

1917

The Dissociation of Double Salts

Harold L. Maxwell
Cornell College

Nicholas Knight
Cornell College

Let us know how access to this document benefits you

Copyright ©1917 Iowa Academy of Science, Inc.

Follow this and additional works at: <https://scholarworks.uni.edu/pias>

Recommended Citation

Maxwell, Harold L. and Knight, Nicholas (1917) "The Dissociation of Double Salts," *Proceedings of the Iowa Academy of Science*, 24(1), 489-499.

Available at: <https://scholarworks.uni.edu/pias/vol24/iss1/69>

This Research is brought to you for free and open access by the Iowa Academy of Science at UNI ScholarWorks. It has been accepted for inclusion in Proceedings of the Iowa Academy of Science by an authorized editor of UNI ScholarWorks. For more information, please contact scholarworks@uni.edu.

THE DISSOCIATION OF DOUBLE SALTS.

HAROLD L. MAXWELL AND NICHOLAS KNIGHT.

The purpose of this work is to study the condition of double salts in aqueous solutions. Graham¹ was the first to show that the double sulphates of the alums could be separated by diffusion. Marignac confirmed this work soon after and reached the conclusion "That double salts are found as such only at the moment of crystallization." Later in 1882, Rüdorff made a study of the diffusion of some of the double bromides and chlorides. He diffused the double salt solutions, using gold beater's skin for a membrane,² and then analyzed the diffusate and in this way determined the proportion in which the double salts came through. If the diffusate contained the various elements in the same proportion that they would be found in the double salt, it would be evident that the double salt did not dissociate in the solution, but if the diffusate contained the elements in a different proportion from that found in the double salt it would be plain that the salt had dissociated in the solution.

From these determinations it is possible to classify double salts in two general classes. First, those which suffer decomposition in aqueous solution and second, those which are not broken down when in a water solution. To the first class belong:

Copper Potassium Chloride $2\text{KCl} \cdot \text{CuCl}_2 + 2\text{H}_2\text{O}$.
 Magnesium Potassium Chloride $\text{KCl} \cdot \text{MgCl}_2 + 6\text{H}_2\text{O}$.
 Copper Ammonium Chloride $2\text{NH}_4\text{Cl} \cdot \text{CuCl}_2 + 2\text{H}_2\text{O}$.
 Sodium Cadmium Chloride $2\text{NaCl} \cdot \text{CdCl}_2 + 3\text{H}_2\text{O}$.
 Zinc Potassium Chloride $2\text{KCl} \cdot \text{ZnCl}_2 + \text{H}_2\text{O}$.
 Barium Cadmium Chloride $\text{BaCl}_2 \cdot \text{CdCl}_2 + 4\text{H}_2\text{O}$.

The following three double chlorides are not decomposed in the presence of water:

Sodium Platonic Chloride $2\text{NaCl} \cdot \text{PtCl}_4 \cdot 8\text{H}_2\text{O}$.
 Potassium Platonic Chloride $2\text{KCl} \cdot \text{PtCl}_2$.
 Mercuric Ammonium Chloride $2\text{NH}_4\text{Cl} \cdot \text{HgCl}_2$.

¹Chem. Pharm. 1n, 56. 1851.

²Ber., 21, 4. 1888.

Later some important work was done on these compounds and others by Kremers,³ Grotian⁴ and Berthelot.⁵ The latter gave us the general proposition founded upon his thermochemical studies: "Double salts formed with the liberation of a small amount of heat are to be regarded as separated, for the most part, into their constituents, by water."

In 1910 Parsons and Evans⁶ made a thorough study of the alums, including in their investigations:

- Ammonium Chrome Alum.
- Potassium Chrome Alum.
- Potassium Aluminium Alum.
- Ammonium Aluminium Alum.
- Ferrie Ammonium Alum.

In summing up the results obtained from their study, the authors said, in a paper presented before the American Chemical Society: "When alums are dissolved in water they are decomposed into the simple sulphates which can be separated from each other by diffusion. The Chrome Alums separate more readily than the Aluminium Alums."

Jones and Ota⁷ used the conductivity method in determining the presence of double salts and by increasing the dilution they were able to determine the rate of dissociation. The work included the study of four double chlorides and those at only a small range of dilution. The same method was employed by Jones and Knight⁸ in a comprehensive study of the double bromides and chlorides. This work included many more double salts than had been studied before and each one was measured over a much wider range of dilution. In several salts the dilution ranged from the molecular weight in two litres to the same in seventeen thousand litres. An important part of this work was the discovery of two new double bromides: sodium cadmium bromide and ammonium zinc bromide. These new salts were analyzed and found to have the composition: $2\text{NaBr} \cdot 3\text{CdBr}_2 + 6\text{H}_2\text{O}$ and $3\text{NH}_4\text{Br} \cdot \text{ZnBr}_2$.

³Ann. Phys. (Pogg), 98, 58.

⁴Ann. Phys. (Wied), 18, 177.

⁵Ann. Chim. Phys. (5), 29, 198.

⁶Journal of the Amer. Chem. Soc., Vol. 32, page 1383, 1910.

⁷Amer. Chem. Journal, 22, 5.

⁸Amer. Chem. Journal, Vol. 21, No. 2, August, 1899.

This work of Jones and Knight included the following four double chlorides and as many double bromides.

Sodium Zinc Chloride.
Strontium Cadmium Chloride:
Ammonium Magnesium Chloride.
Potassium Magnesium Chloride.
Barium Cadmium Bromide.
Potassium Cadmium Bromide.
Sodium Cadmium Bromide.
Ammonium Zinc Bromide.

CONDUCT OF DOUBLE SALTS IN AQUEOUS SOLUTIONS.

The compounds which we have studied are:

Sodium Cadmium Bromide $2\text{NaBr} \cdot 3\text{CdBr}_2 + 6\text{H}_2\text{O}$.

Ammonium Zinc Bromide $3\text{NH}_4\text{Br} \cdot \text{ZnBr}_2$.

Copper Ammonium Chloride $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$.

Iron Ammonium Sulphate $\text{FeNH}_4(\text{SO}_4)_2$.

In the study of these compounds we used the diffusion method. We obtained the porous cups from Carl Schleicher and Schüll and found that the size, 45 mm. wide and 100 mm. high, gave the best results. This article is listed as Diffusions—Hülsen No. 597. These cups are compact enough to permit diffusion only slowly, yet porous enough to pass enough material to admit of accurate analysis. They are placed in 200 cc. beakers and 50 cc. of the five per cent solution of the double salt is placed in each one. Then distilled water is placed in the beaker until it reaches the same level in the beaker that the salt solution has in the diffusion cup.

These beakers must be kept at a constant temperature as this factor plays an important part in determining the amount of material to pass through the walls of the cup. By varying the temperature at one concentration of the salt solution and then by varying the concentration of the salt solution at each temperature, it is possible to secure an endless list of data showing the effect of temperature and dilution upon the rate of dissociation of the salts.

THE DOUBLE BROMIDE OF SODIUM AND CADMIUM.



We brought together the constituent bromides in the proportion two to three to form the salt 2NaBr. 3CdBr₂+6H₂O which was first made by Jones and Knight and described in "Aqueous Solutions of Double Salts."³ The salt crystallized out in long narrow plates with tapering mitre-like ends. We dried the salt and made two analyses of it with the following results:

Cd.	Br.	H ₂ O	Total
PER CENT	PER CENT	PER CENT	PER CENT
32.60	46.51	21.00	100.11
32.77	46.50	20.90	100.17

Since the total per cent of the elements of this salt is 100 it is evident that no sodium salt was present in the compound. By calculation we found that the result from the above salt corresponds to the formula CdBr₂+4H₂O which has the composition:

Cd.	Br.	H ₂ O	Total
PER CENT	PER CENT	PER CENT	PER CENT
32.56	46.51	20.93	100.00

The cadmium bromide which crystallized out of this mixture of salts resembled the original cadmium bromide very closely and when a microscopic examination was made of the two salts it was noted that the two were identical in crystalline form.

The cadmium bromide which we had obtained was returned and redissolved in the mother solution. More of the sodium bromide was added until the amount of the two bromides was proportional to their molecular weights. From this mixture there separated out a salt made up of small six sided plates about the thickness of a ten cent coin.

Analysis of this salt gave the following results:

Cd.	H ₂ O	Br.
PER CENT	PER CENT	PER CENT
30.00	10.09	56.47

This corresponds to the formula 2NaBr. 3CdBr₂+6H₂O which has the percentage composition:

Cd.	H ₂ O	Br.
29.80	9.55	56.59

³American Chemical Journal, Vol. XXII, No. 2, August, 1899.

With this assurance that we had the right salt we proceeded with the diffusion tests using the method outlined in the foregoing. We made these tests at several temperatures and also at different concentrations and time intervals.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	13°C	45 Minutes

We found on the analysis of the diffusate, the following amounts of the salts in solution: (Weight in grams.)

	TEST No. 1	TEST No. 2
CdBr ₂	.04009	.04131
NaBr	.02290	.02320

In the double salt crystals, the proportional parts of the various elements may be represented by the formula: 2NaBr. 3CdBr₂. Since the molecular weights of these are 206 and 810 respectively, it is evident that, if this salt does not dissociate in a water solution, the two salts found in the diffusate will bear the same ratio to each other. From the above molecular weights it is seen that the cadmium bromide should be 3.9 times heavier than the sodium bromide, if the double salt has not dissociated. We find from the analysis of the diffusate that the sodium bromide is a little more than half the weight of the cadmium bromide that diffused through the walls of the porous cup.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	46°C	45 Minutes
	TEST No. 1	TEST No. 2
CdBr ₂	.10045	.10915
NaBr	.04953	.05244

In this we have less than half as much of the sodium bromide as of the cadmium bromide. It seems that less of the salt has dissociated since the ratio is more nearly 1 to 3.9. This may not necessarily point to the fact that the salts break down more easily in cold than in warm water. It may be that the heat has so lessened the internal friction of the solvent that it passes through the walls more easily and in carrying a larger amount of the salt through in the same time, the more cadmium bromide is taken through. This is only a supposition, however.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
25 Per Cent	13°C	45 Minutes
	TEST No. 1	TEST No. 2
CdBr ₂	.12916	.12480
NaBr	.07610	.07052

It is readily noted that the 25 per cent solution with the same time duration and the same temperature has diffused a much larger amount of the salt. We found this true in each case with this salt.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
25 Per Cent	13°C.	45 Minutes
	TEST No. 1	TEST No. 2
CdBr ₂	.13094	.14458
NaBr	.08861	.08690

This test serves only to verify the foregoing one.

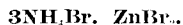
CONCENTRATION	TEMPERATURE	DURATION OF TEST
2½ Per Cent	Room Temp.	24 Hours
	TEST No. 1	TEST No. 2
CdBr ₂	.40921	.36731
NaBr	.19392	.17313

We made an analysis of the contents of the cup also and found that even in the twenty-four hours the solution had not reached its equilibrium, that is, the solution within the cup contained more of the salt per cc. than did the solution surrounding the cup within the beaker.

Conclusions: sodium cadmium bromide dissociates when dissolved in water.

Sodium bromide diffuses faster than cadmium bromide.

THE DOUBLE BROMIDE OF AMMONIUM AND ZINC.



We added the ammonium bromide to the zinc bromide in the proportion of three to one, multiplied by their molecular weights, to form the salt: $3\text{NH}_4\text{Br} \cdot \text{ZnBr}_2$. There separated out a large amount of the salt which we analyzed with the following results:

Br.	Zn.	AMMONIUM	TOTAL
PER CENT	PER CENT	PER CENT	PER CENT
77.19	12.60	10.40	100.19

This compares favorably with the calculated results which are:

Br. PER CENT	Zn. PER CENT	AMMONIUM PER CENT	TOTAL PER CENT
77.07	12.52	10.40	99.99

With the use of the same method employed in the examination of the preceding salt, we diffused the salt and found the following results:

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	Room Temp.	24 Hours
	TEST No. 1	TEST No. 2
ZnBr ₂	.43537	.42142
NH ₄ Br	.78583	.77359

In the double bromide the ratio between the constituent bromides is one of the zinc to 1.3 of the ammonium bromide. Unless it is dissociated by water the diffusate should contain these elements in the same ratio one to the other. We find, however, on analysis that the ammonium bromide is much in excess of this ratio. The results show that the ammonium bromide is to zinc bromide as 1:1.8.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
2½ Per Cent	Room Temp.	24 Hours
	TEST No. 1	TEST No. 2
ZnBr ₂	.30132	.32412
NH ₄ Br	.35455	.37241
5 Per Cent	Room Temp.	12 Hours
	TEST No. 1	TEST No. 2
ZnBr ₂	.28568	.31271
NH ₄ Br	.83258	.84781

It appears from the results that during the first twelve hours the ammonium bromide goes through the porous cup much faster than during the second twelve hours. In the twenty-four hour test the ammonium was not present in large excess but in this analysis of the twelve hour test we find that the ammonium bromide is present in much larger proportions.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	55°C	1 Hour
	TEST No. 1	TEST No. 2
ZnBr ₂	.04428	.04947
NH ₄ Br	.26310	.29190

This test also shows a larger proportion of the ammonium bromide. The raising from "Room Temperature" to 55° C. has also been an active agent of dissociation.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	55° C	15 Minutes
	TEST No. 1	TEST No. 2
ZnBr ₂	.02518	.01972
NH ₄ Br	.08336	.08059

The data here recorded in connection with the preceding tests, give an excellent example which shows how the amount of solid matter that diffuses through the cup per unit of time, is greatest for the first unit of time and becomes smaller and smaller as the solutions become more nearly in an equilibrium. It is noted that half as much of the zinc bromide was diffused in the first fifteen minutes as was diffused during the full hour test. This rate of decrease for each succeeding period diminishes until with long duration of time tests, when the solutions become nearly saturated, the difference or the rate of decrease is very small.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	Room Temp.	12 Hours
	TEST No. 1	TEST No. 2
ZnBr ₂	.27178	.33168
NH ₄ Br	.80585	.832206

This test was made under the same condition as one of the foregoing and similar results were obtained, each serving to check the other.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	Room Temp.	6 Hours
	TEST No. 1	TEST No. 2
ZnBr ₂	.12064	.10240
NH ₄ Br	.46180	.47242

It may be noted when comparing this six hour test with the twelve hour tests, that less than half as much of the zinc bromide was diffused, while more than half as much of the ammonium came through the walls.

Conclusions—(1) Zinc ammonium bromide dissociates in water solution. (2) Ammonium bromide passes through a membrane faster than ZnBr₂. (3) Ammonium bromide dialyzes much faster than ZnBr₂ at the beginning of the test, but the amount dialyzed, per unit time, decreases more rapidly when the time is lengthened.

THE DOUBLE CHLORIDE OF COPPER AND AMMONIUM.



For these tests we used the salt crystals furnished by the Baker Adamson Company. The analysis of this salt compared favorably with the calculated composition which is:

PER CENT	NH ₄	Cl	H ₂ O
Cu	PER CENT	PER CENT	PER CENT
22.89	12.97	51.16	12.97
CONCENTRATION	TEMPERATURE	DURATION OF TEST	
	TEST No. 1	TEST No. 2	
CuCl ₂	.10365	.08954	
NH ₄ Cl	.40470	.37995	

From the formula of the double chloride of copper and ammonium, it is plain that the two salts have combined in such a way that the relative molecular weight is 134 of the copper chloride to 107 of the ammonium chloride. If the salt does not dissociate we will expect then to find the salts in the diffusate in the proportion of (1) one of the ammonium chloride to 1.25 of the copper chloride. The analysis, however, shows the presence of about four times as much ammonium chloride as of the copper chloride.

CONCENTRATION	TEMPERATURE	DURATION OF TEST	
5 Per Cent	Room Temp.	2 Hours	
	TEST No. 1	TEST No. 2	
CuCl ₂	.07820	.06680	
NH ₄ Cl	.23149	.20469	

The ammonium chloride is still present in an excess but not so much as in the first instance.

CONCENTRATION	TEMPERATURE	DURATION OF TEST	
5 Per Cent	Room Temp.	1 Hour	
	TEST No. 1	TEST No. 2	
CuCl ₂	.05428	.05015	
NH ₄ Cl	.10626	.10690	

It is readily seen, from the results of the five, two, and one hour tests, that the difference is less in the shorter time tests.

It is to be expected then that since the CuCl₂ diffuses at a more even rate, the ammonium chloride comes through very much faster during the first part of the test and decreases rapidly until the weight of the copper chloride seems to approximate the weight of the ammonium salt.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	63°C	2¼ Hours
	TEST No. 1	TEST No. 2
CuCl ₂	.16231	.15929
NH ₄ Cl	.35727	.34984

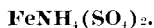
With the rise of temperature it is noticed that the two salts are approaching a different ratio and that the ammonium chloride has taken another marked increase. Instead of the ratio of 1 to 1.25 we have the ratio of 1 to 2.25.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	63°C	1 Hour
	TEST No. 1	TEST No. 2
CuCl ₂	.07259	.08508
NH ₄ Cl	.20596	.20188

This test serves to verify the statement made above concerning the rapid diffusion of the ammonium salt during the first part of the tests. We have in these data more evidence to prove that the decrease of the ammonium chloride is more rapid than the decrease of the copper chloride, for each additional time unit. The ratio between the two salts for the shorter periods is higher than for the longer periods.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	Room Temp.	10 Hours
	TEST No. 1	TEST No. 2
CuCl ₂	.24141	.26204
NH ₄ Cl	.53293	.51076

THE DOUBLE SULPHATE OF IRON AND AMMONIUM.



CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	Room Temp.	2 Hours
	TEST No. 1	TEST No. 2
FeSO ₄	.01039	.01249
(NH ₄) ₂ SO ₄	.03608	.04312

From the above formula we computed the ratio of the two constituent salts and found that they were present in the ratio of 100 of the iron to 33 of the ammonium sulphate. If then the salt does not dissociate we would expect to find three times the weight of the iron sulphate as of the ammonium sulphate, in the diffusate. But from the above data it is evident that the ammonium is much in excess and that the double sulphate dissociates when in a water solution.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	Room Temp.	3 Hours
	TEST No. 1	TEST No. 2
FeSO ₄	.02548	.01824
(NH ₄) ₂ SO ₄	.05709	.04244

We find here an example of how the ammonium salt decreases at a more rapid rate than iron salt for the longer periods.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	Room Temp.	5 Hours
	TEST No. 1	TEST No. 2
FeSO ₄	.03998	.04623
(NH ₄) ₂ SO ₄	.07799	.09438

The ammonium sulphate is still on the ratio decrease and now for the five hour test it is less than twice the weight of the iron, while for the two hour period it was three times greater.

CONCENTRATION	TEMPERATURE	DURATION OF TEST
5 Per Cent	Room Temp.	10 Hours
	TEST No. 1	TEST No. 2
FeSO ₄	.08621	.09196
(NH ₄) ₂ SO ₄	.15411	.16478

The total weight of the salts which came through the walls during the ten hour test is less than twice the weight of the salts which came through during the five hour test. This is another example of how the total amount of salt which passes through a dializer during any period of time, is greatest for the first period and decreases for each additional period. This is only to be expected for as the solutions within and without the porous cup come to approximate an equilibrium, there is less pressure and consequently less force to urge the salts through the membrane.

GENERAL CONCLUSIONS FROM DATA SECURED.

The double salts studied do not exist as such in aqueous solutions, but dissociate into simpler salts.

The rate at which the dissociated ions of a salt pass through a porous membrane is inversely proportional to the size of the ions of that salt.

Some ions, which are of themselves small, hydrate and thus become large and because of this they pass through the more slowly. This is in accordance with the "Hydrate Theory" of Jones and Knight.

DEPARTMENT OF CHEMISTRY,
CORNELL COLLEGE.