

VIII.—*Miscellaneous Observations.*

BY A. W. HOFMANN.

II.

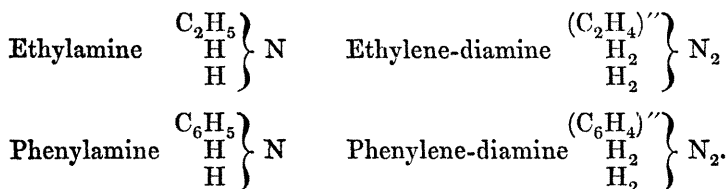
(Continued from Vol. X, p. 211.)

4. *Action of Nitrous Acid upon Nitrophenylene-diamine.*

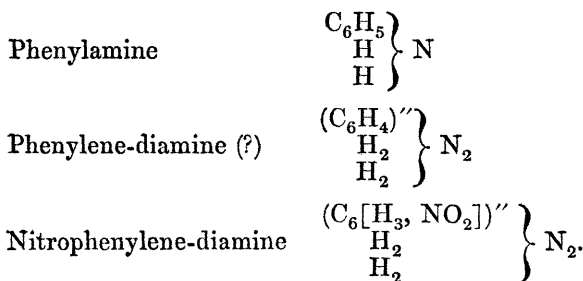
THE experiments of Gottlieb have shown that dinitrophenylamine, when boiled with sulphide of ammonium, is converted into a remarkable base crystallising in crimson needles, generally known as *Nitrazophenylamine*, and for which, in accordance with the views I entertain regarding its constitution, I now propose the name *Nitrophenylene-diamine*. I owe to the kindness of Dr. Vincent Hall a considerable quantity of this substance which is not quite easily procured. In preparing it, Dr. Hall has, in the first place, followed the succession of processes recommended by Gottlieb, viz., treatment of phenyl-citraconimide (citraconanile) with nitro-sulphuric acid, transformation of the nitro-substitute into dinitrophenylamine, and the reduction of the latter by sulphide of ammonium. In other experiments Dr. Hall has availed himself with the same advantage of phenyl-succinimide (succinanile), which, under the influence of a mixture of nitric and sulphuric acid, exhibits a deportment similar to that of the citraconyl-body. Dinitrophenyl-succinimide is readily transformed into dinitrophenylamine, which ultimately yields the crimson-coloured compound.

To the accurate description which Gottlieb has given of the preparation and the properties of this substance, I have scarcely to add a single word. The following remarks refer to an experiment made with the view of obtaining some insight into the molecular construction of the body. If, bearing in mind the numerous analogies of the radicals ethyl and phenyl, we assume that the latter by the loss of hydrogen may be converted into a diatomic molecule phenylene, C_6H_4 ,* corresponding to ethylene, the existence of a group of phenylene-bases corresponding to the ethylene-bases cannot be doubted.

* H=1, C=12, O=16, S=32, etc.



The compound known as semibenzidam or azophenylamine, which Zinin obtained by exhausting the action of sulphide of ammonium on dinitrobenzol, agrees with the last-named body in composition. Those chemists, however, who have had an opportunity of becoming acquainted with the well-defined properties of ethylene-diamine, will not easily be persuaded to consider the uncouth dinitrobenzol-product, sometimes appearing in brown flakes, sometimes as a yellow resin rapidly turning green in contact with the air, as standing to phenylamine in a relation similar to that which obtains between ethylene-diamine and ethylamine. We much more readily admit a connection of this description between phenylamine and Gottlieb's crimson-coloured base, in which the clearly pronounced character of the former is still distinctly visible, although of necessity, modified by the further substitution which has taken place within the radical.



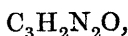
Does the latter formula really represent the molecular constitution of the crimson needles? The degree of substitution of this body might have been determined by the frequently adopted process of ethylation. But even a simpler and shorter method appeared to present itself in the beautiful mode of substituting nitrogen into the place of hydrogen, lately discovered by P. Griess. The red crystals undergo indeed with the greatest facility the transformation, which he has proved already for a great many derivatives of ammonia.

On passing a current of nitrous acid into a moderately concentrated solution of the nitrate of the base, the liquid becomes gently heated, and deposits, on cooling, a considerable quantity of brilliant white needles, the purification of which presents no difficulty; being sparingly soluble in cold, readily soluble in boiling water, the new compound requires only to be once or twice re-crystallised. Thus purified, the new substance forms long prismatic crystals frequently interlaced, white as long as they are in the solution, but assuming a slightly yellowish tint when dried, and especially when exposed to 100° ; they are readily soluble both in alcohol and in ether. The new body exhibits a distinctly acid reaction; it dissolves on application of a gentle heat in potassa and ammonia, without, however neutralizing the alkaline character of these bases; it also dissolves in the alkaline carbonates, but without expelling their carbonic acid. The new acid fuses at 211° C., and sublimes at a somewhat higher temperature, with partial decomposition. The sublimate consists of small prismatic crystals. Analysis gave the following results:—

- I. 0.3290 grm. acid dried at 100° , gave
 0.5298 „ carbonic acid, and
 0.0777 „ water.

- II. 0.2868 grm. acid gave 84 cc. moist nitrogen at 15° , and 0.7583 Bar. (corr.)

These numbers lead to the ratio:—



and, the origin of the substance being taken into consideration, to the formula:—



	Theory.		Experiment.	
			I.	II.
C ₆	72	43.90	43.92	—
H ₄	4	2.44	2.62	—
N ₄	56	34.15	—	34.32
O ₂	32	19.51	—	—
	<hr/>	<hr/>		
	164	100.00		

This formula is confirmed by the analysis of the silver- and of the potassium-compound.

Silver-salt. This salt is obtained in the form of a white amorphous precipitate on mixing the saturated ammonia-solution of the acid with nitrate of silver. *In vacuo* this salt may be dried without decomposition; at 100° it becomes slightly coloured; when gently heated on platinum foil it detonates. The silver therefore had to be estimated as chloride.

- I. 0.4215 grm. silver-salt gave
 0.4068 „ carbonic acid, and
 0.0487 „ water.
- II. 0.2984 „ silver-salt gave
 0.1574 „ chloride of silver.

The formula $C_6[H_3Ag] N_4O_2$ involves the following values :—

		Theory.	Experiment.	
			I.	II.
C_6	72	26.57	26.32	—
H_3	3	1.11	1.28	—
Ag	108	39.85	—	39.67
N_4	56	20.66	—	—
O_2	32	11.81	—	—
<hr/>		<hr/>		
	271	100.00		

Potassium-salt. Obtained in pretty well-formed, flattened prisms, by saturating a moderately concentrated boiling solution of potassa with the acid; the crystals are difficultly soluble in potassa, but exceedingly soluble in pure water and in alcohol; the recrystallization is therefore attended with very considerable loss. The aqueous solution of the salt yields a crystalline precipitate on addition of potassa. The salt, even after four or five recrystallizations from alcohol, retains a distinctly alkaline reaction. Its composition was fixed by a potassium determination.

0.2012 grm. salt dried at 100° gave
 0.0857 „ sulphate of potassium.

The formula $C_6 [H_3K] N_4O_2$ requires the following values :—

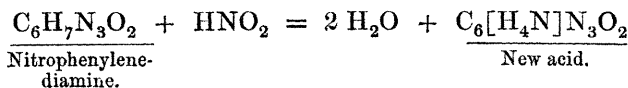
	Theory.		Experiment.
C_6	72	35·64	—
H_3	3	1·48	—
K	39	19·31	19·10
N_4	56	27·72	—
O_2	32	15·85	—
	<hr/>	<hr/>	
	202	100·00	

With regard to the other salts, I have made but few observations.

The ammonium-salt crystallizes in needles. It has, however, but little stability, losing the whole of the ammonia when repeatedly recrystallized. The solution of this salt exhibits with metallic oxides the following deportment.

Barium and calcium-salts are not precipitated. Salts of copper give a light blue, salts of nickel a light green precipitate. The solution of a ferrous salt produces a deep brown-red precipitate, probably with simultaneous decomposition of the acid; the solution of a ferric salt, a light fawn-coloured precipitate. The salts of lead, zinc, manganese, and mercury (*mercurosum* and *mercuricum*), furnish white flaky precipitates.

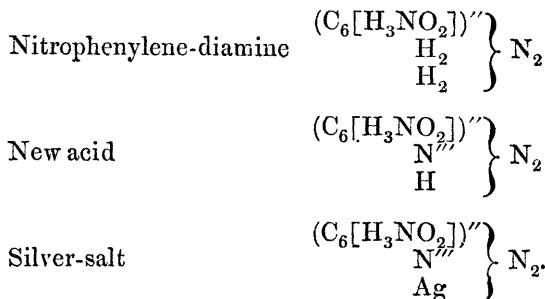
The analysis of the new compound shows that, under the influence of nitrous acid on nitrophenylene-diamine, one molecule of nitrogen is substituted into the place of three molecules of hydrogen, which are eliminated in the form of water



I do not propose a name for the new compound, which can claim but a passing interest, as throwing by its formation some light on the constitution of nitrophenylene-diamine.

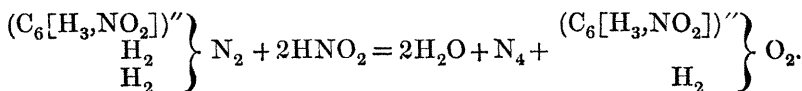
The composition of the new acid and of its salts shows that in the crimson base four hydrogen molecules are still capable of replacement; in other words, that this body still contains four extra-radical molecules of hydrogen. These experiments appear to confirm the view which in the commencement of this note,

I have taken of the constitution of the body; at all events, the mutual relation of the several compounds is satisfactorily illustrated by the formulæ—



If the admissibility of this interpretation be confirmed by further experiments, the reaction discovered by Griess furnishes a new and valuable method of recognising the degree of substitution in the derivatives of ammonia.

The new acid differs in many respects from the substances similarly produced from other nitrogenous compounds. As a class, these substances are remarkable for the facility with which they are changed under the influence of acids and more especially of bases. The new acid exhibits remarkable stability; it may be boiled either with potassa or with hydrochloric acid without undergoing the slightest change. Even a current of nitrous acid passed into either the aqueous or alcoholic solution is without the slightest effect. The latter experiment was repeatedly performed; for if the action of nitrous acid in a second phase of the process had assumed the form so frequently observed by Piria and others, it might have led to the formation of the diatomic nitrophenylene-alcohol, according to the equation



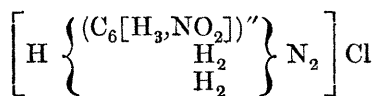
It deserves to be noticed that nitrophenylene-diamine, although derived from two molecules of ammonia, is, nevertheless, a decidedly mono-acid base. Gottlieb's analyses of the chloride, nitrate, and sulphate, left scarcely a doubt on this point. However, as some of the natural bases, quinine, for instance, are

capable of combining either with one or with two molecules of acid, I thought it of sufficient interest to confirm Gottlieb's observations by some additional experiments. The crystals deposited on cooling from a solution of nitrophenylene-diamine in concentrated hydrochloric acid were washed with the same liquid, and dried *in vacuo* over lime.

0.3975 grm. substance gave

0.3005 „ chloride of silver = 18.70 p. c. of chlorine.

The formula

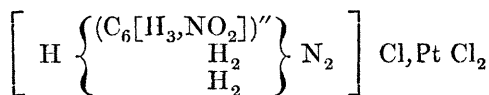


requires 18.73 p. c. of chlorine.

The dilute solution of the previous salt is not precipitated by dichloride of platinum; nor could the double salt of the two chlorides be obtained by evaporating the mixture of the two solutions, which, just as Gottlieb observed, was readily decomposed with separation of metallic platinum. I had, however, no difficulty in preparing a platinum-salt, crystallizing in splendid long brown-red prisms, by adding the platinum solution to the concentrated solution of the hydrochlorate.

0.4225 grm. of the platinum-salt dried *in vacuo*, left on ignition 0.115 grm. = 27.22 p. c. of platinum.

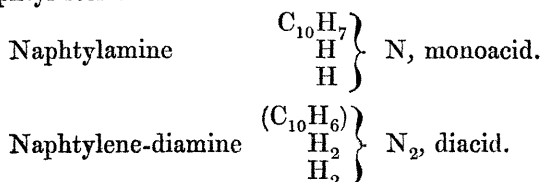
The theoretical percentage of the formula



is 27.48 p. c. of platinum.

These experiments prove that, even under the most favourable circumstances, nitrophenylene-diamine combines with only 1 eq. of acid, while the ethylene-derivatives are decidedly diacid. The diminution of saturating power in nitrophenylene-diamine at the first glance seems somewhat anomalous; but the anomaly disappears if the constitution of the body be more accurately examined. It cannot be doubted that the diminution of the saturating power is due to the substitution which has taken place within the radical

of the diamine. I pointed out some time ago,* that the basic character of phenylamine itself is considerably modified by successive changes induced in the phenyl-radical by substitution. Chlorphenylamine, though less basic than the normal compound, still forms well-defined salts with the acids; the salts of dichlorphenylamine, on the other hand, are so feeble, that under the influence of boiling water they are split into their constituents; and in trichlorphenylamine the basic character has entirely disappeared. Again, on examining the nitro-substitutes of phenylamine, we find that even nitrophenylamine is an exceedingly weak base, whilst dinitrophenylamine is perfectly indifferent. What wonder, then, that a molecular system, to which, in the normal condition, we attribute a diacid character, should, by the insertion of special radicals, be reduced to monoacidity? The normal phenylene-diamine, which remains to be discovered, will, doubtless, be found to be diacid, like the diamines derived from ethylene. Even now the group of diacid diamines is represented in the naphthyl-series.



The body which I designate by the term naphthylene-diamine is the base which Zinin obtained by the final action of sulphide of ammonium upon dinitronaphtalin. This substance, originally designated as seminaphtalidam, and subsequently described as naphtalidine, combines, according to Zinin's experiments, with two equivalents of hydrochloric acid.†

I must add a remark suggested by the perusal of an interesting paper lately published by Kolbe.‡ In this paper, Kolbe refers to an outline of the history of ammonia and its derivatives, which, in the form of an evening lecture, I gave to the members of this Society, and which was subsequently printed in this journal.§ Kolbe regards many of the ammonia-compounds from a different point of view and expresses them by molecular

* Mem. of Chem. Soc., ii, 298.

† Ann. Ch. Pharm. lxxxv, 328.

‡ Ueber den natürlichen Zusammenhang der organischen mit den unorganischen Verbindungen.—Ann. Ch. Pharm. cxiii, 293.

§ Chem. Soc. Qu. J. xi, 252.

formulae different from those which I have adopted. It is not my intention to refer in detail to the several questions which he discusses, more especially since many of the theoretical views in which we differ were brought forward by others, and were simply introduced into the sketch with the view of rendering it as complete as possible; yet I must not allow this opportunity to pass without a word or two in elucidation of a question on which we differ more in appearance than in reality.

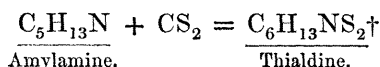
In classifying the basic ammonia-derivatives, I proposed to designate the substances formed by the coalescence of more than one molecule of ammonia, in accordance with the nomenclature adopted for the neutral derivatives, and to distinguish, as monamines, diamines, and triamines, the bases derived from one, two, or three molecules of ammonia. In a classification of this kind the circumstance could not be left unnoticed, that many of the diamines and triamines combine with one equivalent of acid only, instead of saturating, as might have been expected from their construction, two or three equivalents. I was thus naturally led to subdivide again, and to distinguish, for instance, monoacid and diacid diamines, and I added: "It is obvious that the question, whether a diamine is capable of uniting with one or two equivalents of acid, must be intimately connected with the molecular construction of the basic system. As yet the nature of this connection remains unknown."

In the paper quoted, Kolbe remarks: "There appears no reason why, among the bodies derived from two molecules of ammonia, there should be, side by side with the diatomic substances, others yielding monoatomic ammonium-compounds. I cannot, therefore, consent to regard the ureas, melaniline, and other bases containing two atoms of nitrogen, as true diamines."

It is scarcely necessary to state that I entirely agree with my friend if he views as true diamines those bases which unite with two equivalents of acid; for it is proved experimentally, that the ureas and melaniline combine with one equivalent of acid only. All depends upon the definition of the word diamine. I had designated by this name basic compounds derived from two molecules of ammonia, without reference to the degree of saturating power; and even now it appears to me somewhat arbitrary to limit this term to those substances which unite with two equivalents of acid, especially since there are diatomic bases which are capable of combining either with one or with two equivalents of acid.

5. *Action of Bisulphide of Carbon upon Amylamine.*

In a note on the alleged transformation of thialdine into leucine, communicated some time ago* to the Chemical Society, I alluded to a crystalline substance observed by Wagner, when he submitted amylamine to the action of bisulphide of carbon. Wagner had not analysed this substance, but, considering its mode of formation, he had suggested that it might possibly be thialdine :



A simple comparison of the properties of thialdine with those of the substance produced by the action of bisulphide of carbon upon amylamine, had enabled me at once to recognise the difference between the two bodies ; and, satisfied with the result, I had not at the time examined more minutely into the nature of the latter substance.

The new interest conferred by recent researches upon leucine and its homologues, has recalled my attention to the sulphuretted derivative of amylamine.

This body may be readily procured by mixing anhydrous amylamine with a solution of dry bisulphide of carbon in anhydrous ether. The mixture becomes warm, and deposits, on cooling, white shining scales, which are insoluble in ether, and may therefore be purified by washing them with this liquid. The new body is likewise insoluble in water, but readily dissolves in alcohol ; when dry, it may be exposed for a while to a temperature of 100° C. without fusing ; after some time, however, the substance begins to be liquefied and to undergo complete decomposition, sulphuretted hydrogen being evolved. The same change occurs, although more slowly, at the common temperature ; a mixture of free sulphur with a new crystalline body, extremely fusible, insoluble in water, but soluble both in alcohol and ether, remaining behind.

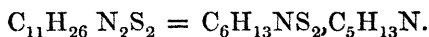
I. 0.274 grm. of the amylamine-body burnt with a mixture of oxide of copper and chromate of lead, gave 0.535 grm. of carbonic acid, and 0.2535 grm. of water.

* Chem. Soc. Qu. J. x, 193.

† H = 1, C = 12, O = 16, S = 32.

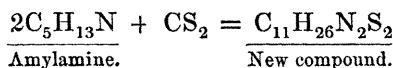
II. 0.429 grm. of substance, dissolved in alcohol and boiled for some time with nitrate of silver, gave 0.837 grm. of sulphide of silver.

These numbers lead to the formula

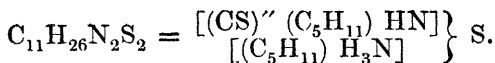


	Theory.		Experiment.	
			I.	II.
C ₁₁	132	52.8	53.25	—
H ₂₆	26	10.4	10.28	—
N ₂	28	11.2	—	—
S ₂	64	25.6	—	25.17
	—	—		
	250	100.0		

The new substance then is formed simply by the union of two molecules of amylamine with one molecule of bisulphide of carbon.



A glance at this formula suffices to characterize this substance as amyl-sulphocarbamate of amylammonium.

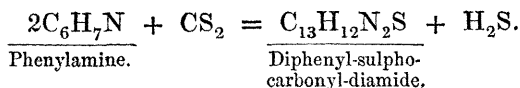


This view is readily confirmed by experiment. Addition of hydrochloric acid to the crystalline compound immediately separates an oily liquid which gradually solidifies, and the acid solution then contains amylamine which may be liberated by potassa. The oily substance is obviously amyl-sulphocarbamic acid. This body is readily soluble in ether, by which it may be separated from the chloride of amylammonium; it dissolves in ammonia and in potassa; mixed with amylamine it reproduces the original crystalline compound.

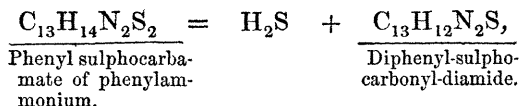
Experiments with ethylamine have furnished perfectly analogous results. I have been satisfied to establish qualitatively the analogy of the reactions.

It is of some interest to compare the deportment of amylamine under the influence of bisulphide of carbon with that of phenylamine in the same conditions. If these two bodies gave rise to

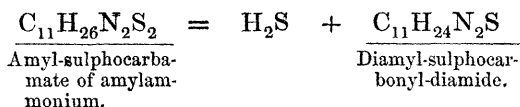
similar changes, we should expect, in the case of phenylamine, the formation of phenyl-sulphocarbamate of phenylammonium. But experiment proves that phenylamine produces diphenyl-sulphocarbonyl-diamide (sulphocarbanilide), sulphuretted hydrogen being evolved :—



Nevertheless it is extremely probable that further experiments will establish the perfect analogy in the deportment of amylamine and phenylamine with bisulphide of carbon. Diphenyl-sulphocarbonyl-diamide is probably the product of decomposition of a very unstable phenyl-sulphocarbamate of phenylammonium—



while a more minute examination of the crystalline substance obtained by the action of heat upon amyl-sulphocarbamate of amylammonium cannot fail to characterize it as diamyl-sulphocarbonyl-diamide.



The apparent dissimilarity of the two reactions would thus be reduced to the unequal stability of the sulphocarbamic acids of the amyl- and phenyl-series.

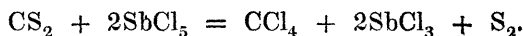
6. On the use of Pentachloride of Antimony in the Preparation of Chlorine-compounds.

Under a cloudless sky nobody would think of preparing the tetrachloride of carbon by any other process than by acting with chlorine upon chloroform. Exposed to direct sunlight, chloroform, when distilled in an atmosphere of chlorine, is rapidly converted into tetrachloride of carbon. A London November sky is, however, rather unfavourable to this process, and when requir-

ing lately, for some experiments, a small quantity of the tetrachloride, I was compelled to have recourse to another method. A well-known process, for which we are indebted to Prof. Kolbe, consists in submitting the bisulphide of carbon to the action of chlorine at a red heat, when chloride of sulphur and chloride of carbon are formed. I have repeatedly availed myself of this process, which, when a large quantity of chloride of carbon is to be prepared, leaves nothing to be desired. When, however, a small amount is rapidly required, the apparatus involved in this process becomes rather inconveniently troublesome.

I have, therefore, endeavoured to substitute chlorine in a state of combination for the free chlorine. Pentachloride of phosphorus, as is well known, exerts so little action upon bisulphide of carbon, that it has been found convenient to prepare the pentachloride of phosphorus by saturating a solution of phosphorus in bisulphide of carbon with chlorine gas. There is likewise, no reaction between pentachloride of phosphorus and bisulphide of carbon at 100° under pressure; it is only at a higher temperature that an action takes place. A very different result is obtained when the latter compound is submitted to the action of pentachloride of antimony, the chlorinating properties of which were first noticed by Wöhler.

On adding pentachloride of antimony to bisulphide of carbon, a transparent mixture is obtained, which exhibits, after a few minutes, a powerful reaction, becoming very hot, and assuming a dark reddish-brown colour; the mixture deposits on cooling a copious crystallization of terchloride of antimony, interspersed with well-formed sulphur-crystals. The liquid poured off from the crystals consists chiefly of tetrachloride of carbon, retaining some bisulphide of carbon, chloride of sulphur, and terchloride of antimony:—



I had expected that the reaction would give rise to the formation of a compound SbCl_3S ; but I have always found that the terchloride of antimony and the sulphur are separately deposited; and the same observation was made by Mr. H. McLeod, who has frequently carried out this reaction in my laboratory, modifying the proportions and the conditions of the experiment to a considerable extent. The small quantity of chloride of sulphur, which is simultaneously formed, appears to be the product of a secondary

reaction, a portion of the pentachloride not yet acted upon being reduced by the separated sulphur.

If the experiment be made with a couple of ounces, the two liquids must be mixed in a flask provided with a vertical cooling apparatus; the reaction is so powerful, that a considerable quantity of the material would be lost without this precaution. Whilst studying this process, I have allowed the two liquids to act upon each other in various proportions: on employing 1 eq. of bisulphide of carbon (1 part by weight) and 2 eq. of pentachloride of antimony (8 parts by weight) the decomposition is pretty complete; on account of the formation of chloride of sulphur, however, the theoretical quantity of chloride of carbon is never reached. The process yields a much more copious result when the pentachloride of antimony is mixed with a considerable excess of bisulphide of carbon, and the mixture, whilst boiling in a retort, is submitted to the action of a current of chlorine gas. In this manner large quantities of bisulphide of carbon may be transformed into the tetrachloride by the intervention of a comparatively small quantity of pentachloride of antimony.

In order to purify the tetrachloride of carbon, the product of the reaction is submitted to distillation; the liquid passing over below 100° is boiled for some time with a solution of potassa, which removes terchloride of antimony and chloride of sulphur, together with any undecomposed bisulphide of carbon. From the product, boiling at a higher temperature, a considerable quantity of pure terchloride of antimony may be recovered.

The tetrachloride obtained by this process exhibits all the properties of the product obtained by other modes of preparation. It boils at 77° . The determination of the chlorine gave the following results:—

0.195 grm. of substance, ignited with lime, furnished 0.730 chloride of silver.

	Theory.		Experiment.	---
C	12	7.79	—	---
Cl ₄	142	92.21	92.56.	
	<hr/>	<hr/>		
	154	100.00		

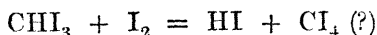
Pentachloride of antimony may be used with advantage in many cases as a carrier of free chlorine. On heating a very moderate quantity of pentachloride of antimony in a retort connected with

an inverted cooling apparatus, and passing simultaneously currents of dry olefant gas and chlorine through the boiling liquid, a very large amount of Dutch liquid may be obtained in an exceedingly short time. In an atmosphere of pentachloride of antimony, the combination of the ethylene and the chlorine goes on with the greatest facility. As soon as the retort is filled with the Dutch liquid, the access of the two gases is interrupted, and the liquid distilled. The portion boiling below 100° requires only to be once more rectified in order to furnish perfectly pure bichloride of ethylene. The residue in the retort consists of a mixture of terchloride and pentachloride of antimony, which may serve for a new experiment.

The preparation of large quantities of pentachloride of antimony presents no difficulty whatever, since antimony combines readily with chlorine at the common temperature. A simple mode of proceeding consists in introducing the antimony, coarsely powdered, into a combustion-tube from 5 to 6 feet long, rising at an angle of 10° or 15° , one end of which is fitted into one tubulature of a two-necked glass globe, the other neck of the globe communicating with a tube supplying dry chlorine gas. The combination taking place in the tube, the product flows backwards into the globe, whilst the long layer of antimony prevents the escape of any chlorine.

7. On Di-iodide of Methylene.

Being engaged in some experiments on the action of chloride of carbon CCl_4 on the phosphorus-bases, I thought it desirable to study likewise the deportment of these substances under the influence of the corresponding iodide. Bearing in mind the facility with which chloroform is converted into chloride of carbon, I had some hope of procuring the iodide by the action of dry iodine upon iodoform:—



When a mixture of iodoform and iodine, in the equivalent proportions of the above equation, was exposed in sealed tubes to a temperature of from 140° to 150°C. , the iodoform was found to be changed after the lapse of some hours. On opening the tubes, an acid gas was evolved; and on distilling the dark solid residue with

water, an aromatic body passed over, which collected in the receiver in the form of heavy oily drops. Decolorized by potassa and freed from water by chloride of calcium, the oily body boiled at about 180° , a considerable portion being decomposed, with evolution of hydriodic acid, and the distillate reassuming the red coloration. The liquid was therefore distilled *in vacuo*; it then passed over colourless, and without decomposition, at a temperature scarcely higher than the boiling point of water.

I. 1.222 grm. of substance, burnt with chromate of lead, gave 0.2077 grm. of carbonic acid, and 0.0800 grm. of water.

II. 0.705 grm. of substance burnt with lime, furnished 1.243 grm. of iodide of silver.

These numbers represent the composition of di-iodide of methylene—



only recently discovered by Boutlerow.*

Theory.			Experiment.	
			I.	II.
C	12	4.48	4.63	—
H ₂	2	0.74	0.73	—
I ₂	254	94.78	—	95.27
	<hr/>	<hr/>		
	268	100.00		

The compound analysed was indeed pure di-iodide of methylene. At a temperature near the freezing point of water, it solidified in large crystalline plates, and exhibited in every respect the properties described by Boutlerow. The analysis of the substance received moreover additional confirmation in a variety of substitutions in which it was subsequently employed.

The idea naturally suggested itself that the free iodine had no share in the formation of the di-iodide of methylene in the process described, but that the transformation of the iodoform was exclusively due to the action of heat. Experiment has verified this anticipation. Iodoform, when heated by itself in sealed tubes, at a temperature of 150°C . for several hours, furnished, on subsequent distillation with water, a very appreciable quantity of di-iodide of methylene. A comparative experiment, in which I followed the plan recommended by Boutlerow (1 eq. of iodoform, and 3 eqs. of ethylate of sodium), leads me to think that the action of heat

* Compt. rend. xlv, 595.

yields a larger product and involves on the whole a far less troublesome operation. The inequality of the amount of product in my experiments, however, may possibly be ascribed to the circumstance that I have repeatedly prepared the methylene-compound by exposing iodoform to the action of heat alone, while Boutlerow's process was only once or twice adopted.

The transformation of iodoform into di-iodide of methlene by one or other of these processes is strange enough, and as yet remains entirely unexplained; there is formed, together with the methylene-compound, a quantity of a brown substance, the nature of which appears anything but attractive.

8. *Dibromide of Ethylene.*

The usual mode of preparing this compound, which of late has acquired considerable interest, consists in passing ethylene into bromine covered with a layer of water. This method is extremely tedious, since, in order to avoid the loss of both bromine and of ethylene, the gas can be but slowly transmitted through the liquid. The compound may, however, be rapidly obtained without the slightest loss, by an exceedingly simple modification of the process.

A strong glass bottle, of 2 or 3 litres capacity, is provided with a perforated cork, through which is fitted a glass tube open at both ends, one of which reaches nearly to the bottom of the bottle, whilst the other, slightly projecting over the cork, communicates by means of a flexible india rubber tube with the gasholder containing the ethylenc. To start the operation, the bottle is detached, and filled over water with ethylene gas, into which are then poured from 100 to 130 grm. of commercial bromine, and about half that quantity of water, the cork with the glass tube being immediately replaced. On gently agitating the bottle, the ethylene is rapidly absorbed, and on turning the stop-cock of the gasholder, the gas rushes into the bottle exactly as into a vacuum. If the agitation be continued, a very large volume of ethylene may be thus united with bromine in an exceedingly short space of time, without the loss of a particle of the constituents or of the compound. As soon as the absorption becomes languid, the bromine is renewed, and the process continued in this manner until the accumulation of the dibromide renders it desirable to interrupt

the operation. When working upon a very large scale, it is convenient to insert between the absorption-bottle and the gasholder a wash-bottle filled with water or dilute potassa, which serves as a gauge for the rapidity of the gas-current, purifying the gas at the same time, if necessary, and intercepting, moreover, any bromine-vapour that may have risen into the india rubber tube, if the mixture should have become hot, in consequence of too rapid absorption.

9. *Metamorphosis of Monobrominated Ethylene.*

A quantity of monobrominated ethylene (bromide of vinyl) was sealed up in a glass tube with the view of preserving it. After the lapse of a night, the colourless extremely mobile liquid was found to have become a white porcelain-like mass, and on opening the tube all pressure had disappeared. The white substance was perfectly amorphous and inodorous, and proved insoluble in water, in alcohol, and in ether. When heated it was charred, with abundant evolution of hydrobromic acid.

Analysis showed, as might have been expected, that the alteration of the monobrominated ethylene had been simply molecular.

0.2954 grm. substance, burnt with chromate of lead, gave
0.24784 grm. of carbonic acid and 0.0780 grm. of
water.

The values corresponding to the formula C_2H_3Br are :—

	Theory.		Experiment.
C_2	24	22.43	22.87
H_3	3	2.80	2.93
Br	80	74.77	—
	<hr/> 107	<hr/> 100.00	

The chemical relations of bromide of vinyl are as yet but slightly examined. From its formula, the body might be considered as the hydrobromic ether of an alcohol homologous to allylic alcohol; this mode of viewing it, however, is not supported by the general deportment of the compound. The peculiar molecular transformation which it undergoes points rather to aldehydic relations, aldehyde being isomeric with the alcohol in question. As in the case of aldehyde, the conditions involving these transformations are utterly unknown; I have vainly tried to fix the

circumstances under which the solid modification of bromide of vinyl is formed. In some cases the liquid bromide was preserved for weeks without the slightest change, when suddenly the liquid was found to have been transformed throughout its entire mass. At one time I thought I had observed that the presence of water favoured the metamorphosis, but I have convinced myself by special experiments that this is not the case. The change takes place as capriciously in the presence as in the absence of water.

It deserves to be noticed that other bodies derived from ethylene by substitution are prone to similar transformations. Thus Regnault,* many years ago, observed analogous phenomena in the case of dichlorinated ethylene.

10. *Iodide of Ethyl.*

The reaction generally used for the preparation of this compound is so simple and elegant, that it would be difficult to propose a better method. Indeed, all the processes which have been suggested differ only as to the proportions of iodine, phosphorus, and alcohol, or as to the manner in which these substances are to be brought into contact with each other. Iodide of ethyl being extensively used as substitution-material in all laboratories, every observation which is calculated to facilitate the preparation of this body may prove acceptable.

The common plan of gradually introducing fragments of phosphorus into the mixture of alcohol and iodine has the disadvantage of occasionally giving rise to powerful reactions, involving considerable loss of materials, even when great care is taken to add the phosphorus slowly and in little fragments. This inconvenience may be readily avoided by introducing the phosphorus, together with about a fourth of the alcohol to be used, into a retort connected with an efficient cooler, into the tubulus of which is fitted a glass globe, provided with tube and stopcock.† The rest of the alcohol is then poured upon the iodine, and the solution thus obtained is introduced through the globe into the retort, which is heated on a sand-bath or in a water-bath. Iodine is but

* Ann. Chim. Phys. lxi, 151.

† The apparatus used in the preparation of triethylphosphine may be conveniently employed.—Chem. Soc., Qu. J., xi, 60.

sparingly soluble in alcohol, but excessively so in iodide of ethyl; it is, therefore, only necessary to pour the first portion which distils upon the residuary iodine, which is readily dissolved, and to allow the concentrated iodine solution thus obtained to flow through the globe into the retort, where it is instantaneously converted into iodide of ethyl. This process is especially convenient when the iodide of ethyl is to be prepared on a rather large scale. In this case I find it convenient to dissolve the iodine at once in iodide of ethyl, and to introduce it slowly through the globe into the retort. The stopcock being appropriately adjusted, the process requires but little attention, and, being continuous, yields a very large product in a comparatively limited time. The iodide generally distils at once perfectly colourless, and requires only to be washed with water in order to become free from traces of alcohol. It deserves to be noticed that the process may be carried out in a very moderate-sized retort, since there is only a very limited portion of material at a time under operation.

Convenient proportions for iodide of ethyl are 1000 grammes of iodine, 700 grammes of alcohol, of spec. grav. 0.84 (83 per cent.), and 50 grammes of phosphorus. From 96 to 98 per cent. of the theoretical quantity of pure iodide of ethyl are obtained. It deserves to be noticed how small a quantity of phosphorus is necessary for the etherification of the iodine, the quantity stated being less than one-half of the amount given in the majority of prescriptions.

Iodide of methyl and iodide of amyl may be prepared in the same manner. In the case of iodide of methyl, the following proportions have been found by experiment to work well. 1000 grammes of iodine, 500 grammes of methylic alcohol (the fraction boiling below 74°), and 60 grammes of phosphorus. The product, owing to the volatility of the compound, is somewhat less than in the previous case, amounting to from 94 to 95 per cent. of the theoretical quantity.

11. *On the deportment of Cyanate of Ethyl with Ethylate of Sodium.*

In a former note* I have stated that cyanate of ethyl, when heated with ethylate of sodium, is converted into triethylamine and carbonate of sodium. But I have pointed out at the same time that, owing to the facility with which the ethylate of sodium

* Chem. Soc., Qu. J., v, 20

undergoes decomposition at comparatively moderate temperatures, the process in question appeared to be of limited application.

I have lately had occasion to resume the study of cyanate of phenyl, which I described several years ago.* It appeared to me to be of some interest to apply the above reaction to the preparation of triphenylamine. On performing the experiment, I found, however, that phenylate of sodium and cyanate of phenyl give rise to a different reaction; no triphenylamine was obtained in this process.

This unexpected result induced me to repeat the experiment on the action of ethylate of sodium upon cyanate of ethyl. I have found that in this case likewise the reaction frequently assumes a form different from that which I had previously observed, and which excludes the production of triethylamine. I am engaged in the study of this transformation, the result of which I propose to lay before the Society on some future occasion.

12. *On Glycerin.*

Before the nature of this interesting compound had been finally established by Berthelot's remarkable inquiries, it had been frequently surmised, that the saponification of the several fatty bodies which are found in nature did not invariably furnish the same kind of glycerin.

This view appeared to receive new support in the researches of Wurtz, who has rendered it probable that glycerin is but the type of a class of homologous triatomic alcohols.

As a contribution towards the elucidation of this question, an experiment may be briefly mentioned which arose from a conversation with my friend Mr. George Ferguson Wilson, the technical director of the great establishment well known as Price's Patent Candle Company. Many hundred weights of glycerin are weekly separated in these works, by simple steam-saponification, from a considerable variety of fatty bodies; and Mr. Wilson, who has studied with predilection the preparation and purification of glycerin on a large scale, has acquired a sum of practical information upon this subject such as will not easily be found again. To my question, whether there is more than one kind of glycerin, Mr. Wilson replied, that in his opinion all the fatty bodies which he had examined contained the same

* Chem. Soc., Qu. J., ii, 323.

variety of glycerin, with the exception of cocoa-nut oil, the glycerin-like constituent of which differed in many respects so much from ordinary glycerin, that he was inclined to consider it as a special variety.

Since this question admitted of a simple experimental solution, Mr. Wilson kindly supplied me with a quantity of glycerin obtained by the saponification of cocoa-nut oil. This substance, although prepared in the same manner, differed in colour and odour from the glycerin furnished by other fatty substances. But notwithstanding the colouring matter, and an odorous principle which adhered with great pertinacity, it was not difficult to identify the compound under examination with ordinary glycerin. Distilled with iodide of phosphorus it furnished iodide of allyl, which exhibited the same boiling point as that obtained from ordinary glycerin, and was also transformed under the successive influence of oxalate of silver and ammonia, respectively, into oxalate of allyl and allyl-alcohol.

These experiments appear to solve the question as far as cocoa-nut oil is concerned.

13. *Dinitrotoluic Acid.*

The nitro-substitutes of the aromatic acids are but slowly transformed into dinitro-compounds. Whoever has made the experiment in the benzoyl-series has had an opportunity of experiencing this difficulty. The same remark applies to the toluyl-series: Noad,* to whom we are indebted for the first knowledge of this group, found that nitrotoluic acid may be dissolved in a boiling mixture of nitric and sulphuric acids without undergoing any alteration.

Whilst studying some reduction phenomena of nitro-compounds, I felt an interest in procuring, if possible, a small quantity of dinitrotoluic acid, and by my desire Mr. William Temple has prepared this substance. Pure nitrotoluic acid was digested for two days with three times its weight of equal parts of fuming nitric and sulphuric acids. The solution being mixed with an equal volume of water, a crystallization of dinitrotoluic acid was obtained on cooling. It was washed, recrystallized from water, and submitted to analysis.

I. 0.582 grm. of acid, burnt with oxide of copper, gave 0.908 grm. of carbonic acid and 0.152 grm. of water.

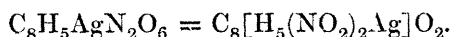
* Mem. Ch. Soc., III. 437.

II. 0.396 grm. of acid gave 0.614 grm. of carbonic acid and 0.103 grm. of water.

These numbers prove that the acid consisted of dinitrotoluic acid $C_8H_6N_2O_6 = C_8[H_6(NO_2)_2]O_2$ in a state of purity.

Theory.			Experiment.		Mean.
			I.	II.	
C ₈	96	42.48	42.54	42.30	42.42
H ₆	6	2.65	2.94	2.88	2.91
N ₂	28	12.39	—	—	—
O ₆	96	42.48	—	—	—
	<hr/>	<hr/>			
	226	100.00			

This result is fully confirmed by the analysis of the silver-salt, which is obtained in the form of a white precipitate on addition of nitrate of silver to a solution of dinitrotoluate of ammonium. The silver-salt contains



I. 0.609 grm. of silver-salt gave on combustion, 0.643 grm. of carbonic acid and 0.094 grm. of water.

II. 0.130 grm. of silver-salt gave 0.042 grm. of silver.

Theory.			Experiment.	
			I.	II.
C ₈	96	28.83	28.78	—
H ₅	5	1.50	1.71	—
Ag	108	32.43	—	32.30
N ₂	28	8.41	—	—
O ₆	96	28.83	—	—
	<hr/>	<hr/>		
	333	100.00		

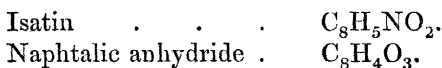
14. On Isatin.

Few bodies have fixed the attention of chemists more generally than indigo. But have their experiments led to a satisfactory view regarding the nature of this colouring matter? The brilliant labours of Erdmann and of Laurent have brought to light a rich

harvest of the most interesting derivatives of indigo, but they have left us in uncertainty with regard to the constitution of this group of compounds.

With the hope of throwing some light upon this subject, I have endeavoured to eliminate the nitrogen from these compounds by processes likely to act without producing too powerful alterations. The mode of action peculiar to nitrous acid appeared to promise some results; and since indigo, owing to its insolubility, is but little adapted to this reaction, I have made some experiments with isatin, which is so closely allied to indigo.

Supposing isatin to undergo a transformation analogous to that first observed by Piria in similar cases, and consisting arithmetically in the exchange of HN for O, there appeared some hope of obtaining in this manner naphthalic anhydride, and of thus opening a passage from the indigo-group into the naphthalin-series.



The history of these two bodies presents some features which conferred a degree of probability on such a transformation. Both isatin and naphthalic anhydride readily assimilate the elements of water, being converted respectively into isatic and naphthalic acids, which, when submitted to the action of alkalis, give both rise to the formation of phenylic derivatives, isatic acid yielding phenylamine, and naphthalic acid being converted into hydride of phenyl (benzol).

Experiment, however, has not confirmed my anticipation, and it might seem superfluous to waste another word upon the subject; nevertheless, I will briefly mention the result of this unsuccessful experiment, since it may probably save some trouble to others.

When studying the deportment of isatin with nitrous acid, I observed the following facts. If finely powdered isatin be suspended in from ten to twenty times its weight of water, and the mixture be then submitted to the action of a current of nitrous acid (disengaged by the action of arsenious acid upon nitric acid, and partially freed from nitric acid by sending it through an empty wash-bottle), the liquid at once begins to effervesce, and the isatin is soon entirely dissolved. The nearly colourless solution invariably contains a considerable quantity of nitric acid generated by the contact of the nitrous acid with the water. To avoid the action of this acid upon the product of the transformation of the

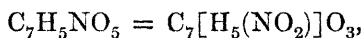
isatin, the liquid, mixed with much water, was evaporated upon the water-bath, the water being repeatedly renewed so as to prevent the nitric acid from getting concentrated. The liquid thus evaporated deposited crystals of an acid which, once or twice recrystallized from boiling water, appeared to be perfectly pure.

On analysis the following numbers were obtained—

I. 0.4308 grm. of the acid gave 0.7203 grm. of carbonic acid, and 0.1094 grm. of water.

II. 0.3164 grm. of the acid gave 0.5306 grm. of carbonic acid, and 0.0874 grm. of water.

These numbers lead to the expression,



which is the formula of nitrosalicylic (indigotic) acid.

	Theory.		Experiment.	
			I.	II.
C ₇	84	45.90	45.60	45.73
H ₅	5	2.73	2.81	2.86
N	14	7.65	—	—
O ₅	80	43.72	—	—
	<hr/>	<hr/>		
	183	100.00		

Assuming the nitrosalicylic acid to be a product of oxidation of the body directly formed from isatin under the influence of nitrous acid, the solution before evaporation was neutralized by means of an alkali. The result remained the same. In another experiment, pea-sized pieces of marble were introduced into the mixture of water and isatin before the nitrous acid was passed, in order to remove the free nitric acid as rapidly as it was formed. In these experiments, likewise, nitrosalicylic acid was obtained. It need scarcely be mentioned that the acid derived from isatin possessed all the properties of nitrosalicylic acid prepared by the ordinary method; it exhibited more especially the characteristic coloration with perchloride of iron.

When the liquid obtained by treatment with nitrous acid was evaporated, without having been previously mixed either with water or with an alkali, the isatin, as might have been expected, was transformed into trinitrophenylic acid. This acid was suffi-

ciently characterised by its properties, and by the analysis of its well-known difficultly-soluble potassium-compound.

0.3399 grm. of the potassium-salt, when burnt with chromate of lead, gave 0.3293 grm. of carbonic acid, and 0.0230 grm. of water.

The formula $C_6H_2KN_3O_7 = C_6[H_2(NO_2)_3K]O$ requires the following values,—

	Theory.		Experiment.
C_6	72	26.97	27.14
H_2	2	0.75	0.76
K	39	14.60	—
N_3	42	15.73	—
O_7	112	41.95	—
	<hr/> 267	<hr/> 100.00	

15. *Spontaneous Decomposition of Gun-cotton.*

Some gun-cotton prepared in the establishment of Messrs. Hall, soon after Schönbein's discovery, and taken out of a cartridge intended for blasting, had been preserved by my friend Dr. Percy since 1847, in a glass bottle provided with a glass stopper. After some time, red vapours had appeared in the interior of the bottle, and the cotton had crumbled down to a loose powder. When lately the bottle was again examined, the powder was found to be converted into a light brown, semi-fluid, gum-like mass, while the side of the bottle had become coated with a net-work of fine needles. It was not difficult to collect a sufficient quantity of these crystals; they exhibited all the characters of oxalic acid. In order to fix their nature by a number, they were converted, first into the ammonium-salt, and then into the silver-salt.

0.2420 grm. of silver-salt gave 0.2275 grm. of chloride of silver = 70.74 p.c. of silver.

Oxalate of silver contains 71.05 p.c. of silver.

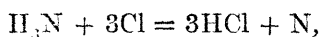
The viscid mass into which the bulk of the gun-cotton had been converted, exhibited all the properties of ordinary gum; it was likewise interspersed with crystals of oxalic acid.

16. *Experimental illustration of the Composition of Ammonia in Lectures.*

The decomposition of ammonia by the spark-current, exhibits in a conspicuous manner the condensation which accompanies the transformation of a mixture of hydrogen and nitrogen into ammonia. It is more difficult to illustrate the relative proportion of the nitrogen and hydrogen which exists in ammonia. The following experiment elucidates, though indirectly, this relation.

A glass tube from 30 to 40 inches in length, and $\frac{3}{4}$ of an inch in width, is sealed at one end and divided without particular care into three equal parts, which are conveniently marked by paper or by india-rubber rings. The tube is then filled over water with pure chlorine, and at once transferred into a test-glass half filled with mercury and half with concentrated solution of ammonia. In this manner a layer of ammonia one or two inches in height, and separated from the bulk of the liquid by mercury, is collected in the tube. A lively reaction immediately sets in, the mercury rises, and the ammonia-solution floating on the metal effervesces, with evolution of nitrogen, while the chlorine disappears, dense white clouds of chloride of ammonium being formed.

According to the equation—



the 3 volumes of chlorine should be replaced by 1 volume of nitrogen, and this result is actually observed. At the common temperature, however, the reaction is but slowly accomplished, the disengagement of nitrogen from the solution of ammonia becoming slower and slower, but often continuing for hours. On the other hand, the decomposition is instantaneous if the tube be gently inclined, and the liquid floating upon the mercury be heated to ebullition. To complete the experiment it is only necessary to transfer the glass tube into a high cylinder filled with water, in which the inner and outer liquids may become level when the 3 volumes of chlorine originally filling the tube, are found to be very accurately replaced by 1 volume of nitrogen gas.

Supposing the composition by volume of hydrochloric acid to be known, the composition of ammonia is fixed by this observation. The experiment furnishes moreover an instructive illustration of the volume-equivalence of chlorine, hydrogen, and nitrogen.

17. *How to exhibit the Inflammability of Ammonia.*

It is well known that ammoniacal gas cannot be inflamed in atmospheric air, but will burn in oxygen gas with a greenish-yellow flame. This flame may be shown by allowing the gas to issue from a bent jet into a vessel containing oxygen. There is, however, some difficulty in lighting the gas, and under the most favourable circumstances the phenomenon is very ephemeral. To avoid this inconvenience, the inflammability of ammonia is generally exhibited by sending a current of the gas into an ordinary flame, the ammonia-gas being allowed to issue from the delivery tube into the lower opening of an Argand gas-burner provided with a glass chimney. The gas burning low and almost invisibly, the high lambent ammonia-flame becomes very conspicuous.

The phenomenon may, however, be observed in a purer and much more brilliant form, when a wide-mouthed flask, containing a strong aqueous solution of ammonia is heated upon a sand-bath, and a rapid current of oxygen gas from a gas-holder forced through the boiling liquid. The mixture of oxygen and ammonia-gas thus formed may be lighted, and burns at the mouth of the flask with the characteristic greenish-yellow flame, which continues until the ammonia is expelled from the liquid.

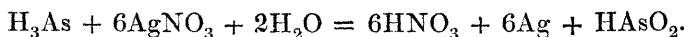
18. *Separation of Cadmium from Copper.*

Having had occasion to perform some experiments on the relative merits of the several processes which have been suggested for the separation of cadmium from copper, I was led to observe a property of sulphide of cadmium, which I do not find noticed in analytical manuals. Sulphide of cadmium dissolves with the greatest facility in boiling dilute sulphuric acid, which has no effect upon the sulphide of copper. On precipitating, by sulphuretted hydrogen, a solution containing not more than 1 milligramme of cadmium mixed with 1000 milligrammes of copper, and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part of concentrated sulphuric acid and 5 parts of water), a colourless filtrate is obtained, in which an aqueous solution of sulphuretted hydrogen produces an unmistakable precipitate of yellow sulphide of cadmium. Another solution of the same composition was mixed with an excess of cyanide of potassium and treated with sulphuretted hydrogen gas. A distinct yellow

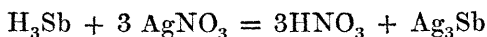
coloration was observed: a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in cyanide of potassium also gives rise to a yellow coloration, when submitted to the action of sulphuretted hydrogen.

19. *Separation of Arsenic from Antimony.*

The separation of these two metals, which presents unusual difficulties, has been a task of predilection with chemists, and a great number of processes have been suggested, the majority of which, it cannot be denied, admit of improvement. Among the many methods, the one which is based upon the dissimilar deportment of arsenetted and antimonetted hydrogen with nitrate of silver, deserves to be favourably mentioned, the former, as is well known, yielding arsenious acid which passes in solution:



the latter giving rise to the formation of antimonide of silver:



which is insoluble in water. This process presents no difficulty as far as the arsenic is concerned, which may be recognized in solution by ammonia, if there be an excess of silver, or by sulphuretted hydrogen, if the silver has been entirely precipitated. It is far less easy to find, according to this process, minute quantities of antimony in the presence of large quantities of arsenic, the silver-compound of antimony being mixed with a bulky precipitate of metallic silver. By treating this precipitate, as might readily suggest itself, with hydrochloric acid, there dissolves, together with antimony, a small quantity of chloride of silver, which is sufficient to darken the precipitate produced in the solution by sulphuretted hydrogen to such a degree as altogether to mask the presence of antimony. This inconvenience may easily be obviated by boiling the mixture of silver and antimonide of silver, after the arsenious acid has been carefully washed out by boiling water, with *tartaric acid*, which dissolves the antimony alone. The solution thus obtained yields at once the characteristic orange-yellow precipitate with sulphuretted hydrogen.

In some experiments made with the view of testing the delicacy of this process, 1 part of antimony in presence of 199 parts of arsenic, and *vice versâ*, 1 part of arsenic, together with 199 parts

of antimony, could be easily detected. Even with minute quantities the process proved successful, inasmuch as 5 milligrammes of either metal in the presence of 100 times the amount of the other could be satisfactorily exhibited. In evolving the hydrogen-compounds of arsenic and antimony, care must be taken to add as little nitric acid as possible to the hydrochloric acid used in dissolving the sulphides of the metals, since the presence of even moderate quantities of this acid greatly interferes with the free disengagement of the gases.

If there be tin with the arsenic and antimony, this metal will be deposited upon the plates of zinc used in evolving the hydrogen, from which it may be mechanically detached, dissolved in hydrochloric acid, and tested by the usual processes.

20. *Analysis of the Saline Water of Christian Malford,
near Chippenham.*

The water used for analysis, was collected November 11, 1858.

The water pumped up from the well is perfectly clear and colourless, and almost inodorous. It has a distinctly saline taste, and effervesces on agitation, exhibiting the presence of a considerable quantity of free carbonic acid. The water contains, in addition to carbonic acid, a minute trace of an inflammable carbonetted hydrogen. The presence of the latter becomes perceptible if a considerable quantity of the water be heated to ebullition, and the gases expelled be passed through a solution of potassa. The gas not absorbed is a mixture of atmospheric air with the carbonetted hydrogen; it burns, owing to the preponderance of the air, with a pale scarcely visible flame. On standing, more readily on boiling, the water deposits a yellowish sediment, consisting of carbonate of calcium, carbonate of magnesium, sesquioxide of iron, and organic matter.

Temperature of the water 12°C , the temperature of the air being nearly the same.

Specific gravity of the water = 1.006.

The analysis was performed in the usual manner; only the determination of the bromine requires a passing notice.

In determining this element, I have availed myself of the method of imperfect precipitation. According to the observations of Lyte and of Field, nitrate of silver produces in a mixture of chloride, bromide, and iodide, a precipitate, first of

iodide, and then of bromide, and a precipitate of chloride only after the whole of the iodine and bromine have been separated ;— a method of separating chlorine, bromine, and iodine, based upon this department, has been proposed by the latter chemist.

The amount of iodine present in the water of Christian Malford, is so exceedingly small, that the quantitative determination appeared useless. The task was, therefore, limited to the determination of the bromine.

For this purpose, 28 litres of the water were evaporated to dryness, and the saline residue was exhausted with dilute alcohol. The alcoholic liquid, when submitted to distillation, left a saline mass, which was dissolved in a small quantity of water. This solution was measured and divided into two equal parts, each of which represented the extract of the saline residue of 14 litres = 14084 grammes of the original water, containing the whole of the bromides and part of the chlorides. Each of the liquids thus obtained was precipitated by a silver-solution, containing 0.4288 grammes of pure silver, whereby the whole of the bromine, and part of the chlorine was thrown down. The two precipitates weighed respectively 0.6355 (I), and 0.6350 (II) grammes.

If P represent the weight of the mixed precipitate, and x the amount of chloride of silver in it, then $P-x$ is the quantity of bromide of silver, and if the total amount of the silver in the precipitate be represented by S , then

$$S = \frac{108}{143.5} x + \frac{108}{188} (P - x)$$

whence

$$x = \frac{S - 0.5745 P}{0.1781}.$$

By substituting the experimental values for S and P in the above expression, we find

	I.	II.
Chloride and bromide of silver (by experiment)	0.6355	0.6350
Chloride of silver (by calculation)	0.3576	0.3593
Bromide of silver	0.2779	0.2757
Corresponding (in 14084 grms. of water) to bromine	0.1182	0.1173
Or in 1000 grms. to	0.0084	0.0083

Direct results of analysis calculated to 1000 grammes of water.

a. BASES.

Experiment.	Sesquioxide of Iron.	Lime.	Magnesia.	Alkaline Chlorides.	Chloride of Potassium.	Chloride of Sodium.
I.	0·0035	0·4234	0·1897	6·9600	0·863	6·097
II.	0·0035	0·4241	0·1903	6·8800	0·897	5·983
Mean....	0·0035	0·4238	0·1900	6·9200	0·880	6·040

b. ACIDS

(or elements replacing them).

Exp.	Sulphuric Acid.	Chlorine.	Bromine, with traces of Iodine.	Silica.	Carbonic Acid free and combined.	Carbonic Acid combined as Carbonate of Calcium and Magnesium.	Carbonic Acid free.
I.	0·2464	4·5630	0·0084	0·0150	0·2921	0·1050	0 1871
II.	0·2452	4·5570	0·0083	0·0145	0·3164	0·1072	0 2092
Mean ..	0·2458	4·5600	0·0084	0·0148	0·3043	0·1061	0·1982

c. RESIDUE LEFT ON EVAPORATION.

Experiment.	Mineral Residue.	Organic Matter.	Total Residue.
I.	8·2000	0·0200	8·2200
II.	8·1900	0·0200	8·2100
Mean	8·1950	0·0200	8·2150

THE SALINE WATER OF CHRISTIAN MALFORD.

83

VERIFICATIONS.

a. VERIFICATION FOR LIME.

Experiment.	Lime precipitated on ebullition. (Carbonate of Calcium.)	Lime left in solution after ebullition. (Sulphate and Chloride of Calcium.)	Total by Calculation.	Total by Experiment
I.	0·1285	0·2895	0·4180	0·4234
II.	0·1307	0·2856	0·4163	0·4241
Mean	0·1296	0·2876	0·4172	0·4238

b. VERIFICATION FOR MAGNESIA.

Experiment.	Magnesia precipitated on ebullition. (Carbonate of Magnesium.)	Magnesia left in solution after ebullition. (Chloride of Magnesium.)	Total by Calculation.	Total by Experiment.
I.	0·0022	0·1852	0·1874	0·1897
II.	0·0025	0·1863	0·1888	0·1903
Mean	0·0024	0·1857	0·1881	0·1900

SALINE CONSTITUENTS.

	In 1000 grammes of water.	In one gallon, (70,000 grains) of water.
	Grammes.	Grains.
Sulphate of calcium	0·4179	29·253
Carbonate of calcium	0·2314	16·198
Chloride of calcium	0·2289	16·023
Carbonate of magnesium	0·0050	0·350
Chloride of magnesium	0·4413	30·891
Bromide of magnesium (with traces of iodide of magnesium)	0·0096	0·672
Carbonate of iron	0·0051	0·357
Chloride of potassium	0·8800	61·600
Chloride of sodium	6·0400	422·800
Silica	0·0148	1·036
Organic matter	0·0200	1·400
	8·2940	580·580

The water contains 29.02 cubic inches in the gallon, or 104.6 cubic centimetres in the litre, of free carbonic acid. The quantity of carbonic acid was determined at the well. It deserves to be mentioned that the water for this purpose was pumped up, whereby probably a minute quantity of gas was lost.

My thanks are due to Mr. E. Millar, of Christian Malford, for his help in collecting the water, and to Dr. Leibius for his assistance in performing the experiments.

21. *Spontaneous Decomposition of Chloride of Lime.*

One morning (I think it was in the summer of 1858), when entering my laboratory, which I had left in perfect order on the previous evening, I was surprised to find the room in the greatest confusion. Broken bottles and fragments of apparatus lay about, several window panes were smashed, and all the tables and shelves were covered with a dense layer of white dust. The latter was soon found to be chloride of lime, and furnished without difficulty the explanation of this strange appearance.

At the conclusion of the Great Exhibition of 1851, M. Kuhlmann, of Lille, had made me a present of the splendid collection of chemical preparations which he had contributed. The beautiful large bottles were for a long time kept as a collection; gradually, however, their contents proved too great a temptation, and in the course of time all the substances had been consumed. Only one large bottle, of about 10 litres capacity, and filled with chloride of lime, had resisted all attacks; the stopper had stuck so fast that nobody could get it out; and after many unsuccessful efforts—no one venturing to indulge in strong measures with the handsome vessel—the bottle had at last found a place on one of the highest shelves of the laboratory, where for years it had remained lost in dust and oblivion, until it had forced itself back on our recollection by so energetic an appeal. The explosion had been so violent that the neck of the bottle was projected into the area, where it was found with the stopper still firmly cemented into it.

I have not been able to learn whether similar cases of the spontaneous decomposition of chloride of lime have been already observed.

22. *Bisulphide of Carbon in Coal Gas.*

It is well known that coal gas, even when submitted to the most improved processes of purification, retains a minute quantity of a sulphur-compound, which yields sulphurous acid when the gas is burned. A commission having been appointed for the purpose of reporting* to the Lords of the Committee of Privy Council on Education on the lighting of picture-galleries by gas, and on any precautions (if necessary) against the escape of gas and of the products of its combustion, the writer of this note undertook a few experiments, with the view of determining the amount of sulphur generally present in the London coal gas.

The object of the inquiry being to ascertain the quantity of sulphurous acid capable of being formed by the combustion of the gas, an exceedingly small jet of gas, carefully washed with acetate of lead—which showed the absence of sulphuretted hydrogen—and measured by an accurate experimental meter, was burned in a large two-necked glass globe. Through one of the necks the gas tube was conveyed into the globe, whilst the other, fitting into a condenser, carried off the product of combustion into a two-necked receiver. To establish a current of air, the receiver was connected with a water-current aspirator, a couple of Woolfe's bottles containing water or dilute ammonia being inserted, for the purpose of fixing any trace of sulphurous acid which might escape condensation, with the water, in the receiver. The experiment being terminated, the liquids in the receiver and in the wash-bottles were united, oxidized with chlorine and precipitated with chloride of barium.

Experiments in July, 1859.

Order of Experiments.	Quantity of Gas consumed. Cubic feet.	Amount of Sulphate of Barium. Grammes	Amount of Sulphur in 100 cubic feet		Amount of Sulphur in 100 cubic metres. Grammes.
			Grammes.	Grains.	
I.	1·98	0·0630	0·437	6·74	15·433
II.	2	0·0840	0·577	8·90	20·371
III.	2	0·0630	0·433	6·68	15·278
IV.	2	0·0740	0·508	7·84	17·944
Mean	0·488	7·54	17·256

* Report on the subject of Lighting Picture Galleries by Gas, by Professors Faraday, Hofmann, and Tyndall, Mr. Redgrave, R.A, and Capt. Fowke, R.E.

Experiments in December, 1859, and January, 1860.

Order of Experiments.	Quantity of Gas consumed. Cubic feet.	Amount of Sulphate of Barium. Grammes.	Amount of Sulphur in 100 cubic feet.		Amount of Sulphur in 100 cubic metres. Grammes.
			Grammes.	Grains.	
V.	2	0·0890	0·611	9·43	21·585
VI.	2	0·0953	0·654	10·10	23·111
VII.	2	0·0975	0·669	10·33	23·644
VIII.	2	0·0935	0·642	9·91	22·677
Mean	0·644	9·94	22·754

These experiments show that the amount of sulphur remaining in the London gas after the removal of the sulphuretted hydrogen is very small, and that in winter it is somewhat greater than in summer. This may possibly arise from the enormously increased production of gas during the winter months, when it will be more difficult to regulate the several processes involved in its manufacture. But the result may also be purely accidental, arising from a change in the nature of the coal used, etc. A much more extended series of experiments would be required to decide this question.

It has long been assumed that the sulphur in purified gas exists in the form of bisulphide of carbon, the conditions for the generation of this compound being in fact given in the ordinary process of producing gas. That coal gas really contains bisulphide of carbon was first elegantly proved by Vogel,* who, at the suggestion of Baron Liebig, passed a current of purified gas through an alcoholic solution of potassa, when xanthate (sulpho-carbonate) of potassium ($K(C_2H_5)CS_2O$) was formed, which produced in copper-solutions the highly characteristic yellow precipitate of xanthate of copper, and yielded, when boiled with a few drops of nitrate of lead in the presence of free potassa, a black deposit of sulphide of lead. When engaged in the above inquiry, I repeated Vogel's experiments, which I can confirm in every particular. The amount of bisulphide of carbon in the London gas is, however, so small, that a very large volume must be passed through the alcoholic solution of potassa in order to produce a sufficient quantity of xanthate of potassium. After a cubic foot of gas had been passed through alcoholic potassa in a bulb apparatus, the

* Liebig's *Annalen* lxxxviii, 369.

solution gave with sulphate of copper a leek-green precipitate, in which the presence of xanthate was but imperfectly indicated. Only after passing several additional cubic feet the yellow colour became more distinct, although still masked to some extent by the hydrated protoxyde simultaneously precipitated. On the other hand, the black precipitate of sulphide of lead was obtained without difficulty, even after the passage of one single cubic foot of gas.

But the presence of bisulphide of carbon in coal gas may be exhibited even more elegantly, and with greater precision, by means of *triethylphosphine*, which produces with the bisulphide a compound crystallizing in splendid prisms of a ruby colour. This body is so characteristic, and forms with so much facility, that bisulphide of carbon has become a most valuable re-agent for triethylphosphine and its homologues. The idea naturally suggested itself to employ the phosphorous-base for the detection of bisulphide of carbon in gas. On distilling a considerable proportion of coal-gas-benzol, I had separately collected a small fraction, which came over in the commencement below 65°. When mixed with triethylphosphine, this liquid solidified into a mass of the well known ruby crystals. Four or five drops of triethylphosphine were dissolved in ether, the ethereal liquid was introduced into a bulb apparatus, and a current of coal gas allowed to bubble through the solution. When 0.2 of a cubic foot had passed, the liquid had assumed a distinctly red coloration, the intensity of which increased as the passage of the gas and the evaporation of the ether continued. After 0.8 of a cubic foot had passed, the whole of the ether had evaporated, and the inner surface of the bulb-apparatus was lined with a beautiful network of the ruby crystals.

23. Remarks on the Changes of Gutta Percha under Tropical Influences.

[From a Report addressed to Sir W. B. O'Shaughnessy, Director-General of Telegraphs in India.]

The peculiar change which gutta percha undergoes when in contact with air for some time is well known, this substance gradually becoming brittle, and ultimately losing all coherence. This effect was experienced on an undesirable scale in construct-

ing the East Indian Telegraphs. Enormous quantities of gutta percha, became in a comparatively short time, entirely useless, involving a loss of thousands of pounds. At the request of Sir W. B. O'Shaughnessy I have made a few experiments with the gutta percha thus altered, the results of which were recalled to my mind by the researches on the alteration of gutta percha lately published by Oudemans. It may be of some interest briefly to mention the analytical results furnished by the changed material submitted to me for examination.

The specimens sent home from India formed a brown, exceedingly brittle substance, softening to a plastic mass in boiling water. Since the gutta percha existing in commerce does not always exhibit the same characters, it was of some importance for the inquiry, that a quantity of the original unchanged substance, with which the wires sent out to India had been coated, was likewise placed at my disposal. In their deportment with solvents the changed and unchanged gutta percha exhibited a marked difference. Whilst the latter proved to be perfectly insoluble in strong alcohol, the changed gutta percha was in a great measure taken up by this solvent. By treating the changed material first with cold, then with boiling alcohol, and ultimately with ether, three substances were obtained, which, although very much alike in their physical properties, differed considerably from each other in their chemical composition.

I.—*Substance soluble in cold Alcohol.*

Cold alcohol readily attacked the outer surface of the coating, and dissolved a considerable portion. On evaporation a brown resinous mass remained behind, which was dried, first over sulphuric acid, and ultimately at 100°; at which temperature it readily fused. The fused mass solidified on cooling to a brittle substance, yielding a highly electrical powder, and exhibiting on combustion the following percentage composition.

	I.	II.	Mean.
Carbon	62·94	62·64	62·79
Hydrogen . . .	9·22	9·36	9·29
Oxygen	27·84	28·00	27·92
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

II.—*Substance soluble in boiling Alcohol.*

By treating with boiling alcohol the residue of the previous operation, which had ceased to yield anything more to cold alcohol, a fresh quantity of substance was obtained in solution. The alcoholic liquid, on evaporation, left a residue very similar to that of the previous operation, which, when dried in the same manner, furnished on analysis the following numbers.

	I.	II.	Mean.
Carbon	68·13	67·29	67·72
Hydrogen	10·01	10·18	10·09
Oxygen	21·86	22·53	22·19
	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00

III.—*Substance insoluble in cold and in boiling Alcohol.*

The residue left after repeated treatment with boiling alcohol, dissolved in ether, a few mechanical impurities remaining behind. The ethereal solution gave with alcohol a precipitate which dried up to a yellowish powder, becoming highly electrical by trituration, and caking when gently heated. It had the general characters of gutta percha, being merely somewhat deeper coloured and less plastic. When analysed, it furnished numbers nearly agreeing with those which were obtained by several observers for gutta percha.

Carbon	88·12
Hydrogen	12·49

The body last analysed was obviously unchanged gutta percha; a view which is also supported by its solubility in chloroform and benzol. The substance in question differed from specimens of gutta percha investigated by others, and especially from that which Payen considers the pure gutta percha, by its solubility in ether. The original substance with which the wires had been coated was, however, likewise soluble in ether. It cannot, therefore, be doubted that gutta percha exists in several modifications.

The experiments which I have quoted prove that the changes which gutta percha undergoes in contact with air depend upon oxidation. Unchanged gutta percha is free from oxygen; the product dissolved by cold alcohol contained nearly 28 per cent.,

and that soluble in boiling alcohol still more than 22 per cent. of oxygen.

I need not mention that I am far from believing that these oxygenated substances are definite chemical compounds. Their mode of preparation altogether precludes such an idea, the object of the experiments having been simply to establish the fact of oxidation having taken place. That the changes of gutta percha are due to the absorption of oxygen, is countenanced by the experience of this substance having been kept for years under water without undergoing any alteration.
