



XLIII. On the diffusion of liquids

Thomas Graham F.R.S. F.C.S.

To cite this article: Thomas Graham F.R.S. F.C.S. (1850) XLIII. On the diffusion of liquids , Philosophical Magazine Series 3, 37:251, 341-349, DOI: [10.1080/14786445008646625](https://doi.org/10.1080/14786445008646625)

To link to this article: <http://dx.doi.org/10.1080/14786445008646625>



Published online: 30 Apr 2009.



Submit your article to this journal [↗](#)



Article views: 2



View related articles [↗](#)

XLIII. *On the Diffusion of Liquids.*

By THOMAS GRAHAM, F.R.S., F.C.S.

[Concluded from p. 281.]

III. DIFFUSION OF SALTS OF SODA.

(1.) **T**HE only salts of soda which I have yet had an opportunity of diffusing in a sufficient variety of circumstances are the carbonate and sulphate. These salts appear to be equidiffusive, but to diverge notwithstanding more widely in the solutions of the higher proportions of salt than the corresponding potash salts. It is a question whether this increased divergence is not due to the less solubility of the soda salts, and the nearer approach consequently to their points of saturation in the stronger solutions.

Table XIII.—Diffusion of Carbonate and Sulphate of Soda.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 64°.		At 37°·7	
		Experi- ments.	Mean.	Experi- ments.	Mean.
Carbonate of soda					
2	1·0202	4·15 4·08 4·21	4·14	2·78 2·62 2·73	2·71
4	1·0405	7·96 7·70 7·68		5·31 4·94 5·35	
6½	1·0653	12·16 12·06 12·45	7·78	8·50 8·45 8·05	5·20
10	1·0957	17·13 16·53 17·00	12·22		8·33
			16·88		
Sulphate of Soda					
2	1·0179	4·35 4·32 4·25	4·31	2·96 3·03 3·09	3·03
4	1·0352	8·14 8·10 8·28		5·63 5·64 5·42	
6½	1·0578	13·26 13·63 13·61	8·17	8·77 8·84	5·56
10	1·0847	18·71 19·73 18·91	13·50		8·80
			19·14		

The range of the thermometer during the continuance of the experiments at the higher temperature was from 64°·5 up to 65° and falling again to 63°; the mean of all the days being 64°. The temperature of the other series, or of the ice-box,

was 42° the first day, 38° the second, and 37° steadily for the remainder of the period; the mean being $37^{\circ}7$.

The mean results at 64° are as follows:—

	2.	4.	6 $\frac{1}{2}$	10.
Carbonate of soda	4.14	7.78	12.22	16.88
Sulphate of soda	4.31	8.17	13.50	19.14

Another series of experiments was made upon a 1 per cent. solution of the same salts at a mean temperature of $64^{\circ}9$. Six phials of each solution were diffused, and the water of two jars afterwards evaporated together, so that the quantities stated are double.

The diffusion product in three experiments with the sulphate of soda was 4.77, 4.75 and 4.80 grs.; mean 4.77 grs. The diffusion product in three experiments with the carbonate of soda was 4.61, 4.68 and 4.67 grs.; mean 4.65 grs. The difference between the carbonate and sulphate is 0.12 gr.; it is less for the present proportion of 1 per cent. of salt, than for 2 per cent., so that the diffusion of the salts may be converging to a perfect equality in very weak solutions. One-half of the preceding quantities, or the mean results for a single diffusion cell, are—

Diffusion of 1 per cent. solutions at $64^{\circ}9$.

Carbonate of soda, 2.32 grs. . . 100
Sulphate of soda, 2.38 grs. . . 102.58

(2.) The diffusion of the carbonate of soda was further compared with the nitrate of the same base, to find whether their times of equal diffusion are related like those of the corresponding potash salts. The mean temperature of the first seven days, which was the period of diffusion for the nitrate of soda, was $66^{\circ}9$; of the last three days, $65^{\circ}2$; and of the whole period of 9.9 days occupied by the carbonate of soda, $66^{\circ}4$. The 4 per cent. solutions were employed.

The nitrate of soda gave a diffusion product, in three experiments, of 11.48, 11.58 and 12.13 grs.; mean 11.73 grs.

The carbonate of soda, in three experiments, gave 11.66, 11.53 and 11.52 grs.; mean 11.57 grs. A slight addition should be made to the latter quantity to raise the diffusion product from $66^{\circ}4$ to $66^{\circ}9$. It will appear from a subsequent experiment that the diffusion of the carbonate of soda increases 0.096 gr. for a rise of one degree of temperature; which will give 0.05 gr. for the half degree in question.

Bringing the diffusion of the two salts to the same temperature of $66^{\circ}9$, we have therefore diffused, of—

Nitrate of soda, in seven days, 11.73 grs. .	100
Carbonate of soda, in 9.9 days, 11.62 grs. .	99.06

The difference in the quantity diffused of the two salts is only 0.11 gr., or 1 per cent., which is quite within the unavoidable errors of observation.

(3.) The diffusion of a 2 per cent. solution of the same salts was repeated at the same inferior temperature of $54^{\circ}3$ as with the salts of potash, and under the same difficulties from fluctuation of atmospheric temperature. Two water-jars were evaporated together, so that the results are double.

Nitrate of soda, diffused for seven days at a mean temperature of $54^{\circ}3$, gave 10.15 , 10.24 and 9.92 grs. in three experiments; mean 10.10 grs.

Carbonate of soda, diffused for 9.9 days at a mean temperature of $53^{\circ}4$, gave 9.93 , 9.54 and 10.10 grs. in three experiments; mean 9.86 grs. But the latter amount is to be increased by 0.09 gr. to bring it to the diffusion of $54^{\circ}3$. We have then for the diffusion product of the two salts at the same temperature of $54^{\circ}3$ —

Nitrate of soda, in 7 days, 10.10 grs. .	100
Carbonate of soda, in 9.9 days, 9.95 grs. .	98.51

The difference is again small, namely, 0.15 gr., or $1\frac{1}{2}$ per cent., and within the limits of unavoidable error.

It appears therefore that the times of equal diffusion of the nitrate and carbonate of soda are related like those of the nitrate and carbonate of potash, or as the square root of 1 and 2, that is, as 1 to 1.4142 .

Relation of Salts of Potash to Salts of Soda.

It appeared probable, from many of the experiments already recorded, that if any relation, in the times of equal diffusibility, existed between the corresponding salts of potash and soda, it was that of the square root of 2 to the square root of 3. They were accordingly diffused for times having this ratio; namely, the nitrate of potash for seven days, the nitrate of soda for 8.57325 days; the sulphate and carbonate of potash for 9.9 days, and the sulphate and carbonate of soda for 12.125 days. If these times are rightly chosen, the eventual diffusion products of all the experiments should be equal. The 1 per cent. solution was selected, and the number of experiments simultaneously made on each salt was eight or six. The liquids of two water-jars were evaporated together, so that each of the

results in the table below represents the diffusion of two cells. These experiments also afford another opportunity of testing the assumed relation between the nitrates and sulphates of the same base.

Table XIV.—Solution: 1 Salt to 100 Water, at $55^{\circ}4$ — $56^{\circ}1$.

	Temperature.	Time in days.	Square of times. Sol. density.	Diffusion product of two cells in grs.				
				Exp. I.	Exp. II.	Exp. III.	Exp. IV.	Mean.
Nitrate of potash	$56^{\circ}1$	7	2	6.67	6.87	6.90	6.57	6.75
Nitrate of soda . . .	$55^{\circ}7$	8.57	3	6.59	6.80	6.94	6.57	6.78
Sulphate of potash	$55^{\circ}4$	9.90	4	6.73	6.77	6.96	6.68	6.78
Sulphate of soda . . .	$55^{\circ}4$	12.125	6	6.43	6.94	6.80	6.68	6.72
Carbonate of potash	$55^{\circ}4$	9.90	4	6.54	6.64	6.40	6.67	6.56
Carbonate of soda	$55^{\circ}4$	12.125	6	6.40	6.63	6.60	6.67	6.54

The range of temperature during the period of these experiments rather exceeded 3 degrees, so that they cannot be considered as fortunate in that respect; but still the similarity between the different sets of experiments, and the near equality of their means, is very remarkable. The two nitrates and the two sulphates may be said to coincide, the extreme difference of the means of the four salts not being quite so much as 1 per cent. The two carbonates fall about 3.4 per cent. below the sulphates and nitrates, but agree perfectly with each other, showing a uniformity in their irregularity. This deviation of the carbonates would appear essential, as it has been observed every time they have been compared with the sulphates.

The double relation between salts of potash and salts of soda, and between the nitrate and sulphate class of each of these bases, will, I believe, be allowed to acquire considerable additional support from this new series of observations.

IV. DIFFUSION OF SULPHATE OF MAGNESIA.

In a set of preliminary experiments upon sulphate of magnesia in comparison with sulphate of potash, the 4 per cent. solutions of both salts were diffused for seven days at a mean temperature of $57^{\circ}9$, with very little fluctuation, the extreme range being from $58^{\circ}5$ to $57^{\circ}75$. The sulphate of magnesia is taken anhydrous in all the following experiments. The diffusion of sulphate of potash in three cells was 9.16, 9.22 and 9.57 grs.; mean 9.32 grs.

The diffusion of sulphate of magnesia in three cells was 5.21, 4.98 and 5.34 grs.; mean 5.18 grs. The diffusion, in

equal times, appears here to be as 100 sulphate of potash to 55·58 sulphate of magnesia. We know, however, when unequally diffusible salts are diffused for equal times, that the diffusion of the slower is exaggerated. Consequently the diffusion of sulphate of magnesia is likely to be represented in excess in these experiments.

In a second preliminary series of experiments the same 4 per cent. solutions were diffused, the sulphate of potash for eight days and the sulphate of magnesia for nineteen days, with the view of discovering their times of equal diffusibility.

During the first period of eight days the temperature fluctuated considerably, beginning at 54° , falling gradually in four days to $50^{\circ}5$, and rising again in four days to 53° ; the average of the whole period was $52^{\circ}2$. The diffusion of sulphate of potash from three cells was 9·36, 9·25 and 10·52 grs.; mean 9·71 grs.

During the second period of nineteen days, which included the first period, the mean temperature was $54^{\circ}6$. The diffusion of sulphate of magnesia from three cells was 11·81, 11·61 and 10·90 grs.; mean 11·44 grs. The variation in the amounts diffused of both salts is greater than usual, owing no doubt to the changes of temperature, which were imperfectly controlled.

Dividing the quantity of salt diffused by the number of days, we have of sulphate of potash 1·214 gr. diffused per day, and of sulphate of magnesia 0·602 gr. per day; or the latter salt exhibits sensibly half the diffusibility of the former in equal times. This suggested the trial of times for these two salts in the proportion of 1 to 2, with the view of obtaining equal diffusions.

(1.) A one per cent. solution of sulphate of magnesia (anhydrous) was diffused for the long period of 19·8 days, at a mean temperature of $54^{\circ}7$, in eight cells. The diffusion products of four pairs of cells were 7·07, 6·71, 7·07 and 7·35 grs.; mean 7·05 grs., or for one cell, 3·53 grs.

A similar solution of sulphate of potash diffused for 9·9 days, or half the preceding period, at a mean temperature of $55^{\circ}4$, or $0^{\circ}7$ higher, gave a mean product, for two cells, of 6·79 grs., as before stated, or for one cell, of 3·40 grs. The diffusion of sulphate of potash being 100, that of sulphate of magnesia is therefore 103·7, a fair approximation to equality.

(2.) In a second series of experiments upon 1 per cent. solutions of the same two salts, diffused in the vault for fourteen and seven days respectively, with a mean temperature of $53^{\circ}8$ for the sulphate of magnesia, and $54^{\circ}3$ for the sulphate of potash, the temperature was remarkably uniform, gradually

falling from $55^{\circ}2$ to 53° during the longer period, but without any injurious oscillation.

From eight cells, evaporated two together, the sulphate of magnesia obtained was 6.12, 6.12, 6.04 and 6.03 grs.; mean 6.08 grs., or 3.04 grs. for one cell.

The sulphate of potash gave from eight cells, in experiments already detailed, a mean result of 5.84 grs. of salt for two cells, or 2.92 grs. for one cell. The diffusion is in the proportion of 100 sulphate of potash to 104.11 sulphate of magnesia, the times being as 1 to 2 for the two salts respectively.

From these two series of experiments, it appears that, at 54° , sulphate of magnesia has nearly, if not exactly, half the diffusibility of sulphate of potash, and consequently one-fourth of that of hydrate of potash. Or, the times of equal diffusion for these three salts appear to be 1, 2 and 4. The squares of these times and the solution densities are 1, 4 and 16. Hydrate of potash may possibly therefore have the same relation to sulphate of magnesia in solution, density and diffusibility, that hydrogen gas has to oxygen gas.

(3.) A two per cent. solution of sulphate of magnesia, diffused for fourteen days, gave at $53^{\circ}9$, for two pairs of cells, 9.57 and 10.00 grs. of salt, of which the mean is 9.79 grs., or 4.85 grs. for one cell.

A similar solution of sulphate of potash diffused for seven days gave a mean result of 4.97 grs. of salt for one cell, at $54^{\circ}2$, as already stated. The result is a diffusion of 100 sulphate of potash to 97.59 sulphate of magnesia.

(4.) A four per cent. solution of sulphate of magnesia, diffused for fourteen days, gave at $53^{\circ}7$, in two pairs of cells, 18.00 and 18.20 grs. of salt; mean 18.10 grs. for two cells, or 9.05 grs. for a single cell.

A similar solution of sulphate of potash, diffused for seven days at $54^{\circ}2$, gave a mean result of 9.30 grs. of salt for a single cell, as already stated. This is a diffusion of 100 sulphate of potash to 97.4 sulphate of magnesia.

The diffusion of the 2 and 4 per cent. solutions of sulphate of magnesia is so nearly equal to the diffusion of the same proportions of sulphate of potash in half the time, that they may be considered as supplying additional support to the assumed relation between the diffusibilities of these salts.

I may add, that a 4 per cent. solution of anhydrous sulphate of zinc was diffused for fourteen days, simultaneously with the similar solution of sulphate of magnesia, and of course at the same temperature of $53^{\circ}7$. Two cells, evaporated two together, gave 17.40 and 17.36 grs. of ignited sulphate of zinc; mean 17.38 grs. The salt remained, after ignition, entirely

soluble. This is a diffusion of 8·69 grs. for one cell, while the sulphate of magnesia gave 9·05 grs.; or of 100 sulphate of zinc to 104·14 sulphate of magnesia. This result is interesting, as we here find two salts which are isomorphous, and of which the equi-diffusion is on that account in a high degree probable, differing between themselves so much as 4 per cent.

Another numerous series of experiments was made at a considerably lower temperature, with the view of testing several of the same relations. The temperature in commencing the diffusion was 41°, but fell in the course of three days to 38°·8, and afterwards rose to 39°, from which it never varied afterwards more than a degree during the diffusion of the salts of potash and soda. The mean temperature for their periods did not vary above 0°·1 or 0°·2 from 39°·7, so that it may be supposed the same for all these salts. For the sulphates of magnesia, the mean temperature was 38°·9, or 0°·8 lower. The times chosen are as the square-roots of 2, 3, 6 and 16.

Table XV.—Solutions of 1 and 2 Salt to 100 Water, at 39°·7.

	Time in days.	Square of times. Sol. density.	Diffusion product of two cells in 1 per cent. solutions, and one cell in 2 per cent. solutions.				
			Exp. I.	Exp. II.	Exp. III.	Exp. IV.	Mean.
Chloride of potassium, 2 per cent....	9	2	6·58	6·79	6·82	6·73
Nitrate of soda, 2 per cent.....	11·022	3	6·66	6·98	6·79	6·81
Chloride of sodium, 1 per cent.....	11·022	3	6·33	6·63	6·73	7·06	6·69
Chloride of sodium, 2 per cent.....	11·022	3	6·50	6·60	6·64	6·74	6·62
Sulphate of soda, 1 per cent.....	15·589	6	6·60	6·56	6·56	6·50	6·55
Sulphate of soda, 2 per cent.....	15·589	6	6·50	6·43	6·33	6·42
Sulphate of magnesia, 1 per cent....	25·456	16	6·36	6·20	6·86	6·59	6·50
Sulphate of magnesia, 2 per cent....	25·456	16	6·42	6·78	6·50	6·84	6·63

Several other salts were diffused in the same circumstances as the preceding, of which the diffusion products have been previously given. Of these salts, both the 1 and 2 per cent. solutions of nitrate of potash gave 6·83 in nine days, or in the same time as chloride of potassium in the table. The latter salt maintains a sensible equality of diffusion with the present series at the low, as well as it was found to do at the former high temperature. Chloride of sodium is here introduced for the first time: it appears to be equi-diffusive with nitrate of soda. If the sulphate of magnesia diffused be increased by 0·07, for its lower temperature, this salt will be in close accordance with the salts of potash and soda.

Taking nitrate of potash 6·83, as 100, for a standard, the

salt which deviates most considerably is sulphate of soda, which for the 1 per cent. solution is 6.55, or 95.9. A low temperature, however, must be unfavourable to diffusion experiments, from increasing the tendency of salts to crystallize.

In conclusion, I may sum up the results of most interest which this inquiry respecting liquid diffusion has hitherto furnished.

1. I would place first the method of observing liquid diffusion. This method, although simple, appears to admit of sufficient exactness. It enables us to make a new class of observations which can be expressed in numbers, and of which a vast variety of substances may be the object, in fact everything soluble. Diffusion is also a property of a fundamental character, upon which other properties depend, like the volatility of substances; while the number of substances which are soluble and therefore diffusible, appears to be much greater than the number of volatile bodies.

2. The novel scale of Solution Densities, which are suggested by the different diffusibilities of salts, and to which alone, guided by the analogy of gaseous diffusion, we can refer these diffusibilities. Liquid diffusion thus supplies the densities of a new kind of molecules, but nothing more respecting them.

The fact that the relations in diffusion of different substances refer to equal weights of those substances, and not to their atomic weights or equivalents, is one which reaches to the very basis of molecular chemistry. The relation most frequently possessed is that of equality, the relation of all others most easily observed. In liquid diffusion we appear to deal no longer with chemical equivalents or the Daltonian atoms, but with masses even more simply related to each other in weight. Founding still upon the chemical atoms, we may suppose that they can group together in such numbers as to form new and larger molecules of equal weight for different substances, or if not of equal weight, of weights which appear to have a simple relation to each other. It is this new class of molecules which appear to play a part in solubility and liquid diffusion, and not the atoms of chemical combination.

3. The formation of classes of equi-diffusive substances. These classes are evidently often more comprehensive than the isomorphous groups, although I have reason to imagine that they sometimes divide such groups; that while the diffusion of salts of baryta and strontia, for instance, is similar, the diffusion of salts of lead may be different.

4. The separation of the whole salts (apparently) of potash

and of soda into two divisions, the sulphate and nitrate groups, which must have a chemical significance. The same division of the salts in question has been made by M. Gerhardt, on the ground that the nitrate class is monobasic and the sulphate class bibasic.

5. The application of liquid diffusion to the separation of mixed salts, in natural and in artificial operations.

6. The application of liquid diffusion to produce chemical decompositions.

7. The assistance which a knowledge of liquid diffusion will afford in the investigation of endosmose. When the diffusibility of the salts in a liquid is known, the compound effect presented in an endosmotic experiment may be analysed, and the true share of the membrane in the result be ascertained.

But on the mere threshold of so wide a subject as liquid diffusion, I must postpone speculation to the determination of new facts and the enlargement of my data, of the present incompleteness of which I am fully sensible.

XLIV. *On the Crystalline Form of Beudantite.*

*By H. J. BROOKE, Esq., F.R.S.**

IN a paper by Dr. Percy in the September Number of this Journal, on the chemical constitution of Beudantite, it is stated that its form is certainly very similar to, if not identical with, that of cube-ore; that Levy maintained it to be an obtuse rhombohedron with the vertical angle truncated; and that Descloizeaux, on the other hand, asserts that the crystals are cubes similar in all respects to those of cube-ore from Cornwall. It is clear from this statement that the crystals examined by Descloizeaux were different in form from those examined and described by Levy, which have *only one* of the solid angles of the supposed cube truncated, the truncating face being large in comparison with the size of the crystals; and instead of being bright, like the other faces, is of such a velvety dullness as scarcely to reflect any light.

The composition seems therefore to have influenced the form and character of the crystals of Levy's specimen, the further distinction of which from those of cube-ore cannot, however, on account of the imperfection of the faces, be made out.

* Communicated by the Author.