label to be affixed, expressing the fact that they were so procured.

4. Every person who takes a book from the Library shall give a receipt for the same to the Librarian or his assistant.

5. Every book shall be returned in good order, regard being had to the necessary wear of the book with good usage. And if any book shall be lost or injured, the person to whom it stands charged shall replace it by a new volume or set, if it belongs to a set, or pay the current price of the volume or set to the Librarian; and thereupon the remainder of the set, if the volume belonged to a set, shall be delivered to the person so paying for the same.

6. All books shall be returned to the Library for examination, at least one week before the Annual Meeting.

CHAPTER VIII.

OF MEETINGS.

1. There shall be annually four stated meetings of the Academy; namely, on the day next preceding the last Wednesday in May (the Annual Meeting), on the second Wednesday in October, on the second Wednesday in January, and on the second Wednesday in March; to be held in the Hall of the Academy, in Boston. At these meetings only, or at meetings adjourned from these and regularly notified, shall appropriations of money be made, or alterations of the statutes or standing votes of the Academy be effected.

2. Fifteen Fellows shall constitute a quorum for the transaction of business at a stated meeting. Seven Fellows shall be sufficient to constitute a meeting for scientific communications and discussions.

3. The Recording Secretary shall notify the meetings of the Academy to each Fellow residing in Boston and the vicinity; and he may cause the meetings to be advertised, whenever he deems such further notice to be needful.

CHAPTER IX.

OF THE ELECTION OF FELLOWS AND HONORARY MEMBERS.

1. Elections shall be made by ballot, and only at stated meetings.

2. Candidates for election as Resident Fellows must be proposed by two or more Resident Fellows, in a recommendation signed by them, specifying the Section to which the nomination is made, which recommendation shall be transmitted to the Corresponding Secretary, and by him referred to the Council for Nomination. No person recommended shall be reported by the Council as a candidate for election, unless he shall have received a written approval, signed at a meeting of the Council by at least eight of its members. All nominations thus approved shall be read to the Academy at a stated meeting, and shall then stand on the nomination list during the interval between two stated meetings, and until the balloting. No person shall be elected a Resident Fellow, unless he shall have been resident in this Commonwealth one year next preceding his election; and any Resident Fellow who shall remove his domicile from the Commonwealth, shall be deemed to have abandoned his Fellowship. If any

person elected a Resident Fellow shall neglect for one year to pay his admission fee, his election shall be void; and, if any Resident Fellow shall neglect to pay his annual assessments for two years, provided that his attention shall have been called to this article, he shall be deemed to have abandoned his Fellowship; but it shall be in the power of the Treasurer, with the consent of the Council, to dispense (*sub silentio*) with the payment both of the admission fee and of the assessments, whenever in any special instance he shall think it advisable so to do.

3. The nomination of Associate Fellows shall take place in the manner prescribed in reference to Resident Fellows; and after such nomination shall have been publicly read at a stated meeting previous to that when the balloting takes place, it shall be referred to a Council for Nomination; and a written approval, authorized and signed at a meeting of said Council by at least seven of its members, shall be requisite to entitle the candidate to be balloted for. The Council may in like manner originate nominations of Associate Fellows, which must be read at a stated meeting previous to the election, and be exposed on the nomination list during the interval.

4. Foreign Honorary Members shall be chosen only after a nomination made at a meeting of the Council, signed at the time by at least seven of its members, and read at a stated meeting previous to that on which the balloting takes place.

5. Three fourths of the ballots cast must be affirmative, and the number of affirmative ballots must amount to eleven to effect an election of Fellows or Foreign Honorary Members.

6. Each section of the Academy is empowered to present lists of persons deemed best qualified to fill vacancies occurring in the number of Foreign Honorary Members or Associate Fellows allotted to it; and such lists, after being read at a stated meeting, shall be referred to the Council for Nomination.

7. If, in the opinion of a majority of the entire Council, any Fellow — Resident or Associate — shall have rendered himself unworthy of a place in the Academy, the Council shall recommend to the Academy the termination of his Fellowship; and, provided that a majority of two thirds of the Fellows at a stated meeting, consisting of not less than fifty Fellows, shall adopt this recommendation, his name shall be stricken off the roll of Fellows.

CHAPTER X.

OF AMENDMENTS OF THE STATUTES.

1. All proposed alterations of the Statutes, or additions to them, shall be referred to a committee, and, on their report at a subsequent meeting, shall require for enactment a majority of two thirds of the members present, and at least eighteen affirmative votes.

2. Standing Votes may be passed, amended, or rescinded, at any stated meeting, by a majority of two thirds of the members present. They may be suspended by a unanimous vote.

CHAPTER XI.

OF LITERARY PERFORMANCES.

1. The Academy will not express its judgment on literary or scientific memoirs or performances submitted to it, or included in its publications.

STANDING VOTES.

1. Communications of which notice has been given to the Secretary shall take precedence of those not so notified.

2. Resident Fellows who have paid all fees and dues chargeable to them are entitled to receive one copy of each volume or article printed by the Academy, on application to the Librarian personally or by written order, within two years from the date of publication. And the current issues of the Proceedings shall be supplied, when ready for publication, free of charge to all the Fellows and Members of the Academy who desire to receive them.

3. The Committee of Publication shall fix from time to time the price at which the publications of the Academy may be sold. But members may be supplied at half this price with volumes which they are not entitled to receive free, and which are needed to complete their sets.

4. Two hundred extra copies of each paper accepted for publication in the Memoirs or Proceedings of the Academy shall be placed at the disposal of the author, free of charge.

5. Resident Fellows may borrow and have out from the Library six volumes at any one time, and may retain the same for three months, and no longer.

6. Upon special application, and for adequate reasons assigned, the Librarian may permit a larger number of volumes, not exceeding twelve, to be drawn from the Library for a limited period.

7. Works published in numbers, when unbound, shall not be taken from the Hall of the Academy, except by special leave of the Librarian.

8. Books, publications, or apparatus shall be procured from the income of the Rumford Fund only on the certificate of the Rumford Committee, that they, in their opinion, will best facilitate and encourage the making of discoveries and improvements which may merit the Rumford Premium.

9. The annual meeting and the other stated meetings shall be holden at half-past seven o'clock, P. M.

10. A meeting for receiving and discussing scientific communications shall be held on the second Wednesday of each month not appointed for stated meetings, excepting July, August, and September.

RUMFORD PREMIUM.

In conformity with the terms of the gift of Benjamin, Count Rumford, granting a certain fund to the American Academy of Arts and Sciences, and with a decree of the Supreme Judicial Court for carrying into effect the general charitable intent and purpose of Count Rumford, as expressed in his letter of gift, the Academy is empowered to make from the income of said fund, as it now exists, at any annual meeting, an award of a gold and silver medal, being together of the intrinsic value of three hundred dollars, as a premium to the author of any important discovery or useful improvement in light or in heat, which shall have been made and published by printing, or in any way made known to the public, in any part of the continent of America, or any of the American islands; preference being always given to such discoveries as shall, in the opinion of the Academy, tend most to promote the good of mankind; and to add to such medals, as a further premium for such discovery and improvement, if the Academy see fit so to do, a sum of money not exceeding three hundred dollars.

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