

1869

8. ON THE COMPOSITION OF THE ACID OXALATES OF POTASSIUM, AMMONIUM AND SODIUM. By WILLIAM RIPLEY NICHOLS, of Boston, Mass.

BINOXALATE OF POTASSIUM.

THE composition of this salt was formerly held to be expressed by the formula* $KO, C_4O_6 + 3HO$ ($C_2KH\Theta_4 + aq.$)

*On the authority of Graham, Phil. Tr. 1837, 50.

and this formula is still given by Gmelin, Watts, and others, as that of the commonly occurring salt.

Rammelsberg,* on the other hand, describes the salt obtained by neutralizing a certain quantity of oxalic acid with carbonate of potassium, and adding an equal amount of oxalic acid, as corresponding to the formula $2(KO, C_4O_6) + 3aq.$ [$4(C_2KH\Theta_4) + aq.$]

Marignac,† having afterwards partially analyzed this salt, concluded that the correct formula was $C_4KH O_8(C_2KH\Theta_4)$ and that the crystals contained no water of crystallization. He differed from Rammelsberg as to the system to which the crystals should be referred, and the latter afterwards‡ acknowledges the correctness of Marignac's views as to the crystalline form and, without repeating the analysis of the salt, seems satisfied to accept the formula assigned by Marignac.

I have prepared this salt in the manner indicated by Rammelsberg, and find that its composition agrees with the formula originally given by him.

	Calculated.			Found.							
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Mean.		
$2K_2\Theta$	188.44	35.53	—	—	35.55	35.05	—	—	35.30		
$4C_2\Theta_3$	288.00	54.29	55.35	55.67	55.76	—	—	—	55.76		
$3aq.$	54.00	10.18	—	—	—	—	10.16	10.39	10.58		
$4(C_2KH\Theta_4) + aq.$	530.44	100.00	—	—	—	—	—	—	—		

In these analyses I determined the potassium as carbonate by igniting a portion of the finely powdered crystals in a covered platinum crucible, raising the heat very gradually in order to avoid loss by projection, to which, as Marignac hints, this salt is particularly liable. The oxalic acid was determined by titration with a solution of permanganate of potassium standardized against pure oxalic acid. The hydrogen was determined by igniting the salt in a combustion tube, in a stream of dry air, and collecting the water in a weighed chloride of calcium tube.

Rammelsberg's					Marignac's				
formula	demands.	own figures	were.		formula	demands.	own figures	were.	
$2KO$	35.53	36.41	35.22	35.36	KO	36.78	36.35	(Mean of four.)	
$2C_4O_6$	54.29	55.31	54.32	54.00	C_4O_6	56.19	55.86		
$3aq.$	10.18	—	—	—	HO	7.03	—		
	100.00					100.00			

* Pogg. Ann. XCH, 24 (1854).

† Mém. de la Soc. d. Phys. et d'Hist. Nat. de Genève, T. XIV, part I. (1855).

‡ Supplement zu dem Handbuch der krystallographischen Chemie. Leipzig, 1857, s. 81.

Had Marignac determined the hydrogen in his salt, he would have found his formula to be inadmissible.

In regard to the acid oxalate described by Graham (loc. cit.),* it is extremely doubtful whether there be such a salt. Rammelsberg† doubts its existence, and I have myself been unable to procure it. I added to a hot solution of a known quantity of oxalic acid, half the carbonate of potassium necessary to neutralize it. The crystals which formed in the hot solution (A), those deposited from the solution at the ordinary temperature (B), as well as those deposited when the solution was artificially cooled to a considerably lower temperature (C), proved to be the quadroxalate $\text{C}_2\text{KH}\Theta_4$, $\text{C}_2\text{H}_2\Theta_4$, + 2aq.

	Calculated.		Found.					
			A.			B.		C.
			I.	II.	III.	I.	II.	I.
$\text{K}_2\Theta$	94.22	18.54	—	—	18.41	—	—	—
$4\text{C}_2\Theta_3$	288.00	56.67	56.23	56.52	—	—	56.86	56.33
$3\text{H}_2\Theta$	54.00	24.79	—	—	—	—	—	—
4aq.	72.00							
$2(\text{C}_2\text{KH}\Theta_4, \text{C}_2\text{H}_2\Theta_4, + 2\text{aq.})$	508.22	100.00						

In these estimations the potassium was determined as carbonate, by ignition, and the oxalic acid by titration, as in the preceding case.

I analyzed several samples of commercial "binoxalate of potash," but each sample proved to be quadroxalate.

BINOXALATE OF AMMONIUM.

This salt was prepared by neutralizing a certain quantity of oxalic acid with ammonia-water, and then adding an equal quantity of oxalic acid. Analysis showed the composition of the salt to be $2(\text{C}_2(\text{NH}_4)\text{H}\Theta_4) + \text{aq.}$

	Calculated.		Found.				Mean.
			I.	II.	III.	IV.	
$(\text{NH}_4)_2\Theta$	52	22.41	—	—	21.54	—	21.54
$2\text{C}_2\Theta_3$	144	62.08	61.35	61.57	—	—	61.46
$\text{H}_2\Theta$	18	7.75	—	—	—	—	—
aq.	18	7.76	—	—	—	7.50	7.50
$2(\text{C}_2(\text{NH}_4)\text{H}\Theta_4) + \text{aq.}$	232	100.00					

	Calc.	Found.
* KO	32.24	32.34
C_4O_6	49.28	—
3HO	18.48	—
	100.00	

Graham deduced this formula from the amount of carbonate of potassium left on ignition (47.45 per cent.).

† Pogg. Ann. XCIII, 24 (supra cit.).

The formula usually given in text-books on chemistry (Gmelin, Watts, etc.), is $C_4(NH_4)HO_8 + 2 aq.$ $\epsilon_2(NH_4)H\Theta_4 + aq.$, that is, with one more molecule of water than I find to be the case. For this formula the calculated percentages would be

$(NH_4)_2\Theta$	52	20.80
$2\epsilon_2\Theta_3$	144	57.60
$H_2\Theta$	18	7.20
$2 aq.$	36	14.40
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100.00	250	

Anderson* says that the binoxalate of ammonium may be obtained by mixing equivalent quantities of chloride of ammonium and oxalic acid (regarded as monobasic; $C_2O_3, HO + 2 aq. = 63$), and gives as the formula $2 C_2O_3, NH_4O, 2 HO [2(\epsilon_2(NH_4, H\Theta_4) + aq.)]$.

He determined the oxalic acid alone, and, from the data that he gives, it would appear that, instead of the binoxalate, he really obtained the quadroxalate mentioned below.

	Percentage of $\epsilon_2\Theta_3$	
in his salt.	in the acid salt above.	in the hyperacid salt below.
61.92	62.08	61.80

I found that by adding a hot solution of 53.5 grm. (1 eq.) chloride of ammonium (NH_4Cl), to a hot solution of 63 grm. ($\frac{1}{2}$ eq.) of crystallized oxalic acid ($\epsilon_2H_2\Theta_4 + 2 aq.$), there were deposited on cooling crystals of the hyperacid salt of the formula $\epsilon_2(NH_4)H\Theta_4, \epsilon_2H_2\Theta_4, + 2 aq.$

	Calculated.	Found.						Mean.
		I.	II.	III.	IV.	V.	VI.	
$(NH_4)_2\Theta$	52	11.16	11.12	11.29	—	—	—	11.20
$4\epsilon_2\Theta_3$	288	61.80	—	—	61.14	61.14	61.09	61.12
$3H_2\Theta$	54	11.59	—	—	—	—	—	—
$4 aq.$	72	15.45	—	—	—	—	15.81	15.81
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$2(\epsilon_2(NH_4)H\Theta_4, \epsilon_2H_2\Theta_4, + 2 aq.)$	466	100.00						

In these analyses the ammonium was determined as chloroplatinate of ammonium, the oxalic acid by titration, and the water of crystallization by drying at $100^\circ C.$, until the weight remained constant.

BINOXALATE OF SODIUM.

Anderson (loc. cit.) says that, by dissolving equivalent proportions of oxalic acid (equiv. = 63) and chloride of sodium (equiv. = 58.5), in hot water, crystals of this salt are obtained

* Qu. Jour. Ch. Soc. I. 231 (1849).

on cooling the solution. He gives the formula for the same $NaO, 2C_2O_3 + 4HO [2(C_2NaH\Theta_4) + 3aq.]$

I found that crystals of the binoxalate were deposited from such a mixture, but that they answered to the commonly received formula $C_4NaHO_8 + 2aq. [C_2NaH\Theta_4 + aq.]$

	Calculated.		Found.		Mean.
			I.	II.	
$Na_2\Theta$	62	23.85			
$2C_2\Theta_3$	144	55.38	55.19	55.24	55.22
$H_2\Theta$ }			—	—	—
$2aq.$ }					
	<hr/>	<hr/>			
$2(C_2NaH\Theta_4 + aq.)$	260	100.00			

9. ON THE SOLUBILITY IN WATER OF THE OXALATES OF SODIUM, POTASSIUM AND AMMONIUM, AT THE ORDINARY TEMPERATURE OF THE AIR. By WILLIAM RIPLEY NICHOLS.

In determining the solubilities of the salts experimented upon, the method employed to obtain solutions, saturated at the observed temperatures, was as follows:—Considerable quantities of the salts operated upon, several times as much as would be likely to dissolve in the amount of water used, were put into glass-stoppered bottles, which were then half filled with distilled water, and placed in a pan of water so as to be immersed up to the necks. The operation was carried on in a room where the variation of temperature was slight, such variation being noted by means of a thermometer suspended in the pan of water.

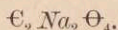
The bottles were shaken conscientiously at frequent intervals for two or three days, and, finally, portions of the solutions were filtered through dry filters, into tared flasks, and weighed. As a rule the thermometer had indicated a constant temperature for several hours previous to the filtration.

The amount of oxalic acid in the weighed solution, was determined by titration with permanganate of potassium, standardized against pure oxalic acid and from this result the amount of salt dissolved was calculated.

In every case but one, the salts were prepared by myself,

and in every case the character and purity of the salt in question was ascertained by titrating a weighed portion of the dry salt with the standard solution of permanganate of potassium.

OXALATE OF SODIUM.



This salt was prepared by neutralizing a hot solution of oxalic acid with pure carbonate of sodium. The oxalic acid used in preparing this, as well as the other salts, left upon ignition 0.03 per cent. ash.

	Calculated.		Found.		Mean.
	I.	II.	I.	II.	
Na_2O	62	46.27			
C_2O_3	72	53.73	54.06	53.62	53.84
	134	100.00			

Solubility.—Temperature at time of filtration, . . 13° C.

Temperature had varied during solution from 11° to 13.5°.

100 parts of the solution saturated at 13° contain :

I.	II.	III.	Mean.	
3.063	3.066	3.047	3.059	parts of the crystallized salt.

Or, 100 parts of water at 13° dissolve 3.156 parts of the crystallized salt.

Or, 1 part of the crystallized salt is soluble in 31.6 parts of water at 13°.

This agrees with the determination of Souchay and Lensen* who say that one part of the salt dissolves in 31.1 parts of water at 15.5°.

Pohl† says that one part of salt dissolves in 26.7 parts of water at 21.8°.

BINOXALATE OF SODIUM.



This salt was prepared by adding 58.5 grm. (1 eq.) of chloride of sodium in solution, to a hot solution of 63 grm. ($\frac{1}{2}$ eq.) of crystallized oxalic acid, and recrystallizing the product deposited from the solution when cold.

* Ann. Ch. u. Ph. XCIX. 33 (1856).

† Wien. Acad. Ber. VI. 596 (1851).

	Calculated.		Found.		Mean.
	I.	II.	I.	II.	
$Na_2 \Theta$	62	23.85	—	—	—
$2 \Theta_2 \Theta_3$	144	55.38	55.08	55.35	55.22
$3 H_2 \Theta$	54	20.77	—	—	—
$2 (\Theta_2 Na H \Theta + aq.)$	260	100.00	—	—	—

Solubility.—Temperature at time of filtration, . . 10°.

Temperature had varied between 5° and 10°.

100 parts of the solution saturated at 10° contain :

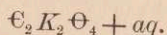
I.	II.	III.	Mean.	
1.40	1.39	1.55	1.45	parts of the crystallized salt.

Or, 100 parts of water at 10° dissolve 1.48 parts of the crystallized salt.

Or, one part of the crystallized salt dissolves in 67.57 parts of water at 10°.

Souchay and Lensen (loc. cit.) say that one part of the salt dissolves in 60.3 parts of water at 15.5°.

OXALATE OF POTASSIUM.



This salt was prepared by neutralizing a commercial sample of quadroxalate of potassium with carbonate of potassium and recrystallizing twice.

	Calculated.		Found.			Mean.
	I.	II.	I.	II.	III.	
$K_2 \Theta$	94.22	51.14	—	—	—	—
$\Theta_2 \Theta_3$	72.00	39.08	38.99	39.63	38.53	39.05
$H_2 \Theta$	18.00	9.78	—	—	—	—
$\Theta_2 K_2 \Theta_4 + aq.$	184.22	100.00	—	—	—	—

Solubility.—Temperature at time of filtration, . . 16°.

Temperature had varied between 12° and 16°.

(The temperature had remained at 16° for several hours.)

100 parts of the solution saturated at 16° contain :

I.	II.	Mean.	
24.73	24.89	24.81	parts of the crystallized salt.

Or, 100 parts of water at 16° dissolve 32.99 parts of the crystallized salt.

Or, one part of the crystallized salt is soluble in 3.03 parts of water at 16°.

BINOXALATE OF POTASSIUM.



This salt was prepared as stated in the preceding paper.

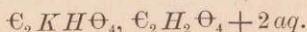
Solubility.—Temperature for three hours preceding filtration, 8°

Temperature had varied between 8° and 10.5°.

100 parts of the solution saturated at 8° contain :

I.	II.	III.	Mean.	
3.680	3.681	3.668	3.676	parts of the crystallized salt.
Or, 100 parts of water at 8° dissolve 3.816 parts of the crystallized salt.				
Or, one part of the crystallized salt is soluble in 26.21 parts of water at 8°.				

QUADROXALATE OF POTASSIUM.



This salt was prepared by recrystallizing a sample of commercial "binoxalate of potash".

	Calculated.		Found.				Mean.
	I.	II.	I.	II.	III.	IV.	
$\text{K}_2\Theta$	94.22	18.54	—	—	—	18.45	18.45
$4\text{C}_2\Theta_3$	288.00	56.67	55.80	55.63	55.77	—	55.75
$3\text{H}_2\Theta$	54.00	} 24.79	—	—	—	—	—
$4aq.$	72.00						
$2(\text{C}_2\text{KH}\Theta_4, \text{C}_2\text{H}_2\Theta_4, + 2aq.)$	508.22	100.00					

Solubility.—Temperature at time of filtration, . . . 13°.

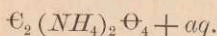
Temperature had varied between 12° and 14.5°.

100 parts of the solution saturated at 13° contain :

I.	II.	Mean.	
1.774	1.784	1.779	parts of the crystallized salt.
Or, one part of the salt is soluble in 55.25 parts of water at 13°.			
Or, 100 parts of water at 13° dissolve 1.81 parts of the crystallized salt.			

Pohl (loc. cit.) says that 100 parts of water at 20.6° dissolve 4.957 parts of the salt dried at 100° (5.775 parts of the crystallized salt), which would go to show that the solubility must increase rapidly with the temperature.

OXALATE OF AMMONIUM.



This salt was prepared by neutralizing a hot solution of oxalic acid with ammonia-water.

	Calculated.		Found.			
			I.	II.	III.	Mean.
$(\text{NH}_4)_2\text{O}$	52	36.62				
C_2O_3	72	50.70	50.72	50.92	51.48	51.04
<i>aq.</i>	18	12.68	—	—	—	—
$\text{C}_2(\text{NH}_4)_2\text{O}_4 + aq.$	142	100.00				

Solubility.—Temperature at time of filtration, . . 15°.

Temperature had varied between 13.5° and 15°.

100 parts of the solution saturated at 15° contain :

I.	II.	Mean.
4.028	4.076	4.052

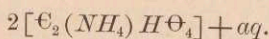
parts of the crystallized salt.

Or, 100 parts of water at 15° dissolve 4.22 parts of the crystallized salt.

Or, 1 part of the crystallized salt dissolves in 23.69 parts of water at 15°.

I verified the statement of Heintz* that this salt is less soluble in a solution of chloride of ammonium than in pure water. I added chloride of ammonium to a concentrated solution of the salt, and there were deposited small crystals which gave by titration 50.93 per cent. C_2O_3 , showing that they were actually the normal oxalate.

BINOXALATE OF AMMONIUM.



This salt was prepared as stated in the previous paper.

Solubility.—Temperature at time of filtration, . . 11.5°.

Variation of temperature—slight.

100 parts of the solution saturated at 11.5° contain :

I.	II.	III.	Mean.
5.89	5.91	5.88	5.896

parts of the crystallized salt.

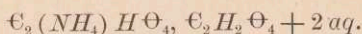
Or, 100 parts of water at 11.5° dissolve 6.26 parts of the crystallized salt.

Or, 1 part of the crystallized salt is soluble in 15.97 parts of water at 11.5°.

* Zeitsch. f. d. ges. Naturw. XX. 29.

In order to ascertain whether this salt dissolved unchanged, a portion of that remaining undissolved, was titrated with the standard permanganate, and the percentage of oxalic acid found agreed with that of the original salt.

QUADROXALATE OF AMMONIUM.



This salt was prepared by adding to half an equivalent of oxalic acid ($C_2H_2\Theta_4 + 2aq.$) an equivalent of chloride of ammonium (NH_4Cl), as described in the preceding paper.

Solubility.—Temperature at time of filtration, 7.75° .

Temperature had varied but slightly.

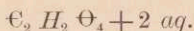
100 parts of the solution saturated at 7.75° contain :

I.	II.	III.	Mean.
2.45	2.46	2.46	2.46 parts of the crystallized salt.

Or, 100 parts of water at 7.75° dissolve 2.52 parts of the crystallized salt.

Or, one part of the crystallized salt is soluble in 39.68 parts of water at 7.75° .

OXALIC ACID.



A portion of pure crystallized oxalic acid was taken, and its solubility determined to be as follows :

Solubility.—Temperature at time of filtration, 14.5° .

Variation of temperature—slight.

100 parts of the solution saturated at 14.5° contain :

I.	II.	III.	Mean.
8.668	8.777	8.754	8.733 parts of the crystallized salt.

Or, 100 parts of water at 14.5° dissolve 9.56 parts of the crystallized salt.

Or, one part of the crystallized salt is soluble in 10.46 parts of water at 14.5° .

THE FOREGOING RESULTS MAY BE TABULATED AS FOLLOWS:—

(169)

NAME OF SALT.	Temperature.	100 parts of the saturated solution contain parts salt.	100 parts water dissolve parts salt.	1 part salt soluble in parts water.
Oxalic Acid, $\text{C}_2\text{H}_2\text{O}_4 + 2 \text{ aq.}$	14.5°	8.73	9.56	10.46
Oxalate of Sodium, $\text{C}_2\text{Na}_2\text{O}_4$	13°	3.06	3.16	31.60
Binoxalate of Sodium, $\text{C}_2\text{Na H O}_4 + \text{ aq.}$	10°	1.45	1.48	67.57
Oxalate of Potassium, $\text{C}_2\text{K}_2\text{O}_4 + \text{ aq.}$	16°	24.81	32.99	3.03
Binoxalate of Potassium, $4 (\text{C}_2\text{K H O}_4) + \text{ aq.}$	8°	3.68	3.82	26.21
Quadroxalate of Potassium, $\text{C}_2\text{K H O}_4, \text{C}_2\text{H}_2\text{O}_4 + 2 \text{ aq.}$	13°	1.78	1.81	55.25
Oxalate of Ammonium, $\text{C}_2(\text{NH}_4)_2\text{O}_4 + \text{ aq.}$	15°	4.05	4.22	23.69
Binoxalate of Ammonium, $2 (\text{C}_2(\text{NH}_4)\text{H O}_4) + \text{ aq.}$	11.5°	5.89	6.26	15.97
Quadroxalate of Ammonium, $\text{C}_2(\text{NH}_4)\text{H O}_4, \text{C}_2\text{H}_2\text{O}_4 + 2 \text{ aq.}$	7.75°	2.46	2.52	39.68