

NOTICES

OF

PAPERS CONTAINED IN THE

“Philosophical Translations” and Foreign Journals.

BY HENRY WATTS, B.A., F.C.S.

On the Diffusion of Liquids.*

By Professor Graham, F.R.S., F.C.S.

The experiments described in the author's former paper on this subject furnished strong grounds for believing that isomorphous salts possess a similar diffusibility. All the salts of potash and ammonia, which were compared, appeared to be equi-diffusive; so also were the salts of certain magnesian bases. A single preliminary observation on the nitrates of lead and baryta, however, opposed the general conclusion, and demanded further inquiry. It is scarcely necessary to say that any new means of recognising the existence of the isomorphous relation between different substances, must prove highly valuable. Let us inquire therefore how far liquid diffusion is available for that purpose.

The salts were still diffused from weak solutions, that is from solutions containing from 1 to 8 per cent of salt; but now a measure of the solution, equal to 100 grs. of water, was made to contain 1 grain of the salt, to form what is called the 1 per cent solution, instead of 1 grain of salt being added to 100 grs. of water, as before, without reference to the condensation which generally occurs. The quantities 1, 2, 4 and 8 per cent thus indicate the parts of salt present in a constant volume of liquid,—as 10, 20, 40 and 80 grs. of the salt in 1000 water grain-measures of the solution. The same phials for the solution and jars for the external water-atmosphere continued to be used, and the manipulations were similar. It is believed, however, that the temperature of the liquids was maintained more uniform in the new experiments than the old, partly by the better regulation of the temperature of the apartment, and partly by placing the jars close together upon a table with upright ledges, and covering the whole

* Philosophical Transactions 1850, p. 805.

over with sheets of paper during the continuance of an experiment. The mass of fluid in 80 or 100 jars, which were employed at once and placed together, made the small oscillations of temperature, which might still occur, slow and less injurious.

The investigation is also extended to several new substances, such as hydrocyanic acid, acetic acid, sulphurous acid, alcohol, ammonia and salts of organic bases, without reference to isomorphous relations. It is very necessary to have data which are minute and accurate respecting the diffusion of a considerable variety of substances. This it is the object of the present investigation to endeavour to supply, leaving speculative deductions in general respecting the nature and laws of liquid diffusion for a future occasion.

The density of all the solutions was observed at a constant temperature, namely, 60° Fahr.

1. *Hydrochloric acid*.—The period of diffusion arbitrarily chosen for this acid was five days. The diffusate, or quantity of acid diffused, was determined by precipitating the liquid of the external reservoirs with nitrate of silver, and weighing the chloride of silver formed. In the 1 and 2 per cent solutions, the liquids of two jars were generally mixed and precipitated together.

The number of cells diffused at once, unless otherwise specified, was always eight cells, of the 1 and 2 per cent solutions, and four cells of the 4 and 8 per cent solutions. In this abstract the means only of these experiments are given.

The diffusates at the same temperature were found to be as follow :

Diffusion in five days at 51° Fahr. ; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·41	0·97
From 2 per cent solution . . .	15·04	2·00
From 4 per cent solution . . .	30·72	4·08
From 8 per cent solution . . .	67·68	9·00

The 2 per cent solution is taken as the standard of comparison for the ratios, instead of the 1 per cent solution, from the greater accuracy with which the diffusion of the former can be observed.

The increasing diffusibility with the larger proportions of acid here observed is unusual, at least in the degree exhibited by the 8 per cent solution. Other substances, as will be immediately observed of nitric acid, appear to lose proportionally in diffusibility as their solutions are concentrated.

Hydrochloric acid belongs to the most diffusive class of substances known ; it appears to exceed hydrate of potash at 53°·5, as 7·56 to 6·12, or as 100 to 80·9*.

* Phil. Trans. 1850, 39.

The rapidity with which hydrochloric acid diffuses, and the facility with which that substance may be estimated, induced the author to examine the progression with which its diffusion takes place with increasing times in a minute manner. The 2 per cent solution was diffused for times increasing by six hours, from twelve hours or 0·5 day to 4·75 days, six cells being diffused for every period. Instead of determining the acid diffused separately in each jar or pair of jars, the contents of the six jars of each experiment were mixed together, and a definite proportion of the liquid precipitated by nitrate of silver, and the chloride of silver weighed, so as to obtain at once the mean result. Another observation for 5·75 days is added, although made at a sensibly higher temperature.

DIFFUSION OF HYDROCHLORIC ACID, 2 PER CENT SOLUTION; ONE CELL.

Time.	Temperature.	Diffusate in grains.	Differences.
days.	°		
0·5	53·75	0·909	
0·75	53·75	1·312	·403
1	53·75	1·766	·454
1·25	53·75	2·353	·587
1·5	53·75	2·596	·243
1·75	53·58	3·178	·582
2	53·58	3·410	·232
2·25	53·42	3·967	·557
2·5	53·58	4·339	·372
2·75	53·50	4·618	·279
3	53·50	4·969	·351
3·25	53·50	5·304	·335
3·5	54·85	5·857	·553
3·75	54·85	6·254	·397
4	54·85	6·407	·153
4·25	54·85	6·795	·388
4·5	54·71	7·034	·239
4·75	54·71	7·473	·339
5·75	56·46	8·363	

The differences are evidently affected by accidental errors of observation. The diffusion in 3·5 days is also increased by a rise of temperature of more than 1° in that and the following experiments. The diffusion always increases with the time, but less rapidly, according to a gradually diminishing progression.

Hydriodic acid.—Time of diffusion five days, as for hydrochloric acid. The acid diffused was estimated from the weight of iodide of silver which it gave when precipitated by nitrate of silver.

Diffusion from 2 per cent solutions at 51° Fahr.

Hydrochloric acid . . .	15·04	100
Hydriodic acid . . .	15·11	100·46

These experiments indicate a similarity of diffusion between the two isomorphous substances, hydrochloric and hydriodic acids.

Hydrobromic acid.—Time of diffusion five days. The diffusate was estimated from the bromide of silver.

Diffusate from 2 per cent solutions at 59°·7 Fahr.

Hydrochloric acid . . .	16·55	100
Hydrobromic acid . . .	16·58	100·18

Hydrobromic acid appears therefore to coincide in diffusibility with hydrochloric acid at this temperature. It may be remarked that these three acids, hydrochloric, hydrobromic and hydriodic, do not exhibit the same correspondence in another physical property, namely, the densities of their aqueous solutions containing the same proportion of acid. The densities of 2 per cent solutions of hydrochloric and hydriodic acids appear to be respectively 1·0104 and 1·0143, at 60° Fahr., and that of hydrobromic acid is an intermediate number. The same acids are also known to differ considerably in the boiling-points of solutions containing the same proportion of acid. A considerable diversity of physical properties appears here to be compatible with equal diffusibility in substances which are isomorphous.

Bromine.—Pure water readily dissolves more than 1 per cent of this substance. The solution prepared, however, contained only 0·864 per cent of bromine, as was ascertained by treating it with sulphurous acid and afterwards precipitating by nitrate of silver. Its density was 1·0070. It was evident, from the slow appearance of the brown colour in the exterior cell, that bromine diffuses less rapidly than hydrobromic acid.

The diffusion-time of bromine was made ten days, or double the time of hydrobromic acid. Two cells contained together a diffusate of 5·80 grs. of bromine; another two cells a diffusate of 5·88 grs.; mean 5·84 grs. at 60°·1 Fahr.; or 6·76 grs. for a 1 per cent solution. Doubling the last result we have 13·52 grs. for a 2 per cent solution, which is still considerably under the diffusate of hydrobromic acid (16·58 grs.) in half the time.

3. *Hydrocyanic acid.*—Time of diffusion five days. The acid diffused was estimated from the cyanide of silver which it gave with nitrate of silver.

Hydrocyanic acid, 1·766 per cent, made up to a density of 1·0142 with sulphate of potash. Diffused at 64°·2, in six cells, 11·40, 11·86, 11·80; mean 11·68 grs. for two cells. Calculated for 2 per cent, 13·23 grs. at 64°·2 in two cells, or about 13·10 grs. at 62°·8,

assuming this acid to be affected in the same way by temperature as hydrochloric acid.

Hydrocyanic acid here appears less diffusive than hydrochloric acid, at the same temperature $62^{\circ}8$, as $13\cdot10$ to $16\cdot40$, or as $79\cdot6$ to 100 , and not to belong therefore to the same class of diffusive substances.

4. *Nitric acid*.—Time of diffusion five days. The quantity of this acid diffused was always determined with great exactness by neutralization by means of a normal solution of carbonate of soda.

The diffusion of the different proportions of this acid at one temperature is as follows :

Diffusion of nitrate of water in five days at $51^{\circ}2$; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·99	0·95
From 2 per cent solution . . .	14·74	2
From 4 per cent solution . . .	28·76	3·90
From 8 per cent solution . . .	57·92	7·86

The usual approach to equality of diffusion, between chlorides and nitrates, is observable in hydrochloric and nitric acids, at least in the 1 and 2 per cent solutions.

Diffusion from 1 per cent solution at $53^{\circ}5$.

Hydrochloric acid	7·56	100
Nitrate of water	7·28	96·3

Diffusion from 2 per cent solution.

Hydrochloric acid at 51° .	15·04	100
Nitrate of water at $51^{\circ}2$.	14·74	98·0

The 2 per cent solutions of both acids were also diffused at higher temperatures.

Diffusion from 2 per cent solution.

Hydrochloric acid at $62^{\circ}8$.	16·46	100
Nitrate of water at $63^{\circ}2$.	16·76	101·8

Here the diffusibility of the two acids is as nearly as possible equal.

Diffusion from 4 per cent solution.

Hydrochloric acid at 51° .	30·72	100
Nitrate of water at $51^{\circ}2$.	28·76	93·7

Diffusion from 8 per cent solution.

Hydrochloric acid at 51° .	67·68	100
Nitrate of water at $51^{\circ}2$.	57·92	85·3

The wide divergence between these two acids, in the 8 per cent

solution, is produced by the remarkably increased diffusion of hydrochloric acid in that high proportion.

5. *Sulphuric acid*.—That time of diffusion arbitrarily chosen for this acid was ten days. The diffusate of this acid was determined in the same manner as that of nitric acid.

The diffusion of the different proportions of sulphuric acid is as follows:—

Diffusion of sulphate of water in ten days at $49^{\circ}7$; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	8·69	1·03
From 2 per cent solution . . .	16·91	2
From 4 per cent solution . . .	33·89	4·01
From 8 per cent solution . . .	68·96	8·16

The diffusibility of different strengths of this acid appears to be pretty uniform, but with a slight tendency to increase in the higher proportions, like hydrochloric acid.

Sulphuric acid is inferior in velocity of diffusion to hydrochloric acid, but still appears to possess considerably more than half the diffusibility of the latter.

6. *Chromic acid*.—Time of diffusion ten days. The diffusates from four cells of the 2 per cent solution were mixed together, and the quantity of chromic acid diffused for two cells reduced by means of hydrochloric acid and alcohol, and weighed as oxide of chromium.

1·762 per cent of anhydrous chromic acid, density 1·01404, diffused at $67^{\circ}3$, gave 19·78 grs. of chromic acid in two cells. Calculated for 2 per cent, 22·43 grs. of chromic acid, in two cells, at $67^{\circ}3$. The diffusion of sulphuric acid at $63^{\circ}5$, was 19·73 grs., which would give about 21 grs. of that acid at $67^{\circ}3$.

7. *Acetic acid*.—Time of diffusion ten days. This acid cannot be determined accurately by the acidimetric method, owing to the acetates of potash and soda being essentially alkaline to test paper, like the carbonates of the same bases, although neutral in composition. The weight of carbonate of baryta dissolved by the acid was had recourse to.

Diffusion of acetate of water in ten days at $48^{\circ}8$; two cells.

	Grs.	Ratio.
From 2 per cent solution . . .	11·31	2
From 4 per cent solution . . .	22·02	3·83
From 8 per cent solution . . .	41·80	7·26

The diffusibility diminishes with the larger proportions of acid. This acid appears to be considerably less diffusive than sulphuric acid. I was led to over-estimate the diffusion of acetic acid in a preliminary

observation of my former paper, by trusting to the acidimetric method of determination. Hydrochloric acid appears to diffuse about two and a half times more rapidly than acetate of water, at the same temperature.

8. *Sulphurous acid*.—The time of diffusion chosen for this acid was ten days, for comparison with sulphuric acid. The usual number of eight cells of the 1 and 2 per cent solutions were diffused, and four cells of the 4 and 8 per cent solutions. The whole diffusates of each proportion were then mixed together, and the proportional quantity of liquid representing two cells in the 1 and 2 per cent solutions, and 1 cell in the 4 and 8, was converted into sulphuric acid by a slight excess of bromine, and determined from the sulphate of baryta.

Diffusion of sulphurous acid in ten days at $68^{\circ}\cdot 1$; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	8·09	0·954
From 2 per cent solution . . .	16·96	2
From 4 per cent solution . . .	33·00	3·821
From 8 per cent solution . . .	66·38	7·827

This substance appears to be less diffusive than sulphuric acid at the same temperature; the diffusion of sulphurous acid at $68^{\circ}\cdot 1$ considerably resembles that of sulphuric acid at $49^{\circ}\cdot 7$.

9. *Ammonia*.—The time of diffusion chosen was 4·041 days, or that of hydrate of potash with chloride of sodium at seven days. The whole diffusates of each proportion were mixed together, and the quantity of ammonia diffused for two cells determined by an alkalimetric experiment, which was always repeated twice. It was necessary for diffusion to have the ammoniacal solution made denser than water, which was effected by the addition of common salt.

Diffusion in 4·04 days at $63^{\circ}\cdot 4$; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	4·93	1·029
From 2 per cent solution . . .	9·59	2
From 4 per cent solution . . .	19·72	4·117
From 8 per cent solution . . .	41·22	8·605

Ammonia appears to have a diffusibility approaching to that of hydrate of potash. It appears somewhat less diffusive than hydrocyanic acid at the same temperature, in the proportion of 12 to 13 nearly; or to possess about three-fourths of the diffusibility of hydrochloric acid.

10. *Alcohol*.—Time of diffusion ten days. The quantity of alcohol diffused was determined by careful distillation.

Diffusion in ten days at 48°·7; two cells.

From 2 per cent solution	8·62
From 4 per cent solution	16·12
From 8 per cent solution	35·50

It would be unsafe to draw any conclusion as to the proportionality of the diffusion of alcohol to the strength of the solution from these experiments.

Alcohol does not appear to belong to the same class of diffusive substances as acetic acid, which might be expected from their similarity of composition, but possesses a considerably lower diffusibility.

Diffusion from 2 per cent solutions in ten days.

Acetate of water at 48°·8	11·51	100
Alcohol at 48°·7	8·62	74·9

The diffusion of alcohol approaches to one-half of that of sulphate of water, at nearly the same temperature.

Alcohol may be substituted for water to dissolve certain salts, and also as an atmosphere into which these salts may diffuse. From experiments which have been commenced on this subject, it appears that the diffusion of hydrate of potash, iodide of potassium, chloride of calcium and others is about four times slower in alcohol of density 0·840 than in water. The salts likewise often exhibit the same relations in their diffusibility in alcohol, as in water, with some singular exceptions, such as chloride of mercury.

11. *Nitrate of baryta*.—Time of diffusion 11·43 days.* The salt diffused was precipitated by sulphuric acid, and calculated from the weight of the sulphate of baryta formed.

Diffusion in 11·43 days at 64°·1; two cells.

	Grs.	Ratio.
From 1 per cent solution	7·72	1·026
From 2 per cent solution	15·04	2
From 4 per cent solution	29·60	3·936
From 8 per cent solution	54·50	7·247

12. *Nitrate of strontia*.—Time of diffusion 11·43 days. Of anhydrous nitrate of strontia 0·82 per cent; density 1·0063. Diffused at 51°·5, in eight cells, 5·59, 5·62, 5·44, 5·69; mean 5·59 grs. for two cells; calculated for 1 per cent, 6·79 grs. at 51°·5 for two cells.

The diffusion of nitrate of strontia almost coincides with that of the isomorphous nitrate of baryta at the same temperature.

* This time is to that of sulphate of magnesia (16·166 days) as the square root of 8 is to the square of 16; but does not appear to express the true relation between these salts.

Diffusion from 1 per cent solutions at 51°5 in 11·43 days.

Nitrate of baryta	6·73	100
Nitrate of strontia	6·79	100·89

13. *Nitrate of lime*.—Time of diffusion 11·43 days. The diffusate was evaporated to dryness with an excess of sulphuric acid, and the nitrate of lime, which is always supposed anhydrous, was estimated from the sulphate of lime produced.

Diffusion in 11·43 days at 64°1; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·66	1·021
From 2 per cent solution . . .	15·01	2
From 4 per cent solution . . .	29·04	3·372
From 8 per cent solution . . .	55·10	7·334

The results throughout for this salt are almost identical with those of nitrate of baryta, although these two salts differ greatly in solubility, and in one being a hydrated, and the other an anhydrous salt.

14. *Acetate of lead*.—Diffused for 16·166 days; the time chosen formerly for sulphate of magnesia, with seven days for chloride of sodium. The solution contained 0·965 per cent of anhydrous salt, with the density 1·0080. As this solution of acetate of lead was found to be precipitated by pure water, about 2 per cent of strong acetic acid was introduced into the solution, and the same acid was added in a less proportion to the water jars. The salt of lead diffused was afterwards determined by means of sulphuric acid. Diffused in eight cells, at 53°1, 7·45, 7·29, 7·46 and 8·07 grs.; mean 7·56; or 7·84 for 1 per cent in two cells.

15. *Acetate of baryta*.—Diffused for 16·166 days. The solution contained 0·977 per cent of anhydrous salt, with the density 1·0073. The same addition of acetic acid was made to it as to the preceding acetate of lead, in order that the circumstances of diffusion might be similar for both salts. The salt diffused was estimated also in the form of sulphate.

Diffusion of 1 per cent solutions in 16·166 days; two cells.

Acetate of baryta at 53°5 . . .	7·50	100
Acetate of lead at 53°1 . . .	7·84	104·53

Here, of two isomorphous salts, that of greatest atomic weight sensibly exceeds the other in diffusibility.

16. *Chloride of barium*.—Time of diffusion 11·43 days. The diffused salt was weighed as sulphate of baryta.

Diffusion in 8·57 days at 63°; two cells.

	Gr.	Ratio.
From 1 per cent solution . . .	6·32	1·047
From 2 per cent solution . . .	12·07	2
From 4 per cent solution . . .	23·96	3·970
From 8 per cent solution . . .	45·92	7·608

17. *Chloride of strontium*.—The diffused salt was weighed as sulphate of strontia.

Diffusion in 8·57 days at 63°; two cells.

	Gr.	Ratio.
From 1 per cent solution . . .	6·09	1·045
From 2 per cent solution . . .	11·66	2
From 4 per cent solution . . .	23·56	4·041
From 8 per cent solution . . .	44·46	7·626

The series of ratios in the preceding table will be found, on comparison, to correspond closely with the ratios of chloride of barium. It may be useful to compare farther the amounts diffused from similar solutions of these two isomorphous compounds.

Diffusion in 8·57 days at 63°; two cells.

Chloride of barium, 1 per cent . . .	6·32	100
Chloride of strontium, 1 per cent . . .	6·09	96·36
Chloride of barium, 2 per cent . . .	12·07	100
Chloride of strontium, 2 per cent . . .	11·66	96·90
Chloride of barium, 4 per cent . . .	23·96	100
Chloride of strontium, 4 per cent . . .	23·56	99·16
Chloride of barium, 8 per cent . . .	45·92	100
Chloride of strontium, 8 per cent . . .	44·46	96·83

The near coincidence of the 4 per cent solutions probably arises from an accidental error of observation in the chloride of barium, for the latter departs here from the progression of its ratios. We appear then to have a small but constant difference of about $3\frac{1}{2}$ per cent in the diffusion of these two isomorphous salts, the chloride of barium, which possesses the highest atomic weight, having the advantage.

The diffusion of the 1 per cent solution of the same salts for the longer period of 11·43 days, gives 7·50 for chloride of barium at 50°·9, and 7°·52 for chloride of strontium at 51°, or nearly the same temperature. For the first time we have in the barytic salts a divergence between chlorides and nitrates, for the nitrates of the same bases have a number about 6·8 only at the same temperature. I am led, however, to believe that this discrepancy becomes much

less at low temperatures by experiments which are at present in progress.

18. *Chloride of calcium*.—Time of diffusion 11·43 days. The salt diffused was weighed as sulphate of lime.

Diffusion in 11·43 days at 63°·8; two cells.

	Gr.	Ratio.
From 1 per cent solution . . .	7·92	1·032
From 2 per cent solution . . .	15·35	2
From 4 per cent solution . . .	30·78	4·010
From 8 per cent solution . . .	61·56	8·021

We may now observe how far the diffusion of the chloride of calcium is analogous to that of nitrate of lime. At the inferior temperatures, the results for the 1 per cent solution of these two salts were as follow:

Chloride of calcium at 50°·9 . . .	6·51	100
Nitrate of lime at 51°·5 . . .	6·54	100·46

While at the higher temperatures, namely 63°·8 for the chloride of calcium, and 64°·1 for the nitrate of lime, the results for the different proportions of salt are:

Chloride of calcium, 1 per cent . . .	7·92	100
Nitrate of lime, 1 per cent . . .	7·66	96·72
Chloride of calcium, 2 per cent . . .	15·35	100
Nitrate of lime, 2 per cent . . .	15·01	97·79
Chloride of calcium, 4 per cent . . .	30·78	100
Nitrate of lime, 4 per cent . . .	29·04	94·35
Chloride of calcium, 8 per cent . . .	61·56	100
Nitrate of lime, 8 per cent . . .	55·10	89·51

The correspondence between the 1 and 2 per cent solutions of chloride and nitrate is sufficiently close, but in the 4 and 8 per cent the salts diverge, as happens also with hydrochloric and nitric acids themselves. The nitrate in both falls off, while the chloride sustains throughout the high diffusibility of the lower proportions.

19. *Chloride of manganese*.—Time of diffusion 11·43 days. The salt diffused was estimated by means of nitrate of silver.

The 1 per cent solution, of density 1·0085, gave at 50°·8, in eight cells, 6·67, 6·26, 6·79 and 6·81 grs.; mean 6·63 for two cells.

20. *Nitrate of magnesia*.—Time of diffusion 11·43 days. The salt diffused was estimated as sulphate.

The 1 per cent solution, of density 1·0073, gave at 50°·8, in eight cells, 6·29, 6·39, 6·52 and 6·76 grs.; mean 6·49 for two cells.

21. *Nitrate of copper*.—Time of diffusion 11·43 days. The salt diffused was estimated from the oxide of copper obtained by ignition.

The 1 per cent solution, of density 1.0075, in eight cells, at 50°8, gave 6.52, 6.36, 6.18 and 6.70 grs.; mean 6.44 for two cells.

Comparing the preceding salts with chloride of calcium diffused at the same temperature, 50°8, we have the following results:

Chloride of calcium	6.51	100
Chloride of manganese	6.63	101.15
Nitrate of magnesia	6.49	99.69
Nitrate of copper	6.44	98.92

This group of salts, belonging to the same isomorphous family of bases, the magnesian, again corresponds closely in diffusibility.

The following additional magnesian chlorides were diffused, all 1 per cent solutions, either in six or in eight cells. The salt diffused was estimated by means of nitrate of silver.

The results referred to chloride of calcium, at nearly the same temperature, 50°8, are as follow:

Chloride of calcium	6.51	100
Chloride of zinc	6.29	96.61
Chloride of magnesium	6.17	94.77
Chloride of copper	6.06	93.08

These salts present a greater latitude in their diffusibility, if belonging to the same class, than is usual.

22. *Protochloride of iron*.—A solution of this salt of 1.023 per cent was diffused at 53°5, a somewhat higher temperature than the corresponding chlorides. It gave 6.45, 6.48, 6.48 and 6.28 grs. in two cells; mean 6.44, or 6.30 for 1 per cent in two cells. This salt appears therefore to belong to the last group.

23. *Sesquichloride of iron*.—A full series of observations was made upon the diffusion of the different proportions of this salt from 1 to 8 per cent, but in all of them decomposition was determined by the diffusion, with turbidity also in the solution-phial, except in the 8 per cent solution.

The mean diffusion from the 1 per cent solution in 11.43 days, at 63°3, was 4.13 grs. of sesquichloride of iron with 1.28 gr. of free hydrochloric acid, in two cells. This result indicates that one-half nearly of the sesquichloride of iron is decomposed in the diffusion.

The mean diffusion from the 8 per cent solution, at 63°3, was 55.88 grs. of sesquichloride of iron, with 6.66 grs. of free hydrochloric acid, in two cells. It appears from this experiment that perchloride of iron approaches the chloride of calcium in diffusibility. That the proto- and persalts of the magnesian metals should have a similar rate of diffusion is not unlikely, from other analogies which they exhibit.

24. *Sulphate of magnesia*.—The time chosen for the diffusion of this salt, namely 16.166 days, is a multiple by 2 of the time of

sulphate of potash, and by 4 of the time of hydrate of potash. The diffusate was evaporated to dryness and weighed.

Diffusion in 16·16 days at 65°·4; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·31	1·144
From 2 per cent solution . . .	12·79	2
From 4 per cent solution . . .	23·46	3·671
From 8 per cent solution . . .	42·82	6·701
From 8 per cent solution at 62°·8 .	42·66	1
From 16 per cent solution at 62°·8	75·06	1·759
From 24 per cent solution at 62°·8	102·04	2·340

25. *Sulphate of zinc*.—Time of diffusion 16·166 days. The diffused salt was evaporated to dryness and weighed.

Diffusion in 16·16 days at 65°·4; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·67	1·091
From 2 per cent solution . . .	12·22	2
From 4 per cent solution . . .	23·12	3·784
From 8 per cent solution . . .	42·26	6·916
From 8 per cent solution at 62°·8 .	39·62	1
From 16 per cent solution at 62°·8	74·40	1·878
From 24 per cent solution at 62°·8	101·42	2·560

It will be remarked that the diffusion of these two isomorphous salts, sulphate of magnesia and sulphate of zinc, differs so much in the 1 per cent solution, as 7·31 to 6·67, that is, as 100 to 91·25; or 8·75 per cent. This, I have no doubt, however, is an accidental error, the disturbances from changes of temperature and other causes of dispersion being in direct proportion to the duration of the experiment, and therefore much increased with these long times; while the 1 per cent solution also appears to be generally the proportion most exposed to such errors. The sulphate of zinc appears to be the truest throughout in its diffusion, of these two salts. The approach to equality becomes close in the 4 per cent and larger proportions of salt, particularly with the unusually high proportions of 16 and 24 per cent, which were observed in these salts. The diffusion of both salts falls off remarkably in the higher proportions. The result of the comparison of these two magnesian sulphates is no doubt favourable to the similarity of diffusion of isomorphous salts.

26. *Sulphate of alumina*.—The time of diffusion chosen was 16·166 days, or the same as that for sulphate of magnesia. The usual number of eight cells of the 1 and 2 per cent solutions were diffused, and four cells of the 4 and 8 per cent solutions. The whole diffusates of each proportion were then mixed together and the quan-

tities of alumina and sulphuric acid, diffused for two cells, determined separately.

Diffusion in 16·166 days at 65°·4; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	5·48	1·074
From 2 per cent solution . . .	10·21	2
From 4 per cent solution . . .	19·28	3·780
From 8 per cent solution . . .	33·52	6·572

The diffusion of sulphate of alumina, it will be observed, is very sensibly less than that of sulphate of zinc at the same temperature.

27. *Nitrate of silver*.—Time of diffusion seven days. The quantity of salt diffused was ascertained by precipitation with hydrochloric acid, and weighing the chloride of silver formed.

Diffusion for seven days at 63°·4; two cells.

	Grs.	Ratio.
From 2 per cent solution . . .	13·61	2
From 4 per cent solution . . .	26·34	3·87
From 8 per cent solution . . .	51·88	7·62

28. *Nitrate of soda*.—Time of diffusion seven days. The quantity of salt diffused was ascertained by evaporation to dryness.

Diffusion in seven days at 63°·4; two cells.

	Grs.	Ratio.
From solution of 2 per cent . .	12·35	2
From solution of 4 per cent . .	23·56	3·82
From solution of 8 per cent . .	47·74	7·72

The ratios of the last column of the preceding Table are sensibly the same as those already obtained for nitrate of silver. But the diffusibility of nitrate of soda appears to be increased less rapidly by temperature than nitrate of silver. Hence the diffusibility of these two salts appears more similar at low than high temperatures.

Diffusion from 2 per cent solutions in seven days at 53°.

Nitrate of silver	11·24	100
Nitrate of soda	10·81	96·17

Diffusion from 2 per cent solutions in seven days at 63°·4.

Nitrate of silver	13·61	100
Nitrate of soda	12·35	90·74

29. *Chloride of sodium*.—Time of diffusion seven days. The salt diffused was treated with nitrate of silver, and the chloride of silver weighed.

Diffusion in seven days at $63^{\circ}\cdot 4$; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·32	1·023
From 2 per cent solution . . .	12·37	2
From 4 per cent solution . . .	24·96	4·036
From 8 per cent solution . . .	48·44	7·832

These numbers resemble closely those obtained in the diffusion of chloride of barium during the longer period of 8·57 days.

The chloride of sodium and nitrate of soda will be seen to exhibit the usual approach to parallelism between the chloride and nitrate of the same metal, by the following comparison :

Diffusion of both at $63^{\circ}\cdot 4$.

Chloride of sodium, 2 per cent . . .	12·37	100
Nitrate of soda, 2 per cent	12·35	99·83
Chloride of sodium, 4 per cent . . .	24·96	100
Nitrate of soda, 4 per cent	23·58	94·48
Chloride of sodium, 8 per cent . . .	48·44	100
Nitrate of soda, 8 per cent	47·74	98·55

As usual, the chloride is slightly more rapid in its diffusion than the nitrate.

30. *Chloride of potassium*.—Time of diffusion 5·71 days. The salt diffused was treated with nitrate of silver, and the chloride of silver weighed.

Diffusion in 5·71 days at 62° ; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·69	1·005
From 2 per cent solution . . .	13·32	2
From 4 per cent solution . . .	25·94	3·895
From 8 per cent solution . . .	53·64	8·054

The ratios are in remarkably close accordance with the proportions of salt diffused.

The times 5·71 and seven days chosen for the chlorides of potassium and sodium, it will be observed, are as the square roots of 2 and 3. A certain deviation from this ratio of the times of equal diffusion, appears on comparing the experimental results obtained at present for these salts.

Diffusion of chloride of potassium in 5·71 days at 62° , and of chloride of sodium in 7 days at $63^{\circ}\cdot 4$.

Chloride of potassium, 1 per cent . . .	6·69	100
Chloride of sodium, 1 per cent . . .	6·32	94·47
Chloride of potassium, 2 per cent . . .	13·32	100

Chloride of sodium, 2 per cent . . .	12·37	92·86
Chloride of potassium, 4 per cent . . .	25·94	100
Chloride of sodium, 4 per cent . . .	24·96	96·23
Chloride of potassium, 8 per cent . . .	53·64	100
Chloride of sodium, 8 per cent . . .	48·44	90·30

The difference would be about 1 per cent greater if the diffusion of both salts were reduced to the same temperature. The chloride of potassium deviates of course from the nitrate of soda in a similar manner. But chloride of potassium corresponds more closely with nitrate of silver than with chloride of sodium and nitrate of soda, at the temperature of the experiments.

Diffusion of chloride of potassium for 5·71 days at 62°, and of nitrate of silver for 7 days at 63°·4.

Chloride of potassium, 2 per cent . . .	13·32	100
Nitrate of silver, 2 per cent . . .	13·61	102·18
Chloride of potassium, 4 per cent . . .	25·94	100
Nitrate of silver, 4 per cent . . .	26·34	101·54
Chloride of potassium, 8 per cent . . .	53·64	100
Nitrate of silver, 8 per cent . . .	51·88	96·71

The coincidence in rate would appear even closer in the 2 and 4 per cent solutions, if the diffusion of the nitrate of silver was diminished about 1 per cent, on account of its higher temperature. It might thus be supposed that the nitrate of silver followed the sodium rate more accurately than the nitrate of soda and chloride of sodium themselves do.

A series of observations were made upon the diffusion of the 1 per cent solution of chloride of potassium at a nearly constant temperature of 56°, but for different times, varying from five days to eight days, and eighteen hours, to discover the progression, which proved to be pretty similar to that of the 2 per cent solution of hydrochloric acid. Six cells were diffused for each period, of which the mean result is given: the times advance by ten hours.

Diffusion of 1 per cent solution; two cells.

Time.	Temperature.	Diffusion in two cells.	Differences.
5 days	55°·71	5·89	
5 days 10 hours	55°·90	6·25	0·36
5 days 20 hours	55°·79	6·55	0·30
6 days 6 hours	55°·79	6·71	0·16
6 days 16 hours	55°·90	6·95	0·24
7 days 2 hours	55°·9	7·48	0·53
7 days 12 hours	55°·9	7·58	0·10
7 days 22 hours	56°·03	8·08	0·50
8 days 8 hours	56°·28	8·34	0·26
8 days 18 hours	56°·15	8·60	0·26

When the quantities of chloride of potassium are placed beside the same quantities of hydrochloric acid in the former table, it is found that the times of diffusion of the salt and acid exhibit an approximately constant ratio. The squares of these times of equal diffusion are as 1 to 2·04 for the shortest period of the chloride of potassium, and as 1 to 2·10 for the longest period but one. The variation in the differences towards the middle of the table is too great to be explained, except I fear by some error of observation, although no ordinary precaution was neglected in the execution of this laborious series of experiments.

31. *Iodides and bromides of potassium and sodium.*

Iodide of potassium.—Time of diffusion, 5·716 days. The diffusate was estimated by means of nitrate of silver.

(1). Iodide of potassium, 1·977 per cent; density 1·0145. Diffused at 53°·5, in eight cells, 11·415, 11·506, 10·942 and 11·062 grs.; mean 11·24 for two cells, and 11·36 for 2 per cent.

Comparing this salt with the isomorphous chloride of potassium, we have :

Diffusion of 2 per cent solutions in 5·716 days

Chloride of potassium at 55°	. .	11·48	100
Iodide of potassium at 53°·5	. .	11·36	99·65

The diffusion of the iodide would slightly exceed that of the chloride, instead of falling below it as in the table, if the temperatures were made equal.

(2). Again, iodide of potassium 1·971 per cent; observed density 1·01486. Diffused at 59°·8, in eight cells, and the mean diffusate of the whole cells determined, it gave 12·33 grs. of iodide of potassium for two cells; or 12·51 grs. for a 2 per cent solution.

Bromide of potassium.—Time of diffusion and mode of estimating diffusate as above. The solution contained 1·975 per cent of salt, and had a density of 1·014850. Diffused at 59°·8, in eight cells, it gave a mean diffusate of 12·30 grs. for two cells; or 12·46 grs. for 2 per cent.

For comparison, a solution of *chloride of potassium*, containing exactly 2 per cent of salt and having the density 1·0133, was diffused in the same circumstances of time and temperature as the two preceding salts. The mean diffusate of eight cells was 12·24 grs. for two cells.

Hence the following result of the diffusion of three isomorphous salts :

Diffusion of 2 per cent solutions in 5·716 days, at 59°·8.

	Grs.	Ratio.
Chloride of potassium . . .	12·24	100
Bromide of potassium . . .	12·46	101·80
Iodide of potassium . . .	12·51	102·21
Mean	12·40	

Iodide of sodium.—Time of diffusion seven days, temperature 59°·8. A solution of 2·011 per cent and density 1·01618, diffused in eight cells, gave a mean diffusate of 12·24 grs. for two cells; that is, 12·18 grs. for 2 per cent solution.

Bromide of sodium.—Time of diffusion and temperature as above. A solution of 2·146 per cent, of density 1·01726, diffused in eight cells, gave a mean diffusate of 12·80 grs.; that is, 11·93 grs. for 2 per cent.

A comparative experiment was made with a solution of *chloride of sodium*, containing 1·917 per cent of salt and of density 1·01376, in eight cells, at 60°. The diffusates for four pairs of cells were 11·65, 11·75, 11·63 and 11·47 grs.; mean 11·63 grs., which gives by proportion 12·14 grs. for a 2 per cent solution. As the present salt differs only 0°·2 Fahr. in diffusion-temperature from the two preceding salts, which is inadequate to produce an assignable difference of diffusion, the three salts may be supposed to be diffused at the same temperature, without sensible error.

Diffusion of 2 per cent solutions for seven days.

	Grs.	Ratio.
Chloride of sodium at 60° . .	12·14	100
Bromide of sodium at 59°·8 . .	11·93	98·27
Iodide of sodium at 59°·8 . .	12·18	100·33
Mean	12·08	

In both these isomorphous groups of salts of potassium and sodium, there is certainly a near approach to equality of diffusion. The times for the salts of the two bases being in the empirical proportion of the square roots of 2 and 3, the mean diffusates also approach pretty closely; namely, 12·40 grs. for the salts of potassium and 12·08 grs. for the salts of sodium, which are as 100 to 97·42. Here the members of each group are certainly very similar to each other in density and probably other physical properties, which was not the case with the equidiffusive group containing the hydrogen acids of the same salt-radicals.

32. *Chloride of ammonium.*—Time of diffusion 5·716 days. The salt diffused was estimated by means of nitrate of silver.

Solution 0·988 per cent; density 1·0036. Diffused at 53°, in

eight cells, 6.09, 6.07, 5.67, 5.87; mean 5.92 grs., and 5.99 for 1 per cent in two cells. This is somewhat more than 5.68, one-half of the diffusate of the 2 per cent solution of iodide of potassium, at nearly the same temperature. The diffusion, however, of the small proportions of salts of ammonium, such as the 1 per cent solution, is apt to be given in excess, from their low density.

33. *Dichloride of copper*.—Time of diffusion seven days, or that of chloride of sodium. The salt diffused was obtained by evaporation to dryness, in an air-bath, after treating the liquid with an excess of chlorine, in the form of chloride, from which the dichloride was calculated.

It was an object of interest to discover whether the dichloride of copper ($\text{Cu}_2 \text{Cl}$), which should be isomorphous with the chloride of sodium, may separate from the protochloride of copper and other magnesian salts, and assume the high diffusibility of the salts of alkaline metals. But the salt in question is entirely insoluble in water. A solution, however, was obtained by dissolving an equivalent quantity of the red suboxide of copper recently precipitated, in hydrochloric acid, of density 1.033, so as to give one grain of dichloride in every hundred water-grain measures of the solution. This acid solution did not precipitate by dilution with water. The salt was diffused into pure water at a mean temperature of $53^\circ.2$.

1. Dichloride of copper diffused, 6.66, 6.57, 7.01 and 6.48 grs.; mean 6.68 grs. in two cells. Chloride of sodium at $53^\circ.4$, nearly the same temperature, gave 5.90 grs. in the same time. Reducing the result to the temperature of 51° by an approximative correction, we should have 6.48 grs. of dichloride of copper for that temperature, at which chloride of calcium gave 6.51 grs. in 11.43 days, and protochloride of copper (Cu Cl) 6.06 grs. at nearly the same temperature, also in 11.43 days.

So far as we can judge from an experiment at a single temperature, it would appear that the diffusion of dichloride of copper is more rapid than that of the chloride (Cu Cl), in a proportion which supposes the former compound to possess half the "solution-density" of the latter, the times of equal diffusion 7 and 11.43 days, being when squared as 1 to 2.

With the view of discovering whether the large proportion of hydrochloric acid, amounting to 7 per cent, present in the preceding solution of dichloride of copper, modified the diffusion of the salt, a portion of the same acid solution was treated with chlorine-gas, to convert the copper-salt into chloride, and diffused into water, after the excess of chlorine was removed by agitation of the solution with air. The proportion of salt present was thus increased in weight from 1 to 1.36 per cent. The time of diffusion was 11.43 days, and the temperature 53° .

2. Chloride of copper diffused from a 1.36 per cent solution of the

salt in hydrochloric acid, 5·83, 5·66, and 5·30 grs. in two cells; mean 5·60 grs.

The corresponding diffusion from a 1 per cent solution may be supposed to be less than 5·6 grs., in the proportion of 1·36 to 1, without any great error. The results thus become chloride of copper diffused, 3·98, 3·85 and 3·58 grs.; mean 3·80 grs. in two cells.

It hence appears that the diffusion of chloride of copper is much diminished by the presence of a great excess of hydrochloric acid in the same solution. Different causes suggest themselves for this result, such as the possibility of a combination existing of chloride of copper with chloride of hydrogen, in the acid solution; or the influence which must be admitted of the more soluble substance, in a mixture of two similar substances, in repressing the diffusion of the less soluble. The present result, however, is entirely opposed to the idea that the high diffusibility of the dichloride of copper, observed before is due to the hydrochloride acid present.

3. The diffusion of chloride of sodium also appears to be repressed by contact with a large excess of hydrochloric acid. One per cent of chloride of sodium raised the density of dilute hydrochloric acid from 1·035 to 1·0408. Diffused into pure water for seven days at 52°·9, in eight cells, the diffusates of chloride of sodium were 3·80, 3·87, 4·00 and 3·86 grs.; mean 3·88 for two cells. The diffusion of chloride of sodium is thus reduced in a corresponding measure with that of chloride of copper by association with seven times its weight of hydrochloric acid.

These results are interesting in a very different point of view. I have always watched for the appearance of some absorbent or imbibing power on the part of the acids, more analogous to an endosmotic attraction for water, as usually conceived. If such an attraction existed, it would complicate the phenomena of diffusion, for the volume of water absorbed by the acid would displace and project a portion of the latter into the reservoir, the phial not being extensible. The high diffusibility of hydrochloric and nitric acids would be thus explained. But by such a mechanical displacement, the chloride of sodium would be thrown out in the preceding experiment, as well as the hydrochloric acid, which is not the case.

4. Even in hydrochloric acid, of density 1·124 (25 per cent), the diffusion of 1 per cent of chloride of sodium for seven days, at 56°·6, was found to amount to 4·7 grs. only in two cells, and is less than from a solution in pure water.

5. In comparing the influence of nitric acid with that of hydrochloric acid upon the diffusion of chloride of sodium, it was found that in a 7 per cent solution of nitric acid, the chloride of sodium (1 per cent) was entirely decomposed in the diffusive process, at 56°·6, and gave hydrochloric acid in the full diffusive equivalent of that acid, together with nitrate of soda.

34. *Bicarbonate of potash*.—Time of diffusion 8·083 days, or double that of hydrate of potash. The water of the jars was partially charged with carbonic acid gas, to prevent the decomposition of this and the other bicarbonates in the act of diffusion. The whole diffusates of each proportion were mixed together, and the quantity of bicarbonate of potash diffused for two cells, converted into the chloride of potassium, evaporated to dryness and weighed.

Diffusion in 8·08 days at 68°·2; two cells.

	Grs.	Ratio
From 1 per cent solution . . .	7·23	1·029
From 2 per cent solution . . .	14·05	2
From 4 per cent solution . . .	26·72	3·806
From 8 per cent solution . . .	52·01	7·408

35. *Bicarbonate of ammonia*.—Time of diffusion 8·083 days. The whole diffusates of each proportion were mixed together, and the quantity of bicarbonate of ammonia, diffused for two cells, determined by an alkalimetric experiment, which was always repeated twice.

Diffusion in 8·08 days at 68°·2; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·91	1·013
From 2 per cent solution . . .	13·65	2
From 4 per cent solution . . .	27·00	3·959
From 8 per cent solution . . .	50·10	7·346

The amount and progression of the diffusion of this salt correspond well, for all the proportions diffused, with the preceding isomorphous bicarbonate of potash.

36. *Bicarbonate of soda*.—Time of diffusion 9·875 days. The whole diffusates of each proportion were mixed together, and the quantity of bicarbonate of soda, diffused for two cells, converted into chloride of sodium, evaporated to dryness and weighed.

Diffusion in 9·87 days at 68°·1; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·31	1·059
From 2 per cent solution . . .	13·81	2
From 4 per cent solution . . .	26·70	3·869
From 8 per cent solution . . .	52·38	7·590

A remarkable approach to equality in the diffusion of the bicarbonates of potash and soda, in the times chosen, is observed equally in all the proportions of salt from 1 to 8 per cent.

The results for the three bicarbonates may be stated as follow,

the diffusate of the 2 per cent solution of bicarbonate of potash being made equal to 200, as a standard of comparison.

Diffusion of bicarbonates of potash and ammonia in 8·08 days, at 68°·2, and of bicarbonate of soda in 9·875 days, at 68°·1 :

	Bicarbonate of potash.	Bicarbonate of ammonia.	Bicarbonate of soda.
From 1 per cent solution .	102·9	98·3	104·0
From 2 per cent solution .	200·0	194·3	196·4
From 4 per cent solution .	380·6	384·3	380·0
From 3 per cent solution .	740·8	712·6	748·3

Or, making the diffusate from each proportion of the bicarbonate of potash equal to 100 :

	Bicarbonate of potash.	Bicarbonate of ammonia.	Bicarbonate of soda.
From 1 per cent solution .	100	95·53	101·07
From 2 per cent solution .	100	97·15	98·20
From 4 per cent solution .	100	100·97	99·84
From 8 per cent solution .	100	96·19	101·03

The bicarbonate of ammonia is slightly lower in general than the bicarbonate of potash, possibly from a small loss of the former salt by evaporation in the different operations. The times chosen for these two bicarbonates is to that of the bicarbonate of soda, as the square root of 2 to the square root of 3, and the remarkable agreement observed in the diffusion of these salts gives support, therefore, to that relation. In alluding to this relation, however, it is proper to add that the carbonates of potash and soda deviate from it in a sensible degree, and the hydrates of potash and soda very considerably. If the relation, therefore, has a real foundation, it must be masked in the salts last named by differences existing between them in certain properties, the discovery and investigation of which is of the last importance for the theory of liquid diffusion.

37. *Hydrochlorate of morphine*.—Time of diffusion 11·43 days. The crystallised salt was assumed to be of the composition $C_{34}H_{18}NO_6 \cdot HCl + 6HO$, with the equivalent 374·5. The quantity diffused was determined from the chlorine, which was precipitated as chloride of silver in an acid solution. Hydrochlorate of morphine, 1·88 per cent of the salt supposed anhydrous, diffused at 64°·1, in six cells, 11·03, 10·72, 11·01; mean 10·92 grs. of the anhydrous salt for two cells. Calculated for 2 per cent, 11·60 grs. at 64°·1 for two cells.

38. *Hydrochlorate of strychnine*.—Time of diffusion 11·43 days. The crystallised salt was assumed to be of the composition $C_{42}H_{22}N_2O_4 \cdot HCl + 3HO$, with the equivalent 397·5. Hydrochloro-

rate of strychnine, 2 per cent, density 1.0065, diffused at $64^{\circ}1$, in six cells, 11.54, 11.62, 11.31; mean 11.49 grs. for two cells. The quantities refer to anhydrous salt, and were estimated from the chlorine, as with hydrochlorate of morphine.

These two analogous salts appear to approach very closely in diffusibility.

Diffusion from 2 per cent solutions at $64^{\circ}1$; two cells.

Hydrochlorate of morphine . .	11.60	100
Hydrochlorate of strychnine . .	11.49	99.05

For a similar period of 11.43 days, but at a lower temperature, $53^{\circ}4$, the 1 per cent solution of hydrochlorate of morphine gave a mean result of 5.49 grs. from two cells and the hydrochlorate of strychnine 5.77 grs. from two cells. But the weights of chloride of silver from which these numbers are deduced were too small to admit of much precision.

The diffusion of these salts of organic bases in 11.43 days, is exceeded by the diffusion of chloride of ammonium or potassium in 5.71 days, or half the former time. The *vegeto-alkalies* appear thus to be divided from ammonia and potash.

The new observations of the present paper are favourable to the existence of a relation amounting to close similarity or equality in diffusibility between certain classes of substances.

The chlorides and nitrates of the same metal generally exhibit this correspondence, as in the chloride of calcium and nitrate of lime, the chloride of sodium and nitrate of soda, and also in hydrochloric and nitric acids.

Isomorphous salts exhibit the same relation, as has been observed in the chlorides, bromides and iodides of potassium, sodium and hydrogen, in various salts of baryta, strontia and lead, in numerous magnesian salts, in the salts of silver, soda, and probably those of suboxide of copper, and in several additional salts of potash and ammonia.

Corresponding salts of two of the *vegeto-alkalies* are also found to be equidiffusive.

Before discussing the relations between the different groups of equidiffusive substances which are thus formed, it will be necessary to examine their diffusion at widely different temperatures, a subject attended with considerable difficulty.

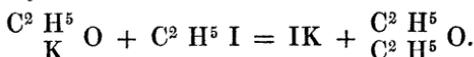
Theory of Etherification.**By A. W. Williamson, Ph.D.***

When sulphuric acid is brought in contact with alcohol under certain circumstances, a new arrangement is effected in the elements of the alcohol, which divide into two groups, forming ether and water. Now it is well known that the process by which this change is effected may be represented in two ways, the difference of which consists in their respectively selecting for starting-point a different view of the constitution of alcohol. According to the one view, an atom of alcohol weighs 23, and is made up of $C^2 H^6 O$; so that to form ether, two atoms of it are needed, one of which takes $C^2 H^4$ from the other, setting free the water with which these elements were combined; whereas, according to the other view, alcohol weighs 46, and *contains* ether and water. These are not the only points of difference which are urged; but they are the most real and tangible, and their consideration is sufficient for our present purpose. If by any direct fact we could decide which of these two expressions is the correct one, the ground would be clear for an examination of the process of etherification itself.

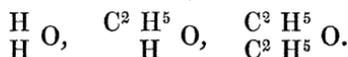
The following experiments were made with the view of obtaining new alcohols, by substituting carburetted hydrogen for hydrogen in a known alcohol. With this view an expedient was adopted, which may render valuable services on similar occasions. It consisted in replacing the hydrogen first by potassium, and acting upon the compound thus formed by the chloride or iodide of the carburetted hydrogen which was to be introduced in the place of that hydrogen. The process was first tried with common alcohol, which, after careful purification, was saturated with potassium, and as soon as the action had ceased, mixed with a portion of iodide of ethyl equivalent to the potassium used. Iodide of potassium was readily formed on the application of a gentle heat, and the desired substitution was effected; but, contrary to expectation, the compound thus formed had none of the properties of an alcohol—it was nothing else than common ether, $C^4 H^{10} O$.

Now this result at once appeared to be inconsistent with the higher formula of alcohol; for if that body contained twice as many atoms of oxygen as are in ether, the product ought clearly to have contained twice as much oxygen as ether does. The alternative was evident; for having obtained ether by substituting $C^2 H^5$ for H in alcohol, the relative composition of the two bodies is represented by expressing that fact in our formula. Thus alcohol is $\begin{matrix} C^2 H^5 \\ H O, \end{matrix}$

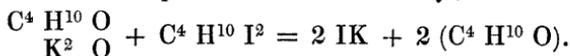
and the potassium compound is $\begin{matrix} C^2 H^5 \\ K \end{matrix} O$; and by acting upon this by iodide of ethyl, we have



Of course, the proportion between the two bodies is the only point here considered, and the same reasoning would be applicable to any multiple of the formulæ assumed. Some chemists may perhaps prefer doubling them, in order to avoid the use of atoms of hydrogen, potassium, &c.; but the author has not felt himself justified in doing so, because that would involve doubling the usual formula for water; for, as will be presently shown, water is formed in etherification by replacing the carburetted hydrogen of alcohol by hydrogen, which, of course, obliges us to assume the same unity of oxygen in both. Alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and ether is water in which both atoms of hydrogen are replaced by carburetted hydrogen, thus:



This formation of ether might, however, be explained, after a fashion, by the other theory—by supposing the potassium compound to contain ether and potash, which separate during the action of the iodide of ethyl; so that half the ether obtained would have been contained in that compound, and the other half formed by double decomposition between potash and iodide of ethyl, thus:



But although the insufficiency of this explanation becomes evident on a little reflection, a further and more tangible method of arriving at a conclusion was devised. It consisted in acting upon the potassium compound by iodide of methyl, in which case, if that compound were ether and potash, the resulting mixture should consist of ether and oxide of methyl; whereas, in the contrary case, a body of the composition $C^3 H^8 O$ should be formed. Now this substance was actually obtained, and neither ether nor oxide of methyl.

In this experiment, the two theories cross one another, and must lead to different results; for it is evident that, in the first-mentioned decomposition by which ether was formed, the only difficulty in explaining the process decisively, consisted in our inability to prove that the carburetted hydrogen introduced instead of the hydrogen did not have in the product an atom of oxygen to itself, but that, on the contrary, it was coupled with the carburetted hydrogen already contained in the alcohol—the two in combination with one

atom of oxygen. It is clear that if alcohol *contains* ether and water, and the carburetted hydrogen in the first experiment formed a second atom of ether by taking the place of the hydrogen of this water, the process being the same in the second experiment, we should then have obtained two ethers; whereas, if the formation of ether from alcohol be effected by synthesis, a new carburetted hydrogen being added to the one already contained in the alcohol, we ought to obtain the new intermediate ether which was really produced.

The boiling-point of this remarkable body, is a little above 10° C.; it has a very peculiar smell, distinctly different from that of common ether; and, like that body, it is only slightly soluble in water. It is not acted upon by the alkali-metals at the common atmospheric temperature.

By acting upon the potassium-alcohol in like manner by iodide of amyl, a similar substitution was effected of the elements of that carburetted hydrogen in the place of the hydrogen of alcohol, and an ether obtained which boiled at 111° C., and had the composition $C^7 H^{16} O$. There is some reason to believe that this body is the same which Balard obtained by decomposition of chloride of amyl by an alcoholic solution of hydrated potash, and which that distinguished chemist took for oxide of amyl.

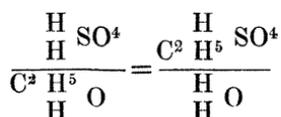
From the perfect analogy of properties between the known terms of the alcoholic series, it was to be expected that similar substitutions might be effected in the others; and this expectation has been verified by experiment. Of course, the formulæ of the other alcohols must be reduced to half, for the same reasons as that of common alcohol. Methylic alcohol is, therefore, expressed by the formula $C H^3 O$, as common alcohol is $C^2 H^5 O$; and in the same manner amylic alcohol is $C^5 H^{11} O$, and the same of the higher ones. In

conformity to this fact, we must be able to obtain the same intermediate ethers by replacing hydrogen in these alcohols (methylic and amylic) by the carburetted hydrogen of iodide of ethyl, as by the inverse process described above. This has been verified in the case of the three-carbon ether, which may be obtained indifferently by replacing one-fourth of the hydrogen of methylic alcohol by $C^2 H^5$, or by replacing one-sixth of the hydrogen of common alcohol by CH^3 . Its rational formula is, therefore, $C^2 H^5 O$.

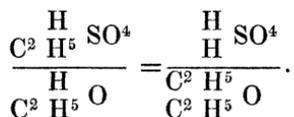
By acting upon the compound $C H^3 O$ by iodide of amyl, a third ethereal compound was obtained, of which the formula is $C H^3 O$. This is evidently the only one of the three new ethers, which, containing an even number of carbon atoms, might be conceived to have

been formed from one alcohol; but when treated with monobasic acids, as the hydrochloric, it cannot be expected to act in the same manner as its homogeneous isomeric, the ether $\frac{C^3 H^7}{C^3 H^7} O$ of the three-carbon alcohol $\frac{C^3 H^7}{H} O$.

The next thing to be done is to explain the process of etherification by the action of sulphuric acid ($SO^4 H^2$) upon alcohol; and in order to accomplish that, we must show the connexion between those substances and the reagents used in the above-described experiments. With this view, we have merely to add to the above facts, the acknowledged analogy of the simple and compound radicals in their compounds. It must first be shown how a substance analogous to the iodide of ethyl is formed, and then how by double decomposition with alcohol it produces ether. This is very easy; for sulphovinic acid is strictly analogous to iodide of ethyl plus iodide of hydrogen, which we should obtain by replacing SO^4 in its formula by an equivalent of iodine; and in order to represent the formation of this sulphovinic acid, which is well known to precede that of ether, the simplest mode is at the same time the one most free from hypothesis; it consists in stating the fact, that sulphuric acid and alcohol are transformed into sulphovinic acid and water, by half the hydrogen of the former changing places with the carburetted hydrogen of the latter; thus:



Now from this point it is clear that the process is the same as in the decompositions above described; for by this sulphovinic acid coming in contact with an atom of alcohol, it reacts exactly in the same manner as the iodide did, forming of course sulphuric acid and ether:



The sulphuric acid thus reproduced comes again in contact with alcohol, forming sulphovinic acid, which re-acts as before; and so the process goes on continuously, as found in practice.

We thus see that the formation of ether from alcohol is neither a process of simple separation, nor one of mere synthesis; but that it consists in the substitution of one molecule for another, and is effected by double decomposition between two compounds. This

view of the matter is therefore consistent with the contact theory, inasmuch as it acknowledges the circumstance of contact as a necessary *condition* of the reaction of the molecules upon one another. By reducing the formulæ of the alcohols to one atom of oxygen, it also retains the equality of volumes which the contact theory insists upon between the vapours of these bodies and their ethers, so that ether truly contains the elements of olefiant gas in addition to those of alcohol in one atom. But, on the other hand, it attaches equal importance to all the essential facts of the chemical theory, and rests the explanation of the process as much upon them as upon those of the contact theory; for, one-sixth of the hydrogen in alcohol truly exhibits different reactions from the remaining five, and must therefore be contained in that compound in a different manner from them; and the alternate formation and decomposition of sulphovinic acid is in this, as well as in the chemical theory, the key to explaining the process of etherification.

Innovations in science frequently gain ground *only* by displacing the conceptions which preceded them, and which served more or less directly as their foundation; but, if the view here presented be considered a step in our understanding of the subject, the author begs leave to disclaim for it the title of innovation; for the conclusion here deduced consists in showing the compatibility of views which have hitherto been considered contrary; and the best possible justification of the eminent philosophers who have advocated either one of the two contending theories, is thus afforded by reconciling their arguments with those of their equally illustrious opponents.

Let us now direct our attention to the transfer of homologous molecules in alternately opposite directions, which, as we have endeavoured to show, is the cause of the continuous action of sulphuric acid in this remarkable process. It may naturally be asked, why do hydrogen and carburetted hydrogen thus continuously change places? It cannot be from any such circumstance as superior affinity of one molecule over another, for one moment sees reversed with a new molecule the transfer effected during the preceding one. Now, in reflecting upon this remarkable fact, it strikes the mind at once that the facility of interchange must be greater the more close the analogy between the molecules exchanged; that if hydrogen and amyl can replace one another in a compound, hydrogen and ethyl, which are more nearly allied in composition and properties, must be able to replace one another more easily in the same compound; and that the facility of interchange of hydrogen and methyl, which are still more similar, will be still greater. But if this be true, must not the exchange of one molecule for another of *identical* properties be the most easily effected of all? Surely it must, if there be any difference at all; and if so, the law of analogy forbids our imagining the fact to be peculiar to hydrogen among

substances resembling it in other respects. We are thus forced to admit, that, in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition Cl H , the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine. Of course this change is not directly sensible to us, because one atom of hydrochloric acid is like another; but suppose we mix with the hydrochloric acid some sulphate of copper (of which the component atoms are undergoing a similar change of place), the basyous elements, hydrogen and copper, do not limit their change of place to the circle of the atoms with which they were at first combined,—the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and sulphuric acid. Thus it is, that at any moment of time in which we examine the mixture, the bases are divided between the acids; and in certain cases, where the difference of properties of the analogous molecules is very great, it is found that the stronger acid and stronger base remain almost entirely together, leaving the weaker ones combined. This is well known in the case of a mixture of sulphuric acid and borax, and is a confirmation of our fundamental assumption, that the greater the difference of properties, the more difficult is the alternate interchange of one molecule for another.

But suppose now, that instead of sulphate of copper, we mixed sulphate of silver with our hydrochloric acid in aqueous solution, and that a similar division of the bases between the acids established itself in the first moment, forming four compounds, $\text{SO}^4 \text{H}^2$, $\text{SO}^4 \text{Ag}^2$, ClH , Cl Ag ; it is clear, that this last-mentioned compound, being insoluble in water, must, on its formation, separate out and remove from the circle of decompositions which solubility established. But, of course, the three compounds remaining in solution continue the exchange of their component parts, and give rise successively to new portions of chloride of silver, until as much of that compound is precipitated as the liquid contained equivalents of its component parts, a very small quantity remaining in solution and in the circle of decompositions.

Such is the general process of chemical decomposition. Of course a compound is removed as effectually from the circle of decompositions by assuming the gaseous form under the circumstances of the experiment, or even by being a liquid insoluble in the menstruum. This explanation coincides in its second part with that

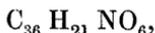
which was proposed many years ago by Berthollet; but not making use of the atomic hypothesis, upon which the preceding explanation is based, that eminent philosopher went no farther back than the division of the acids between the bases on the mixture of salts, a fact here deduced from the motion of atoms. It is well known, that the general fact upon which Berthollet founded his view is denied by some eminent chemists of the present day; but the instances which they adduce are perhaps only apparent exceptions to the law, and will, on further examination, be found to afford additional confirmation of the truth of the great Savoysien's conception, as already shown in the case of boracic and sulphuric acids.

In using the atomic theory, chemists have added to it of late years an unsafe, and perhaps unwarrantable hypothesis, namely, that the atoms are in a state of rest. This hypothesis the author of the present paper discards, and reasons upon the broader basis of atomic motion.

On the Constitution of Codeine, and its Products of Decomposition.

By T. Anderson, M.D.*

The composition of codeine has been variously stated by different chemists. According to Regnault, the formula of anhydrous codeine is $C_{35}H_{20}NO_5$, and that of the crystallised base $C_{35}H_{20}NO_5 + 2HO$. Gerhardt, however, objects to this formula, because the numbers of equivalents of carbon and oxygen are uneven, and the sum of the equivalents of hydrogen and nitrogen is likewise indivisible by two. From his own analysis, Gerhardt deduces the formula :



and this formula is fully confirmed by the recent researches of Dr. Anderson.

The codeine with which the author's experiments were made was prepared, as usual, from the mother-liquor from which morphia had been precipitated by ammonia. This liquid was evaporated to crystallisation, and the crystals pressed, to separate the hydrochlorate of ammonia, which is more soluble than the hydrochlorate of codeine, these operations being repeated till the greater part of the sal-ammoniac was got rid of. The crystals of hydrochlorate of codeine were then dissolved in boiling water, and the solution treated with caustic potash, whereby the codeine was precipitated as an oil, which afterwards concreted into a solid mass and was partly deposited in crystals as the solution cooled.

Another crop of crystals may be obtained by evaporating the solution, and the mother-liquor, when concentrated to a small bulk, becomes

* Transactions of the Royal Society of Edinburgh.

filled on cooling with long silky needles of morphia, which had been retained in solution by the excess of potash. The crystals of codeine are purified by solution in hydrochloric acid, boiling with animal charcoal and reprecipitation by potash; and the resulting precipitate is finally dissolved in hydrous ether free from alcohol, to separate any morphia that may adhere to it. Anhydrous ether dissolves codeine much less easily; the solution when evaporated yields small crystals of anhydrous codeine. Codeine, crystallised from water or hydrous ether, forms crystals belonging to the right prismatic system, and containing 2 equivalents of water, which are given off at 212° .

Codeine is an extremely powerful base, rapidly restoring the blue colour of reddened litmus, and precipitating the oxides of lead, copper, iron, cobalt, nickel, &c., from their solutions. It is precipitated by potash from its salts, and is generally stated to be insoluble in that alkali; but this is true only of very highly concentrated solutions, as a considerable quantity of strong potash may be added to a saturated solution of codeine in water without producing precipitation, and even when a very large amount of potash is added, a certain quantity of the base is still retained in solution. Codeine is soluble in ammonia, but not more so than in water; 100 parts of a moderately strong solution of ammonia at 60° dissolve 1.40 parts of codeine; and, according to Robiquet, 100 parts of water at 59° dissolve 1.26 parts. Codeine is precipitated from all its solutions by ammonia; it does not, however, fall immediately, but is slowly deposited in small transparent crystals.

SALTS OF CODEINE.

Hydrochlorate.— $C_{36}H_{21}NO_6 \cdot HCl$. Obtained by saturating hot hydrochloric acid with pure codeine. A concentrated solution becomes nearly solid on cooling; but a more dilute solution yields radiated groups of short needles, which under the microscope are found to be four-sided prisms with dihedral summits. The crystals are soluble in 20 parts of water at 60° , and in less than their weight of boiling water. The salt dried in the air retains 4 equivs. of water; one which goes off at 212° , and the other three at 250° ; the salt at the same time losing acid and acquiring an alkaline reaction. The salt is also sometimes deposited from its solution in anhydrous crystals.

Hydriodate of Codeine.— $C_{36}H_{21}NO_6 \cdot HI$. Obtained by dissolving codeine in hot hydriodic acid, and leaving the solution to cool, whereupon it is deposited in long slender needles which fill the whole liquid, if it has been sufficiently concentrated. Soluble in 60 parts of cold water; more soluble in boiling water. The crystals contain 2 atoms of water.

Sulphate of Codeine.— $C_{36}H_{21}NO_6 \cdot HO \cdot SO_3$. Crystallises in radiated groups of long needles, or by spontaneous evaporation in flattened four-sided prisms. Dissolves in 30 parts of cold water; very

soluble in hot water. Neutral to test paper, when pure; but very apt to retain a small quantity of acid, which can only be got rid of by repeated crystallisation. The crystallised salt contains 5 equivalents of water, which are given off at 212° ; the formula of the crystallised salt is $C_{36}H_{21}NO_6 \cdot HO \cdot SO_3 + 5 Aq.$

Nitrate of Codeine.— $C_{36}H_{21}NO_6 \cdot HO \cdot NO_5.$ Formed by slowly adding nitric acid of specific gravity 1.060 to powdered codeine, an excess of acid being carefully avoided. Easily soluble in boiling water, from which it is deposited in small prismatic crystals on cooling. When heated on platinum, it melts, and on cooling concretes into a brown resinous mass; at a higher temperature, it is rapidly decomposed, leaving a bulky coal difficult of incineration.

Phosphate of Codeine.— $C_{36}H_{21}NO_6 \cdot HO \cdot 2 HOPO_5.$ When tribasic phosphoric acid is saturated with powdered codeine, and the solution mixed with strong spirit, this salt is obtained in small scales or short thick prisms, which are readily soluble in water. They contain 3 equivalents of water of crystallisation, which are given off at 212° .

Oxalate of Codeine.— $C_{36}H_{21}NO_6 \cdot HO \cdot C_2O_3.$ Deposited, on cooling its hot saturated solution, in short prisms, or sometimes in scales. Soluble in 30 times its weight of water at 60° , and about half its weight at 212° . The crystals heated to 212° gave off 3 equivalents of water. At 250° the salt turns brown, and at a higher temperature is entirely decomposed.

Hydrosulphocyanate of Codeine.— $C_{36}H_{21}NO_6 \cdot HC_2NS_2.$ Deposited in beautiful radiated needles, on mixing the solutions of hydrochlorate of codeine and sulphocyanide of potassium. The crystals contain 1 equivalent of water, which they give off at 212° .

Chloride of Platinum and Codeine.—A moderately concentrated solution of hydrochlorate of codeine, mixed with bichloride of platinum, deposits a pale-yellow pulverulent precipitate; a more dilute solution yields no immediate precipitate, but after a time deposits minute tufts of silky needles. The salt is soluble in water, and on cooling is deposited partly in grains, partly as a powder; not, however, without partial decomposition. By ebullition with excess of chloride of platinum, it is completely decomposed. To obtain it pure, it must be precipitated in the cold, and without excess of chloride of platinum. The formula of the crystallised salt is $C_{36}H_{21}NO_6 \cdot HCl + PtCl_2 + 4 HO.$ At 212° it gives off 3 equivalents of water, and the remainder is expelled at 250° , the salt at the same time turning brown and being partially decomposed.

Codeine forms many other crystallisable salts, none of which, however, have been completely examined. The chromate forms fine yellow needles. With solution of corrosive sublimate, codeine forms a white precipitate, soluble in boiling water and alcohol, and deposited in stellate groups of crystals on cooling. With chloride of palladium,

a yellow precipitate is obtained, which is decomposed on boiling, and yields metallic palladium. The tartrate and hydrocyanate of codeine are uncrystallisable.

PRODUCTS OF DECOMPOSITION OF CODEINE.

Action of Sulphuric Acid.—Amorphous Codeine.—When codeine is dissolved in moderately strong sulphuric acid, the mixture digested for a while on the sand-bath, and then treated with carbonate of soda, a grey precipitate is obtained, consisting of codeine in an amorphous state. The precipitate must be collected on a filter, washed with water, dissolved in alcohol, and precipitated from the solution by water. It then forms a grey powder, with more or less of a green shade, insoluble in water, readily soluble in alcohol, and precipitated by ether from the alcoholic solution. Fuses at 212° to a black resinous mass. Readily soluble in acids, forming salts which are amorphous, and dry up by evaporation into brown resins. Analysis shows it to be identical in composition with codeine in its ordinary state. The action of sulphuric acid upon codeine is indeed analogous to that which it produces upon quinine, but the resulting amorphous codeine is not so stable a substance as quinoidine. Moreover, the action does not stop at the point at which amorphous codeine is produced; for if it be continued, a deep-green substance is formed containing sulphur, and analogous to the sulphomorphide described by Arppe, and the corresponding sulphonarcotide of Laurent and Gerhardt.

Action of Nitric Acid.—Nitrocodeine— $C_{36}H_{20}NO_4NO_6$. When strong nitric acid is poured upon codeine, and heat applied, violent action takes place, nitrous fumes are abundantly evolved, and the solution acquires a red colour. If the fluid be evaporated over the water-bath, a yellow resinous acid is left, soluble, with a red colour, in ammonia and potash; but when dilute acid is used, a nitro-base is obtained having the composition above given. The best mode of preparing it, is to add finely powdered codeine to nitric acid of specific gravity 1.060, kept at a moderate heat in a flask, small portions of the liquid being taken out every now and then and tested with ammonia, till the precipitate formed on neutralising the acid, no longer increases in quantity. The liquid is then to be saturated with ammonia, and stirred rapidly, whereupon it will become filled with a bulky precipitate of nitrocodeine. The action is very rapid, and great care must be taken not to let it go too far, otherwise the resinous substance above-mentioned will be produced, its formation being indicated by the escape of red fumes; it is best to stop the action before the whole of the codeine is decomposed; but even then it is impossible to avoid the formation of a small quantity of the resinous substance, its

presence being indicated by the dark colour which the liquid assumes on the addition of ammonia. The precipitate formed by ammonia is in the form of minute silvery plates, with a very slight shade of yellow. It is purified by solution in hydrochloric acid, boiling with animal charcoal, and reprecipitating with ammonia, and subsequently crystallised from a solution in alcohol, or in a mixture of alcohol and ether.

Nitrocodeine crystallised from alcohol is deposited in the form of slender silky needles, which have a pale fawn colour, and, on drying, mat together into a silky mass. From alcohol and ether it is obtained by spontaneous evaporation in small yellowish crystals, which, under the microscope, are seen to consist of four-sided prisms terminated by dihedral summits. Nitrocodeine is sparingly soluble in boiling water, from which it is deposited in minute crystals on cooling. It dissolves abundantly in boiling alcohol, but sparingly in ether. It is soluble in acids, forming salts which are neutral to test paper, and yield the base in the form of a crystalline powder on the addition of potash or ammonia. When heated carefully, it melts into a yellow liquid, which concretes on cooling into a highly crystalline mass. At a higher temperature it decomposes suddenly without flame, leaving a bulky charcoal. Crystallised nitrocodeine is anhydrous.

Hydrochlorate of Nitrocodeine is obtained by dissolving nitrocodeine in hydrochloric acid, and evaporating the solution, whereupon the salt is left in the form of a resinous mass, which cannot be made to crystallise.

Sulphate of Nitrocodeine, $C_{36}H_{20}(NO_4)NO_6 \cdot HO \cdot SO_3$, forms radiated groups of short-pointed needles, neutral to test-paper, and very soluble in boiling water.

Oxalate of Nitrocodeine crystallises in short prisms of a fine yellow colour, readily soluble in water.

Platinochloride of Nitrocodeine, $C_{36}H_{20}(NO_4)NO_6 \cdot HCl + PtCl_3 + 4HO$, is precipitated from the solution of the hydrochlorate in the form of a yellow powder, insoluble in water and alcohol.

By treating an alcoholic solution of nitrocodeine with hydrosulphate of ammonia, a new base is obtained, which, from its analogy with other compounds similarly prepared, is probably composed of $C_{36}H_{22}N_2O_6$, and may be called *Azocodeine*; it has not yet, however, been completely examined, on account of the great difficulty of preparing and purifying it.

Action of Bromine on Codeine.—Bromocodeine— $C_{36}H_{20}BrNO_6$. When bromine-water is added in small successive portions to finely powdered codeine, the base is rapidly dissolved, the solution losing its colour of bromine, and acquiring a peculiar and characteristic red shade. After a certain quantity of bromine has been added, small crystals make their appearance, which are hydrobromate of codeine; but these

are only observed if the bromine-water has been thoroughly saturated, and are deposited in a small quantity only, the remainder being retained in solution. When the whole of the codeine has been dissolved, ammonia is added, and bromocodeine is immediately thrown down as a silvery-white powder; in this state it contains a small quantity of unchanged codeine. It is collected on a filter, washed several times with cold water, and redissolved in hydrochloric acid, from which it is precipitated by ammonia, and finally crystallised from boiling spirit. Bromocodeine is scarcely soluble in cold water; but by boiling, a somewhat larger quantity is taken up, and deposited again on cooling in minute prisms terminated by dihedral summits. It is readily soluble in alcohol, particularly on boiling, and is best crystallised from spirit diluted with its own bulk of water. The crystals are always very small, but brilliantly white. It is soluble in ether. When heated, it melts into a colourless liquid, which is destroyed at a temperature somewhat above its melting-point. It dissolves in cold sulphuric acid, and the solution becomes dark-coloured when heated. It is attacked by nitric acid, but much less rapidly than codeine itself. Bromocodeine forms two hydrates, the first containing one, and the second two equivalents of water. Hydrochlorate of bromocodeine forms radiated needles closely resembling those of hydrochlorate of codeine. The hydro-bromate is sparingly soluble in cold water, readily soluble in boiling water, and is deposited from the solution in small prismatic crystals. It contains two equivalents of water, which are not expelled at 212° .

Tribromocodeine.— $C_{36}H_{28}Br_3NO_6$. By continuing the addition of bromine-water beyond the point at which bromocodeine is formed, a further action takes place, and a bright-yellow precipitate makes its appearance, which at first re-dissolves in the liquid, but after a time becomes permanent and goes on gradually increasing, till a very large quantity of bromine has been added, when at length a point is reached at which no further precipitate is produced. If the solution be left till next day, however, bromine again causes a precipitate; and if it be added as long as anything falls, and the solution be again left standing, another precipitate is produced, identical in all respects with that before obtained; and this may be repeated day after day for a very considerable time. The yellow precipitate thus obtained is the hydrobromate of tribromocodeine. It is collected on a filter and washed with water, in which it is very sparingly soluble. When this salt is dissolved in dilute hydrochloric acid, and ammonia added, the tribromocodeine is immediately precipitated as a flocculent powder, which must be washed with water, and purified by solution in alcohol and precipitation by water.

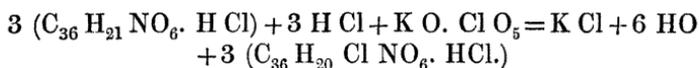
Tribromocodeine, as thus obtained, is a bulky white precipitate, perfectly amorphous, and when dry, more or less grey in its colour. It is insoluble in water and ether, but readily soluble in alcohol.

Hydrochloric acid dissolves it sparingly in the cold, but more readily on boiling; in this process, however, it appears to undergo a partial decomposition, as a small quantity is always left insoluble. Heated on platinum-foil it becomes brown, and is entirely decomposed at its melting-point, leaving a coal difficult of incineration.

In such cases as have been hitherto examined, the substitution of three equivalents of bromine in a base has entirely destroyed its basic properties; but tribromocodeine is a base, though a very feeble one. Its salts are all sparingly soluble in water, and amorphous. The *hydrochlorate* is obtained by dissolving the base in hot dilute hydrochloric acid, and is deposited on cooling as an amorphous powder. The *hydrobromate* is the substance deposited during the preparation of the base. It is a bright-yellow powder, perfectly amorphous, and very sparingly soluble in cold water; on boiling, however, a larger quantity is taken up, and is again deposited on cooling. Its composition appears to be $2(C_{36}H_{18}Br_3NO_6) + HBr$. The *platinochloride* is a brownish-yellow powder, soluble in water and alcohol.

The action of bromine on codeine does not terminate with the production of the base just described, but the author has not pursued the investigation any further. There must also exist a *dibromocodeine*, $C_{36}H_{19}Br_2NO_6$, but it has not yet been actually obtained.

Action of Chlorine on Codeine.—Chlorocodeine— $C_{36}H_{20}ClNO_6$. The action of chlorine on codeine is more complex than that of bromine. When chlorine gas is passed into an aqueous solution of codeine, or chlorine-water added to it, the liquid turns brown, becoming continually deeper in colour, and on the addition of ammonia yields an amorphous resinous base. As there were no means of determining when the action was complete, the product was not further examined. A definite compound, analogous to bromocodeine was, however, obtained by dissolving codeine in excess of dilute hydrochloric acid at about 150° or 160° Fahr., adding finely pounded chloride of potash—agitating the liquid—continually testing with ammonia, and adopting precautions similar to those required in the preparation of nitro-codeine, and finally precipitating by ammonia. The reaction is as follows:



The chlorocodeine is precipitated in the form of a silvery crystalline powder, closely resembling bromocodeine. It has generally a yellowish colour, and retains a small portion of codeine, from which it is purified by dissolving in hydrochloric acid, boiling with animal charcoal, and reprecipitating with ammonia. It is finally obtained in crystals from its solution in boiling spirit.

Chlorocodeine is sparingly soluble in boiling water, and the solution

on cooling deposits minute crystals exactly similar to and isomorphous with those of bromocodeine. It is readily soluble in strong alcohol, especially with the aid of heat, and sparingly soluble in ether. It dissolves in sulphuric acid in the cold, without change, but the solution is charred by heating. Nitric acid dissolves it, and the solution is decomposed by boiling, but not by any means so readily as codeine. Red fumes are evolved, together with a peculiar and excessively pungent vapour.

The salts of chlorocodeine are exactly similar to those of bromocodeine. The *hydrochlorate* crystallises in groups of needles, readily soluble in water. The *sulphate*, $C_{36}H_{20}ClNO_6 \cdot HO \cdot SO_3 + 4 Aq$, is deposited from its hot solution in radiated groups of short prisms, which dissolve abundantly in boiling water and alcohol. The *platinochloride* is obtained in the usual way, in the form of a pale-yellow precipitate, scarcely soluble in water.

Action of Cyanogen on Codeine.—Dicyanocodeine— $C_{36}H_{21}NO_6 \cdot 2 C_2N$.—When cyanogen is passed into a solution of codeine in the smallest possible quantity of alcohol, the gas is rapidly absorbed, the liquid acquiring first a yellow, and by continued action, a brown colour. If the solution be then left to itself for some time, the smell of cyanogen disappears and is replaced by that of hydrocyanic acid, and crystals are gradually deposited. If the cyanogen be passed through the solution in a slow continuous current, the deposit of crystals is very abundant. These are collected on a filter, and washed with a small quantity of alcohol; and the filtrate, on being again exposed to the action of cyanogen, yields an additional quantity of crystals, but not so pure as the former. The product is purified by solution, with the aid of heat, in a mixture of alcohol and ether, from which it is deposited in crystals which are colourless or slightly yellow. Obtained in this way, however, they are apt to retain a small quantity of codeine, and it is therefore advantageous to pass cyanogen into the mixture to be used for their solution, by which means the last traces of codeine are converted into the new compound.

Dicyanocodeine is soluble in boiling absolute alcohol or a mixture of alcohol and ether, and is deposited on cooling in anhydrous, thin, six-sided plates, having a brilliant lustre. It is difficultly soluble in water, but is dissolved on the addition of alcohol. Nothing, however, is deposited from the solution on standing, and by evaporation it is decomposed, and crystals of codeine are left behind. With hydrochloric acid it is converted into a crystalline salt, but decomposition takes place immediately; for, on the addition of potash to the liquid, ammonia escapes, and, if it be left for twenty-four hours, hydrocyanic acid is evolved. With sulphuric and oxalic acid, dicyanocodeine likewise forms sparingly soluble compounds, which decompose rapidly, with evolution of ammonia and hydrocyanic acid. The instability of these compounds prevented their further examination.

Dicyanocodeine belongs to the same class of compounds as cyaniline, but differs from that substance in containing two equivalents of cyanogen.

ACTION OF ALKALIS ON CODEINE.

Codeine, when treated at moderate temperatures with potash, yields more than one volatile base, according to the circumstances under which the experiment is made. Similar results are obtained by the use of hydrate of potash, or of potash-lime or soda-lime, prepared in the usual way. The method employed in the experiment was to mix codeine with four or five times its weight of potash-lime or soda-lime, and introduce the mixture into a retort with a tubulated receiver, having a doubly bent tube attached to its tubulature, the end of which passed into a small flask containing hydrochloric acid, in order to retain any of the very volatile base which might not be condensed in the receiver. The retort was introduced into an oil-bath, and kept at a uniform temperature of 250° Fahr. As soon as this temperature is reached, a slight peculiar odour is observed, which soon becomes more powerful, and a small quantity of water, retaining the bases in solution, collects in the receiver. The decomposition at 250° , however, is excessively slow, and even after many days, bases are evolved apparently in undiminished quantity; but the mixture was maintained steadily at this point, in hopes of obtaining the product free from ammonia, which the preliminary trials had shown to be produced at higher temperatures; but even with this low heat, it was evolved always in appreciable and, in some experiments, even in considerable quantity. The temperature was, therefore, gradually raised to about 350° , when a larger quantity of base was obtained; and after the heat had been sustained for some time, small crystals made their appearance, which deposited themselves in a line round the retort, just above the level of the oil in the bath, but soon rose into, and collected in the neck of the retort.

These crystals resemble benzoic acid in their external appearance, and are at first perfectly colourless, but soon acquire a brownish shade by exposure to light and air. They are a base, and rapidly restore the colour of reddened litmus. They are sparingly soluble in water, but readily in acids, and give a precipitate with bichloride of platinum. The quantity of this substance obtained was excessively minute; and though considerable quantities of codeine were operated upon, all that was obtained served only to make the few qualitative experiments now detailed.

The watery fluid which collected in the receiver possessed a pungent and peculiar smell; it restored the colour of reddened litmus with great rapidity, and gave abundant fumes with hydrochloric acid. On the addition of solid potash, a highly volatile and pungent oily base

collected as a layer on the surface of the fluid, and at the same time a gaseous base escaped along with ammonia. From the small quantity of these substances obtained, it was impossible to obtain any of them in a pure state. Their constitution was, therefore, determined by the analysis of their platinum-salts, which can be separated from one another, though not without difficulty. In order to prepare these salts, the basic fluid was saturated with hydrochloric acid, and evaporated to dryness in the water-bath, when it left behind a beautifully crystalline mass, highly soluble in water, and deliquescent in moist air. This was dissolved in absolute alcohol, to separate ammonia, and the filtered solution mixed with an alcoholic solution of bichloride of platinum, when the platinum-salts were immediately thrown down as a pale-yellow powder, very sparingly soluble in absolute alcohol, but readily dissolved on the addition of water. The separation of the two bases is best effected by heating the washed precipitate with boiling absolute alcohol, and adding water in small quantities until the whole is dissolved. The crystals which deposit on cooling consist of one of the salts in a state of purity, if the process has been properly managed, or, at all events, only require a repetition of the process to make them absolutely pure. The salt thus obtained is scarcely soluble in absolute alcohol or ether, but is readily soluble in water and dilute spirit, and is thrown down from the latter solution by ether, in the form of fine yellow scales. Its analysis gave results agreeing with the formula $C_2H_5N \cdot HCl \cdot PtCl_2$. The base is, consequently, the methylamine of Wurtz, with whose description of that substance and its platinum-salt it perfectly agrees.

The preparation of the platinum-salt of the other base was attended with much greater difficulty; and it could not be obtained quite free from methylamine. In order to obtain it, the fluid which had deposited the methylamine-salt must be evaporated to a small bulk, the salt which separated filtered off, and ether added to the mother-liquor. Immediately a precipitate is obtained, generally in the form of minute yellow needles, but sometimes in scales. It is sparingly soluble in alcohol and ether, and highly soluble in water, from which it crystallises in long needles, and with such facility that a few drops evaporated on a watch-glass, leave the salt they contain in the form of five or six needles crossing the whole space occupied by the solution. The quantity of this salt was too small to admit of carrying its purification by recrystallisation as far as was to be desired, and consequently a small quantity of methylamine remained in those subjected to analysis.

The results of the analysis approach most closely to the formula $C_6H_9N \cdot HCl \cdot PtCl_2$; consequently that of the base itself C_6H_9N . The base, then, obviously belongs to the same series as methylamine, and forms the term of the series corresponding to metacetic acid, and, in accordance with the system of nomenclature adopted by Wurtz, it

receives the name of metacetamine. No examination was made of the salts of this base, as it was not obtained in sufficient quantity, but the author takes the opportunity of stating, that before obtaining it from codeine, he had ascertained its existence among the products of destructive distillation of animal substances.*

The residue in the retort after these bases have been evolved, is dark-cinnamon-brown and slightly coherent; it dissolves in water, with a dark-brown, almost black colour, and gives with acids a flocculent brown precipitate of a humus-like substance, and perfectly amorphous, which was not examined. It still contains nitrogen; and by exposure to a heat gradually raised to low redness, it gives an additional quantity of volatile bases, among which ammonia becomes more and more abundant as the temperature rises. A non-basic oil also makes its appearance, but only in very small quantity.

Wertheim† has lately examined the action of soda-lime on certain organic bases. He has obtained metacetamine from narcotine, and methylamine from morphia; and considering these substances to be directly eliminated from the bases, he expects to obtain the residual atoms in the form of a definite compound. Dr. Anderson entertained a similar idea with regard to codeine, until he detected the formation of two different bases, which seemed to him rather to indicate that these substances appear as the result of a true destructive distillation; and that possibly by varying the circumstances of the experiment, other bases may be obtained.

The author has also observed another remarkable decomposition of codeine, by which volatile bases are obtained. The formation by the action of nitric acid, of a resinous acid, has already been mentioned. This acid, which is insoluble in water, dissolves readily in dilute potash, with a red colour; and the solution, on boiling, evolves a volatile base in great abundance. The further examination of the circumstances under which this change takes place, is reserved for a future communication.

Dr. Anderson has likewise examined the action of iodine on codeine, which yields a magnificent crystalline compound, presenting the phenomena of pleochroism in a remarkable manner.

* The author has likewise convinced himself that the petinine described by him two years since as existing in bone-oil, is represented by the formula $C_8 H_{11} N$, and not by $C_3 H_{10} N$, which he then gave for it. He has also ascertained the existence of ethylamine and methylamine in bone-oil.

† Ann. Ch. Pharm. LXXIII, 208.