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Graduating Thesis

- 1869 -

540.89

Contributions
to the History of the Compounds of
Oxalic Acid; - By William Ripley Nichols,
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Chemistry.

A Graduating Thesis.

31812

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I. On the Composition of the Acid
Oxalates of Potassium, Ammonium and
Sodium.

Binoxalate of Potassium.

The composition of this salt was formerly held to be expressed by the formula $\text{KO}, \text{C}_4\text{O}_6 + 3\text{HO}^*$ ($\text{C}_2\text{KHO}_4 + \text{aq.}$) and this formula is still given by Wätts, Gmelin 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 $2(\text{KO}, \text{C}_4\text{O}_6) + 3\text{aq.}$ ($4(\text{C}_2\text{KHO}_4) + \text{aq.}$)

Maignac^{xxx}, having afterwards partially analyzed this salt, concluded that the correct formula was C_4KHO_8 (C_2KHO_4) and
[that

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

** Pogg. Ann. 23, 24.

xxx Mem. de la Soc. d. Phys. et d'Hist. nat.
de Genève, T. XIV. part. I.

that the crystals contained no water of crystallization. He differed from Rammeisberg 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 Rammeisberg, and find that its composition agrees with the formula originally given by him to it.

		calculated.	Found.								Mean.
			I.	II.	III.	IV.	V.	VI.	VII.	VIII.	
1 K ₂ O	100.44	35.53	---	---	---	35.55	35.05	---	---	---	35.30
4 Cr ₂ O ₃	288.	54.29	55.35	55.67	55.76	---	---	---	---	---	55.76
3 H ₂ O	54	10.18	---	---	---	---	---	10.16	10.39	10.58	10.34
4(C ₂ KKCr ₂) + H ₂ O	530.44	100.00									

In the 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

* Supplement zu dem Handbuch der Kristallographischen Chemie. Leipzig, 1857. S. 81.

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	form.	demands	own figures	
2 KO	35.53	36.41	35.22	35.36	KO	36.78	36.35 (mean of 4)
2 C ₄ O ₆	54.29	55.31	54.32	54.00	C ₄ O ₆	56.19	55.86
3 ag.	10.18	—	—	—	KO	7.03	—
	<u>100.00</u>						

Had Marignac determined the hydrogen in his salt he would have found that his formula is inadmissible.

In regard to the acid oxalate described by Graham* 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

x	Calculated	
KO	32.24	Graham (loc. cit.) deduced this formula from the amount of carbonate of potassium left in ignition (47.45%).
C ₄ O ₆	47.28	
3HO	18.48	
	<u>100.00</u>	

lution 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 hyperacid salt ($C_2KHO_4, C_2H_2O_4, + 2aq.$).

		Calculated	I.	A.	III.	Found. B.	II.	C.
K_2O	94.22	18.54	18.41	18.53	---	---
$4C_2O_3$	288.	56.67	56.23	56.52	---	---	56.86	56.33
$3H_2O$	54	} 24.79	---	---	---	---	---	---
4aq.	72.		---	---	---	---	---	---
$(C_2KHO_4, C_2H_2O_4, + 2aq.)$	500.22	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 $2(C_2(NH_4)HO_4) + aq$

	Calculated	Found.				Mean
		I.	II.	III.	IV.	
$(NH_4)_2O$ 52	22.41	---	---	21.54	---	21.54
$2C_2O_3$ 144	62.08	61.35	61.57	---	---	61.46
H_2O 18	7.75	---	---	---	---	---
aq 18	7.76	---	---	---	---	---
<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
$2(C_2(NH_4)HO_4) + aq.$ 232	100.00	---	---	---	7.50	7.50

The formula usually given in text-books on chemistry (Gmelin, Watts, etc.) is $C_4(NH_4)HO_8 + 2aq$ ($C_2(NH_4)HO_4 + aq$); that is, with one more molecule of water than I find to be the case. For this formula the calculated percentages would be

$(NH_4)_2O$ 52	20.80
$2C_2O_3$ 144	57.60
H_2O 18	7.20
$2aq$ 36	14.40
<hr/>	<hr/>
$2[C_2(NH_4)HO_4 + aq]$ 250	

Anderson⁺ says that binopalate of ammonium may be obtained by mixing equivalent quantities of chloride of ammonium and of oxalic acid (monobasic. $C_2O_3.HO + 2aq = 63$) (and

⁺ *Qu. Journ. Chem. Soc.* I, 231. (1849)

and gives as the formula $2(C_2O_3)NH_4O, 2H_2O$.
 [$2(E_2(NH_4)HO_4) + aq.$] He determined the oxalic acid alone, and from the data that he gives it would appear that, instead of the bioxalate, he really obtained the quadroxalate mentioned below.

in this salt	Percentage of E_2O_3 in the acid salt above	in the hyperacid salt above
61.92	62.08	61.80

I found that, by adding a hot solution of 53.5 gram. chloride of ammonium to a hot solution of 63 gram. crystallized oxalic acid, there were deposited on cooling crystals of the hyperacid salt of the formula $E_2NH_4HO_4, E_2H_2O_4 + 2aq.$

		Calculated	Found.						Mean.
			I.	II.	III.	IV.	V.	VI.	
$(NH_4)_2O$	52	11.15	11.12	11.29	---	---	---	---	11.20
$4E_2O_3$	288	61.80	---	---	61.14	61.14	61.09	---	61.12
$3H_2O$	54	11.59	---	---	---	---	---	---	---
$4aq.$	72	15.45	---	---	---	---	---	15.81	15.81
$(E_2NH_4HO_4, E_2H_2O_4 + 2aq.)$	466	100.00	---	---	---	---	---	---	---

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

Binoxalate of Sodium

Andersen (loc. cit.) says that by dissolving equivalent proportions of oxalic acid (eq. 63) and chloride of sodium (eq. 58.5) in hot water, crystals of this salt are obtained on cooling the solution. He gives the formula for the same $NaO, 2C_2O_3 + 4HO$ ($2(C_2NaHO_4) + 3aq.$)

I found that crystals of the binoxalate were deposited from such a solution but that they answered to the commonly received formula $C_4NaHO_3 + 2aq$

		Calculated	Found.		Mean
			I.	II.	
Na_2O	62	33.85			
$2C_2O_3$	144	55.88	55.19	55.24	55.22
H_2O	54	20.77			
$2aq$					
$2(C_2NaHO_4 + aq.)$		100.00			

II. On the Solubility of the Oxalates of Sodium, Potassium and Ammonium at the Ordinary Temperature of the air.

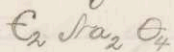
In determining the solubilities of the salts experimented upon the method employed to obtain solutions saturated at the observed temperatures, was as follows;— considerable quantities of the salts operated upon, several times as much as would be likely to dissolve in the amount of water used, were put 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

The thermometer had indicated a constant temperature for several hours previous to the filtration. The amount of oxalic acid in the weighed solutions was determined by titration with permanganate of potassium standardized against pure oxalic acid and from this result the amount of the salt dissolved was calculated.

In every case but one the salts were prepared by myself, and in every case the purity and character 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% ash.

Calculated.

Found

Mean.

Na_2O	62	46.27	I.	II.	
C_2O_3	72	53.73	54.06	53.62	53.84
	134	100.			

Solubility.

Temperature at time of Filtration 13°C

Temperature had varied from 11° to 13.5°C

100 parts of the solution saturated at 13° contain

I.	II.	III.	Mean.
3.064	3.066	3.047	3.059

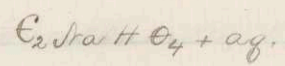
Or, 100 parts of water at 13° dissolve 3.156 parts of the crystallized salt.

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

This agrees with the determination of Leuchay^{2d} and Lensen^x who say that 1 part of the salt dissolves in 31.1 part of water at 15.5°

Pohl^{xx} says that 1 part of the 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 (2 eq.) of crystallized oxalic acid, and recrystallizing the crystals deposited from the solution when cold.

^x Ann. Ch. u. Ph. 99, 33.

^{xx} Min. Acad. Ber. 6, 596

	Calculated		Found.		
			I.	II.	Mean
Na_2O	62	23.05			
$2\text{Cr}_2\text{O}_3$	144	55.38	55.00	55.35	55.22
$3\text{H}_2\text{O}$	54	20.77			
$(\text{C}_2\text{H}_5\text{O}_4 + \text{aq.})$	260	100.00			

Solubility:—

Temperature at Filtration 10°
Variation 5°-10°

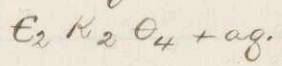
100 parts of the solution saturated at 10° contain
I. 1.40 II. 1.39 III. 1.55 Mean 1.45 parts of the crystallized salt

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

Or, 1 part of the crystallized salt dissolves in 67.57 parts of water at 10°

Souchay and Sersen (loc. cit.) say that 1 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 with carbonate of potassium and recrystallizing.

Twice	Calculated		Found.			
			I.	II.	III.	Mean.
K_2O	94.22	51.14				
Cr_2O_3	72.	39.08	38.99	39.63	38.53	39.05
H_2O	18.	9.78				
$\text{C}_2\text{K}_2\text{O}_4 + \text{aq.}$	184.22	100.00				

Quadrosalate of Potassium.



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

	Calculated		Found.				Mean.
			I.	II.	III.	IV.	
H_2O	94.22	10.54	---	---	---	10.45	10.45
$4E_2O_3$	288.	56.67	55.80	55.63	55.77	---	55.75
$3H_2O$	54						
$4aq$	72	14.79					
$2KHO_4, C_2H_2O_4 + 2aq$	500.22	100.00					

Solubility :-

Temperature at Filtration 13°

Variation $12^\circ - 14.5^\circ$

100 parts of a solution saturated at 13° contain

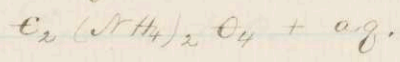
I.	II.	Mean.	
1.774	1.784	1.779	parts of the crystallized salt.

Or, 1 part of the salt is soluble in 55.25 parts of water at 13° .

Or, 100 parts of water at 13° dissolves 1.81 parts of the crystallized salt.

Pohl (loc. cit.) says that 100 parts of water at 20.6° dissolves 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			Mean
		I.	II.	III.	
$(\text{NH}_4)_2\text{O}$	52	36.62			
C_2O_3	72	50.70	50.72	50.92	51.04
aq.	18	12.68			
$\text{C}_2(\text{NH}_4)_2\text{O}_4 + \text{aq}$	142	100.00			

Solubility: - Temperature at Filtration. 15°
Variation 13.5° - 15°

100 parts of a solution saturated at 15° contain

I.	II.	Mean.
4.028	4.076	4.052

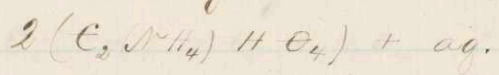
 parts of the crystallized salt.

100 parts of water at 15° dissolves 4.22 parts of the crystallized salt.

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

I verified the statement made by Keintz* 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% C_2O_3 , showing that they were actually the normal oxalate.
 * Zeitschr. f. d. ges. Naturw. 20: 29.

Binoxalate of Ammonium



This salt was prepared as described in the preceding paper.

Solubility:

Temperature at Filtration 11.5°
Variation slight.

100 parts of the solution saturated at 11.5° contain			
I.	II.	III.	Mean
5.89	5.91	5.88	5.89
parts of the crystallized salt.			

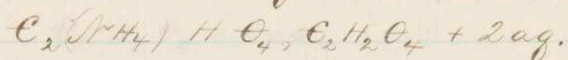
100 parts of water at 11.5° dissolves 6.26 parts of the crystallized salt.

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

In order to ascertain whether this salt dissolved in water 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.

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Quadruplicate of Ammonium.



This salt was prepared by adding to half an equivalent of oxalic acid ($C_2H_2O_4 + 2aq$) an equivalent of NH_4Cl , as described in the preceding paper.

Solubility: Temp. at Filtration $7\frac{3}{4}^\circ$
Variation slight.

100 parts of the solution saturated at $7\frac{3}{4}^\circ$ contain

I.	II.	III.	Mean.
2.45	2.46	2.46	2.46

parts of the crystallized salt.

100 parts of water at $7\frac{3}{4}^\circ$ dissolves 2.52 parts of the crystallized salt.

Or, 1 part of the crystallized salt is soluble in 39.68 parts of water at $7\frac{3}{4}^\circ$.

Oxalic Acid.



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

Temp. at Filtration 14.5°

Variation 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, 1 part of the crystallized salt dissolves in 10.46 parts of water at 14.5° .

The foregoing results may be tabulated as follows:—

Name of Salt.	Temp.	100 pts. of the sat ^d solution contain parts salt.	100 pts water dissolve parts salt.	1 part salt sol. in parts water.
Oxalic Acid — $C_2H_2O_4 + 2aq$	14.5°	9.733	9.56	10.46
Oxalate of Sodium — $C_2Na_2O_4$	13°	3.059	3.156	31.6
Binoxalate of Sodium — $C_2NaHO_4 + aq$	10°	1.45	1.48	67.57
Oxalate of Potassium — $C_2K_2O_4 + aq$	16°	24.81	32.99	3.031
Binoxalate of Potassium — $4(C_2KH_2O_4) + aq$	8°	3.676	3.816	26.21
Quadoxalate of Potassium — $C_2KHO_4, C_2H_2O_4 + 2aq$	13°	1.779	1.81	55.25
Oxalate of Ammonium — $C_2(NH_4)_2O_4 + aq$	15°	4.052	4.22	23.69
Binoxalate of Ammon. — $2(C_2(NH_4)HO_4) + aq$	11.5°	5.89	6.25	15.97
Quadoxalate of Ammon. — $C_2(NH_4)HO_4, C_2H_2O_4 + 2aq$	7.75°	2.46	2.52	39.68