

CXLVIII. *On Atomic Volume and Specific Gravity.*
By LYON PLAYFAIR, Esq., Ph.D. and J. P. JOULE, Esq.

SECTION I.

THE discovery of Gay-Lussac, that gaseous bodies combine in equal or in multiple volumes, and that the resulting compounds stand in a similar simple relation to their constituents, is one of the most important discoveries ever made in physical science. Its utility has been diminished by its supposed inapplicability to liquid and solid bodies, as its own exactitude at different temperatures is entirely owing to the equal expansibility of the same volumes of different gases by equal increments of heat.

In its most simple form, therefore, it was *à priori* impro-

bable that the law of Gay-Lussac should apply to the liquid and solid forms of matter. But, as the larger number of substances are either liquid or solid, and incapable of passing into the gaseous state, even at very high temperatures, the importance of discovering the law which governs the volumes of these forms of matter, has long been recognised, and for some time past has much engaged the attention of philosophers.

The first chemist who drew attention to this subject was Dr. Thomson, who published a Table*, in the year 1831, of the specific volumes of certain of the metals, obtained by dividing their atomic weights by their specific gravities. In this table a remarkable coincidence of volume is observed in several of the metals most nearly allied in chemical characters.

More recently the subject has been examined in detail by Kopp, Schröder and Persoz, whose researches have thrown considerable light on this obscure department of physics.

Kopp† drew attention to the circumstance, that in many cases isomorphous bodies possess the same atomic volume, the law being correct when the isomorphism is strictly accurate, but approximating only when this is not the case. He admits also that perfect equality of the volume exists only at particular temperatures, on account of the unequal expansion of isomorphous crystals.

Schröder‡ made the interesting observation, that the remainder is the same when the primitive volume of the corresponding member of a series of analogous compounds is subtracted from them; thus AO, BO and CO leave a constant remainder when the known volumes of A, B and C are subtracted respectively from the known atomic volumes of the compounds.

Kopp§ confirms this discovery to a certain extent, believing, however, that the primitive volumes A, B and C must be assumed in certain classes of salts to be different when in combination with O from their volumes when isolated. He also announces the discovery|| of a great regularity in the physical properties of analogous organic compounds, so much so, that the study of the physical characters of the compounds of one body enables us to predicate those of the corresponding compounds of another substance.

The discoveries of Schröder and Kopp, with regard to

* Chemistry of Inorganic Bodies, vol. i. p. 14.

† Poggendorff's *Annalen*, Band xlvii.; and *Annalen der Chemie*, Band xxxvi. S. 1.

‡ Poggendorff's *Annalen*, Band l. S. 554.

§ *Ueber das Specifische Gewicht der Chemischen Verbindungen*. Frankfurt, 1841.

|| *Annalen der Chemie*, Band xli. S. 79.

the atomic volumes of liquid and solid bodies, do not, except in a very few instances, indicate an approach to a simple multiple ratio of volumes, and are therefore only in a small degree connected with the law of gaseous volume. We therefore thought it desirable to enter into a series of inquiries on this most important subject, and we have now the honour to lay before the Society the First Part of these researches.

Hitherto the inquiry has been principally confined to solid bodies, on the just ground that their diminished rate of expansion offers less difficulty to the discovery of the law regulating volumes. But there is an objection to the use of solids, which to a certain extent counterbalances this advantage, viz. that they do not present matter in a perfectly uniform condition, free from cohesion. On consideration, therefore, we were led to believe this objection to be so powerful, that we conceived it to be preferable, so to separate the particles of the body under examination, as to destroy their cohesion, without at the same time altering their chemical properties. Solution in water was the obvious means of effecting this purpose, according to the notions generally entertained of solution, and it was therefore resolved to experiment principally upon soluble bodies of well-known and defined constitution. At the same time, it was necessary to examine the relation of the solid volume to the volume of the body when in solution, so as to indicate the connection between the solid and the liquid atom.

The specific gravities of salts are little known, and even when recorded are described so differently by different observers, that it was necessary to determine the specific gravity in each of the cases upon which the experiments were instituted. Hitherto the volumes of solids had always been referred to an equal volume of water; in other words, the *solid* form of matter had been referred to its *liquid* form. This difference of conditions was no small impediment to the discovery of a law which might be modified for each form of matter*. By determining the volume of the substance in solution, we compared it in its liquid state to the liquid form of matter in

* Before leaving the notice of the labours of those who have preceded us in inquiring into the nature of specific gravity, we must not omit to notice the speculations of the ingenious Persoz, who (in vol. xl. of the *Ann. de Ch. et de Phys.*, p. 119) drew attention to the equality in volume of isomorphous bodies, and even of some which were not isomorphous. Persoz also believes that the volumes of all bodies are multiples of 56, or half the atomic weight of water; but this idea does not agree with recorded observations, and is directly contradicted by accurate estimations of specific gravities.—See the work of M. Persoz, *Introduction à l'Etude de la Chimie Moléculaire*, page 834 *et seq.*

which it was dissolved; and by contrasting the volume of the solids with each other, and also with their volume when rendered liquid by water, we conceived that we might be placed in more favourable conditions for elucidating a law.

Bishop Watson* was the first chemist who endeavoured to estimate the increase of volume when salts dissolve in water; for, although both Gassendus† and the Abbé Nollet‡ had written, and Ellis§ had experimented upon the same subject, they had arrived at conclusions entirely erroneous, which were removed by Watson's more accurate experiments. Watson's apparatus was rude enough, being a matrass capable of holding 67 ounces of water, into which he projected 24 penny-weights of each of the salts upon which he experimented, and noted the rise in the neck of the matrass. He completely exploded, however, the idea that saline substances dissolve in water without increasing its bulk.

Between the time of Bishop Watson, whose investigations on this subject are most profound, when we consider the period at which he wrote, and that of Dalton, there were no labourers in this field to whom we need draw especial attention. In the year 1840, Dalton|| made the interesting discovery, that sugar and certain salts on being dissolved in water increase its bulk only by the amount of water pre-existing in them. He generalized this observation by asserting that all hydrated salts dissolve in water, increasing its bulk merely by their amount of water of hydration, while anhydrous salts do not at all increase the bulk of the water in which they are dissolved.

But it must not be forgotten, that when Dalton published this paper, he was much enfeebled by illness, and on this account it does not derogate from the acuteness of the philosopher, that Mr. Holker was unable to confirm Dalton's results in repeating the experiments in 1843**. He did so, however, in the case of sulphate of magnesia, and approximately in that of one or two other salts. As Mr. Holker's paper has not been published, we are unable to state his claims in the progress of this subject; but we believe that an attempt was made to show a multiple relation in the increments of *isomorphous* salts, although his experiments were conducted

* Philosophical Transactions, 1770.

† *Gass. Phys.* lib. i. sect. 1. cap. 3.

‡ *Leçons de Physique*, vol. iv.

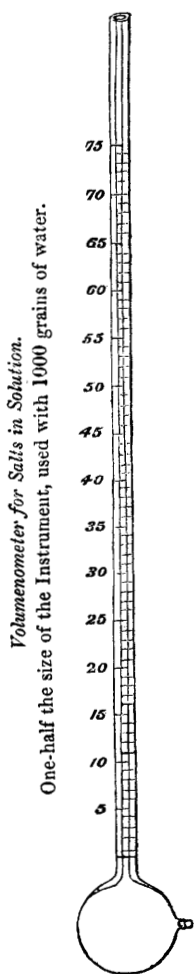
§ Berlin Memoirs, 1750.

|| "On the quantity of Acids, Bases and Waters in Salts, and a new mode of measuring them," read to the Manchester Literary and Philosophical Society, 6th October 1840, and published as a pamphlet.

** Paper read to the Manchester Literary and Philosophical Society, but not published.

without reference to the density or temperature of the solution on which he operated.

In the experiments about to be described, the apparatus for estimating the volume of bodies when dissolved, consisted of a glass bulb, to which a stem was attached. The bulbs varied in capacity from 1000 to 4000 grains of water, and the diameter of the stem was from one-eighth to one-sixteenth of an inch, according to the character of the experiment. In the bulbs employed for ordinary purposes, each grain of water occupied about a quarter of an inch in the stem, and as the graduation was made in grains of water at 60°, the experiment could be made to the tenth of a grain of increase in volume. In every case care was taken that the salts used were rigidly pure, and in their proper state of hydration. The distilled water employed to dissolve them was deprived of air by long-continued boiling, and preserved for use in stoppered bottles. The salt was introduced by a tubulure in the side of the bulb in the following manner. The bulb was filled with water until it reached a fixed point in the stem, when it was reclined and the stopper removed. A weighed quantity of salt was then introduced by a dry funnel, and the stopper reinserted, care being taken that no air was admitted during the operation; the increase in the stem, after the salt was dissolved, gave the volume of the quantity of salt used in the experiment. It was found by repeated trials that no loss of volume or error was occasioned by the moistening of the tube during the time it was in the reclining posture, for the precaution was always taken to moisten the walls of the tube previous to the

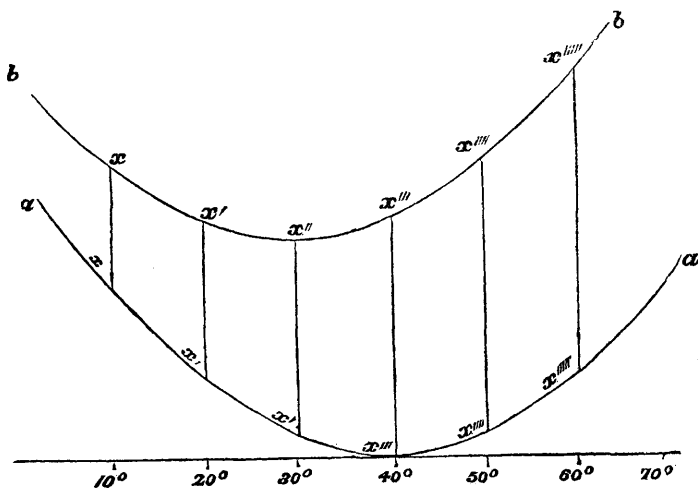


experiment. It is evident that the volume occupied by a salt in solution must be modified by the position of the point of its maximum density. Despretz has shown* that the temperature at which solutions are most dense becomes lower in proportion to the quantity of matter held in solution. It is also known, from the experiments of Dalton and others, that from the point of maximum density to about 30° above or below it,

* *Annales de Chimie*, tome lxx. an. 1839, p. 81.

water and dilute solutions expand according to the square of the temperature from that of greatest density. From Despretz's table of the expansion of water, it appears that the law is not true as far as 212° . As far however as it does hold good, it is evident, from the properties of the parabola, that the volume occupied by a salt in solution will increase in arithmetical progression with the temperature at which the experiment is made.

For instance, let $a a$ in the following diagram be a parabola representing the expansion of water, and let $b b$ be a similar parabola representing the expansion of a solution. Let the latter parabola have its vertex or point of greatest density opposite 30° , while the former parabola has its vertex at 40° ; then $x, x', x'', x''', \&c.$, quantities which increase in arithmetical progression, will represent the volumes occupied by the salt in solution at the temperature of $10^{\circ}, 20^{\circ}, 30^{\circ}, 40^{\circ}, 50^{\circ}, 60^{\circ}, \&c.$



In a similar manner it may be shown that the volume occupied by each equivalent of a salt in solution at any given temperature will increase with the density of the solution. In order to ascertain the amount of influence exercised by a change in the position of the point of maximum density, we have made a series of experiments on the expansion of water and of solutions by heat, which we propose to lay before the Society in a succeeding memoir. In order, however, to render evident the augmentation of volume caused by increased density, we have constructed the following table of the volumes

occupied by 172 grains, or one equivalent of sugar, in solutions of different degrees of density.

TABLE I.

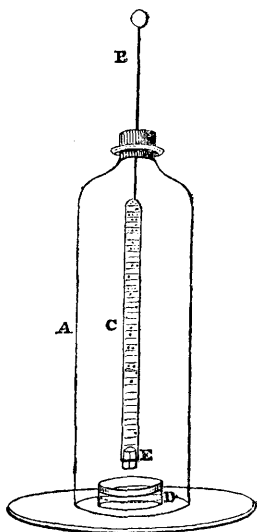
Ratio of the quantity of sugar to the quantity of water in which it was dissolved.	Temperature.	Volume in grain measures of water.
1 : 120	60°	99.00
1 : 10	52	105.09
1 : 1	52	107.01
3 : 1	52	108.06

As the rate of expansion of dilute solutions is so near that of water, it was in most cases sufficient, for a very close approximation to absolute accuracy, to take the observation within a few degrees below 60°, the temperature of the graduation of our volumenometers. Whether this temperature of graduation is the best to adopt, is a point which we shall have to discuss in our future communications; but at present it may be sufficient to state that its convenience was considerable, as being the average temperature of our laboratories. In all cases, then, in the following experiments, unless where it is otherwise stated, the temperature of the solution was about 60°, which was also, of course, the temperature of the water before the salt was introduced. In the case of the sulphates of the magnesian class of metals, the temperature chosen was higher than 60°, in order to make up for a diminished rate of expansion, owing to a greater degree of dilution in the solution.

The specific gravity of the salts was determined in an equally simple manner. A saturated solution of the salt about to be experimented upon (made by dissolving an excess of the salt by heat and allowing the solution to cool) was placed in the apparatus already described, and a weighed portion of the salt was then introduced, care being taken that the temperature did not vary during the experiment. As the new portion of salt could not dissolve, the increase in the stem indicated the volume due to the quantity of salt introduced, and afforded data for calculating the specific gravity. In many cases oil of turpentine was used instead of the saline solution.

It was frequently desirable, especially in the case of hydrated salts rendered anhydrous, to avoid the use of water, and in the case of organic compounds, also of turpentine; and to meet such cases we constructed the following simple apparatus, which we believe to possess various advantages.

A is the receiver of an air-pump, furnished at the top with a collar and sliding rod. B C is a small graduated tube filled with the substance, the volume of which is to be determined; it is closed with a stopper E, perforated with a hole of dimensions so small as to prevent any of the salt from falling out. D is a cup of mercury placed immediately below the graduated tube C. The sketch indicates the position of the apparatus on an air-pump when the experiment is about to be performed. The receiver is then exhausted as thoroughly as possible, and the indication of the siphon-gauge is accurately noted. The graduated tube is then lowered by means of the sliding rod until it touches the bottom of the cup containing the mercury, which, after the admission of air, flows into the tube until it is filled. The whole contents of the tube are then thrown into water, and the salt is washed away by decantation. The mercury is dried by bibulous paper, and restored to the tube. If the temperature be different from that which it possessed in the first part of the experiment, it is restored to the original temperature, or a correction is made for the difference. It is now obvious that the space in the tube unoccupied by the mercury is that which was formerly filled with the salt. To this, however, must be added a slight correction for the imperfect nature of the vacuum, which is not Torricellian,—a correction which need not exceed $\frac{1}{200}$ th of the volume observed. With these preliminary descriptions and observations, we now proceed to describe the details of our experiments, throwing them into various classified groups of salts, for the purpose of easy reference.



The first group described is remarkable for containing a large amount of water of hydration.

Sulphate of Copper, $\text{CuO}, \text{SO}_3 + 5\text{HO} = 124.88$.—The third part of an equivalent of this salt, 41.62 grains, dissolved in 3140 grains of water at 32° , with an increase of 13.15, but dissolved in water at 90° , with an increase of 15.0.

$\text{CuO}, \text{SO}_3 + 5\text{HO}$, vol. in solution 45.0.

Half an equivalent of this salt, 62.44 grains, being immersed in a saturated solution, occupied the volume of 27.7 water-grain measures.

	Sp. vol.	Sp. gr.
CuO, SO ₃ + 5HO, vol. of salt	55·4 ...	2·254

Kopp found for the specific gravity of this salt the number 2·274.

Sulphate of Alumina, Al₂O₃, 3SO₃ + 18HO = 333·7.—The salt used in the experiments was carefully prepared, and obtained in tolerably good crystals. The eighth part of an equivalent, 41·7 grains, dissolved in 1000 of water, with an increase of 20·0 in one experiment, and 19·9 in another, the temperature of observation being 51°.

I. Sulphate of alumina, vol. in solution	160·0
II.	159·2
Mean . .	159·6

The same quantity of salt thrown into turpentine caused in two experiments an increase of 25·0, and in a third of 24·9.

I. Sulphate alumina, vol. of salt	200·0 ...	Sp. gr.
II.	199·2 ...	1·675
Mean . .	199·6 ...	1·671

Sulphate of Soda, NaO, SO₃ + 10HO = 161·48.—Sulphate of soda, crystallized out of a strong warm solution, carries down 10 atoms of water. Of this salt, about one-fourth of an equivalent (40·4 grains), on being dissolved in 1000 grains of water, caused in two experiments an increase of 23·0, at a temperature of 59°; and in a third experiment of 22·8 at the same temperature.

I. II. NaO, SO ₃ + 10HO, vol. in solution =	91·8
III.	91·2
Mean . .	91·5

The same quantity of the salt being immersed in a saturated solution occasioned an increase of 27·8; and on a second experiment, of 27·2 at a temperature of 62°.

I. NaO, SO ₃ + 10HO, vol. of salt	111·1 ...	Sp. gr.
II.	108·7 ...	1·485
Mean . .	109·9 ...	1·469

When sulphate of soda crystallizes from a weak cold solution, it carries down a quantity of water, corresponding to eleven equivalents. In two experiments, the volume in solution of salt procured in this way was 98; but we apprehend that the water is merely mechanical, for reasons which will be seen hereafter, as the volume of the salt itself, by a mean of several experiments, came out to 119·5, whereas had this

eleventh atom of water been combined it should have been 121.

Biborate of Soda, $\text{NaO}, 2\text{BO}_3 + 10\text{HO} = 191.23$.—On dissolving 40 grains of this salt in 1000 of water, the increase was 19.2 at a temperature of 55° .

$\text{NaO}, 2\text{BO}_3 + 10\text{HO}$, vol. in solution 91.7 .

Half an equivalent, or 95.61 grains, on being placed in a saturated solution, occasioned an increase of 55.5 ; and 47.8 grains caused an increase of 27.5 ; both experiments being made at a temperature of 55° .

I.	$\text{NaO}, 2\text{BO}_3 + 10\text{HO}$, vol. of salt	111	...	Sp. gr.
				1.722
II.	110	...	1.738
	Mean . .	110.5	...	1.730

Chloride of Strontium, $\text{Sr}, \text{Cl} + 6\text{HO} = 133.32$.—There are two hydrates of chloride of strontium, the one with nine, and the other with six equivalents of water. To determine which of these hydrates was under examination, 4.324 grammes were heated to redness with a loss of 1.75 gramme = 40.47 per cent., showing that the hydrate was that with six equivalents of water, which gives by calculation 40.50 per cent.

On dissolving 40 grains of this salt in 1000 of water, the increase occasioned at a temperature of 56° was 16.0 ; a second experiment, in which the same quantities were used, gave exactly the same result.

I. II. $\text{Sr Cl} + 6\text{HO}$, vol. in solution 53.3 .

The same quantity of salt (40 grains), immersed in a saturated solution, caused an increase of 20.0 at a temperature of 57° ; and on a second experiment of 19.7 .

I.	$\text{Sr Cl} + 6\text{HO}$, vol. of salt	66.6	...	Sp. gr.
				2.000
II.	65.6	...	2.030
	Mean . .	66.1	...	2.015

Chloride of Calcium, $\text{Ca Cl} + 6\text{HO} = 109.92$.—On dissolving 55 grains, or the half of an equivalent of this salt, in 1000 grains of water, an increase of 28.0 was obtained at the temperature of 70° ; and in a second experiment 27.6 at 60° .

I.	$\text{Ca Cl} + 6\text{HO}$, vol. in solution	56.0
II.	55.2
	Mean . .	55.6

The same quantity of salt thrown into turpentine caused an increase of 32.7 and 32.8 in two experiments.

I.	$\text{Ca Cl} + 6\text{HO}$, vol. of salt	65.4	...	Sp. gr.
				1.682
II.	65.6	...	1.677
	Mean . .	65.5	...	1.680

Chloride of Magnesium, $\text{Mg Cl} + 6\text{HO} = 102\cdot16$.—Millon has lately described this salt as containing $6\frac{1}{2}$ atoms of water; but, as we have not been successful enough to obtain this hydrate, we retain the old formula. $25\cdot54$ grains, or the fourth of an equivalent, dissolved in 1000 grains of water at 53° , with an increase of $14\cdot0$.

$\text{Mg Cl} + 6\text{HO}$, vol. in solution = $56\cdot0$.

The same quantity, $25\cdot54$ grains, gave, in four experiments, respectively, $16\cdot5$; $16\cdot0$; $16\cdot4$; $16\cdot5$.

						Sp. gr.
I.	$\text{Mg Cl} + 6\text{HO}$	volume of salt	$66\cdot0$...		$1\cdot548$
II.	$64\cdot0$...		$1\cdot595$
III.	$65\cdot6$...		$1\cdot557$
IV.	$66\cdot0$...		$1\cdot548$
Mean . .			$65\cdot4$...		$1\cdot562$

The salts now examined are not calculated, on account of the deliquescent character of several of them, to produce absolutely accurate experimental results; but, notwithstanding this circumstance, the determination of their volumes is sufficiently uniform to indicate the theory. The actual volume observed for each of the salts in solution, when divided by 9, the atomic volume of water, yields as the quotient the same number as that representing the atoms of water in the salt. Hence it is quite certain that the salts now described dissolve in water without adding to its bulk more than is due to the liquefaction of the water in chemical combination with them.

The volumes of the salts in their solid state possess a number considerably higher than that representing the liquid volume, but affect a divisor, which is the same for all the salts, allowing for errors of experiments, or for alterations caused by incidental circumstances. This divisor is a number either equal or approximating to 11. When the volumes of the salts in the solid state are divided by this number, the quotient represents the number of atoms of water attached to the salt. The most natural view of this circumstance is to suppose that water in combination as a solid with a salt possesses a higher volume than liquid water, just as in the case of ice. If this view be correct, the atomic volume of the salts described is the same in the state of a solid as when in solution, the only difference being, that in the one case the volume is expressed by liquid, in the other by solid water. In this case, however, water in combination with a salt does not possess the same volume as ice, which, according to our experiments, detailed in another part of this paper, has a volume of $9\cdot8$, and not of a number approaching to 11.

Yet there is nothing extravagant in the idea that water combined with a salt may have a volume different from that of ice. Indeed, we are inclined to be of the opinion that ice itself represents nearly the mean of the volume of water uncombined and that of combined water. Be this as it may, it will be observed, as we proceed, that the number 11 is the best exponent of one class of our experiments on specific gravity; and therefore, without resting its claims to acceptance entirely on the present experiments, we assume it in the following tables as the theoretical result for each class of salts. With these views we tabulate the experiments which have been already detailed.

TABLE II.—Showing the volumes occupied by certain salts containing a large amount of hydrate water.

Designation.			Volume in solution.			Volume as salt.				
Name.	Formula.	Atomic Weight.	Volume in solution.	9, or volume of water as unity.	Volume by calculation.	Volume of salt by experiment.	11, an assumed number as unity.	Volume by calculation.	Specific gravity by calculation.	Specific gravity by experiment.
Sulphate of copper	$\text{CuO}, \text{SO}_3 + 5\text{HO}$	124.88	45.	5	45	55.4	5	55	2.270	2.254
Sulphate of alumina	$\text{Al}_2\text{O}_3, 3\text{SO}_3 + 18\text{HO}$	333.7	159.6	18	162	199.6	18	198	1.685	1.671
Sulphate of soda	$\text{NaO}, \text{SO}_3 + 10\text{HO}$	161.48	91.6	10	90	109.9	10	110	1.468	1.469
Biborate of soda	$\text{NaO}, 2\text{BO}_3 + 10\text{HO}$	191.23	91.7	10	90	110.5	10	110	1.738	1.730
Chloride of strontium ..	$\text{SrCl} + 6\text{HO}$	133.33	53.3	6	54	66.1	6	66	2.020	2.015
Chloride of calcium	$\text{CaCl} + 6\text{HO}$	109.92	55.6	6	54	65.5	6	66	1.665	1.680
Chloride of magnesium.	$\text{MgCl} + 6\text{HO}$	102.16	56.0	6	54	65.4	6	66	1.548	1.562

There are some salts which do not take up any space in solution, except that due to their water, but which assume a volume due to one of their constituents on becoming solid; the potash and ammonia alums are examples of this class.

Sulphate of Alumina and Potash, $\text{Al}_2\text{O}_3, 3\text{SO}_3 + \text{KO SO}_3 + 24\text{HO} = 474.95$.—59 grains of alum dissolved in 1000 grains of water, gave the increase of 27.0 in one experiment and 27.1 in another, both at the temperature of 60° .

I.	Alum, volume in solution	217.3
II.	...	218.1
	Mean . .	217.7

Atomic Volume and Specific Gravity.

413

On throwing 59·37 grains into a saturated solution, an increase of 34·4 was obtained in the first experiment; of 34·7 in a second; of 34·3 in a third; and of 34·2 in a fourth, all at a temperature about 60°.

				Sp. gr.
I.	Alum, vol. of salt	275·2	...	1·726
II.	...	277·6	...	1·711
III.	...	274·4	...	1·730
IV.	...	273·6	...	1·735
	Mean . .	275·2	...	1·726

Sulphate of Alumina and Ammonia, $\text{Al}_2\text{O}_3, 3\text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 24\text{HO} = 454·26$.—20 grains of this salt dissolved in 4100 grains of water with an increase of 10·0 at 58°.

Ammoniacal alum, vol. in solution 227·1

The eighth part of an equivalent, 56·78 grains, immersed in turpentine, caused a rise in the stem of 34·9 in one experiment and 35·0 in another, the temperature being 60°.

				Sp. gr.
I.	Ammonia alum, vol. of salt	279·2	...	1·627
II.	...	280·0	...	1·623
	Mean . .	279·6	...	1·625

Chrome Alum, $\text{Cr}_2\text{O}_3, 3\text{SO}_3 + \text{KO}, \text{SO}_3 + 24\text{HO} = 504·1$.—On dissolving 32 grains of this salt in 4100 grains of water, an increase of 13·7 was effected at 37°.

Chrome alum, vol. in solution 215·8

In two experiments 63 grains of this salt thrown into turpentine caused an increase of 34·5.

				Sp. gr.
	Chrome alum, volume of salt	276	...	1·826

Iron Ammonia-alum, $\text{Fe}_2\text{O}_3, 3\text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 24\text{HO} = 481·03$.—On dissolving 30·06 grains in 1000 grains of water, an increase of 14·3 was obtained at a temperature of 37°.

Iron alum, vol. in solution 228

The eighth part of an equivalent, 60·13 grains, produced an increase of 35·0 measures when thrown into turpentine.

				Sp. gr.
	Ammoniacal iron alum, vol. of salt	280·0	...	1·718

Pyrophosphate of Soda, $2\text{NaO}, \text{PO}_5 + 10\text{HO} = 224·15$.—The eighth part of an equivalent of the crystallized pyrophosphate, 28 grains, dissolved in 1000 grains of water with an increase of 11·2 in one experiment and of 11·3 in another, the temperature in both cases being 58°.

Pyrophosphate of soda, vol. in solution	89.6
... ..	90.4
Mean . .	90.0

On immersing 56.04 grains of the salt in a saturated solution, an increase of 30.5 was obtained in two experiments.

Pyrophosphate of soda, vol. of salt 122.0 ... 1.836 Sp. gr.

By tabulating the results thus obtained we find the following relationship between the class of alums.

TABLE III.—Showing the volumes of certain Alums*.

Designation.			Volume in solution.			Volume in state of salt.				
Name.	Formula.	Atomic weight.	Vol. in solution by experiment.	9, or vol. of water as unity.	Vol. by theory.	Vol. of salt by experiment.	11, taken as unity.	Vol. of salt by theory.	Specific gravity by theory.	Specific gravity by experiment.
Potash alum ...	$\{ \text{Al}_2\text{O}_3, 3\text{SO}_3, \text{KO}, \text{SO}_3 + 24\text{HO} \}$	474.95	217.7	24	216	275.2	25	275	1.727	1.726
Ammonia alum.	$\{ \text{Al}_2\text{O}_3, 3\text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 24\text{HO} \}$	454.26	227.1	25	225	279.6	25	275	1.652	1.625
Chrome alum...	$\{ \text{Cr}_2\text{O}_3, 3\text{SO}_3 + \text{KO}, \text{SO}_3 + 24\text{HO} \}$	504.1	215.8	24	216	276.0	25	275	1.833	1.826
Iron alum ...	$\{ \text{Fe}_2\text{O}_3, 3\text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 24\text{HO} \}$	481.03	228	25	225	280.0	25	275	1.749	1.718
Pyrophosphate of Soda ...	$2\text{NaO}, \text{PO}_5 + 10\text{HO}$	224.15	90	10	90	122	11	121	1.852	1.836

The peculiarity of the salts described in the above table is, that the quotient of the divisor for the potash alums in the solid state is not the same as in the state of solution, and that the ammoniacal alums possess one volume in solution greater than the corresponding potash alums, both of which peculiarities will find an explanation as we proceed. Pyrophosphate of soda shares this peculiarity, and is therefore introduced into the table.

We now proceed to describe a class of hydrated salts, in which the divisor for the solid volume is certainly not the number 11.

Carbonate of Soda, $\text{NaO}, \text{CO}_2 + 10\text{HO} = 143.4$.—On dissolving 35.85 grains of this salt in 1000 grains of water, the increase was 22.5 in one experiment at 64° , and 22.9 in a second experiment at 65° .

I. $\text{NaO}, \text{CO}_2 + 10\text{HO}$, vol. in solution	90.0
II.	91.6
Mean . .	90.8

* *Vide* conclusion for explanation of the high volume of ammonia alums.

On throwing 35·8 grains of the salt into turpentine, the increase was 24·7, 24·5, 24·6, and 24·8 in consecutive experiments with different specimens.

					Sp. gr.
I.	Carbonate of soda,	vol. of salt	98·8	...	1·451
II.	98·0	...	1·463
III.	98·4	...	1·457
IV.	99·2	...	1·446
Mean . .			98·6	...	1·454

Rhombic Phosphate of Soda, $2\text{NaO HO}, \text{PO}_5 + 24\text{HO} = 359·1$.—The eighth part of an equivalent of this salt, 44·9 grains, dissolved in 1000 grains of water with an increase of 27·0 in one experiment, and 27·1 in a second; by some mistake the temperature of the solution has not been recorded.

I.	Phosphate of soda,	vol. in solution	216·0
II.	216·8
Mean . .			216·4

The same quantity of salt thrown into turpentine caused an increase of 29·4 in two experiments, and 29·5 in a third.

					Sp. gr.
I.	Phosphate of soda,	vol. of salt	235·2	...	1·527
II.	235·2	...	1·527
III.	236·0	...	1·521
Mean . .			235·5	...	1·525

Sub-phosphate of Soda, $3\text{NaO}, \text{PO}_5 + 24\text{HO} = 381·6$.—The eighth part of an equivalent of this salt, 47·7 grains, dissolved in 1000 grains of water, with an increase of 27·1 in two experiments at 48°.

I. II. Sub-phosphate of soda, vol. in solution 216·8

The same quantity of salt thrown into turpentine produced an increase of 29·4 in two experiments under favourable circumstances, although in another experiment, in which we were not satisfied with the state of hydration of the salt, the increase was only 28·9.

Sub-phosphate of soda 235·2 ... 1·622

Arseniate of Soda, $2\text{NaO}, \text{HO}, \text{AsO}_5 + 24\text{HO} = 402·9$.—On dissolving 50·36 grains, the eighth part of an equivalent, in 1000 grains of water, an increase of 27·2 was obtained at a temperature of 54°.

Arseniate of soda, vol. in solution 217·6

The same quantity of salt thrown into a saturated solution caused an increase of 29·0 in several experiments. This salt

loses its water with such facility that it is almost impossible to obtain it in a state well-fitted for experiment. In two specimens of salts, prepared at different times, the volume for the above quantity of salt was 29·7 and 29·8; but as in most cases it was only 29·0, we give the result most generally obtained.

Arseniate of soda, vol. of salt 232·0 ... 1·736

Sub-arseniate of Soda, $3\text{NaO}, \text{AsO}_5 + 24\text{HO} = 425·2$.—The eighth part of an equivalent, 53·15 grains, of this salt dissolved in 1000 grains of water, with an increase of 27·0 in one experiment, and 26·9 in another, at a temperature about 55°.

I.	Sub-arseniate of soda	216·0
II.	...	215·2
Mean . .		215·6

The same quantity of salt immersed in turpentine caused an increase of 29·4 and 29·5 in two experiments.

I.	Sub-arseniate of soda, vol. of salt	235·2	1·808
II.	...	236·0	1·801
Mean . .		235·6	1·804

Cane-Sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11} = 171·60$.—25·8 grains of sugar dissolved in 3140 grains of water caused an increase of 14·8 at 32°; 42·9 grains, or the fourth of an equivalent, gave an increase of 25·0 at 60° in two experiments.

I.	Cane-sugar, vol. in solution	98·4
II.	...	100·0
III.	...	100·0
Mean . .		99·5

300 grains of sugar-candy thrown into alcohol previously saturated with it, caused an increase in the first experiment of 188·0, in the second of 188·75; in a third experiment, 49·65 grains thrown into turpentine caused an increase of 31·0; and the same quantity, in a fourth experiment, of 31·1, the temperature in all the cases being about 60°.

				Sp. gr.
I.	Cane-sugar, vol. of solid	107·5	...	1·596
II.	...	107·9	...	1·590
III.	...	107·1	...	1·602
IV.	...	107·5	...	1·596
Mean . .		107·5	...	1·596

In this section a class of salts presents itself, in which the volumes are clearly not represented by any multiple of 11; yet they are uniform in their isomorphous relations, and are sensibly multiples of the same number. To discover whether

the solid volume have any relation to that occupied by ice, we have determined the specific gravity of the latter with great care. The distilled water, which we converted into ice, was deprived of air by long-continued boiling, and a weighed portion of the ice was quickly immersed in water at 32° , the balance being kept at the same temperature during the weighing of the ice. The rise in the stem of the volumenometer, in which fragments of ice had previously been placed, indicated the volume due to the quantity of ice immersed. On treating in this manner 54.2 grains of ice, a rise in the stem of 59.0 was produced; and in a second experiment 52.8 grains of ice occasioned an increase of 57.5, the temperature in both cases being exactly 32° .

	Specific volume.	Specific gravity.
I. Ice volume	9.797	...
II.	9.801	...
Mean . .	9.799	...

As the true specific gravity of ice is a subject of much importance, we place here all the recorded results, as given in Bottger's most useful work on specific gravity, and in the first volume of Scoresby's Arctic Regions.

Specific gravity of ice	0.888	Dulk.
...	0.937	Irvine.
...	0.945	Williams.
...	0.885	Meineke.
...	0.905	Heinrich Kraft.
...	0.927	Osann.
...	0.950	Roger and Dumas.
...	0.920	Scoresby.
Mean . .	0.919	

The mean of all these experiments, differing only $\frac{1}{1000}$ from our own determination, warrants us in concluding that our result is accurate, and that 9.80 may safely be taken as the specific volume of an atom of ice. Now it must at once strike the observer of the previous experiments, that this number forms the divisor for the volumes of the salts described in the present section.

TABLE IV.—Showing the volumes occupied by certain Phosphates, Arseniates, Carbonate of Soda and Cane-sugar.

Designation.			Volume in solution.			Volume of salt.				
Name.	Formula.	Atomic weight.	Volume in solution by experiment.	9, or volume of water as unity.	Volume by theory.	Volume of salt by experiment.	9's, or volume of ice as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Carbonate of soda	$\text{NaO}, \text{CO}_2 + 10\text{HO}$	143.4	90.8	10	90	98.6	10	98.0	1.463	1.454
Phosphate of soda	$\left\{ \begin{array}{l} 2\text{NaO}, \text{HO}, \text{PO}_5 \\ + 24\text{HO} \end{array} \right\}$	359.1	216.4	24	216	235.5	24	235.2	1.527	1.525
Sub-phosphate of soda	$3\text{NaO}, \text{PO}_5 + 24\text{HO}$	381.6	216.8	24	216	235.2	24	235.2	1.622	1.622
Arseniate of soda	$\left\{ \begin{array}{l} \text{HO}, 2\text{NaO}, \text{AsO}_5 \\ + 24\text{HO} \end{array} \right\}$	402.9	217.6	24	216	232.0	24	235.2	1.713	1.736
Sub-arseniate of soda	$3\text{NaO}, \text{AsO}_5 + 24\text{HO}$	425.2	215.6	24	216	235.6	24	235.2	1.808	1.804
Cane-sugar	$\text{C}_{12} \text{H}_{11} \text{O}_{11}$	171.6	99.5	11	99	107.5	11	107.8	1.591	1.596

Connected with the latter group, there is a class of salts which come out uniformly with themselves, but the divisor of which is not 11 in the solid state. We subjoin them in the following group.

Sulphate of Magnesia, $\text{MgO}, \text{SO}_3 + 7\text{HO} = 123.86$.—When this salt is dissolved in a large quantity of cold water, the volume observed after solution is always less at ordinary temperatures than that due to the water contained in the salt. That this diminution is due to a contraction caused by an affinity of the salt for water is shown by the fact, that anhydrous sulphate of magnesia dissolved in a large quantity of water actually lessens, instead of increasing the bulk of the water; and to compensate for this contraction, a certain temperature has to be given to the water. In the following experiments with the sulphates of magnesia, zinc and iron, this circumstance has been attended to, and the temperature is given at which the results come out exact.

31 grains of crystallized sulphate of magnesia were dissolved in 3140 grains of water at 32° , and caused an increase of 15.22 ; at 85° the increase was 15.75 .

$\text{MgO}, \text{SO}_3 + 7\text{HO}$, vol. in solution 63.

Half an equivalent, 61.93 grains, being placed in a saturated solution of the salt, caused an increase of 37.5 in one experiment, but in three other experiments the increase was not greater than 37.2 ; the temperature in all the cases being 54° .

						Sp. gr.
I.	MgO,	SO ₃	+ 7HO,	vol. of salt	75·0	... 1·651
II.	74·4	... 1·664
III.	74·4	... 1·664
IV.	74·4	... 1·664
Mean . . .					74·55	... 1·660

Sulphate of Zinc, ZnO, SO₃ + 7HO = 143·43.—This salt possesses the same property as sulphate of magnesia, of causing a contraction when the anhydrous salt is dissolved in a large quantity of cold water.

35·9 grains were dissolved in 3140 grains of water at a temperature of 32°, causing a rise in the stem of 14·03. At 90° the rise was 15·77.

ZnO, SO₃ + 7HO, vol. in solution 63.

The half of an equivalent of this salt, 71·71 grains, being thrown into a saturated solution, caused an increase of 37·1; and 35·85 grains produced a rise in the stem of 18·6 in two experiments, and of 18·5 in a fourth.

						Sp. gr.
I.	ZnO,	SO ₃	+ 7HO,	vol. of salt	74·2	... 1·933
II.	74·4	... 1·928
III.	74·4	... 1·928
IV.	74·0	... 1·937
Mean . . .					74·25	... 1·931

Sulphate of Iron, FeO, SO₃ + 7HO = 138·3.—The fourth part of an equivalent, 34·6 grains, dissolved in 3140 grains of water at 32° with an increase of 15·25, which became 15·75 at 80°.

FeO, SO₃ + 7HO, vol. in solution 63.

The same quantity of salt thrown into turpentine gave in one experiment an increase of 18·6, in another of 18·7, and in a third of 18·6.

						Sp. gr.
I.	FeO,	SO ₃	+ 7HO,	vol. of salt	74·4	... 1·860
II.	74·8	... 1·850
III.	74·4	... 1·860
Mean . . .					74·5	... 1·857

Sulphate of Nickel, NiO, SO₃ + 6HO = 131·74.—This salt we found to contain only 6 atoms of water instead of 7 atoms, as usually described; but it is known to crystallize with both proportions. On dissolving 35 grains in 1000 of water, the increase obtained was 14·0 at a temperature of 55°.

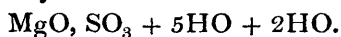
NiO, SO₃ + 6HO = vol. in solution 52·7.

We have not ourselves obtained the specific gravity of this

salt, but this has been determined by Kopp, who gives it at 2·037, without however describing the character of the hydrate which he examined. It is possible, therefore, that it may not be the same as that which we have examined; but presuming it to be so, the volume of this salt, according to Kopp, would be

NiO, SO ₃ + 6HO, vol. of salt	64·6	...	Sp. gr. 2·037.
--	------	-----	-------------------

The volumes of the magnesian sulphates with 7 atoms of water are obviously less than those which would result were they multiples of the volume 11. But as we have already seen that the water of hydration does not always enter into combination with the volume 11, but occasionally with that of 9·8, or the volume of ice, the results obtained may be explained on this view. Graham*, in his researches on the phosphates, and on the heat of combination, drew attention to the fact, that the atoms of water seem to be attached together in *twos*. Millon† more lately has shown that the two last atoms of water in sulphate of magnesia are less firmly attached than the five remaining atoms; that a magnesian sulphate in fact may be viewed as



That 5 atoms of water form the natural numbers for the magnesian sulphates we have evidence in the salts of copper and manganese, both of which possess these 5 atoms of water in combination with a volume of 11, at least.

CuO, SO ₃ + 5HO vol. of salt	55·4	(P. and J.)
MnO, SO ₃ + 5HO	...	57·6 (Kopp.)

As then the two additional atoms of water are retained by a less feeble affinity than the remaining five, may we not assume that they are present, as in the case of other salts possessing a feeble affinity for water, with the volume of ice, whilst the original 5 atoms possess the higher volume of 11? The following table will show that this hypothesis gives results by calculation which do not differ widely from those obtained by experiment.

* Phil. Trans., part 1. 1837, page 67.

† *Annales de Chimie*, 3 série, t. xii. p. 134.

Atomic Volume and Specific Gravity.

421

TABLE V.

Designation.			Volume in solution.			Volume of salt.				
Name.	Formula.	Atomic Weight.	Volume in solution.	9, or volume of water as unity.	Volume by theory.	Volume of salt by experiment.	11 as unity for 5 atoms, and the volume of ice for 2 atoms.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Sulphate of magnesia	$\text{MgO}, \text{SO}_3 + 5\text{HO}$	123.86	63	7	63	74.55	5+2	74.6	1.660	1.660
Sulphate of zinc	$\text{ZnO}, \text{SO}_3 + 5\text{HO}$	143.43	63	7	63	74.25	5+2	74.6	1.926	1.931
Sulphate of iron	$\text{FeO}, \text{SO}_3 + 5\text{HO}$	138.3	63	7	63	74.5	5+2	74.6	1.854	1.857
Sulphate of nickel ...	$\text{NiO}, \text{SO}_3 + 5\text{HO}$	131.74	52.7	6	54	64.6	5+1	64.8	2.033	2.037

Before leaving this section we would sum up some of the principal facts observed. In the first place, it is of much importance to know that these salts dissolve in water without increasing its bulk more than is due to the water attached to them as crystallized water. The acid and bases entirely disappear in the water which is attached to them; and so closely does this rule prevail, that the atom of basic water in the tri-basic arseniates and phosphates has ceased to play the part of water, either in solution or in the solid state. In the condition of solid salts, we find four classes to which we have drawn attention. The first of these is represented by salts having their water firmly attached, and possess as a divisor for their atomic volume a number equal or approaching to 11; and we have concluded, as the quotient of this divisor is always the same as the number of atoms of water attached to the salt, that 11 is the volume of an atom of water in combination; and hence that the salts have disappeared in this attached water, adding to its weight, but not to its observed bulk.

The second class of salts in this section is represented by potash alum, in which the astonishing result is obtained, that the 23 anhydrous atoms of this salt have combined in some way with the 24 atoms of water, so as to cease to occupy bulk in solution. The peculiarity of this group is, that an additional 11 becomes attached to the solid salt, so that the quotient of the divisor is 25 instead of 24. This fact, and that connected with the ammoniacal alums in the same group, cannot be discussed with propriety in the present place.

The third group of salts in this section is one of high interest, and is represented by salts having their hydrate water attached by a feeble affinity. In them the volume of the

water is exactly the same as that of ice itself. Sugar belongs to this category, not because the $H_{11}O_{11}$ are feebly attached, for it has yet to be shown that they are present *quasi* water. The fact however that these 11 atoms of hydrogen and oxygen take up the same space as liquid water in solution, and as ice in the solid state of sugar, and that the 12 atoms of carbon have ceased to occupy space, is a matter of supreme interest, and cannot fail to lead to important results when we come to the consideration of organic compounds.

The fourth class in this section finds its representatives in the sulphates of the magnesian class of metals, and perhaps ought to include the magnesian chlorides also. They possess their constitutional water with the usual volume of 11, while the water feebly attached is present with the volume of ice.

Although, then, we have four distinct groups in the section of salts possessing a large amount of hydrate water, we have only two modifications of volume, the one represented by a number equal or approximating to 11, the other by the volume of ice itself, viz. 9·8.

We now proceed to the consideration of salts which either are destitute of water, or contain it in small proportion only. The volumes affected by them must be volumes peculiar to themselves, and not, as in the present section, to the water with which they are combined.

SECTION II.

Sulphates with a small proportion of Water of Hydration, Anhydrous and Double Sulphates.

Sulphate of Potash, $KO, SO_3 = 87\cdot25$.—Half an equivalent of this salt, dissolved in 3140 grains of water of 37° , increased $7\cdot2$, and at 80° , $9\cdot0$; the same quantity dissolved in 1000 grains of water at 66° , increased $9\cdot0$.

I. II. KO, SO_3 , vol. in solution 18·0

A whole equivalent of the salt being placed in its saturated solution effected a rise in the stem of $33\cdot0$ at a temperature of 55° ; and a repetition of the experiment gave the increase $33\cdot1$.

				Sp. gr.
I.	KO, SO_3	vol. of salt	$33\cdot0$...	$2\cdot644$
II.	$33\cdot1$...	$2\cdot636$
	Mean	. .	$33\cdot05$	$2\cdot640$

Sulphate of Potash and Sulphate of Water, $KO, SO_3 + HO, SO_3 = 136\cdot35$.—The fourth of an equivalent ($34\cdot08$ grains), being dissolved in 1000 grains of water, caused an increase of

9.0 at a temperature of 59° , and 33 grains dissolved in the same quantity of water occasioned a rise of 8.75 at 44° .

I.	KO, $\text{SO}_3 + \text{HO}$, SO_3 , vol. in solution	36.0
II.	36.1
	Mean . .	36.05

Half an equivalent (68.2 grains) of the salt, previously fused, immersed in a saturated solution, produced a rise in the stem of 27.5; and a second experiment with the same quantity, but with salt which had not been fused, of 27.6, the temperature on both occasions being 55° .

I.	KO, $\text{SO}_3 + \text{HO}$, SO_3 , vol. of salt	55.0	...	Sp. gr. 2.479
II.	55.2	...	2.470
	Mean . .	55.1	...	2.475

Sulphate of Ammonia, NH_4O , $\text{SO}_3 + \text{HO} = 75.25$.—In three separate experiments, in which 75.25 grains of this salt were dissolved in 1000 grains of water, the increase was exactly 36.0 at 60° .

I. II. III. NH_4O , SO_3 , HO , vol. in solution 36.0

Half an equivalent (37.6 grains) being immersed in a saturated solution at 49° , caused, in two experiments, an increase of 21.5.

I. II.	NH_4O , $\text{SO}_3 + \text{HO}$, vol. of salt	43.0	...	Sp. gr. 1.750
--------	--	------	-----	------------------

Sulphate of Ammonia and Sulphate of Water, NH_4O , $\text{SO}_3 + \text{HO}$, $\text{SO}_3 = 115.35$.—Half an equivalent (57.7 grains) of this salt, dissolved in 1000 grains of water, gave a rise in the stem of 23.0 at 56° , in two separate experiments.

I. II. NH_4O , $\text{SO}_3 + \text{HO}$, SO_3 , vol. in solution 46.0

The same quantity of salt being placed in its saturated solution, caused an increase of 32.5 in one experiment and of 33.0 in a second, the temperature in both cases being 58° .

I.	NH_4O , HO , 2SO_3 , vol. of salt	65.0	...	Sp. gr. 1.775
II.	66.0	...	1.747
	Mean . .	65.5	...	1.761

Sulphate of Soda and Sulphate of Water, NaO , $\text{SO}_3 + \text{HO}$, $\text{SO}_3 = 120.64$.—The fourth of an equivalent (30.16 grains) dissolved in 1000 grains of water, in the first experiment with an increase of 4.6, in the second of 4.7, both at a temperature of 56° .

I.	NaO, SO ₃ + HO, SO ₃ , vol. in solution	18.4
II.	18.8
	Mean . .	18.6

The same quantity of salt thrown into a saturated solution caused, in two experiments, an increase of 11.0 at a temperature of 54°.

		Sp. gr.
I. II.	Bisulphate of soda, vol. of salt	44.0 ... 2.742

Ammoniacal Sulphate of Copper, CuO, SO₃, HO + 2NH₃ = 123.0.—The fourth of an equivalent (30.8 grains) of this substance in beautiful large indigo-blue crystals, dissolved in 1000 grains of water, with an increase of 13.3 in one experiment and 13.0 in another, the temperature being 54 and 50°.

I.	CuO, SO ₃ , HO + 2NH ₃ , vol. in solution	53.2
II.	52.0
	Mean . .	52.6

61.5 grains of this salt placed in the solution from which it had crystallized, caused an increase of 34.3, and on a repetition of the experiment of 34.4, at a temperature of 60°.

		Sp. gr.
I.	CuO, SO ₃ , HO + 2NH ₃ , vol. of salt	68.6 ... 1.793
II.	68.8 ... 1.788
	Mean . .	68.7 ... 1.790

Sulphate of Copper and Sulphate of Potash, CuO, SO₃ + KO, SO₃ + 6HO = 221.31.—The fourth of an equivalent (55.32 grains) dissolved in 3140 grains of water at 32°, increased to 16.3, and at 72° to 18.0.

CuO, SO ₃ + KO, SO ₃ + 6HO, vol. in solution	72.0
--	------

The same quantity of the salt placed in its saturated solution, caused an increase of 24.7 in one experiment and of 24.6 in a second, the temperature on both occasions being 55°.

		Sp. gr.
I.	CuO, SO ₃ + KO, SO ₃ + 6HO, vol. of salt	98.8 . 2.239
II.	98.4 . 2.249
	Mean . .	98.6 . 2.244

Sulphate of Copper and Sulphate of Ammonia, CuO, SO₃ + NH₄O, SO₃ + 6HO = 199.88.—On dissolving 50 grains of this salt in 1000 grains of water, an increase was occasioned in the first experiment of 20.2, in the second of 20.3, both at a temperature of 59°.

I.	Sulphate of copper and ammonia, vol. in solution	80.8
II.	81.2
	Mean . .	81.0

On immersing the same quantity in a saturated solution, an

increase of 26·4 was obtained in the first experiment, and of 26·45 in the second, both at a temperature of 59°.

I.	CuO, SO ₃ + NH ₄ O, SO ₃ + 6HO, vol. of salt	105·6	..	Sp. gr. 1·892
II.	105·8	.	1·889
	Mean . .	105·7	..	1·891

Sulphate of Zinc and Sulphate of Potash, ZnO, SO₃ + KO, SO₃ + 6HO = 221·86.—The fourth of an equivalent of this salt (55·46 grains), on being dissolved in 1000 grains of water, increased to 18 at a temperature of 60° in two experiments.

I. II. ZnO, SO₃ + KO, SO₃ + 6HO, vol. in solution 72.

The same quantity immersed in a saturated solution, caused an increase also in two experiments of 24·7, the temperature being 56°.

I. II.	ZnO, SO ₃ + KO, SO ₃ + 6HO, vol. of salt	98·8	...	Sp. gr. 2·245
--------	--	------	-----	------------------

Sulphate of Zinc and Sulphate of Ammonia, ZnO, SO₃ + NH₄O, SO₃ + 6HO = 200.—On dissolving 45 grains of this salt in 1000 of water, an increase of 18·0 was occasioned in three separate experiments at a temperature of 58°.

I. II. III. ZnO, SO₃ + NH₄O, SO₃ + 6HO, vol. in solution 80

On adding the fourth of an equivalent (50 grains) to a saturated solution, an increase of 26·4 was occasioned in the first experiment, and of 26·3 in the second, both at a temperature of 55°.

I.	Sulph. zinc and ammonia, vol. of salt	105·6	...	Sp. gr. 1·894
II.	105·2	...	1·901
	Mean . .	105·4	...	1·897

Sulphate of Magnesia and Sulphate of Potash, MgO, SO₃ + KO, SO₃ + 6HO = 202·29.—When a quarter of an equivalent of this salt (50·57 grains) is dissolved in as many as 3140 grains of water, the volume at 32° is only 15·45, but is 18 at 80°. This gives for the salt in very dilute solution—

MgO, SO ₃ + KO, SO ₃ + 6HO, vol. in solution	63 at 40°
... ..	72 at 80°

The same quantity of salt after immersion in a saturated solution gave in the first experiment an increase of 24·3, and in the second of 24·4, both at a temperature of 57°.

I.	Sulph. magnesia and potash, vol. of salt	97·2	.	Sp. gr. 2·081
II.	97·6	.	2·071
	Mean . .	97·4	.	2·076

Sulphate of Magnesia and Ammonia, MgO, SO₃ + NH₄O, SO₃ + 6HO = 181·12.—The fourth of an equivalent (45·28

grains) being dissolved in 1000 grains of water, caused an increase of 20.0 at 60° ; and a repetition of the experiment at the same temperature gave the increase 20.1 .

I.	Sulph. magnesia and ammonia, vol. in solution	80.0
II.	80.4
	Mean . .	80.2

The same quantity of salt placed in a saturated solution, gave on two occasions a rise in the stem of 26.3 at a temperature of 60° .

		Sp. gr.
I. II.	Sulph. magnesia and ammonia, vol. of salt	$105.2 \quad 1.721$

Sulphate of Iron and Potash, $\text{FeO}, \text{SO}_3 + \text{KO}, \text{SO}_3 + 6\text{HO} = 216.73$.—The eighth of an equivalent (27.09 grains), when dissolved in 1000 of water, caused an increase of 9 at a temperature of 65° .

Sulph. iron and potash, vol. in solution 72 .

The same quantity immersed in a saturated solution occasioned a rise in the stem in two experiments 12.3 at a temperature of 61° .

		Sp. gr.
I. II.	Sulph. iron and potash, vol. of salt	$98.4 \quad 2.202$

Sulphate of Iron and Ammonia, $\text{FeO}, \text{SO}_3 + \text{NH}_4\text{O SO}_3 + 6\text{HO} = 195.55$.—On dissolving 33.45 grains of this salt in 1000 of water, the increase in the first experiment was 13.4 , in the second 14 , both at a temperature of 59° ; a third experiment with 66.9 grains, gave the increase 28 at the same temperature.

I.	Sulph. iron and ammonia, vol. in solution	78.3
II.	81.8
III.	81.8
	Mean . .	80.7

48.89 grains of the salt being projected into a saturated solution, caused in the first experiment an increase of 26.4 , in the second of 26.5 .

		Sp. gr.
I.	Sulph. iron and ammonia, vol. of salt	$105.6 \quad 1.851$
II.	$106.0 \quad 1.845$
	Mean . .	$105.8 \quad 1.848$

In the last section we gave the volumes occupied by those salts which did not occupy any space of themselves, but merely that due to their combined water. The divisor for the volumes observed in solution was therefore necessarily 9 , or the atomic volume of water itself. But in this section we have experimented upon salts which take up space quite inde-

pendent of their water of crystallization, even when they contain water, and yet the most interesting result follows, that the same divisor, 9, continues for the volumes ascertained by experiment. The volumes in solution of the salts examined, allowing for errors of observation, are therefore always multiples of 9,—the atomic volume of water. The volumes of the solids are, like those of the previous section, multiples of one and the same number, that number being also, as in the former case, 11; but the ammonia salts do not arrange themselves under this divisor for reasons which will be explained presently. The averages of the experiments on all the salts are thrown into the following table, into which is also introduced the exact numbers which would have resulted had there been a strict accordance with the law obviously indicated by experiment.

TABLE VI.—Showing the volumes of certain Sulphates with a small proportion of Water of Hydration, Anhydrous and Double Sulphates.

Designation.			Volume in solution.			Volume in state of salt.				
Name.	Formula.	Atomic weight.	Volume in solution by experiment.	9, or volume of water as unity.	Volume by theory.	Volume of salt by experiment.	11, or supposed vol. of combined water as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Sulphate of potash ..	KO, SO ₃	87.25	18.0	2	18	33.05	3	33	2.644	2.640
Bisulphate of potash.	KO, SO ₃ + HO, SO ₃	136.35	36.05	4	36	55.1	5	55	2.479	2.475
Sulphate of ammonia	NH ₄ O, SO ₃ + HO	75.25	36.0	4	36	43.0	4	44	1.710	1.750
Bisulphate of ammonia	NH ₄ O, SO ₃ + HO, SO ₃	115.35	46.0	5	45	65.5	6	66	1.747	1.761
Bisulphate of soda...	NaO, SO ₃ + HO, SO ₃	120.64	18.6	2	18	44.0	4	44	2.742	2.742
Ammoniacal sulphate of copper	CuO, SO ₃ HO + 2NH ₃	123.00	52.6	6	54	68.7	1.790
Sulphate of copper and potash	CuO, SO ₃ + KOSO ₃ + 6HO	221.31	72.0	8	72	98.6	9	99	2.235	2.244
Sulphate of copper and ammonia...	CuO, SO ₃ + NH ₄ O, SO ₃ + 6HO	199.88	81.0	9	81	105.7	9	99	2.019	1.891
Sulphate of zinc and potash	ZnO, SO ₃ + KO, SO ₃ + 6HO	221.86	72.0	8	72	98.8	9	99	2.241	2.245
Sulphate of zinc and ammonia...	ZnO, SO ₃ + NH ₄ O, SO ₃ + 6HO	200.00	80.0	9	81	105.4	9	99	2.020	1.897
Sulphate of magnesia and potash	MgO, SO ₃ + KO, SO ₃ + 6HO	202.29	72.0	8	72	97.4	9	99	2.043	2.076
Sulphate of magnesia & ammonia	MgO, SO ₃ + NH ₄ O, SO ₃ + 6HO	181.12	80.2	9	81	105.2	9	99	1.829	1.721
Sulphate of iron and potash	FeO, SO ₃ + KO, SO ₃ + 6HO	216.73	72.0	8	72	98.4	9	99	2.190	2.202
Sulphate of iron and ammonia...	FeO, SO ₃ + NH ₄ O, SO ₃ + 6HO	195.55	80.7	9	81	105.8	9	99	1.975	1.848
Sulphate of nickel and potash	NiO, SO ₃ + KO, SO ₃ + 6HO	218.99	71.5	8	72	100.0	9	99	2.212	2.190

The correspondence between the observed and calculated results in the preceding table, as far as regards the potash salts, is so striking as to remove any doubt of the basis upon which the calculations are made. It is therefore of interest to consider the results indicated by the table a little more in detail. The first point of remark is, that in every case the ammoniacal salt has one volume greater in solution than the corresponding potash salt. Sulphate of potash possesses two volumes in solution; sulphate of ammonia divested of one volume for its atom of water possesses three. These volumes are respectively carried through the whole class of double sulphates. The volumes of these double sulphates are made up of the sum of the volumes of their constituent salts, which appear, therefore, to be united unchanged. We saw in the previous section that the magnesian sulphates dissolve in water without increasing its bulk more than is due to their water of combination. The same takes place in their double sulphates, for subtracting the volumes of the atoms of water which have been carried by the sulphates into their union with sulphate of potash, the remainder shows the volumes belonging to the latter salts, as indicated by direct experiment. This is strikingly exemplified also by bisulphate of soda. Sulphate of soda was shown in the last section to possess no volume in solution, and in this acid salt we find that the sulphate of soda has in solution ceased to occupy space, for the resulting volume of the acid salt is only 18 or 9×2 , which is the atomic volume of sulphate of water, as ascertained by the volume occupied by it in bisulphate of potash and bisulphate of ammonia, and as determined also by a calculation, which we have made, of the volume occupied by hydrated sulphuric acid in a *dilute* solution, founded upon recorded specific gravities.

Although the ammoniacal sulphates, on account of their analogy to the potash salts, have been introduced into the above table, it is obvious that the numbers representing their volumes are too wide from the theoretical numbers to be considered multiples of 11. Hydrated sulphate of ammonia affects four volumes, 11×4 , but the anhydrous salt obeys a different law. On immersing in turpentine 33·15 grains of anhydrous NH_4O , SO_3 , the increase was 19·6 and 19·5, the mean being 19·55 water-grain measures. This gives 39·1 as the vol. of the equivalent, and $9·8 \times 4 = 39·2$. Anhydrous sulphate of ammonia affects, therefore, 4 vol. of ice; and the double salts consist of the magnesian sulphates with 6 equivalents of water attached to an equivalent of anhydrous sulphate of ammonia, as will be seen from the following table of their solid volumes and specific gravities.

Name.	Solid volume by experiment.	Solid volume by theory.	Specific gravity by experiment.	Specific gravity by theory.
Sulphate of ammonia.....	39.1	39.2	1.695	1.691
Sulphate of copper and ammonia.....	105.7	105.2	1.891	1.900
Sulphate of zinc and ammonia.....	105.4	105.2	1.887	1.901
Sulphate of magnesia and ammonia...	105.2	105.2	1.721	1.721
Sulphate of iron and ammonia.....	105.8	105.2	1.848	1.858

As one of the members of the group of double salts here described takes up no space of itself, it became of importance to ascertain the volume of the salt when deprived of water, and also the space occupied by the double salt reduced to the same state. In this examination it was quite unnecessary to obtain the volumes in solution, because it was obvious that salts not occupying in solution a greater volume than that due to their water of hydration, would, in their anhydrous condition, take up no space at all. In fact, we had ascertained that not only was there no increase in dissolving such salts in water, but that actually there was a contraction if the water were in large proportion to the salt; when this is not the case, the increased expansibility of the solution prevents the contraction being observed.

In the following examination will be found almost all the salts previously described in their hydrated condition, with the exception of the phosphates and arseniates, which we reserve for another paper.

Sulphate of Magnesia, MgO , $\text{SO}_3 = 60.86$.—Half an equivalent of this salt, 30.43 grains, thrown into turpentine, caused an increase of 11.0; but in a second experiment the increase was 11.5, the temperature in both cases being 65° .

			Sp. gr.
MgO , SO_3 , vol. of salt	22.0	...	2.766
...	23.0	...	2.646
Mean . .	22.5	...	2.706

Sulphate of Zinc, ZnO , $\text{SO}_3 = 80.43$.—Half an equivalent of this salt, 40.22 grains, projected into turpentine, caused an increase of 11.05 and, in another experiment, of 10.8.

			Sp. gr.
ZnO , SO_3 , vol. of salt	22.1	...	3.639
...	21.6	...	3.723
Mean . .	21.85	...	3.681

Sulphate of Copper, CuO , $\text{SO}_3 = 79.88$.—Half an equivalent, 39.94 grains, of the salt placed in turpentine, caused in several successive experiments an increase of exactly 11.0.

	Sp. gr.
CuO, SO ₃ , vol. of salt 22·0 ...	3·631

Sulphate of Iron, FeO, SO₃=75·3.—Half an equivalent of this salt, 37·65 grains, caused, in two experiments with the same salt, a rise of 12·0, which gives for the equivalent 24·0 and a specific gravity of 3·138.

Sulphate of Cobalt, CoO, SO₃=77·69.—On immersing 19·42 grains of this salt in turpentine, an increase of 5·5 was obtained in two experiments; this gives for the equivalent 22·0, and for the specific gravity 3·531.

Sulphate of Soda, NaO, SO₃=71·43.—On throwing a whole equivalent of this salt into turpentine, the increase was only 27·5 in several successive experiments, which gives for the specific gravity 2·597. Karsten found its specific gravity to be 2·631, a result approximating to our own; attention is drawn to this circumstance because both results are anomalous.

Sulphate of Silver, AgO, SO₃=156·48.—On immersing in turpentine 78·24 grains of this salt, the increase was 14·7, which gives as the volume of the equivalent 29·4, and a specific gravity of 5·322.

Chromate of Silver, AgO, CrO₃=168·49.—The fourth of an equivalent of this salt, 42·12 grains, gave an increase, when thrown into turpentine, of 7·3 in two successive experiments. This gives 29·2 for the volume of the equivalent, and 5·770 for the specific gravity of the salt.

Sulphate of Copper and Potash, CuO, SO₃ + KO, SO₃=167·31.—41·82 grains, the fourth of an equivalent, thrown into turpentine, caused an increase of 14·9 in one experiment and of 15·0 in another, the temperature in both cases being 54°.

		Sp. gr.
CuO, SO ₃ + KO, SO ₃ , vol. of salt	59·6 ...	2·807
... ..	60·0 ...	2·788
Mean . .	59·8 ...	2·797

Sulphate of Nickel and Potash, NiO, SO₃ + KO, SO₃ = 164·99.—41·54 grains caused an increase of 14·2 in one experiment and 14·5 in a second, the temperature in both cases being 54°.

		Sp. gr.
NiO, SO ₃ + KO, SO ₃ , vol. of salt	56·4 ...	2·925
... ..	57·5 ...	28·69
Mean . .	56·95 ...	2·897

Sulphate of Zinc and Potash, ZnO, SO₃ + KO, SO₃ = 167·86.—41·96 grains, the fourth of an equivalent, placed in turpentine, caused an increase of 14·9 in two experiments.

$\text{ZnO}, \text{SO}_3 + \text{KO}, \text{SO}_3$, vol. of salt 59.6 ... $\text{Sp. gr. } 2.816$
Sulphate of Magnesia and Potash, $\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3$
 = 148.29.—37.07 grains, or the fourth of an equivalent,
 caused in one experiment an increase of 13.9, and in a second
 of 13.8, the temperature being 55° .

$\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3$, vol. of salt	55.6	...	$\text{Sp. gr. } 2.667$
...	2.686
Mean	55.4	...	2.676

Sulphate of Manganese and Potash, $\text{MnO}, \text{SO}_3 + \text{KO}, \text{SO}_3$
 = 163.07.—40.8 grains of this salt, one-fourth of an equivalent,
 placed in turpentine, caused an increase of 13.5 in one
 experiment and 13.6 in another, at a temperature of 55° .

$\text{MnO}, \text{SO}_3 + \text{KO}, \text{SO}_3$, vol. of salt	54.0	...	$\text{Sp. gr. } 3.020$
...	2.996
Mean	54.2	...	3.008

Sulphate of Copper and Ammonia, $\text{CuO}, \text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3$
 = 145.88.—36.53 grains of this salt thrown into turpentine,
 caused an increase of 16.7 in one experiment and 16.6 in another,
 at a temperature of 60° .

I. <i>Sulphate of copper and ammonia</i>	66.6	...	$\text{Sp. gr. } 2.190$
II.	2.204
Mean	66.4	...	2.197

Sulphate of Zinc and Ammonia, $\text{ZnO}, \text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3$
 = 146.0.—30 grains of this salt thrown into turpentine, caused
 an increase of 13.5 at 60° .

<i>Sulphate of zinc and ammonia</i> , vol. of salt	65.7	...	$\text{Sp. gr. } 2.222$
--	------	-----	-------------------------

Sulphate of Magnesia and Ammonia, $\text{MgO}, \text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3$
 = 127.12.—The fourth of an equivalent (31.78 grains)
 placed in turpentine, caused an increase of 16.5 in the first
 experiment, and of 16.4 in the second.

I. <i>Sulphate of magnesia and ammonia</i>	66.0	...	$\text{Sp. gr. } 1.926$
II.	1.938
Mean	65.8	...	1.932

Sulphate of Alumina, $\text{Al}_2\text{O}_3.3\text{SO}_3$ = 171.95.—This salt, and
 the anhydrous alums, offer difficulties to the correct estimation
 of their specific gravity on account of their great porosity
 and liability to carry down air. The best mode of obviating
 this source of error is to introduce a metallic wire previously

moistened with turpentine into the volumenometer, and employ this to break the numerous air bubbles which arise on immersing the salts. The following estimations were taken with great care, but from this source of error may possibly be inaccurate.

The eighth part of an equivalent (21.49 grains), immersed in turpentine and treated as described above, gave results varying from 9.8 to 10.0, the mean result being 9.9.

			Sp. gr.
$\text{Al}_2\text{O}_3\cdot 3\text{SO}_3$, vol. of salt	79.2	...	2.171

Sulphate of Alumina and Potash, $\text{Al}_2\text{O}_3\cdot 3\text{SO}_3 + \text{KO}$, $\text{SO}_3 = 259.36$.—The eighth part of an equivalent (32.42 grains) of anhydrous alum, immersed in turpentine and treated as described in the case of sulphate of alumina, gave an increase of 14.5 and 14.6 in two experiments.

			Sp. gr.
I. Alum, vol. of salt	116.0	...	2.236
II.	116.8	...	2.220
Mean . . .	116.4	...	2.228

Ammonia Alum, $\text{Al}_2\text{O}_3\cdot 3\text{SO}_3 + \text{NH}_4\text{O}$, $\text{SO}_3 = 238.2$.—The eighth part of an equivalent of this salt (29.77 grains), treated as in the previous cases, gave an increase of 14.6 in two experiments.

			Sp. gr.
Ammonia alum, vol. of salt	116.8	...	2.039

Carbonate of Soda, NaO , $\text{CO}_2 = 53.47$.—The equivalent of this salt, thrown into turpentine, gave an increase of exactly 22.0, which makes its specific gravity 2.430.

Chloride of Magnesium, $\text{MgCl} = 48.12$.—The anhydrous chloride of magnesium used in the experiment was made by saturating equal portions of muriatic acid with magnesia and ammonia, mixing together, evaporating to dryness, and heating to redness.

Half an equivalent (24.06 grains), thrown into turpentine, caused an increase of 11.0 in one experiment and of 11.1 in a second.

			Sp. gr.
I. MgCl , vol. of salt	22.0	...	2.187
II.	22.2	...	2.167
Mean . . .	22.1	...	2.177

Chloride of Calcium, $\text{CaCl} = 55.92$.—This salt was rendered anhydrous by fusing it in a platinum crucible for some time. 28 grains of the fused salt, thrown into turpentine, caused an increase of 11.3 at a temperature of 63° .

Atomic Volume and Specific Gravity.

433

CaCl, vol. of salt 22·5 ... Sp. gr.
2·480

Chloride of Cobalt, $\text{CoCl} = 65\cdot0$.—On throwing the fourth of an equivalent (16·25 grains) of anhydrous chloride of cobalt into turpentine, an increase of 5·5 was obtained in two experiments, and of 5·6 in a third trial.

I. CoCl , vol. of salt 22·0 ... Sp. gr.
2·954
II. ... 22·0 ... 2·954
III. ... 22·4 ... 2·902
Mean . . 22·13 ... 2·937

TABLE VII.—Showing the volume occupied by certain Hydrated Salts rendered Anhydrous.

Designation.			Volumes of anhydrous salts.				
Name.	Formulae.	Atomic weight.	Volume of salt by experiment.	11, taken as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Sulphate of magnesia	MgO, SO ₃	60·86	22·5	2	22	2·766	2·706
Sulphate of zinc	ZnO, SO ₃	80·43	21·85	2	22	3·656	3·681
Sulphate of copper...	CuO, SO ₃	79·88	22·0	2	22	3·631	3·631
Sulphate of iron.....	FeO, SO ₃	75·3	24·0	2	22	3·423	3·138
Sulphate of cobalt ...	CoO, SO ₃	77·69	22·0	2	22	3·531	3·531
Sulphate of soda.....	NaO, SO ₃	71·43	27·5	2·597
Sulphate of silver	AgO, SO ₃	156·48	29·4	5·322
Chromate of silver...	AgO, CrO ₃	168·49	29·2	5·770
Sulphate of alumina .	Al ₂ O ₃ 3SO ₃	171·95	79·2	2·171
Sulphate of copper and potash	CuO, SO ₃ + KO, SO ₃	167·31	59·8	5	55	3·042	2·797
Sulphate of nickel and potash	NiO, SO ₃ + KO, SO ₃	164·99	56·95	5	55	2·998	2·897
Sulphate of zinc and potash	ZnO, SO ₃ + KO, SO ₃	167·86	59·6	5	55	3·034	2·816
Sulphate of mag- nesia and potash	MgO, SO ₃ + KO, SO ₃	148·29	55·4	5	55	2·694	2·676
Sulphate of manga- nese and potash	MnO, SO ₃ + KO, SO ₃	163·07	54·2	5	55	2·964	3·008
Sulphate of copper and ammonia ...	CuO, SO ₃ + NH ₄ O, SO ₃	145·88	66·4	6	66	2·192	2·197
Sulphate of zinc and ammonia ...	ZnO, SO ₃ + NH ₄ O, SO ₃	146·0	65·7	6	66	2·212	2·222
Sulphate of magne- sia and ammonia }	MgO, SO ₃ + NH ₄ O, SO ₃	127·0	65·8	6	66	1·924	1·932
Potash alum	Al ₂ O ₃ 3SO ₃ + KO, SO ₃	259·36	116·4	2·228
Ammonia alum	Al ₂ O ₃ 3SO ₃ + NH ₄ O SO ₃	238·2	116·8	2·039
Carbonate of soda ...	NaO, CO ₂	53·47	22·0	2	22	2·427	2·427
Chloride of cobalt ...	Co, Cl	65·0	22·1	2	22	2·955	2·937
Chloride of magne- sium	Mg, Cl	48·12	22·1	2	22	2·187	2·177
Chloride of calcium .	Cu, Cl	55·92	22·5	2	22	2·542	2·485

The preceding table exhibits various points of great interest as regards isomorphism. Hydrogen has for a long time been recognised by chemists as equivalent to a magnesian metal; and hence the sulphate of a metal of this class should possess the volume of sulphate of water. The volume of bisulphate of potash is 55·0 by experiment, which leaves 22·0 for that of sulphate of water, on deducting the volume of sulphate of potash, which is 33·0; and the same result follows when the volume of sulphuric acid is deduced from bisulphate of soda, if we suppose the sulphate of soda to enter that salt with two volumes. Thus we have—

$$\text{Sulphate of water} \quad . \quad . \quad . \quad . = 22 \div 11 = 2$$

$$\text{Sulphate of a magnesian oxide} = 22 \div 11 = 2$$

We now see that bisulphate of potash (sulphate of water and sulphate of potash) is exactly equivalent to the double sulphates of the magnesian class. (*Vide* Section V.)

Bisulphate of potash ($\text{HO}, \text{SO}_3 + \text{KO}, \text{SO}_3$) = 55

Sulphate of magnesia and potash ($\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3$) = 55.

It is now comprehensible why bisulphate of soda should have a volume of 44·0 in the solid state and only of 18·0 in a state of solution; because sulphate of soda which assumes a volume in the solid state becomes added to the same volume possessed by sulphate of water, while in the state of solution the proper volume of sulphate of soda disappears altogether.

Bisulphate of ammonia possesses a volume due to a combination of sulphate of water and sulphate of ammonia, with a volume of 11×4 , and it will be observed that the same result attends the double sulphates of the magnesian metals with sulphate of ammonia.

Bisulphate of ammonia ($\text{NH}_4\text{O}, \text{SO}_3 + \text{HO}, \text{SO}_3$) = 66

Sulphate of ammonia and copper ($\text{NH}_4\text{O}, \text{SO}_3 + \text{CuO}, \text{SO}_3$) = 66.

The cause of this singular result is in the mutual convertibility of the primitive volumes 9·8 and 11.

It is very curious to observe the large number of volumes which have disappeared when the salt combines with water. Thus sulphate of alumina in its anhydrous state possesses a bulk equal to 79·2, which has ceased to occupy space in the hydrated salt; and still more remarkable instances of this are seen in the alums, which add to this the volumes of their alkaline sulphates. A curious result obtained in the examination of the hydrated alums is now explicable. We found that the potash alums took up in solution only the space due to their water; but that the space occupied by them in the state of salts was one volume in addition to this quantity. In the pre-

ceding section we observed that sulphate of potash possessed the singular property of expanding one volume in becoming solid; 9×2 in a state of solution becoming 11×3 in the state of a salt. It is impossible to refrain from accepting this as an explanation of the increase of one in the quotient obtained by dividing the volumes by their proper numbers 9 and 11— 24×9 becoming 25×11 .

The difficulties, to which we have already alluded, prevent us placing much confidence in our results for the anhydrous alums. Sulphate of alumina seems to affect eight volumes of ice, $9.8 \times 8 = 78.4$; in ammonia alum the latter becomes united to the volume of anhydrous sulphate of ammonia, $9.8 \times 8 + 9.8 \times 4 = 117.6$; while potash alum should consist of $9.8 \times 8 + 11 \times 3 = 111.4$. It is unnecessary to remark that these theoretical numbers possess only an approximation to our experimental results. (*Vide* remarks on Section V.)

The sulphates of soda and silver and the corresponding chromate are also obviously exceptions to the general rule of the solid volume being multiples of 11. But in the last section we had similar exceptions in salts which ranged themselves under 9.8 or the volume of ice. The sulphates now under consideration have the same divisor, if sulphate of soda be not considered an exception, as the variation is decidedly too great to be attributed to a mere error of experiment; it ought however to be observed that Mohs gives for the specific gravity of this salt 2.462, a number much more in accordance with theory than our own result; but as our experiments have been often repeated, they may perhaps be viewed as an argument in favour of an opinion, deduced from other considerations, that sulphate of soda has a double atom $27.5 \times 2 = 55$, which is 11×5 .

Name.	Volume by experiment.	9.8, or volume of ice as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Sulphate of soda	27.5	3	29.4	2.430	2.597
Sulphate of silver	29.4	3	29.4	5.322	5.322
Chromate of silver.....	29.2	3	29.4	5.711	5.770

SECTION III.

Nitrates, &c.

The nitrates do not in general affect a large proportion of water of hydration, and are therefore well-calculated to show

the volume occupied by anhydrous salts. It will be observed that they present some peculiarities.

Nitrate of Potash, $\text{KO}, \text{NO}_5 = 101.3$.—The half of an equivalent of this salt, 50.65 grains, being dissolved in 1000 grs. of water, gave an increase of 18.05 at 45° .

KO, NO_5 , vol. in solution 36.1

The same quantity of salt, 50.65 grains, thrown into turpentine, caused a rise in the stem of 24.5, 24.4, 24.5 in three successive experiments.

I.	KO, NO_5 , vol. of salt	49.0	...	Sp. gr. 2.067
II.	...	48.8	...	2.075
III.	...	49.0	...	2.067
Mean . .		48.9	...	2.070

Nitrate of Ammonia, $\text{NH}_4\text{O}, \text{NO}_5 = 80.3$.—The volume of nitrate of ammonia in solution was determined by dissolving 40.15 grains of this salt in 1000 grains of water. In one experiment the increase in the stem was 22.5, the temperature being 57° ; in a second the rise was 23.0 at 63° .

I.	$\text{NH}_4\text{O}, \text{NO}_5$, vol. in solution	45.0
II.	...	46.0
Mean . .		45.5

Half an equivalent of this salt, well-dried (40.15 grains), on being immersed in turpentine produced an increase in three experiments of 24.7, 24.5, 24.5.

I.	$\text{NH}_4\text{O}, \text{NO}_5$, vol. of salt	49.4	...	Sp. gr. 1.625
II.	...	49.0	...	1.639
III.	...	49.0	...	1.639
Mean . .		49.1	...	1.635

Nitrate of Soda, $\text{NaO}, \text{NO}_5 = 85.45$.—On dissolving 85.45 grains, or one equivalent, of this salt in 1000 grains of water, an increase of 27.1 was obtained, the temperature being 59° ; but on repetition of the experiment at the same temperature the increase was only 26.0.

I.	NaO, NO_5 , vol. in solution	27.1
II.	...	26.0
Mean . .		26.5

The half of an equivalent of this salt, 42.72 grains, well-dried, produced an increase on being thrown into turpentine of 19.6 in three experiments and 19.5 in a fourth trial.

Atomic Volume and Specific Gravity.

437

			Sp. gr.
I.	NaO, NO ₅ vol. of salt	39·2 ...	2·180
II.	39·2 ...	2·180
III.	39·2 ...	2·180
IV.	39·0 ...	2·190
	Mean . .	39·1	2·182

Nitrate of Silver, AgO, NO₅ = 170·0.—On dissolving 42·5 grains of this salt in 1000 grains of water, an increase of 6·8 was effected at a temperature of 59°.

AgO, NO₅, vol. in solution 27·2.

The same quantity of salt, 4·25 grains, thrown into turpentine, produced an increase of 9·8.

		Sp. gr.
	AgO, NO ₅ vol. of salt 39·2 ...	4·336

Nitrate of Lead; PbO, NO₅ = 165·75.—This salt gives very unsatisfactory results on being dissolved in water; at low temperatures the volume for the atom is equal to nearly 18·0, or 9×2 . But at higher temperatures the volume in solution approaches nearly to 27·0, or 9×3 ; and, although the results do not come out exact, unless corrected for expansion, we are inclined to view the latter as the true result. 83 grs. dissolved in water gave an increase of 12·5; in a second experiment of 12·7, both at a temperature of 65°.

	PbO, NO ₅ , vol. in solution	25·0
	25·4
	Mean . .	25·2

The fourth part of an equivalent, 41·43 grains, immersed in turpentine, gave an increase of 9·7; 82·87 grains gave the increase 19·2; and in a third experiment 19·0.

			Sp. gr.
I.	PbO, NO ₅ , vol. of salt	38·8 ...	4·272
II.	38·4 ...	4·316
III.	38·0 ...	4·362
	Mean . .	38·4 ...	4·316

Nitrate of Barytes, BaO, NO₅ = 130·85.—Half an equivalent of this salt, 65·42 grains, dissolved in 1000 grains of water with an increase of 13·5 at a temperature of 60°; and a repetition of the experiment was attended with the same result.

BaO, NO₅, vol. in solution 27·0.

The same quantity of salt, immersed in turpentine, caused an increase of 19·8 in three experiments, and 20·0 and 20·2 in two other experiments; the salts being all different specimens, and decrepitated previously to the experiment.

				Sp. gr.
I.	BaO, NO ₅ , vol. of salt	39.6	...	3.304
II.	39.6	...	3.304
III.	39.6	...	3.304
IV.	40.0	...	3.271
V.	40.4	...	3.238
Mean . .		39.84	...	3.284

Nitrate of Strontia = 106.0.—Half an equivalent of this salt, 53 grains, was dissolved in 1000 grains of water, with an increase of 13.0, the temperature being 62°; 106 grains dissolved in 1000 grains of water, with an increase of 27.0 at a temperature of 63°.

I.	SrO, NO ₅ , vol. in solution	26.0
II.	27.0
Mean . .		26.5

53 grains immersed in turpentine gave an increase of 19.6; and this result was confirmed by a second experiment.

	SrO, NO ₅ , vol. of salt	39.2	...	2.704
--	-------------------------------------	------	-----	-------

Nitrate of Black Oxide of Mercury, Hg₂O, NO₅ + 2HO = 282.0.—This salt, in beautiful large transparent crystals, was dissolved in water containing nitric acid, to prevent the formation of a subsalt; 70.5 grains thus treated caused an increase of 13.5.

Protonitrate of mercury, vol. in solution 54.0

On immersing the same quantity of salt in turpentine, the increase in three experiments was 14.8, 14.7, and 14.7.

				Sp. gr.
I.	Protonitrate of mercury, vol. of salt	59.2	...	4.763
II.	58.8	...	4.796
III.	58.8	...	4.796
Mean . .		58.9	...	4.785

Nitrate of Copper, CuO, NO₅ + 3HO = 120.8.—Half an equivalent (60.4 grains) dissolved in 1000 grains of water with an increase of 22.4 at 60°, and in a second experiment of 22.6; in a third experiment, 30.2 grains, dissolved in the same quantity of water, gave an increase of 11.4.

I.	CuO, NO ₅ , vol. in solution	44.8
II.	45.2
III.	45.6
Mean . .		45.2

In two experiments, 60.4 grains thrown into turpentine

caused an increase of 29.5, which gives for an equivalent of the salt the volume 59.0, and a specific gravity 2.047.

Nitrate of Magnesia, $\text{MgO}, \text{NO}_5 + 6\text{HO} = 128.8$.—The fourth part of an equivalent of crystallized nitrate of magnesia (32.2 grains) dissolved in 1000 grains of water at 60° , with an increase of 18.1 and 18.3 in two experiments.

I.	$\text{MgO}, \text{NO}_5 + 6\text{HO}$	vol. in solution	73.2
II.	72.4
Mean . .			72.8

The same quantity thrown into turpentine produced an increase of 22.0, which gives for the volume of an equivalent of the salt 88.0, and for its specific gravity 1.464.

Nitrate of Bismuth, $\text{BiO}, \text{NO}_5 + 3\text{HO} = 160.33$.—This salt, being decomposed when thrown into water, is not fitted for determining volume by solution; but when 80.16 grains were thrown into turpentine, the increase was obtained in two experiments of 29.2 and of 29.4.

I.	$\text{BiO}, \text{NO}_5 + 3\text{HO}$	vol. of salt	58.4	...	Sp. gr. 2.745
II.	58.8	...	2.727
Mean . .			58.6	...	2.736

Basic Nitrate of Mercury, $2\text{HgO}, \text{NO}_5 + 2\text{HO} = 291.0$.—This salt cannot be dissolved in water without the formation of a subsalt, unless the water is used in small proportion; it is therefore unfitted for our experiments, as far as regards the volume in solution. On immersing 68.7 grains in turpentine, an increase of 16.2 was obtained in two successive experiments. This gives 68.6 as the volume of the equivalent, and a specific gravity of 4.242.

Basic Nitrate of Lead, $2\text{PbO}, \text{NO}_5 = 277.72$.—This salt is so insoluble, that it is difficult to determine its volume in solution with any great degree of accuracy. The sixteenth part of an equivalent dissolved in 1000 grains of water gave an increase of 2.6, which seems to indicate a volume of 9×5 .

69.43 grains, being immersed in turpentine, gave an increase of 12.3 in several experiments.

Basic nitrate of lead, vol. of salt	49.2	...	Sp. gr. 5.645
-------------------------------------	------	-----	------------------

The same multiple relation of 9 is carried through all the salts of this class dissolved in water. The divisor for the solid volume is, however, different from the salts of the previous sections. Exceptional cases were pointed out in their examination, in which 9.8, or the volume of ice, became the divisor; and in the present group of salts we observe a wonderful uniformity in this respect.

TABLE VIII.—Showing the volumes occupied by certain Nitrates.

Designation.			Volume in solution.			Volume in state of salt.				
Name.	Formula.	Atomic weight.	Volume by experiment.	9 taken as unity.	Volume by theory.	Volume of salt by experiment.	98. or volume of ice as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Nitrate of potash ...	KO, NO ₅	101.3	36.1	4	36	48.9	5	49.0	2.067	2.070
Nitrate of ammonia	NH ₄ O, NO ₅	80.3	45.5	5	45	49.1	5	49.0	1.639	1.635
Nitrate of soda	NaO, NO ₅	85.45	26.5	3	27	39.1	4	39.2	2.180	2.182
Nitrate of silver ...	AgO, NO ₅	170.0	27.2	3	27	39.2	4	39.2	4.336	4.336
Nitrate of lead	PbO, NO ₅	165.75	25.4	3	27	38.4	4	39.2	4.228	4.316
Nitrate of barytes ..	BaO, NO ₅	130.85	27.0	3	27	39.8	4	39.2	3.338	3.284
Nitrate of strontia ..	SrO, NO ₅	106.0	26.5	3	27	39.2	4	39.2	2.704	2.704
Nitrate of black oxide of mercury	Hg ₂ O, NO ₅ +2HO	282.0	54.0	6	54	58.9	6	58.8	4.796	4.785
Basic nitrate of mercury	2HgO, NO ₅ +2HO	291.0	68.6	7	68.6	4.242	4.242
Basic nitrate of lead	2PbO, NO ₅	277.72	49.2	5	49.0	5.667	5.645
Nitrate of bismuth.	BiO, NO ₅ +3HO	160.33	58.6	6	58.8	2.727	2.736
Nitrate of copper ...	CuO, NO ₅ +3HO	120.8	45.2	5	45	59.0	6	58.8	2.054	2.047
Nitrate of magnesia	MgO, NO ₅ +6HO	128.8	72.8	8	72	88.0	9	88.2	1.460	1.464

It is almost superfluous to offer any remarks upon this group of salts, especially as we shall have to consider several of them in a future section. It cannot escape attention, that the nitrates of soda, silver, lead, strontia and barytes possess the same atomic volume, as might have been expected from the isomorphism of several of them. Nitrates of soda and potash do not possess the same atomic volume, and therefore their alleged isomorphism, deduced from the observation by Frankenheim* of microscopic crystals of nitrate of potash similar to those of nitrate of soda, is highly questionable. The principal exception to the volumes of the nitrates now described being multiples of ice is that of nitrate of lead, which has a volume of 38.4, instead of 39.2; but this must be due to the nature of the salt, which comes out as unsatisfactorily in a state of solution as in the solid state.

SECTION IV.

Chlorides, Bromides and Iodides.

Chloride of Potassium, KCl = 74.7.—On dissolving 37.5 grains of this salt in 1000 grains of water, the increase was 13.3 at a temperature of 57°; a second experiment with the

* Poggendorff's *Ann.*, Band xl. S. 447.

Atomic Volume and Specific Gravity.

441

same quantity gave the increase 13·5 at 58°; and a third experiment gave 13·7 at 65°.

I.	KCl, vol. in solution	26·5
II.	26·8
III.	27·2
Mean . .		26·8

The whole of an equivalent thrown into turpentine (the salt having been decrepitated) increased 39·6, and 39·3 in two experiments. Half an equivalent, 37·35 grains, caused a rise in the stem of 19·6 in two experiments.

			Sp. gr.
I.	KCl, vol. of salt	39·6 ...	1·887
II.	39·3 ...	1·900
III.	39·2 ...	1·905
IV.	39·2 ...	1·905
Mean . .		39·3 ...	1·900

Chloride of Ammonium, NH_4Cl = 53·66.—Half an equivalent, 26·83 grains, dissolved in 1000 grains of water with an increase of 17·5 at a temperature of 60°; in two other experiments at 63°, the increase was 18·0.

I.	NH_4Cl , vol. in solution	35·0
II.	36·0
III.	36·0
Mean . .		35·7

Our experiments on the specific gravity of this salt gave 1·578 as an uniform result, indicating a volume of 34·0.

Bromide of Potassium, KBr = 117·6.—The fourth part of an equivalent, 29·4 grains, on being dissolved in water at 49°, gave in two experiments an increase of 7·2; which gives for the volume of the salt in solution 28·8. The same quantity of salt, immersed in turpentine at 63°, caused an increase of 11·0 in two experiments.

		Sp. gr.
	KBr , vol. of salt	44·0 ... 2·672

Iodide of Potassium, KI = 165·82.—This salt was decrepitated, and on dissolving 41·5 grains gave an increase of 11·0 at 57°; a second experiment with 83 grains gave an increase of 22·0 at 55°.

I.	KI, vol. in solution	44
II.	44
Mean . .		44

On projecting 41·45 grains of this salt, previously decrepitated, into turpentine, an increase of 13·6 and 13·5 was produced in two successive experiments.

I.	KI, vol. of salt	54.4	...	Sp. gr. 3.048
II.	54.0	...	3.070
	Mean . .	54.2	...	3.059

Chloride of Sodium, $\text{NaCl} = 58.78$.—The whole of an equivalent of this salt, previously decrepitated, dissolved in 1000 grains of water at 60° with a rise of 18.0 ; and in a second experiment of 18.2 ; in a third experiment 118 grains of salt were dissolved in 1000 grains of water at 62° with an increase of 38.0 .

I.	NaCl , vol. in solution	18.0
II.	18.2
III.	18.9
	Mean . .	18.3

80 grains of salt were treated as described (page 405), in the mercurial volumometer, and the empty part of the tube, after the restoration of the mercury, showed a volume of 40.0 . The same quantity thrown into alcohol previously saturated with it, gave an increase of 39.5 . The whole of an equivalent, 58.78 grains, thrown into a saturated solution, caused an increase of 29.3 .

I.	NaCl , vol. of salt	29.4	...	Sp. gr. 2.000
II.	29.0	...	2.026
III.	29.3	...	2.006
	Mean . .	29.23	...	2.011

Bromide of Sodium, $\text{NaBr} + 3\text{HO} = 128.70$.—On dissolving 25.7 grains of this salt in water, an increase of 9.2 was occasioned in two experiments at a temperature of 53° .

I. II. $\text{NaBr} + 3\text{HO}$, vol. in solution 46

The same quantity of salt put into turpentine caused an increase of 11.

$\text{NaBr} + 3\text{HO}$, vol. of salt 55 ... 2.340

Chloride of Barium, $\text{BaCl} + 2\text{HO} = 122.83$.— 30.7 grains dissolved in 1000 grains of water, increased 7.0 at a temperature of 58° ; a second experiment, in which 20 grains of the salt were dissolved, gave an increase of 4.5 .

I.	$\text{BaCl} + 2\text{HO}$ vol. in solution	28.0
II.	27.6
	Mean . .	27.8

The fourth of an equivalent, 30.7 grains, being immersed in a saturated solution, gave an increase of 9.7 at a temperature of 60° ; and the same quantity in two other experiments gave an increase of 9.8 .

				Sp. gr.
I.	Ba Cl + 2HO	vol. of salt	38·8 ...	3·166
II.	39·2 ...	3·133
III.	39·2 ...	3·133
Mean . . .				3·144

Perchloride of Mercury, $\text{Hg Cl} = 136·9$.—The fourth of an equivalent, 34·2 grains, of corrosive sublimate, on being dissolved in 1000 grains of water, gave an increase of 4·6 at a temperature of 62° ; a second experiment with the same quantity was attended with the same result.

I. II. Hg Cl , vol. in solution 18·4

Half an equivalent (68·45 grains), thrown into a saturated solution of the salt, caused an increase of 11·0 at a temperature of 56° .

I.	Hg Cl , vol. of salt	22 ...	Sp. gr.
			6·223

Chloride of Hydrogen, $\text{HCl} = 36·47$.—It was of interest to ascertain the volume of hydrochloric acid, in order to compare it with the other chlorides of the magnesian metals when dissolved in water. It was natural to expect that the volume of muriatic acid in dilute solutions would be different from that possessed by it in its concentrated state; and therefore the following experiments must be viewed in this light. Peligot's salt, the bichromate of the chloride of potassium, on dissolving in water, was decomposed into bichromate of potash and muriatic acid, and the volume of the latter was obtained by deducting that due to the former salt and adding the volume of water. The fourth part of an equivalent of this salt, 44·75 grains, dissolved in 1000 grains of water with an increase of 13·5 at 65° ; and of 13·6 in another experiment at 68° . This result gives for the whole volume of the salt when dissolved 54·0 and 54·4, from which must be deducted 45·0 for the volume of bichromate of potash, and 9 must be added on account of the equivalent of water.

I.	Muriatic acid, in dilute solutions	18·0
II.	18·4
	Mean . . .	18·2

Chloride of Copper, $\text{Cu Cl} + 2\text{HO} = 85·18$.—Half an equivalent, 42·6 grains, was dissolved in 1000 grains of water with an increase of 13·4 at a temperature of 60° ; on a second experiment, 47 grains occasioned an increase of 14·0 at a temperature of 58° .

I.	$\text{CuCl} + 2\text{HO}$, vol. in solution	26·8
II.	25·4
	Mean . . .	26·1

Half an equivalent, 42·6 grains, being immersed in a saturated solution at 62°, caused an increase of 17·0; a second experiment with the same quantity of salt gave an increase of 16·6.

I.	CuCl + 2HO, vol. of salt	33·2	...	Sp. gr. 2·566
II.	...	34·0	...	2·505
	Mean . .	33·6	...	2·535

Chloride of Copper and Ammonium, $\text{CuCl} + \text{NH}_4\text{Cl} + 2\text{HO} = 138·84$.—34·7 grains of this salt, being dissolved in 1000 grains of water, gave an increase of 15·5 in the first experiment and of 15·4 in the second, both at a temperature of 68°.

I.	CuCl + NH ₄ Cl + 2HO, vol. in solution	62·0
II.	...	61·6
	Mean . .	61·8

32·46 grains, thrown into a saturated solution, caused an increase of 16·1 in two experiments at a temperature of 60°, and a repetition of the experiment confirmed this result.

Chloride of copper and ammonium, vol. of salt 68·8 ... 2·018

Chloride of Copper and Potassium, $\text{CuCl} + \text{KCl} + 2\text{HO} = 159·88$.—34·7 grains of this salt, being dissolved in 1000 grains of water, caused an increase of 11·5 at 62°.

$\text{CuCl} + \text{KCl} + 2\text{HO}$, vol. in solution 53·0

The same quantity (34·7 grains), thrown into a saturated solution, caused an increase of 14·3.

$\text{CuCl} + \text{KCl} + 2\text{HO}$, vol of salt 65·9 ... 2·426

Chloride of Tin, $\text{SnCl} + 3\text{HO} = 121·39$.—One-fourth of an equivalent (30·35 grains) was dissolved in 1000 grains of water, acidulated with muriatic acid, with an increase of 9·0 at a temperature of 60°; a second experiment, with the same quantity of salt and at the same temperature, gave an increase of 9·2.

I.	SnCl + 3HO, vol. in solution	36·0
II.	...	36·8
	Mean . .	36·4

The same quantity, 30·35 grains, of the salt being immersed in a saturated solution, yielded an increase of 11·0, the temperature being 60°; and exactly the same result attended the repetition of the experiment.

$\text{SnCl} + 3\text{HO}$, vol. of salt 44·0 ... Sp. gr.
2·759

Chloride of Tin and Ammonium, $\text{SnCl} + \text{NH}_4\text{Cl} + 3\text{HO} = 175·05$.—On dissolving 44 grains of this salt in 1000 grains of water, the increase was 18·3 at a temperature of 60°; a

second experiment with the same quantity and at the same temperature, gave an increase of 18.5.

I.	Chloride of tin and ammonium, vol. in solution	72.7
II.	73.5
	Mean . .	73.1

On immersing 43.76 grains of the salt in a saturated solution, an increase of 20.8 was obtained at a temperature of 60°, which gives 83.2 as the volume of the equivalent, and 2.104 as the specific gravity of the salt.

Chloride of Tin and Potassium, $\text{SnCl} + \text{KCl} + 3\text{HO} = 196.09$.—On dissolving 24.3 grains of the salt in 1000 grains of water, an increase of 8.0 was obtained at a temperature of 60°; and 48.5 grains, dissolved in the same quantity of water, gave an increase of 15.5.

I.	Chloride of tin and potassium, vol. in solution	64.5
II.	62.7
	Mean . .	63.6

On throwing the fourth part of an equivalent, 49 grains, into a saturated solution, an increase of 19.5 was obtained at a temperature of 54°.

Sp. gr.

$\text{SnCl} + \text{KCl} + 3\text{HO}$, vol. of salt 78.0 ... 2.514

A. *Chloride of Mercury and Ammonium*, $\text{HgCl} + \text{NH}_4\text{Cl} + \text{HO} = 199.8$.—On dissolving 49.95 grains of this salt in 1000 grains of water, an increase was obtained of 16.0, and in a second experiment of 16.2, the temperature being about 60° in both cases.

I.	A. Chloride of mercury and ammonium, vol. in sol.	64.0
II.	64.8
	Mean . .	64.4

The same quantity of salt, thrown into a saturated solution at 60°, occasioned an increase of 17.0 in two experiments, which makes the volume of the equivalent 68.0, and the specific gravity 2.938.

B. *Chloride of Mercury and Ammonium*, $\text{NH}_4\text{Cl} + 2\text{HgCl} + \text{HO} = 336.4$.—On dissolving 42 grains of this salt in 1000 grains of water, an increase of 10.1 was occasioned in two experiments at 54°, and of 10.2 in a third experiment at 60°.

I.	II.	$\text{NH}_4\text{Cl} + 2\text{HgCl} + \text{HO}$, vol. in solution	80.9
III.	81.6
	Mean	81.2

42 grains, or one-eighth of an equivalent, thrown into a saturated solution of the salt, caused a rise in the stem of 11 in two experiments.

I. II. B. Chloride of mercury and } Sp. gr.
ammonium, vol. of salt . } 88.0 ... 3.822.

Chloride of Mercury and Potassium, $\text{KCl} + 2\text{HgCl} + 2\text{HO}$
= 366.5.—The eighth part of an equivalent, 45.8 grains,
being dissolved in 1000 grains of water, caused in two experi-
ments an increase of 10.1 at a temperature of 53°.

I. II. Chloride of mercury and potassium, }
vol. in solution } 80.8.

The same quantity of salt, 45.8 grains, thrown into a satu-
rated solution, caused an increase of 12.0 in one experiment
and of 12.4 in two other trials, the temperature in all the
cases being 58°.

I. Chloride of mercury and potassium, } Sp. gr.
vol. of salt } 96.0 ... 3.818
II. 99.2 ... 3.694
III. 99.2 ... 3.694
Mean . . . 98.1 ... 3.735

Chloride of Mercury and Sodium, $\text{NaCl} + 2\text{HgCl} + 4\text{HO}$
= 368.5.—On dissolving 46.06 grains of this salt in 1000 grains
of water, the increase was 12.4 at 63°. This gives for the
equivalent a volume of 99.2, or 11 equivalents. The same
quantity of salt thrown into turpentine produced an increase
of 15.3, which gives for the equivalent 122.4, and for the spe-
cific gravity 3.011.

A careful consideration of the previous experiments shows
that there are two distinct classes of chlorides, &c. The first
of these is placed in Table IX., and possesses 11 as the divi-
sor of the solid.

TABLE IX.

Designation.			Vol. in solution.			Volume of solid.				
Name.	Formula.	Atomic weight.	Volume by experiment.	9, taken as unity.	Volume by theory.	Volume by experiment.	11, taken as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Bromide of potassium .	K Br	117.6	28.8	3	27	44.0	4	44	2.672	2.672
Chloride of ammonium.	NH_4Cl	53.66	35.7	4	36	34.0	3	33	1.626	1.578
Iodide of potassium ...	K I	165.82	44.0	5	45	54.2	5	55	3.015	3.059
Bromide of sodium ...	$\text{Na Br} + 3\text{HO}$	128.70	46.0	5	45	55.0	5	55	2.340	2.340
Chloride of mercury ...	Hg Cl	136.9	18.4	2	18	22.0	2	22	6.223	6.223
Chloride of hydrogen...	H Cl	36.47	18.2	2	18
Chloride of copper.....	$\text{Cu Cl} + 2\text{HO}$	85.18	26.1	3	27	33.6	3	33	2.581	2.534
Chloride of tin	$\text{Sn Cl} + 3\text{HO}$	121.39	36.4	4	36	44.0	4	44	2.759	2.759
Chloride of mercury } and sodium	$2\text{Hg Cl} + \text{Na Cl}$ } + 4HO }	368.5	99.2	11	99	122.4	11	121	3.045	3.011

In the second class (Table IX.A.) the primitive volume is 9·8, or, as in the case of the double chlorides of tin, the metallic salt enters into combination with the volume 11; while NH_4Cl remains a multiple of 9·8. It is interesting to observe that NH_4Cl affects in combination as a solid the same number of volumes which it has as a liquid.

TABLE IX.A.—Showing the Volumes in solution and in the solid state of certain Chlorides.

Designation.			Vol. in solution.			Volume of salt.				
Name.	Formula.	Atomic weight.	Volume by experiment.	9, or volume of water as unity.	Volume by theory.	Volume of salt by experiment.	9·8, or volume of ice as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Chloride of potassium	K Cl	74·7	26·8	3	27	39·3	4	39·2	1·905	1·900
Chloride of sodium.....	Na Cl	58·78	18·3	2	18	29·2	3	29·4	2·000	2·011
Chloride of barium ...	Ba Cl + 2HO	122·83	27·8	3	27	39·07	4	39·2	3·133	3·144
Chloride of copper and potassium	Cu Cl + KCl + 2HO	159·88	53·0	6	54	65·9	7	68·6	2·331	2·426
Chloride of copper and ammonium ...	Cu Cl + NH_4Cl + 2HO	138·84	61·8	7	63	68·8	7	68·6	2·024	2·018
Chloride of tin and ammonium	Sn Cl + NH_4Cl + 3HO	175·05	73·1	8	72	83·2	8	83·2	2·104	2·104
Chloride of tin and potassium	Sn Cl + KCl + 3HO	196·09	63·6	7	63	78·0	8	78·4	2·501	2·514
A. Chloride of mercury and ammonium	Hg Cl + NH_4Cl + HO	199·8	64·4	7	63	68	7	68·6	2·912	2·938
B. Chloride of mercury and ammonium	2Hg Cl + NH_4Cl + HO	336·4	81·2	9	81	88	9	88·2	3·814	3·822
Chloride of mercury and potassium.....	2Hg Cl + KCl + 2HO	366·5	80·8	9	81	98·1	10	98·0	3·739	3·736

The results of the experiments detailed in this section afford strong proofs of the law of multiple proportions, and exhibit at the same time that remarkable alteration of the divisor of the solid volumes which we have already noticed so frequently. Thus, while many of the chlorides and bromides are multiples of 11, we have decided exceptions in chlorides of potassium and sodium, which possess for their divisor the volume of ice, viz. 9·8; and this reappears in the double salts.

It is impossible, however, not to see that these results are somewhat singular, for in the double salts the chloride of potassium forces the double salt with which it is associated to assume the multiples of 9·8, and then exhibits its natural isomorphous relation to chloride of ammonium, which *per se* it did not possess. Chloride of ammonium, anomalous, in being a multiple of 11 in the solid state, assumes four volumes,

multiples of 9·8, in the double chlorides, and then presents the same number for its solid volume as chloride of potassium. The isomorphism of potassium and sodium is so entirely hypothetical, that it will not excite surprise to find the volumes of the chlorides so different. We were less prepared to detect the difference between iodide and chloride of potassium; but have confirmed it by an examination of iodide of ammonium, 50 grains of which dissolved in 1000 of water with an increase of 18·7, which gives $\frac{54\cdot1}{9}$ = six volumes for the equivalent, a result confirmatory of our determination of five volumes for iodide of potassium; the increase of one volume being in conformity with the usual behaviour of ammoniacal salts. We shall return to the consideration of the chlorides in a future section.

SECTION V.

Chromates.

The chromates present a class of salts which offer some peculiarities with regard to their volumes, in elucidating which we had occasion to repeat our experiments very often, and, therefore, give the mean of the results, instead of taking up unnecessary space in the Transactions of the Society by describing each experiment individually.

Chromic Acid, $\text{CrO}_3 = 52\cdot19$.—The chromic acid used in our experiments was obtained by adding sulphuric acid to bichromate of potash. It was in beautiful distinct crystals of nearly a quarter of an inch in length, being the finest and purest specimen which we have obtained in many preparations of this acid.

The half of an equivalent, 26·09 grains, dissolved in 1000 of water with an increase of 9·0 at 72°; this gives 18·0 as the volume of chromic acid in solution.

The same quantity of acid, thrown into the solution from which it had crystallized, gave an increase of 9·7 and 9·8 in two experiments.

I.	Chromic acid, volume	19·4	...	2·690
II.	...	19·6	...	2·663
	Mean	19·5	...	2·676

Yellow Chromate of Potash, $\text{K}_2\text{CrO}_4 = 99\cdot50$.—On dissolving 50 grains of this salt in 1000 grains of water, the increase was 9·0 at a temperature of 58°; this gives 17·9 as the volume of the equivalent in solution.

The mean result of ten experiments, on immersing 49·75

grains in turpentine, was an increase of 18.55, which gives 37.1 for the volume of the equivalent, and 2.682 as the specific gravity of the salt.

Sesquichromate of Potash, $2\text{KO}, 3\text{CrO}_3 = 251.09$.—This salt, which will be described in a future communication by one of us, is obtained by boiling a solution of bichromate of potash with an excess of finely pounded litharge. The oxide of lead removes only one-fourth of the chromic acid of the bichromate, and the solution on cooling deposits the sesquichromate in flattened prisms of a paler but more resplendent colour than the bichromate of potash. On dissolving the fourth part of an equivalent, 62.77 grains, in 1000 grains of water, the increase in four experiments at 58° was exactly 18.0; this gives 72.0 as the volume of the equivalent in solution.

The mean of six experiments, placing the fourth of an equivalent, 62.77 grains, in turpentine, was an increase of 23.7, which gives 94.8 as the volume of the equivalent, and 2.648 as the specific gravity of the salt.

Bichromate of Potash, $\text{KO}, 2\text{CrO}_3 = 151.70$.—On dissolving 76 grains of this salt in 1000 grains of water, an increase of 22.5 and 23.0 were obtained in two experiments at 60° and 65° .

I.	$\text{KO}, 2\text{CrO}_3$, vol. in solution	44.9
II.	45.8
	Mean . .	45.3

Half an equivalent of the salt, 75.84 grains, immersed in turpentine, gave an increase, the mean of *ten* experiments, of 28.9, which gives 57.8 as the volume of an equivalent, and 2.624 as the specific gravity of the salt.

Terchromate of Potash, $\text{KO}, 3\text{CrO}_3 = 203.92$.—This salt was obtained by mixing a solution of bichromate of potash with nitric acid and crystallizing. On dissolving 51 grains of the salt in 1000 grains of water, an increase was occasioned of 18.0 at 60° ; this gives 71.9 as the volume of the equivalent in solution.

On immersing 50.98 grains in turpentine, the increase was 19.3 in two experiments, and 19.0 in a third trial.

I.	$\text{KO}, 3\text{CrO}_3$, vol. of salt	77.2	...	2.641
II.	77.2	...	2.641
III.	76.0	...	2.683
	Mean . .	76.8	...	2.655

Bichromate of Chloride of Potassium, $\text{KCl} + 2\text{CrO}_3 = 179.08$.—The fourth part of an equivalent, 44.77 grains, being

dissolved in 1000 grains measure of a dilute solution of muriatic acid, gave an increase of 15·7 in two experiments at 57°; this result makes the volume of an equivalent in solution 62·8.

The mean of various experiments on this salt gave an increase of 18·15 on immersing the above quantity of salt in turpentine, which yields 72·6 as the volume of the equivalent, and 2·466 as the specific gravity of the salt.

The results now described show that the chromates form a group different from the classes of salts hitherto given.

TABLE X.—Showing the Volumes occupied by certain Chromates.

Designation.			Volume of salt in solution.			Volume of salt.	
Name.	Formula.	Atomic weight.	Volume in solution by experiment.	9, taken as unity.	Volume by theory.	Volume of salt.	Specific gravity.
Chromic acid	CrO ₃	52·19	18·0	2	18·0	19·5	2·676
Chromate of potash	KO, CrO ₃	99·50	17·9	2	18·0	37·1	2·682
Sesquichromate of potash.	2KO, 3CrO ₃	251·07	72·0	8	72·0	94·8	2·648
Bichromate of potash.....	KO, 2CrO ₃	151·70	45·3	5	45	57·8	2·624
Terchromate of potash ...	KO, 3CrO ₃	203·92	71·9	8	72	76·8	2·655
Bichromate of chloride of potassium	K Cl + 2CrO ₃	179·08	62·8	7	63	72·6	2·466

An inspection of the previous table will show clearly that the chromates differ from the salts described in the former sections. In the volumes in solution there is no difference; they are multiples of 9, and follow the usual law of the sum of the volumes, being made up of the volumes of the constituents of the salt. Chromate of potash possesses two volumes in solution, exactly as is the case with its analogue sulphate of potash. The latter salt affects three volumes in the solid state, and so naturally should chromate of potash. In bichromate of potash we see these three volumes appearing in solution, united to two volumes possessed by the chromic acid attached to the chromate of potash; in sesquichromate of potash they again reappear, and so also in terchromate of potash. The fact that the number of volumes possessed in the solid state by the lowest member of a series of salts passes over into the higher members when in solution, finds examples in the carbonates and oxalates, and is not peculiar to the chromates.

The solid volumes of the chromates possess decided peculiarities, being neither multiples of 11 nor of 9·8. Chromic acid

itself is obviously twice the volume of ice, $9.8 \times 2 = 19.6$, the experimental number being 19.5. But all the other salts in this group refuse to arrange themselves under either of the heads which we have found to explain most of the salts in the previous sections. In an exception of this kind we are entitled to make an assumption which will in all probability be near the truth, if by means of it we can bring into one uniform system a whole group of anomalous salts. Sesquichromate of potash is of great importance in the history of the chromates, from its frequent occurrence, although hitherto it has been altogether neglected by chemists. Chromic acid is actually able to displace sulphuric acid from sulphate of potash, in order to gratify its love for the potash in the peculiar condition of the sesquichromate. In numerous instances of decomposition, as will be pointed out by one of us in another paper, this sesquichromate appears. The sesquichromate is not formed readily, if indeed it is ever formed, by crystallizing chromate of potash with chromic acid in the proportion of sesquichromate, the result being bichromate of potash and chromate of potash, which crystallize separately. Here then is a remarkable point in the constitution of the chromates, which can only be explained by supposing that sesquichromate of potash contains a double atom of chromate of potash united to one of chromic acid. The decomposition of bichromate of potash by oxide of lead necessarily implies that its atom should also be doubled; $2\text{KO}, 3\text{CrO}_3 + \text{CrO}_3$ boiled with litharge, gives $2\text{KO}, 3\text{CrO}_3 + \text{PbO}, \text{CrO}_3$.

We have found the volume of KO, CrO_3 to be 37.1, not 33.0, as in the case of sulphate of potash. Karsten obtained the specific gravity 2.640, which gives the volume 37.6; and Thomson states the specific gravity to be 2.612, which gives the volume 38.1; the mean of all these experiments is 37.6, which, multiplied by 2, for the reasons already stated, gives as the volume of $2(\text{KO}, \text{CrO}_3)$, 75.2. The natural volume of chromate of potash, deduced from its analogy to sulphate of potash, would be 11×3 , or on the double atom $11 \times 6 = 66$. Now, the assumption we make to explain this class of salts is, that the double atom of chromate of potash enjoys its anomalous character by adding to its natural volume the volume of ice, thus $66.0 + 9.8 = 75.8$, which is not very far from the volume ascertained by experiment. This assumption of a volume of ice, in addition to other volumes of 11, has been shown to exist in the magnesian sulphates, and therefore its hypothetical existence in the chromates is by no means extravagant. Sesquichromate of potash must then be the double chromate of potash united to an equivalent of chromic acid, $75.8 + 19.6$

=95.4, which is not very far from 94.8, the volume determined by experiment. Bichromate of potash would consist of a double atom of chromate of potash and 2 of chromic acid, or $75.8 + 39.2 = 115.0$, which agrees pretty closely with the experimental determination of 115.6; and terchromate of potash, in like manner, is 1 atom of double chromate of potash with 4 of chromic acid, or $75.8 + 78.4 = 154.2$, which is almost exactly the same as 154.4, found in the two consecutive experiments, and not far distant from 153.6, the mean of the three experiments.

This view receives confirmation from the volume of Peligot's salt, which certainly consists of the volume of KCl, when in combination, added to that of 2 atoms of chromic acid, $33.0 + 39.2 = 72.2$, a number very close to the experimental result 72.6. It is quite true that we have made a gratuitous assumption at the outset of our explanation; but it is not surprising to find an unusual law prevailing in a class of salts so anomalous as the chromates. When the experimental numbers, and those calculated on the assumption, are so near as we have shown them to be, there is, we think, a good argument for the truth of the hypothesis.

TABLE X.A.

Name.	Formula.	Volume by experiment.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Chromic acid	CrO_3	19.5	19.6	2.663	2.676
Chromate of potash, doubled	$(2\text{KO}, 2\text{CrO}_3)$	75.2	75.8	2.627	2.646
Sesquichromate of potash	$(2\text{KO}, 2\text{CrO}_3) + \text{CrO}_3$	94.8	95.4	2.658	2.648
Bichromate of potash ...	$(2\text{KO}, 2\text{CrO}_3) + 2\text{CrO}_3$	115.6	115.0	2.638	2.624
Terchromate of potash ...	$(2\text{KO}, 2\text{CrO}_3) + 4\text{CrO}_3$	154.4	154.2	2.644	2.641
Bichromate of chloride of potassium	$\text{KCl} + 2\text{CrO}_3$	72.6	72.2	2.480	2.466

A singular result obtained in the examination of the anhydrous double sulphates seems to be explained by the behaviour of the chromates. We found sulphate of copper and potash and sulphate of magnesia and potash to affect a volume of 59.8 instead of 55.0, and we ascertained, by many experiments, that this high number was not due to an error of observation. Now, if we suppose the KO , SO_3 in these salts to behave like KO , CrO_3 in assuming one volume of ice on the double atom, then $2\text{KO}, \text{SO}_3 = 75.8 + 2\text{MO}, \text{SO}_3 = 44.0 = \frac{119.8}{2} = 59.9$,

a number almost identical with the experimental result. On this view, then, anhydrous double sulphates are constituted on the type of red chromate of potash, the *two volumes* of CrO_3 being replaced by the *two volumes* of MO , SO_3 . Anhydrous alum was found to have a volume of 116.4 instead of 111.4, but would be reconciled with theory, if we supposed it to contain the peculiar KO , SO_3 analogous to KO , CrO_3 ; in this case the theoretical volume would be 116.3.

SECTION VI.

Carbonates.

Carbonate of Potash, KO , $\text{CO}_2 = 69.4$.—On dissolving 34.7 grains of carbonate of potash in 1000 grains of water, the increase was 4.6 at 62° ; the atomic volume in solution is therefore 9.2. The same quantity of salt thrown into turpentine caused, in various experiments, an increase of 16.5; this makes the volume of the equivalent 33.0, and the specific gravity of the salt 2.103.

Bicarbonate of Potash, KO , HO , $2\text{CO}_2 = 100.6$.—The fourth part of an equivalent (25.1 grains) dissolved in 1000 grains of water, at 61° , with an increase of 8.9, and in another experiment of 9.0. The mean of these results, 8.95, gives as the volume of the equivalent in solution, 35.8. The same quantity of salt, thrown into turpentine, gave an increase of 12.0, in various experiments, which gives for the specific volume of the salt 48.0, and for its specific gravity 2.092. As this salt was one of the very few substances used in this inquiry not prepared by ourselves, we take the mean of our own result, and the only other recorded specific gravity of which we are aware, viz. that by Gmelin, 2.012, and adopt 49.0 as the correct volume, and 2.052 as the specific gravity.

Bicarbonate of Ammonia, HO , NH_4O , $2\text{CO}_2 = 79.3$.—This salt was made by exposing the carbonate of the shops to the air until it ceased to emit smell, and then crystallizing the remainder. On dissolving 19.82 grains, the fourth of an equivalent, in 1000 grains of water, the increase was 9.0 at 55° , and 9.4 in another experiment at 62° . The mean result gives 36.8 as the volume of the salt in solution.

On immersing 19.82 grains of the salt in turpentine, an increase of 12.5 was effected, which gives as the volume of the salt 50.0, and for its specific gravity 1.586.

Bicarbonate of Soda, NaO , HO , $2\text{CO}_2 = 84.64$.—On dissolving 42.32 grains of this salt in 1000 grains of water at 67° , an increase of 9.0 was obtained; this gives for the volume of an equivalent in solution 18.0. On immersing the same quantity of salt in turpentine, the increase was 19.4 and 19.2 in two experiments.

I.	NaO, HO, 2CO ₂ , vol. of salt	38·8	...	2·181
II.	...	38·4	...	2·204
	Mean . .	38·6	...	2·192

Although we have examined other carbonates, we purposely avoid bringing them into the present paper, because they involve considerations upon which we are at present engaged in minute study, and do not wish to hazard without sufficient proof. We subjoin the few carbonates here examined in a tabular form.

TABLE XI.—Showing the Volumes occupied by the Alkaline Carbonates.

Designation.			Vol. in solution.			Volume of salt.	
Name.	Formula.	Atomic Weight.	Volume in solution.	9, taken as unity.	Volume by theory.	Volume of salt by experiment.	Specific gravity by experiment.
Carbonate of potash	KO, CO ₂	69·4	9·2	1	9	33·0	2·103
Carbonate of soda	NaO, CO ₂	53·47	22·0	2·427
Bicarbonate of potash ...	HO, KO, 2CO ₂	100·6	35·8	4	36	49·0	2·052
Bicarbonate of soda	HO, NaO, 2CO ₂	84·64	18·0	2	18	38·6	2·192
Bicarbonate of ammonia .	HO, NH ₄ O, 2CO ₂	79·3	36·8	4	36	50·0	1·586

The results shown in this table will appear perplexing, unless the facts already observed in the previous sections be borne in mind. We find in carbonate of potash an astonishing difference between the liquid and the solid volume; and this is still more marked in the case of carbonate of soda, which ceases to occupy volume in solution. Both of these salts have 11 as the divisors of their solid volume, KO, CO₂ affecting three, and NaO, CO₂ two volumes. In the last section we saw that the three volumes possessed by chromate of potash in its solid state passed over into bichromate of potash; and in bicarbonates of potash and ammonia we observe the same circumstance, except that the volumes change from multiples of 11 to multiples of 9·8, and in solution are one less than in the state of a salt. It is probably owing to this circumstance that we do not in this case observe the usual increase of one volume in the ammoniacal over the corresponding salt of potash. The bicarbonates of potash, soda and ammonia are probably multiples of 9·8, or the volume of ice.

Vol. by experiment. Vol. by theory.

Bicarbonate of potash	49·0 .. 2·052	9·8 × 5 = 49·0 .. 2·052
... ammonia	50·0 .. 1·586	9·8 × 5 = 49·0 .. 1·618
... soda	38·6 .. 2·192	9·8 × 4 = 39·2 .. 2·159

SECTION VII.

Oxalates.

The oxalates offered an interesting group of salts for examination, especially on account of the accurate determination of their composition and hydration by Graham.

Oxalate of Water, $\text{HO}, \text{C}_2\text{O}_3 + 2\text{HO} = 63.26$.—32 grains of oxalic acid, dissolved in 1000 grains of water, caused an increase of 18.5° at a temperature of 55° ; the same quantity, being subjected to a second experiment, caused an increase of 19° ; and a third experiment, in which 21 grains were dissolved in $9\frac{1}{2}$ ounces of water, occasioned an increase of 12 at 40° .

I.	$\text{HO}, \text{C}_2\text{O}_3 + 2\text{HO}$	vol. in solution	36.5
II.	37.5
III.	36.0
Mean . .			36.6

A whole equivalent thrown into turpentine caused, in various experiments, an increase of 39.0° , which gives for its specific gravity 1.622. Richter states the specific gravity to be 1.507; but it is impossible that he can have operated upon a pure specimen, as we have repeated the experiments upon this acid very frequently.

Oxalate of Potash, $\text{KO}, \text{C}_2\text{O}_3 + \text{HO} = 92.39$.—A quantity of salt, 42.5 grains, being dissolved in 1000 grains of water, gave an increase of 13.0° ; and the same result attended a repetition of the experiment, the temperature in both cases being at 60° .

$\text{KO}, \text{C}_2\text{O}_3 + \text{HO}$, vol. in solution 28.2

46.2 grains of the same salt, being put into a saturated solution, caused a rise in the stem of 22.0° ; a repetition of the experiment with the same quantity gave the increase 21.9° , the temperature in both cases being 61° .

I.	$\text{KO}, \text{C}_2\text{O}_3 + \text{HO}$	vol. of salt	44.0	...	Sp. gr.
II.	43.8	...	2.100
Mean . .			43.9	...	2.109
					2.104

Oxalate of Ammonia, $\text{NH}_4\text{O}, \text{C}_2\text{O}_3 + \text{HO} = 71.43$.—Half an equivalent of this salt (35.71 grains) was dissolved in 1000 grains of water with an increase of 18.0° at a temperature of 55° ; and a repetition of the experiment with the same quantities and at the same temperature, gave exactly the same result.

I. II. $\text{NH}_4\text{O}, \text{C}_2\text{O}_3 + \text{HO}$, vol. in solution 36

35·71 grains, being immersed in a saturated solution, gave in the first experiment an increase of 24·5, in the second of 24·4; the first experiment being at 48°, the second at 50°.

				Sp. gr.
I.	$\text{NH}_4\text{O}, \text{C}_2\text{O}_3 + \text{HO}$	vol. of salt	49·0	... 1·458
II.	48·8	... 1·464
	Mean	. .	48·9	... 1·461

Binoxalate of Potash, $\text{KO}, \text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3 + 2\text{HO} = 146·63$.—To determine the volume of this salt, 18·33 grains were dissolved in 1000 grains of water with a rise of 6·8 at a temperature of 57°; and the same result attended a repetition of the experiment; in a third experiment, 25 grains at the same temperature caused an increase of 9·0.

I. II.	Binoxalate of potash	vol. in solution	54·4
III.	52·8
	Mean	. .	53·6

Half an equivalent of the salt (73·31 grains), being immersed in a saturated solution, caused an increase of 37·4 in the first experiment, and of 37·2 in the second, the temperature in both cases being 55°.

				Sp. gr.
I.	Binoxalate of potash	vol. of salt	74·8	... 1·960
II.	74·4	... 1·971
	Mean	. .	74·6	... 1·965

Oxalate of Copper and Potash, $\text{KO}, \text{C}_2\text{O}_3 + \text{CuO}, \text{C}_2\text{O}_3 + 2\text{HO} = 177·25$.—On account of the sparing solubility of this salt, 11·08 grains, or the sixteenth part of an equivalent, were dissolved in water, and caused an increase of 3·4 in two experiments at a temperature of 59°.

I. II. $\text{KO}, \text{C}_2\text{O}_3 + \text{CuO}, \text{C}_2\text{O}_3 + 2\text{HO}$, vol. in solution 54·4

The fourth of an equivalent (44·3 grains), placed in a saturated solution, caused an increase in one experiment of 19·5; in another of 18·9; and in a third of 19·7; all at a temperature varying from 54° to 57°.

				Sp. gr.
I.	Oxalate of copper and potash	vol. of salt	78·0	... 2·272
II.	75·6	... 2·344
III.	78·8	... 2·249
	Mean	. .	77·5	... 2·288

Binoxalate of Ammonia, $\text{NH}_4\text{O}, \text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3 + 2\text{HO} = 125·69$.—31·42 grains of this salt, dissolved in 1000 grains of water, caused in the first experiment an increase of 18·0 at 60°; in the second, of 18·2 at 61°; in a third experiment, of

17.8 at 54°; in a fourth, 42 grains dissolved in 4100 grains of water increased 24.0 at 53°.

I.	Binoxalate of ammonia, vol. in solution	72.0
II.	72.8
III.	71.2
IV.	71.8
Mean . .		71.9

The half of an equivalent (62.84 grains), being immersed in a saturated solution, caused an increase of 40.3 in two experiments, and of 40.0 in a third.

		Sp. gr.
I.	Binoxalate of ammonia, vol. of salt	80.6 ... 1.559
II.	80.6 ... 1.559
III.	80.0 ... 1.571
Mean . .		80.4 ... 1.563

Oxalate of Copper and Ammonia, $\text{NH}_4\text{O}, \text{C}_2\text{O}_3 + \text{CuO}, \text{C}_2\text{O}_3 + 2\text{HO} = 156.38$.—The solution of 18.3 grains gave an increase of 8.6 at 65°; this gives 73.3 as the volume of this salt when in solution.

On immersing 20 grains in turpentine, an increase of 10.4 was obtained, which gives for the volume of the equivalent 81.3, and for the specific gravity of the salt 1.923.

Quadroxalate of Potash, $\text{KO}, \text{C}_2\text{O}_3 + 3\text{HO}, \text{C}_2\text{O}_3 + 4\text{HO} = 255.11$.—32.0 grains dissolved in water, gave an increase of 15.0 at 60°; and a second experiment, in which 16 grains were dissolved in 1000 grains of water, gave the increase of 7.2 at a temperature of 44°.

I.	Quadroxalate of potash, vol. in solution	119.4
II.	114.8
Mean . .		117.1

63.8 grains, the fourth part of an equivalent, thrown into a saturated solution, caused a rise of 35.1 in two experiments.

		Sp. gr.
I.	II. Quadroxalate of potash, vol. of salt	140.4 ... 1.817

Quadroxalate of Ammonia, $\text{KO}, \text{C}_2\text{O}_3 + 3\text{HO}, \text{C}_2\text{O}_3 + 4\text{HO} = 234.15$.—On dissolving 20 grains of this salt in 3500 grains of water at 50°, the increase is 11.5, which gives 134.5 as the volume of the equivalent in solution.

58.5 grains of the salt, thrown into a saturated solution, caused in the first experiment an increase of 36.8, in the second of 36.9, both at a temperature of 62°.

		Sp. gr.
I.	Quadroxalate of ammonia, vol. of salt	147.2 ... 1.591
II.	147.6 ... 1.586
Mean . .		147.4 ... 1.589
		2 H 2

The volumes of the oxalates can only be explained by an attentive consideration of the previous results. We have already seen numerous instances in which the primitive volumes 9·8 and 11·0 become mutually convertible; this is strikingly the case with the salts of the present section. Hydrated oxalic acid has a volume $9\cdot8 \times 4$; oxalate of potash possesses the volume 11×3 , and passes with this volume into the binoxalate and quadroxalate of potash, the oxalic acid in the binoxalate being associated as two volumes of ice, although the water of crystallization possesses the volume 11. Quadroxalate of potash is to be viewed as anhydrous binoxalate *plus* 2 equiv. hydrated oxalic acid, the latter having become 11×4 instead of $9\cdot8 \times 4$. The same explanation applies to the binoxalate and quadroxalate of ammonia, the only difference being that anhydrous oxalate of ammonia, $9\cdot8 \times 4$, takes the place of oxalate of potash. On these views the following table is constructed.

TABLE XII.—Showing the volumes occupied by certain Oxalates.

Designation.			Vol. in solution.			Volume in state of salt.				
Name.	Formula.	Atomic weight.	Volume in solution by experiment.	9, or volume of water as unity.	Volume by theory.	Volume by experiment.	11 and 9·8, taken as unity, as above described.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Oxalic acid	$\text{HO}, \text{C}_2\text{O}_3 + 2\text{HO}$	63·26	36·6	4	36	39·0	4	39·2	1·616	1·622
Oxalate of potash...	$\text{KO}, \text{C}_2\text{O}_3 + \text{HO}$	92·39	28·2	3	27	43·9	4	44·0	2·100	2·104
Oxalate of ammonia	$\text{NH}_4\text{O}, \text{C}_2\text{O}_3 + \text{HO}$	71·43	36·0	4	36	48·9	5	49·0	1·458	1·461
Binoxalate of potash	$\text{KO}, 2\text{C}_2\text{O}_3 + 3\text{HO}$	146·63	53·6	6	54	74·6	7	74·6	1·965	1·965
Binoxalate of ammonia	$\text{NH}_4\text{O}, 2\text{C}_2\text{O}_3 + 3\text{HO}$	125·67	71·9	8	72	80·4	8	80·8	1·555	1·563
Oxalate of copper and potash	$\text{KO}, \text{C}_2\text{O}_3 + \text{CuO}, \text{C}_2\text{O}_3 + 2\text{HO}$	177·25	54·4	6	54	77·5	7	77·0	2·301	2·288
Oxalate of copper and ammonia	$\text{NH}_4\text{O}, \text{C}_2\text{O}_3 + \text{CuO}, \text{C}_2\text{O}_3 + 2\text{HO}$	156·38	73·3	8	72	81·3	8	80·8	1·935	1·923
Quadroxalate of potash	$\text{KO } 4\text{C}_2\text{O}_3 + 7\text{HO}$	255·11	117·1	13	117	140·4	13	140·6	1·814	1·817
Quadroxalate of ammonia	$\text{NH}_4\text{O}, 4\text{C}_2\text{O}_3 + 7\text{HO}$	234·15	134·5	15	135	147·4	14	146·8	1·595	1·589

The examination of the volumes occupied by the oxalates presents several points of great interest. The volume of oxalic acid itself is a multiple of the volume of ice, or $9\cdot8 \times 4$.

Oxalate of potash in its solid state possesses four volumes, 11×4 , but loses one volume on passing into solution, as usually is the case with neutral salts of potash. As one of

these volumes is due to its combined water, the proper number of volumes in anhydrous oxalate of potash is three, and these it carries into binoxalate of potash, which is therefore a simple combination of oxalate of potash and hydrated oxalic acid, the crystalline water of the latter having assumed the volume 11.

	In solution.	As a salt.
$\text{KO}, \text{C}_2\text{O}_3 \dots \dots \dots$	18 ...	33·0
$\text{HO}, \text{C}_2\text{O}_3 + 2\text{HO} \dots \dots$	36 ...	41·6
Binoxalate of potash . . .	54 ...	74·6

The only difference between the volumes of this salt and those of its constituents, when uncombined, is that the crystalline water of the hydrated oxalic acid has assumed the volume 11. Quadroxalate of potash consists of anhydrous binoxalate of potash united to hydrated oxalic acid, as Graham has already announced in his researches on the oxalates. The three volumes affected by oxalate of potash in its solid state pass into solution with it in quadroxalate of potash, just as we saw in the case of chromate and bichromate of potash; and the attached oxalic acid affects 11×4 instead of $9 \cdot 8 \times 4$.

	In solution.	As a salt.
I. Anhydrous binoxalate of potash	45 ...	52·6
II. Hydrated oxalic acid	72 ...	88·0
Quadroxalate of potash . . .	117 ...	140·6

The assumption of two volumes in solution above those of binoxalate of potash was already characteristic of binoxalate of ammonia, and the same increase is seen in the quadroxalate, showing clearly that that salt must contain its ammonia *quasi* binoxalate and not as oxalate of ammonia. It is very possible that the volumes in solution of quadroxalate of ammonia should be 14, instead of 15, but the temperature 31° , at which it comes out 14 volumes, is so low, that it is more natural to keep the volumes we have given in the table.

It is interesting to observe how closely oxalate of copper relates itself to oxalate of water.

	Volumes in solution.	Volumes as salt.
Oxalate of copper and potash .	6 ...	7
... water and potash .	6 ...	7
... copper and ammonia .	8 ...	8
... water and ammonia .	8 ...	8

Thus, even in the apparently anomalous behaviour of binoxalate of ammonia, in assuming two volumes more than the corresponding salt of potash, we find oxalate of copper and ammonia imitating its example. The reason of their increase will be explained in the next section.

SECTION VIII.

Subsalts and Ammoniacal Salts.

The salts which we have hitherto examined have been those soluble in water, and having a constitution to a certain degree well-defined. We have now to consider the insoluble subsalts, and, in some cases, their neutral insoluble types, and also to ascertain how far the results thus obtained serve to throw light on the constitution of ammoniacal salts.

Subsulphate of Copper, $\text{CuO}, \text{SO}_3, 4\text{HO} + 3\text{CuO} = 234.9$.—This well-known salt was made by adding ammonia to a solution of sulphate of copper. The fourth part of an equivalent, 58.7 grains, thrown into water, caused an increase of 19.1 and 19.0 in two successive experiments.

I. Subsulphate of copper, vol. of salt	76.4	...	Sp. gr.
II. ...	76.0	...	3.074
Mean . .	76.2	...	3.090
			3.082

Subsulphate of Zinc, $\text{ZnO}, \text{SO}_3, 3\text{ZnO}, 4\text{HO} = 237.3$.—This salt is apt to combine with more water than four atoms, but may be obtained with four by drying at 212° . On placing 29.66 grains, the eighth part of an equivalent, in turpentine, an increase of 9.5 was obtained; and on treating 22.8 in a similar manner, the rise in the stem was 7.3. Both of these experiments exactly agree in making—

Subsulphate of zinc, vol. of salt	76.0	...	Sp. gr.
			3.122

Sulphate of Protoxide of Mercury, $\text{Hg}_2\text{O}, \text{SO}_3 = 251.0$.—This salt was prepared in the usual way by digesting one part of mercury in $1\frac{1}{2}$ part of sulphuric acid. The fourth of an equivalent, 62.75 grains, thrown into turpentine, increased 8.3.

$\text{Hg}_2\text{O}, \text{SO}_3$, vol. of salt	33.2	...	Sp. gr.
			7.560

Sulphate of Peroxide of Mercury, $\text{HgO}, \text{SO}_3 = 149.6$.—The salt used in the experiment was prepared by heating five parts of sulphuric acid mixed with a little nitric acid, with four parts of mercury until the whole became a dry saline mass. On immersing 37.5 grains of the salt thus prepared in turpentine, an increase of 5.8 was obtained, which gives 23.1 for the volume of the equivalent, and 6.466 for the specific gravity of the salt.

Subsulphate of Mercury, $\text{HgO}, \text{SO}_3 + 2\text{HgO} = 368.46$.—The last salt thrown into water and washed with warm water is converted into the beautiful yellow powder known as tur-

peth mineral. On throwing 57.4 grains of this salt thus prepared into water, an increase of 6.9 was obtained, which gives 44.3 as the volume of the equivalent, and 8.319 as the specific gravity of the salt.

Chromate of Lead, $\text{PbO}, \text{CrO}_3 = 163.97$.—On throwing 81.98 grains of the chromate of lead, previously well-dried, into turpentine, an increase of 14.5 was effected; this gives 29.0 as the volume of the equivalent, and 5.653 as the specific gravity of the salt.

Subchromate of Lead, $\text{PbO}, \text{CrO}_3 + \text{PbO} = 275.7$.—This salt was prepared by projecting chromate of lead into melted nitre, and afterwards washing out all soluble matter. On immersing 68.92 grains, the fourth part of an equivalent, an increase of 11.0 was obtained in two experiments. This gives 44.0 for the volume of the equivalent, and 6.266 as the specific gravity of the salt.

Sesquibasic Chromate of Lead, $2(\text{PbO}, \text{CrO}_3) + \text{PbO} = 439.67$.—The mineral, melanchroit, is of the composition expressed by the above formula, and has a specific gravity of 5.75 according to Hermann; this gives the number 76.5 as the atomic volume of the compound.

Subnitrate of Copper, $\text{CuO}, \text{NO}_5, \text{HO}, 2\text{CuO} = 182.17$.—The fourth part of an equivalent, 45.54 grains, caused an increase of 16.5 in two experiments, and of 16.4 in a third.

						Sp. gr.
I.	$\text{CuO}, \text{NO}_5, \text{HO} + 2\text{CuO}$	vol. of salt	66.0	...	2.760	
II.	66.0	...	2.760	
III.	65.6	...	2.777	
	Mean	.	65.87	...	2.765	

A. *Subnitrate of Bismuth*, $\text{BiO}, \text{NO}_5, \text{HO} + 2\text{BiO} = 300.4$.—This salt was prepared in the same manner as subnitrate of copper, viz. by heating the nitrate to 400° or 500° . The fourth part of an equivalent, 75.1 grains, thrown into water, caused, in various experiments, an increase of 16.5, which gives 66.0 as the atomic volume, and 4.551 as the specific gravity of the salt.

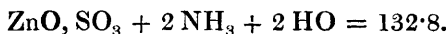
B. *Subnitrate of Bismuth*, $\text{BiO}, \text{NO}_5 + 2\text{BiO} = 291.4$.—This salt was prepared by adding nitrate of bismuth to a large quantity of water; the white powder which falls by this treatment, is composed, according to Phillips, of three equivalents of oxide of bismuth united to one of nitric acid. It is therefore the same salt as the one last described, deprived of its constitutional water. On immersing 72.85 grains of the salt in water, a rise in the stem of 13.9 was effected, and 36.42 grains treated in the same way gave an increase of 6.9.

				Sp. gr.
I.	3BiO, NO ₅ , vol. of salt	55.6	...	5.241
II.	55.2	...	5.279
	Mean . .	55.4	...	5.260

Subnitrate of Mercury, HgO, NO₅ HO + 2HgO = 391.49.—This salt was obtained in a yellow powder by adding the crystallized subnitrate of mercury to water, and washing it, according to the directions of Kane, with hot, but not boiling water. The fourth part of an equivalent, 97.87 grains, thrown into turpentine, caused an increase of 16.4, which gives 65.6 as the atomic volume of the salt, and 5.967 as the specific gravity.

Ammoniacal Sulphate of Copper, CuO, SO₃ HO, + 2NH₃ = 123.0.—This salt has already been described in a previous section; it had a volume of 54.0 or 9 × 6 in a state of solution, and of 68.6 or 9.8 × 7 in the solid state. The salt examined in that case was in fine large indigo blue crystals, and was prepared by ourselves. Another portion, made by Mr. Morson in small crystals, we found to possess a volume of 68.0 and specific gravity of 1.809. When this salt is heated it loses one equivalent of water and one of ammonia, being converted into a green powder, the formula of which is CuO, SO₃ + NH₃; 24.27 grains of this, thrown into turpentine, caused an increase of 9.8, which gives 39.2 as the volume of the equivalent, and 2.476 as the specific gravity of the salt. The latter salt on being moistened with water absorbs three equivalents, and therefore assumes the atomic weight of 124.07; the fourth part of which, 31.0 grains, thrown into turpentine, caused an increase of 15.9, making the atomic volume of CuO, SO₃ + NH₃ + 3HO, 63.6, and its specific gravity 1.950.

Ammonia-Sulphate of Zinc.—Kane describes several ammonia-sulphates of zinc, obtained by passing a stream of ammonia through a hot solution of sulphate of zinc, until the precipitate at first formed is redissolved. The solution thus obtained deposited transparent crystals in a few hours, but these effloresced so quickly after being dried, that we did not determine their specific gravity. The effloresced crystals have, according to Kane, the formula—



We fear, however, that we have not been successful in procuring this salt in its proper state, as the determination of its volume varied between 57.5 and 64.0, results so discordant, that it would not be safe to take their mean as a correct result. On heating this salt it loses water and ammonia, being

converted into ZnO , $\text{SO}_3 + \text{NH}_3$; 26.7 grains of which (the fourth of an equivalent), thrown into turpentine, caused an increase of 10.8, which gives 39.5 as the volume of the salt, and 2.479 for its specific gravity.

Ammonia-Sulphate of Mercury, HgO , $\text{SO}_3 + \text{HgAd} + 2\text{HgO} = 486.0$.—This salt, which Kane calls the Ammonia Turpeth, was prepared by heating turpeth mineral with ammonia until it became changed to a heavy white powder. The eighth part of an equivalent, 60.75 grains, immersed in water, caused an increase of 8.3 in two experiments; this makes the volume of the compound 66.4, and its specific weight 7.319.

Ammonia-Sulphate of Silver, AgO , $\text{SO}_3 + 2\text{NH}_3 = 190.86$.—This salt was obtained in the usual way, by dissolving sulphate of silver in ammonia and crystallizing. The first specimen tried was in small, indistinct crystals, in the second instance the crystals were large and well-defined. 25.62 grains gave an increase of 8.6, and 37.7 grains of the better specimen of salt gave the increase 13.2.

					Sp. gr.
I.	AgO , $\text{SO}_3 + 2\text{NH}_3$, vol. of salt	64.0	...	2.979	
II.	66.8	...	2.857	
	Mean . .	65.4	...	2.918	

Ammonia-Chromate of Silver, AgO , $\text{CrO}_3 + 2\text{NH}_3 = 202.8$.—This salt was obtained in fine large crystals, in the same manner as the last salt. On immersing 25.35 grains in turpentine, the increase was 8.3, and on treating 50.7 grains in the same way, the increase was 16.5.

					Sp. gr.
I.	AgO , $\text{CrO}_3 + 2\text{NH}_3$, vol. of salt	66.4	...	3.054	
II.	66.0	...	3.073	
	Mean . .	66.2	...	3.063	

Ammonia-Nitrate of Copper, CuO , $\text{NO}_5 + 2\text{NH}_3 = 128.4$.—On dissolving 64.2 grains, half an equivalent, in 1000 grains of water, the increase was 32.0 in two experiments at a temperature of 60° ; this makes the atomic volume in solution 64.0. On putting the same quantity into turpentine, there was a rise in the stem, in three experiments, of 34.0, 34.0, and 34.8.

					Sp. gr.
I.	CuO , $\text{NO}_5 + 2\text{NH}_3$, vol. of salt	68.0	...	1.888	
II.	68.0	...	1.888	
III.	69.6	...	1.845	
	Mean . .	68.5	...	1.874	

Ammonia-Sub-Nitrate of Mercury, HgO , $\text{NO}_5 + 2\text{HgO} + \text{NH}_3 = 399.7$.—This salt was prepared by adding a dilute

solution of ammonia to nitrate of mercury, and was of a pure milk-white colour, as described by Kane. On throwing 40 grains of this compound into water, an increase of 6·7 was obtained; this gives a volume of 67·0 on the equivalent, and 5·970 as the specific gravity of the salt.

Chloride of Copper, $\text{CuCl} = 67\cdot18$.—The volume of hydrated chloride of copper was shown to be 33 or 3×11 ; but we have not yet examined the bulk occupied by the anhydrous chloride. The chloride was deprived of its water by a heat considerably below that of redness, in order to prevent the formation of any sub-chloride. On throwing 33·59 grains, or half an equivalent, into turpentine, the increase in two experiments was exactly 11·0, which gives 22·0 as the volume of the salt, and 3·054 as its specific gravity.

Ammonia-Chloride of Copper, $\text{CuCl} + 2\text{NH}_3 + \text{HO} = 110\cdot3$.—This salt was made by passing a stream of ammonia through a solution of chloride of copper until the precipitate formed had completely redissolved. The crystals, which deposited as the solution cooled, were dried in a receiver containing slaked lime, so as to prevent the carbonic acid of the atmosphere acting upon the ammonia; but in spite of this precaution the crystals had slightly effloresced on the surface. The effloresced matter was removed, and the pure crystals employed. 27·6 grains of them, when thrown into turpentine, produced in two experiments an increase of 16·5, making the volume of the salt 66·0, and its specific gravity 1·672. On dissolving the same quantity of salt, 27·6 grains, in 1000 grains of water, the rise was 15·9 at 62°, making the volume of the salt when in solution 63·6.

On exposing this salt to heat, water and ammonia are expelled, and a green powder remains, having the formula $\text{CuCl} + \text{NH}_3$. 21·07 grains of this salt thrown into turpentine produced an increase of 9·6, making the volume of the equivalent 38·4, and the specific gravity of the salt 2·194.

Subchloride of Copper, $\text{Cu}_2\text{Cl} = 98\cdot89$.—The subchloride used in the experiment was made by adding protochloride of tin to a solution of chloride of copper. During the desiccation of the salt it became slightly green, showing that a little chloride had been formed by the absorption of oxygen; but the change was so slight as probably not to interfere materially with the result; 42·2 grains, thrown into turpentine, caused an increase of 12·5, which gives 29·2 as the volume, and 3·376 as the specific gravity of the salt.

Subchloride of Mercury, $\text{Hg}_2\text{Cl} = 238\cdot33$.—The fourth part of an equivalent, 59·58 grains, thrown into turpentine, caused an increase of 8·3.

Atomic Volume and Specific Gravity.

465

			Sp. gr.
Calomel, vol. of salt	33.2	...	7.178

Hassenfratz states the specific gravity to be 7.176, a result very near our own determination.

Subchloride and Amide of Mercury, $\text{Hg}_2\text{Cl} + \text{Hg}_2\text{Ad} = 458.1$.—The eighth part of an equivalent, 57.26 grains, thrown into water, caused an increase of 8.3 and 8.4 in two experiments.

			Sp. gr.
I. Black compound of calomel	67.2	...	6.816
II.	6.899
Mean	. .	66.8	...

The salt used in the experiments was prepared in the usual way, by acting upon calomel with ammonia.

Chloride and Amide of Mercury, $\text{HgCl} + \text{HgAd} = 254.5$.—The excellent researches of Kane, so often alluded to, have shown that the above formula represents the composition of white precipitate. It must be dried by a pretty strong heat, to get rid of all its hygrometric water. On projecting 63.8 grains, the fourth of an equivalent, into water, an increase of 11.2 was obtained in two experiments; this gives 44.6 as the specific volume of the compound, and 5.700 as its specific gravity.

Basic Chloride and Amide of Mercury, $\text{HgCl} + \text{HgAd} + 2\text{HgO} = 473.3$.—This yellow compound was made in the usual way, by boiling white precipitate with water. On throwing 59.2 grains into water, the rise was 8.2 in one experiment, and 8.3 in another.

			Sp. gr.
I. The above salt, volume	65.5	...	7.220
II.	7.132
Mean	. .	65.9	...

TABLE XIII.—Showing the Volumes occupied by certain Subsals and Salts of Ammonia.

Designation.			Volume in solution.			Volume of salt.				
Name.	Formula.	Atomic weight.	Volume of salt in solution.	9, taken as unity.	Volume by theory.	Volume of salt by experiment.	11, taken as unity.	Volume by theory.	Specific gravity by theory.	Specific gravity by experiment.
Subsulphate of copper	$\left\{ \begin{array}{l} \text{CuO, SO}_3, 3\text{CuO} \\ + 4\text{HO} \end{array} \right\}$	234.9	76.2	7	77	3.051	3.082
Subsulphate of zinc	$\left\{ \begin{array}{l} \text{ZnO, SO}_3, 3\text{ZnO} \\ + 4\text{HO} \end{array} \right\}$	237.3	76.0	7	77	3.082	3.122
Protosulphate of mercury ...	$\text{Hg}_2\text{O, SO}_3$	251.0	33.2	3	33	7.606	7.560
Persulphate of mercury.....	HgO, SO_3	149.6	23.1	2	22	6.800	6.466
Subsulphate of mercury ...	$\text{HgO, SO}_3 + 2\text{HgO}$	368.46	44.3	4	44	8.374	8.319
Chromate of lead	PbO, CrO_3	163.97	29.0	5.653
Subchromate of lead	$\text{PbO, CrO}_3 + \text{PbO}$	275.7	44	4	44	6.266	6.266
Melanchroit	$2\text{PbO, 2CrO}_3 + \text{PbO}$	439.67	76.5	7	77	5.710	5.750
Subnitrate of copper	$\text{CuO, NO}_5 \text{ HO} + 2\text{CuO}$	182.17	65.9	6	66	2.760	2.765
A. Subnitrate of bismuth ...	$\text{BiO, NO}_5, \text{HO} + 2\text{BiO}$	300.4	66.0	6	66	4.551	4.551
B. Subnitrate of bismuth ...	$\text{BiO, NO}_5 + 2\text{BiO}$	291.4	55.4	5	55	5.298	5.260
Subpernitrate of mercury ...	$\left\{ \begin{array}{l} \text{HgO, NO}_5, \text{HO} \\ + 2\text{HgO} \end{array} \right\}$	391.49	65.6	6	66	5.932	5.967
A. Ammonia-sulphate of copper	$\text{CuO, SO}_3, \text{HO} + 2\text{NH}_3$	123.0	54	6	54	68.7	1.790
B. Ammonia-sulphate of copper	$\text{CuO, SO}_3 + \text{NH}_3$	97.08	39.2	2.476
Hydrate of ammonia-sulphate of copper	$\left\{ \begin{array}{l} \text{CuO, SO}_3 + \text{NH}_3 \\ + 3\text{HO} \end{array} \right\}$	124.07	63.6	1.950
Ammonia-sulphate of zinc...	$\text{ZnO, SO}_3, \text{NH}_3$	97.8	39.5	2.479
Ammonia-turpeth ..	$\left\{ \begin{array}{l} \text{HgO, SO}_3 + \text{Hg} \\ \text{Ad} + 2\text{HgO} \end{array} \right\}$	486.0	66.4	6	66	7.363	7.319
Ammonia-sulphate of silver.	$\text{AgO, SO}_3 + 2\text{NH}_3$	190.86	65.4	6	66	2.890	2.918
Ammonia-chromate of silver	$\text{AgO, CrO}_3 + 2\text{NH}_3$	202.8	66.2	6	66	3.073	3.063
Ammonia-nitrate of copper .	$\text{CuO, NO}_5 + 2\text{NH}_3$	128.4	64	7	63	68.5	1.874
Ammonia-nitrate of mercury	$\left\{ \begin{array}{l} \text{HgO, NO}_5 \\ + 2\text{HgO} + \text{NH}_3 \end{array} \right\}$	399.7	67.0	5.970
Chloride of copper.....	Cu Cl	67.18	22	2	22	3.054	3.054
Ammonia-chloride of copper	$\text{Cu Cl} + 2\text{NH}_3 + \text{HO}$	110.3	63.6	7	63	66	6	66	1.671	1.671
B. Ammonia-chloride of copper	$\text{Cu Cl} + \text{NH}_3$	84.11	38.4	2.194
Subchloride of copper	$\text{Cu}_2 \text{Cl}$	98.89	29.2	3.376
Subchloride of mercury.....	$\text{Hg}_2 \text{Cl}$	238.33	33.2	3	33	7.221	7.178
Subchloride and amide of mercury	$\text{Hg}_2 \text{Cl} + \text{Hg}_2 \text{Ad}$	458.1	66.8	6	66	6.941	6.858
Chloride and amide of mercury	$\text{Hg Cl} + \text{Hg Ad}$	254.5	44.6	4	44	5.784	5.700
Basic chloride and amide of mercury	$\left\{ \begin{array}{l} \text{Hg Cl} + \text{Hg Ad} \\ + 2\text{HgO} \end{array} \right\}$	473.3	65.9	6	66	7.171	7.176

The important researches of Graham have shown that water plays a most important part in the constitution of salts; and that salts with an excess of base may be viewed as hydrates, in which oxide of hydrogen becomes replaced by a metallic oxide. The previous experiments will be found to give this theory the fullest confirmation. Sulphate of zinc crystallizes with seven atoms of water and affects a volume of 74·6; and sulphate of copper assumes the same state of hydration, when crystallized with the latter salt, although *per se* it assumes only five atoms. Placing together the subsulphates and hydrated sulphates of these metals, we perceive not only a close similarity in their formulæ but also in their volumes, as ascertained by experiment.

		Difference.
ZnO, SO ₃ , 3HO, 4HO, vol.	74·6	1·4
ZnO, SO ₃ , 3ZnO, 4HO, ..	76·0	
CuO, SO ₃ , 3HO, 4HO, vol.	74·6	1·6
CuO, SO ₃ , 3CuO, 4HO, ..	76·2	

The difference between the two states of the sulphates is probably greater as stated than it actually is. We have already shown that the magnesian sulphates with seven atoms of water do not possess a volume of 77·0, because two of the atoms possess a volume of 9·8 instead of 11·0; and perhaps a similar circumstance tends to reduce the volume of the subsulphates. Similar instances of replacement of water by a metallic oxide are seen in other parts of the table. We have already shown that nitrates of copper and bismuth possess a volume of 58·8 or $9·8 \times 6$. We have also seen instances in which 9·8, the volume of ice, in feeble compounds, became changed into the volume 11 when the salt entered into combination. In this point of view, the subsalts MO, NO₅ + HO + 2MO become assimilated to the hydrated nitrates MO, NO₅ + HO + 2HO, the number of volumes in both cases being the same, the only difference being, that, in the former case, the salts are multiples of 11, and in the latter of 9·8, or the volume of ice. The hydrated type affects six volumes, and so do the subnitrates, as will be seen by the following table.

CuO, NO ₅ , HO + 2CuO, volume	65·9	or	11 × 6
BiO, NO ₅ , HO + 2BiO, ..	66·0	...	11 × 6
HgO, NO ₅ , HO + 2HgO ..	65·6	...	11 × 6

We have further evidence of the equivalency of water to the metallic oxide in anhydrous nitrate of bismuth, which has a volume of 55·0 or $66 - 11$; the formula for the salt being BiO, NO₅ + 2BiO. The conversion of the volume 9·8 into 11

is by no means uncommon, and is again seen in the subchromates of lead. Chromate of lead has a volume sensibly the multiple of 9.8.

	By experiment.			By calculation.	
Chromate of lead	29.0	...	5.653	...	$9.8 \times 3 = 29.4$... 5.577

Boullay gives the specific gravity of oxide of lead as 9.5, which indicates the volume 11.7, a number not far from 11, which we take as the unit volume. Subchromate of lead consists of one equivalent of the neutral chromate united to one of oxide of lead, but the three volumes of ice in the former have changed in the subsalt to 11×3 , and the same is the case in the mineral melanchroit, which contains two equivalents of chromate of lead united to one of oxide of lead.

Subchromate of lead, $\text{PbO}, \text{CrO}_3 + \text{PbO} = 44$ or 11×4

Melanchroit, $2 (\text{PbO}, \text{CrO}_3) + \text{PbO} = 76.5$ or 11×7

In these salts we clearly see that oxide of lead takes up the volume and plays the part of an atom of water, although we are ignorant of their hydrated types. The same function of an oxide is seen in turpeth mineral, in which the 2HgO , attached to HgO, SO_3 , assumes the volume of two atoms of water, $22 + 22 = 44$. There can be little doubt from the previous examples of the equivalency of CuO , ZnO , BiO , HgO , and PbO , not only to each other but also to water; and this will be still more strongly seen by placing the volumes of these and other anhydrous magnesian sulphates along with the volume of sulphate of water itself, as deduced from bisulphate of potash.

Sulphate of Water, vol. by experiment	22.0
... Zinc	21.8
... Copper	22.0
... Iron	24.0
... Cobalt	22.0
... Mercury	23.1

The only cases in which there is an appreciable difference from sulphate of water are those of sulphates of iron and mercury, neither of which salts can be obtained without difficulty perfectly pure in an anhydrous state.

But if the equivalency of the magnesian metals to each other and to hydrogen be left in any doubt by the preceding table, this doubt would be entirely removed by a consideration of the magnesian chlorides. The strongest muriatic acid obtained has, according to Thomson, a specific gravity of 1.203, and contains 40.66 per cent. of dry muriatic acid; which is equal to 5.91, obviously six atoms of water to one of muriatic

acid, as pointed out by Kane. The atomic weight of this compound, divided by its specific gravity, is $\frac{90.47}{1.203} = 75.2$, which is not far from 72.0 or 9×8 , considering that the result remains uncorrected for expansion; this gives a volume of 18.0 or 9×2 for muriatic acid. The acid which possesses a constant boiling-point and distils over unchanged has a specific gravity of 1.094 , and contains 19.19 per cent. of absolute acid, according to Davy, and 20.44 per cent. according to Thomson. The mean of their results indicates the acid to contain 16.4 , or nearly 16 atoms of water. Now $\frac{180.47}{1.094} = 165$, which is not far from 162 , the volume of 9×18 , making for the volume of muriatic acid in strong solutions 18.0 or 9×2 , a result the same as that obtained by the last calculation. These results, and that given in a previous section, along with the fact that hydrochloric acid gas has twice the volume of steam, leave no doubt that muriatic acid affects two volumes; and converting the liquid into the solid volume, we have a volume of 22.0 or 11×2 as the atomic volume of solid muriatic acid. By contrasting this volume with the experimental results on the magnesian chlorides, we find a very great similarity.

Chloride of Hydrogen, volume		22.0 or 11×2	
...	Cobalt ...	22.2	...
...	Magnesium ...	22.1	...
...	Calcium ...	22.4	...
...	Copper ...	22.0	...
...	Mercury ...	22.0	...

In dilute solutions muriatic acid affects only one volume, and this has been shown to be also the case with chlorides of copper and cobalt. Whether nitrate of water and nitrate of a magnesian oxide possess the same volume it is difficult to decide. Nitrate of water in the acid of specific gravity 1.42 seems to affect four volumes, and this acid, $\text{HO}, \text{NO}_5, + 3\text{HO}$ is constituted on the same type as $\text{CuO}, \text{NO}_5 + 3\text{HO}$; yet $\frac{90.2}{1.42} = \frac{63}{9} = 7$, which gives four volumes for HO, NO_5 , while nitrate of copper certainly does not possess more than three volumes. Nitrate of water calculated on weak acids has three volumes; but there being no good fixed point upon which to make the calculation, we must leave at present this point undetermined.

An important question now arises as to the truth of the supposition that two atoms of a magnesian metal are equal to

one of the family of which potassium stands as the type. In calomel and chloride of ammonium we have a direct case in point, and the similarity of volumes is very striking.

Chloride of ammonium, NH_4Cl . . .	34.0	Diff. } 0.8
Calomel, Hg_2Cl	33.2	

In this case we have taken chloride of ammonium, because KCl assumes the volume of four atoms of ice.

Subchloride of copper, like NH_4Cl , possesses three volumes, according to Karsten's experiments and our own, but these three volumes are multiples of 9.8, and not of 11.0.

	By experiment.	By calculation.
Subchloride of copper, vol.	$\overbrace{29.2 \quad 3.376}$	$\overbrace{9.8 \times 3 = 29.4 \quad 3.363}$

Another illustration is furnished in sulphate of protoxide of mercury and sulphate of potash.

Protosulphate of mercury, vol.	33.20	Diff. } 0.15
Sulphate of potash	33.05	

These are instances in which two atoms of a magnesian metal are at once shown to be equivalent to one of a metal of the potash family; but it does not thereby preclude the possibility of two atoms of a magnesian *oxide* being equivalent to one atom of potash. For example, a magnesian sulphate, MgO , SO_3 , affects a volume 22, or 11×2 , while the same salt united to an atom of constitutional water has the volume 33, or MgO , SO_3HO becomes equal to KO , SO_3 , which also possesses a volume of 33. The most striking case, however, is seen when crystallized subnitrate of lead is compared with nitrate of potash.

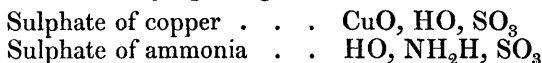
Nitrate of potash, KO , NO_5 , vol.	49.0
Subnitrate of lead, PbO , $\text{NO}_5 + \text{PbO}$, vol. . .	49.0

The fact that two atoms of a magnesian oxide are equivalent to one of potash, appears to find its explanation in the circumstance that we uniformly find the salt of potash assuming one volume greater than the corresponding salt of magnesia. Hence, as the volume of the oxides corresponding to the latter body is equal to unity, the equivalency of two of their atoms to one of potash becomes a matter of necessity.

To sum up these remarks, we conceive (1.) that Graham has taken the correct view in supposing subsalts to represent hydrated salts, in which water has been replaced by a metallic oxide; and (2.) that the volume of two atoms of a metal of the magnesian family, in which we include hydrogen, is equal in volume to one of the potassium group; or two atoms

of the former oxide, when combined, to one of the latter. We are now in a condition to consider the salts of ammonia.

It is quite unnecessary to remind chemists that there are two rival theories regarding the constitution of ammoniacal salts. One of them, proposed by the profound Berzelius, is that the salts of ammonia contain a hypothetical radical termed ammonium, consisting of one equivalent of nitrogen and four equivalents of hydrogen. Sulphate of ammonia is to be viewed as sulphate of oxide of ammonium, the latter hypothetical body being equivalent to potash; and hence the isomorphism between the salts of potash and ammonia. The other view of the constitution of ammonia is that proposed by Kane, and so elaborately supported by him in his paper on subsalts and ammoniacal compounds*. Dr. Kane supposes that an ammoniacal salt is formed on the type of a magnesian salt, carrying along with it constitutional water.



On this view, amide of hydrogen is equivalent to, and plays the part of an atom of water. If this be the case, amidogene must be analogous to oxygen, and ammonia and a magnesian oxide must possess the same atomic volume. At present all this is purely hypothetical, and must be subjected to the test of experiment before we can admit it as a safe foundation on which to rear a theory. The means of deciding this question seemed to present itself in an examination of the amides of mercury, and of the crystallized salts of copper and zinc, in which the ammonia is present *quasi* ammonia; and such compounds have been described in the beautiful researches of Kane on this subject. Wöhler's white precipitate, $\text{HgCl} + \text{NH}_3$ seems to be constituted in the most simple manner, and possesses a volume of 33·0, which, deducting the volume 22·0 for HgCl , leaves 11·0, or unity, as the volume of NH_3 . But again, white precipitate, $\text{HgCl} + \text{HgNH}_2$, affects a volume of 44·6 by experiment, which, deducting 22·0 for HgCl , leaves HgNH_2 also equal to 22·0, and yet the latter compound should correspond in volume to NH_2H . The heavy yellow powder obtained by boiling white precipitate with water has a volume of 66·0, and is constituted according to the formula $(\text{HgCl} + \text{HgAd}) + 2\text{HgO}$; so that deducting 44·0, the ascertained volume of the double amide and chloride, 22 or 11×2 remains for *two* atoms of HgO , giving the same result as in the former subsalts, viz. the equivalency of HgO to HO , but not to HgNH_2 ; and another proof of this is afforded in the

* Transactions of the Royal Irish Academy, vol. xix. part 1.
Chem. Soc. Mem. VOL. II.

reduction of the volume of ammonia turpeth. From this circumstance, the view would appear probable that amide and chloride of mercury are equivalent, and hence would follow the equivalency of chlorine to amidogene. This receives further support from the volume of the double subamide and subchloride of mercury, $\text{Hg}_2\text{Cl} + \text{Hg}_2\text{Ad}$, which has a volume of 66.8, according to experiment. Calomel itself possesses the volume 33.2, which, deducted from that of the salt just described, gives 33.6 as the volume of Hg_2Ad , showing the complete equivalency of the latter to the subchloride.

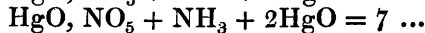
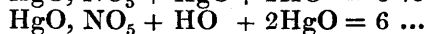
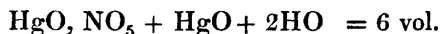
It has been shown that chloride of mercury and chloride of hydrogen are equivalent, and it now remains to be shown by direct proof that amide of hydrogen (ammonia) is embraced in the same category. Ammonia-chloride of copper, $\text{CuCl} + \text{NH}_3$, was found with a volume of 39.2 or 9.8×4 ; chloride of copper itself affects two volumes, which leaves for Ad, H, as deduced from this salt, also two volumes. But the ammonia in $\text{CuCl} + 2\text{NH}_3 + \text{HO}$, if we were to suppose the salts constituted in a manner so simple as expressed by their empirical formulæ, would only have a volume of 33.0 for two atoms, or $1\frac{1}{2}$ volume for each.

In proceeding further, it will be seen that we involve ourselves in inextricable difficulties, if we insist upon the equivalency of NH_2H to HO ; or suppose the ammoniacal salts, such as those described, to be constituted on the type of the hydrated salts. Thus, ammonia-sulphate of copper, $\text{CuO}, \text{SO}_3 + 2\text{NH}_3 + \text{HO}$, has a volume of 68.6 or 9.8×7 in its solid state, and of 54 or 9×6 when in solution. Deducting 19.6 for CuO, SO_3 , and 9.8 for HO , there is again left 39.2, or 9.8×4 for *two* atoms of ammonia. The simple salt, $\text{CuO}, \text{SO}_3 + \text{HN}_3$, has a volume of 39.2, which leaves 19.6, or 9.8×2 for one atom of ammonia; but the same salt, when combined with three atoms of water, yields the volume 63.6, which would lead us to suppose that one atom of water is equal to one atom of ammonia. We also find ammonia with the volume 11, or unity, when calculated from the observed volume of hydrated sulphate of ammonia. But in the ammonia-chromate of silver, $\text{AgO}, \text{CrO}_3 + 2\text{NH}_3$, and in its corresponding sulphate, we find on deducting 33.0, or 11×3 for the salts themselves, the residual 33.0 for *two* atoms of ammonia. Again, however, we become perplexed by finding that the ammonia in ammonia-pernitrate of mercury possesses the volume of an atom of water. Thus, then, by considering the volumes of the ammoniacal salts as containing their ammonia *quasi* ammonia, and as constituted on the type of the hydrated salts, we obtain the contradictory and absurd result, that ammonia, though

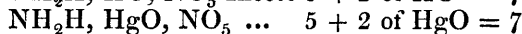
often taking a volume equal to unity, sometimes possesses a volume of $1\frac{1}{2}$, and occasionally two volumes. It is pretty certain, from these contradictory results, that the salts are not constituted on the hydrated type.

Graham has thrown out the ingenious idea*, that the salts now referred to may actually contain an ammonium in which the fourth equivalent of hydrogen is replaced by an equivalent of a magnesian metal. Thus CuO , $\text{SO}_3 + \text{NH}_3$ is constituted, according to Graham, NH_3Cu , O , SO_3 , on the type of sulphate of ammonia, NH_3H , O , SO_3 . There is nothing whatever opposed to this view in Kane's researches, as he himself admits, the only difference being that he considers the said salts to contain oxide of copper and water united to amide of hydrogen, instead of to *cuprammonium* and oxide of ammonium, according to the views of Berzelius and Graham. While, therefore, Kane admits that amide of hydrogen is very closely allied to chloride of hydrogen, he claims for the former body an equally close alliance to water, by asserting that it is equivalent to a magnesian oxide, although it is difficult to conceive why chloride of hydrogen has not a right to a similar claim. Amide and chloride of mercury have undoubtedly the same volume, viz. 22.0, and chloride of hydrogen also enjoys the same number; but water does not in any case do so. On this point alone, then, are we at issue with Kane, for there are many proofs that there is extreme probability in the view propounded by him of the presence of NH_2H and HO in ammoniacal salts. On the former view alone do we contest the accuracy of the opinion, leaving for future consideration and research, to which we are now devoting ourselves, a more defined notion of the reason why NH_2H and HO are equivalent in many instances, *not in all*, to potash. We have already stated the incongruous results which would flow from the conception that ammonia was simply attached to the salts examined. It is true that Kane gives to some of them a constitution more intimate, and when he does so his theory accords with our results. But his conception of the equivalency of NH_2H to HO has led him in other instances to attach the ammonia to the salt in place of water, and it is from these cases that we dissent. If he merely means that NH_2H can replace HO in a compound, as KO , SO_3 does in a magnesian sulphate, then we cease to differ, because the resulting compounds do not remain in strict parallelism; the only point we argue against being that HO and NH_2H are equivalent. Thus we have, supposing all of them to affect the primitive volume 9.8,—

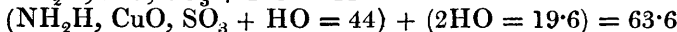
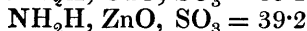
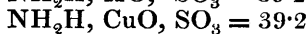
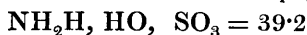
* Graham's Elements of Chemistry, p. 416.



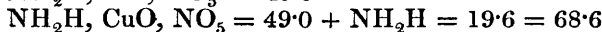
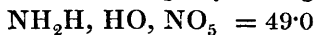
The first two members of the series have the same number of volumes, because HgO and HO are equivalent, and the last salt should also affect the same, if $\text{NH}_2\text{H} = \text{HO}$. But if we consider the last salt as equal to nitrate of ammonia, in which HgO replaces HO, then it becomes intelligible.



On the same principle we would arrange the other ammoniacal compounds. Thus $\text{CuO}, \text{SO}_3 + \text{NH}_3$ obviously ought to be arranged $\text{NH}_2\text{H}, \text{CuO}, \text{SO}_3$, corresponding to $\text{NH}_2\text{H}, \text{HO}, \text{SO}_3$, anhydrous sulphate of ammonia, and both affect, as they should do on this formula, four volumes. We observed a very decided peculiarity in sulphate of ammonia; for while in its hydrated condition the $\text{NH}_4\text{O}, \text{SO}_3$ could only be equal to three volumes, in its anhydrous state, or when in combination with salts, it assumed four volumes. The latter peculiarity attends the *alpha* ammonia-sulphate of copper, and is shared also by ammonia-sulphate of zinc, while the hydrate assimilates itself to $\text{NH}_4\text{O}, \text{SO}_3 + \text{HO}$.

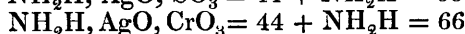
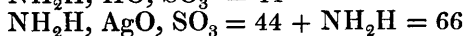
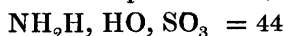


In ammonia-nitrate of copper we have an instance in which the ammonia may be present either as nitrate of ammonia or as ammonia; for if we suppose the volume 68.5, which obviously indicates $9.8 \times 7 = 68.6$, to be made up of $\text{CuO}, \text{NO}_5 + 2\text{NH}_3$, we must assume that two atoms of ammonia are equal to four atoms of ice, for we already have seen that CuO, NO_5 affects three volumes. On the supposition that the compound contains a substance equivalent to nitrate of ammonia, the volumes are equally intelligible.

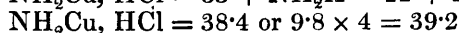


Perhaps, however, the clearest instances are seen in the ammoniacal chromate and sulphate of silver. AgO, CrO_3 and AgO, SO_3 affect a volume of 9.8×3 , and supposing a transformation into multiples of 11, of which we have seen frequent instances, $2\text{NH}_3 = 33.0$, or $\text{NH}_3 = 16.5$, or $1\frac{1}{2}$ times the

number which we assume as unity. But on the supposition that AgO takes the place of HO , the difficulty ceases.



Perhaps the most anomalous salt in the whole series examined is chloride of ammonium, which actually decreases one volume in becoming solid, 9×4 in solution being 11×3 in the state of a salt. Chloride of potassium refuses to share this anomaly, and we accordingly find it 9.8×4 , and NH_4Cl associates itself to KCl in the double salts. Four volumes for NH_4Cl is undoubtedly what we should expect from its composition, and from that number being affected in solution and in its double salts. We also see the three volumes entering into *alpha* ammonia-chloride of copper, although the beta, according to our results, seems singularly enough to affect the proper four volumes.



The double amides and chlorides, as we have already shown, affect the same number of volumes as NH_4Cl when in solution, and might be placed on the same type as $\text{NH}_2\text{Hg}, \text{HCl}$. Without denying that NH_2H and HO may be so intimately associated in the ammoniacal salts as to form the hypothetical body oxide of ammonium, we would call attention to the facts, which show that the resulting volumes of the ammoniacal salts are made up of the volumes of the hydrated acid and amide of hydrogen. It by no means militates against that view, that in hydrated sulphate of ammonia we have one volume in solution less, and also in the state of a solid, than should result from the combination of these two. CuCl has undoubtedly *per se* two volumes, just as HCl has in a concentrated state, or as NH_2H has in combination. But the CuCl in $\text{CuCl} + 2\text{HO}$ possesses only one volume, the other having disappeared in the water; and HCl itself has only one volume in dilute solutions. The disappearance of one volume in combination with water is by no means so surprising as the disappearance of the volumes of 23 atoms of the constituents of alum in the water in which it is dissolved, especially when we find the salt under consideration, sulphate of ammonia, vindicating its proper volume when in combination. The oxalate of ammonia has its *proper* volume, just as has anhydrous sulphate of ammonia; the only exception is the decidedly anomalous salt—chloride of ammonium, although this also ceases

to be anomalous in the double chlorides. By placing together the volumes of the hydrated acids and those of the ammoniacal salts, it will be seen that the latter are made up of the volumes of the hydrated acid united to amide of hydrogen affecting two volumes, like HCl.

Sulphate of ammonia = $\text{HO}, \text{SO}_3 = 2 + \text{NH}_2\text{H} = 2 = 4$

Nitrate of ammonia = $\text{HO}, \text{NO}_5 = 3 + \text{NH}_2\text{H} = 2 = 5$

Oxalate of ammonia = $\text{HO}, \text{C}_2\text{O}_3 = 2 + \text{NH}_2\text{H} = 2 = 4$

All the ammoniacal salts which we have described in this section may be arranged in a similar way with a like result.

We do not profess to have resolved the cause of the equivalency $\text{HO} + \text{NH}_3$ to KO ; nor do we insist that they do not enter into more intimate union to form NH_4O . It must not be left out of consideration, however, that in almost every instance the ammoniacal salt affects one volume in solution more than the corresponding salt of potash, and that the number of volumes of the latter becomes augmented by one in passing from the liquid to the solid state, while the number of volumes of the ammoniacal salt remains unchanged. It requires a more minute knowledge of the constitution of salts than we now possess to decide the question at issue.

Conclusion.

Although we have examined many other salts than those described in the previous pages, with results quite confirmatory of our views, we do not feel warranted in extending our memoir, already much too long. We therefore conclude by summing up, in the form of propositions, the laws which we consider regulate the volumes of salts. At the same time we do so with strict reference to the salts which we have described, deprecating their hasty generalization, being ourselves quite satisfied that there are peculiarities in other cases, which must be subjected to close examination. This being only the first of several memoirs on the same subject which we intend to lay before the Society, we do not present this investigation as being in itself complete.

Prop. I.—*Compounds dissolved in water increase its volume for every equivalent either by 9, or by multiples of 9.*

This, in other words, signifies that the volumes of salts in solution are either equal to each other, or are multiples of each other; for 9, being the volume of nine grains, or an equivalent of water, is merely assumed as the standard of comparison.

a. Certain salts, such as the magnesian sulphates, the

alums, &c., dissolve in water without increasing its bulk more than is due to the liquefaction of the water which they themselves contain; the anhydrous salt taking up no space in solution.

b. Anhydrous salts, or salts containing a small proportion of water, affect a certain number of volumes in solution, which pass along with them unchanged into their union with other salts.

c. The volume occupied by double salts when dissolved is the sum of volumes occupied by their constituents when separate, with the exception of certain cases described in the previous sections.

Prop. II.—*The volume occupied by a salt in the solid state has a certain relation to the volume of the same salt when in solution; and has also a fixed relation to the volume occupied by any other salt.*

a. The volume of an equivalent of any salt is either 11, or a multiple of 11, or of a number very nearly approaching the number 11.

b. Or the volume of a salt is 9·8, or a multiple of 9·8, or, in other words, of the volume occupied by an equivalent of solid water (ice).

c. Or the volume of a salt is made up of a certain multiple of the number 11, added to a certain multiple of the number 9·8.

On each of these heads we would offer a few remarks.

With two assumptions we have been enabled to connect with each other the volumes occupied by all the salts examined by us in the previous sections. These assumptions are, that the divisor for the volumes of salts is either 11, or a number very nearly approaching to it, or that the divisor is 9·8, the volume of ice itself.

We have been guarded in stating positively that the first divisor is absolutely 11, because we do not in the present memoir enter into the connection between this number and the volume of ice, 9·8. To show, however, that our experiments agree with those of recent accurate experimenters, and that the number 11, which we have at present to announce empirically, cannot be wide from the truth, we append the theoretical and experimental results upon the alums, which we stated to possess twenty-five volumes, in which therefore any considerable error in the number 11 would be multiplied by 25, and plainly show itself in the results. Notwithstanding this severe test, it will be seen that the theoretical and experimental numbers are actually within the errors of the balance.

	Theoretical. sp. gr.	By Kopp's* experiments.	By our experiments.	Mean of experiments.
Potash alum .	1·727 ...	1·724 ...	1·726 ...	1·725
Chrome alum	1·833 ...	1·848 ...	1·826 ...	1·837

The number 11 must then be very near the truth, if it be not absolutely the truth. We now append an equally severe test for our view that the volumes of many salts are multiples of 9·8, the number representing the volume of ice. If there be an error in this number, it must become very notable in the phosphates and arseniates, when multiplied by 24, or in carbonate of soda when multiplied by 10. Perhaps sugar itself will form as severe a test as could be desired, for we proceed on the extraordinary fact that the 12 atoms of carbon in sugar have ceased to occupy space, and that the bulk of an atom of sugar is just the bulk of $H_{11}O_{11}$, or its 11 atoms of hydrogen and oxygen, *quasi* water, frozen into ice.

	Theoretical sp. gr.	Sp. gr. ac- cording to our expe- riments.	Other author- ities.
Carbonate of soda .	1·463	1·454	1·423 Haidinger.
Phosphate of soda .	1·527	1·525	1·514 Tünnerman.
Subphosphate of soda	1·622	1·622	none
Arseniate of soda .	1·713	1·736	1·759 Thomson.
Subarseniate of soda	1·808	1·804	none
Cane-sugar . . .	1·591	1·596	1·600 Schübler & Renz.

Thus even in salts so difficult to obtain in a proper degree of hydration free from mechanical water, as those given in the above table, the difference between the theoretical and experimental numbers is not greater than might have been expected.

We give one other class of salts to illustrate position *c* in Prop. II., there being in these salts a certain number of volumes represented by 11, and a certain number by 9·8, CuO , SO_3 representing the number of volumes with the divisor 11.

	Theoretical sp. gr.	Sp. gr. by our experiments.	Sp. gr. by other authorities.
Sulphate of copper .	2·270	2·254	2·274 Kopp.
... zinc . .	1·926	1·931	1·912 Hassenfratz.
... iron . .	1·854	1·857	1·840 <i>Idem</i> .
... magnesia	1·660	1·660	1·660 <i>Idem</i> .
... nickel .	2·033	...	2·037 Kopp.

We have selected these three classes of salts as being the most severe tests which we could apply to our theory, and any chemist who has had experience in this subject will at once admit that the theoretical and experimental numbers are

* *Annalen der Pharmacie*, Bd. xxxvi. S. 10.

as near each other as the estimation of specific gravities by any two different experimenters. We do not rest the claims of our theories on our own experiments, but are willing to admit the accuracy of other experimenters, especially of Karsten, Hassenfratz, Kopp, and others who have preceded us on this subject*; while at the same time we believe that our methods of taking specific gravities have enabled us to introduce more uniformity into the results. The simplicity of the methods themselves is due to Bishop Watson, who was the first to take specific gravities by the increase in the stem of an instrument; and to Holker the suggestion is due of using a saturated solution instead of the water employed by Watson.

We conceive that the primitive volume 9.8 is transformable into the primitive volume 11, and *vice versa*, and for this reason we sometimes see sulphate of ammonia 9.8×4 , at other times, in combination as in bisulphate of ammonia or the anhydrous double sulphates, it is 11×4 ; and numerous other instances of transformation are presented in the previous sections.

The liquid volume being to the solid volume either as 9 : 11 or as 9 : 9.8, these numbers, used as the divisor for the liquid and solid volumes respectively, usually yield the same quotient. Thus the liquid volume of sulphate of cop-

per is 45, its solid volume is 55. $\frac{45}{9} = 5$, and $\frac{55}{11} = 5$;

so that we say the salt affects the same number of volumes in the liquid and in the solid state. In the same manner subphosphate of soda has a volume of 216 in solution and of

235 in the state of salt. Now $\frac{216}{9} = 24$ and $\frac{235}{9.8} = 24$, so

that the number of volumes affected in solution and in the solid state are exactly the same. This is a general rule and a powerful argument of the accuracy of our position. The rule has exceptions in salts of potash, in which the volumes are increased by one volume on becoming solid; thus KO , SO_3

$= \frac{18}{9} = 2$ in solution, and $\frac{33}{11} = 3$ in the solid state. This is

* The only decided difference which we found from other experimenters is in the case of hydrated salts. Thus our determination of the volumes of the double magnesian sulphates and sulphate of potash (Table VI.) differs from Kopp's experiments as 99 : 103. These salts contain from 3 to 4 per cent. of mechanical water, as Graham long ago pointed out (Trans. R. S. E. vol. xiii. p. 12), and the neglect of this in Kopp's experiments has probably caused the difference. We take this opportunity of stating that when more than one specific gravity is given by us, the salts have been prepared at different times; in many instances this is not the case, but in much the largest proportion it is so.

not an accidental variation, but an actual augmentation of one volume, as is proved by the potash alums, in which KO, SO_3 has ceased to occupy space in solution, but on the crystallization of the alum the volume becomes increased by one, obviously owing to this peculiarity of KO, SO_3 ; thus alum in solution $\frac{216}{9} = 24$, becomes $\frac{275}{11} = 25$ in the state of a salt.

This peculiarity is very striking, especially in the case KO, CO_2 , which with a volume of $\frac{33}{11} = 3$ as a solid, becomes $\frac{9}{9} = 1$ as a liquid. Let us endeavour to conceive the extraordinary amount of power exerted in this case; the water in the volumenometer, on dissolving an equivalent of KO, CO_2 , descends from 33 to 9, so that a bulk of solid matter = 24 grains of water disappears within it. If we would compare the force to that which would be required to compress the water into this diminished bulk, we must deal in numbers of a magnitude truly immense. We have always been accustomed to view as an exception the expansion of water on becoming solid, but now we see with Longchamp, that the rule is universal; the salt (muriate of ammonia excepted?) takes up more space as a solid than it does in its liquid state in solution.

We have stated that we desire not to be held responsible for any rash generalization of these laws, which we do not extend at present beyond the salts examined by us. Let us consider the volumes of the ammonia alums, as an example of the danger of applying either of the laws without a proper comprehension of them. These volumes are certainly above 275, the volumes of the potash alums, and are between 279 and 280, according to our experiments and those of Kopp. Now let us suppose that the four volumes of $\text{NH}_4\text{O}, \text{SO}_3$ are represented in the alums, and that only $\text{Al}_2\text{O}_3, 3\text{SO}_3$ has ceased to occupy space, as it in fact does when hydrated, then an ammonia alum $\text{Al}_2\text{O}_3, 3\text{SO}_3 + \text{NH}_4\text{O}, \text{SO}_3 + 24\text{HO}$ may be viewed as $9 \cdot 8 \times (24 + 4) = 279 \cdot 4$, and the specific gravities would countenance this idea.

	Sp. gr. by Theory.	Sp. gr. by our experiments.	Sp. gr. by Kopp' experiment.
Ammonia alum . .	1·626	1·625	1·626
Ammonia iron alum	1·721	1·718	1·712

These results certainly approach the theoretical number very closely; and the theory may represent the truth. But at the same time it is difficult to believe that the ammonia alum is constituted on a different type from the potash alum. We might suppose that the only variation between them is the

difference between the volumes of KO , SO_3 and NH_4O , SO_3 , or the difference between 11×3 and 9.8×4 . This difference, 6.2 , added to the volume of potash alum $275 + 6.2 = 281.2$, which is not very wide from the experimental results, and would give the specific gravity by theory for ammonia alum 1.616 , and for ammonia iron alum 1.711 . These are points which require further inquiry.

We do not refer here to the minor views embraced in the preceding investigation, being anxious principally for inquiry and confirmation into the three main theories propounded. With one assumption for the volume in solution, and with two assumptions for the volumes of solids, we have been enabled to explain, as we trust, the specific gravities detailed in the previous sections. We might perhaps with propriety indulge in speculation, and apply these laws in explanation of isomorphism and dimorphism, but we prefer the safer course of trusting to experimental investigation, part of which we shall in a short time lay before the Society in an inquiry upon the expansion of solutions, and on some other points connected with this important subject.