

to which reference has been made in this paper is completely confirmed. But to what extent the activity of an organic compound determined by physical means, that is, the fugacity, corresponds with its activity as measured by its rate of reaction, that is, its reactivity or enhanced tendency to unite with the molecules of some other chemical species, is as yet unsettled. Certain experiments in this direction are at present in progress.

Summary

1. The solubilities of the nitrobenzoic acids have been measured in isoamyl alcohol, xylene, water and aqueous solutions of sodium chloride and magnesium sulfate, all at 50°

2. Measurements have been made at 50° of the partition ratios of the nitrobenzoic acids between the amyl alcohol and *N*-5 *N* aqueous solutions of sodium chloride and magnesium sulfate.

3. Activity coefficients have been calculated from the solubility and partition ratio measurements.

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The System Zinc Oxalate, Potassium Oxalate, Water. I. At 25°¹

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There is some confusion with respect to the complex salts formed from zinc oxalate and the alkali oxalates. Kayser² prepared a compound that analysis indicated to be either $K_2Zn(C_2O_4)_2 \cdot 4H_2O$ or $K_2Zn(C_2O_4)_2 \cdot 5H_2O$ and another for which the analysis did not distinguish clearly between $(NH_4)_2Zn(C_2O_4)_2 \cdot xH_2O$ and $(NH_4)_4Zn(C_2O_4)_3 \cdot xH_2O$. Kunschert³ concluded that the oxalato-zincate ion in solution is $Zn(C_2O_4)_3^{=}$ when the oxalate concentration is larger than 0.15 molar. In more dilute solutions he thought there was evidence of the ion $Zn(C_2O_4)_2^{=}$. Scholder and Linström⁴ prepared an anhydrous compound of the formula $K_2Zn(C_2O_4)_2$.

According to the theory of Mann⁵ four-covalent zinc compounds should be more stable than six-covalent ones.

Further data seemed desirable and it was undertaken to determine what solid phases can exist in equilibrium with saturated solutions of potassium and zinc oxalates at 25°.

(1) A thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

(2) Kayser, *Ann. Physik*, **60**, 140 (1843).

(3) Kunschert, *Z. anorg. Chem.*, **41**, 337 (1904).

(4) Scholder and Linström, *Ber.*, **63**, 2831 (1930).

(5) Mann, *J. Chem. Soc.*, 551 (1929).

Materials and Apparatus

Zinc oxalate was prepared by slow precipitation from zinc chloride and oxalic acid. Analysis by ignition to oxide and by permanganate titration gave 42.98% zinc oxide and 46.49% oxalate as compared with the theoretical values 42.96 and 46.46, respectively. The crystals ranged in size from 0.08 to 0.2 mm. diameter.

Potassium thiocyanato-mercurate solution was prepared by adding mercuric chloride to an equivalent quantity of potassium thiocyanate solution. Other materials were of C. P. quality.

A thermostat regulated at $25 \pm 0.02^\circ$ was used, with a device for rotating several bottles at a time. The glass stoppers of the bottles were covered with rubber caps while in the thermostat.

Methods of Analysis

Oxalate was determined by permanganate titration. For determining zinc the thiocyanato-mercurate method was used.⁶

The method was checked by determining zinc in pure zinc ammonium sulfate. To an acidified solution of the sample an excess of 0.1 molar thiocyanato-mercurate solution was added slowly with stirring. Solution and precipitate were allowed to stand at least one hour. The precipitate was washed twice on a Gooch crucible with a 0.01 molar solution of the reagent and twice with a 0.001 molar solution and dried at 105° .

The results were about two parts in a thousand too low when 1-g. samples were present in solutions of about 200 cc. volume containing 0.05 mole of sulfuric acid per liter and 70 cc. of the reagent added. More acid caused still lower results.

In analyzing the saturated solutions, the samples were diluted to 200 cc. and 9 molar sulfuric acid solution was added to the turning point of methyl orange and 1 cc. in excess. In the analysis of the solid phases, the samples were dissolved in an excess of sulfuric acid and the excess neutralized to the blue-green color of methyl violet.

Preparation of the Complex Salts

Attempts to prepare potassium oxalato-zincate resulted in two compounds. A solution of potassium oxalate saturated at 25° was heated to the boiling point and zinc oxalate added slowly until a small excess was present. The hot solution was filtered,⁷ allowed to cool to 40° , and the resulting crystals separated from the mother liquor. The crystals were well-formed hexagonal plates, very thin and transparent. The compound was shown to be a complex salt. It is sparingly soluble in water and is decomposed by dilute acids. It effloresces in air. This compound is being further investigated by one of the authors.

Another compound can be obtained from the mother liquor after the filtration. When this solution is allowed to stand for three or four days at 20 to 25° large crystals form. Analysis after washing with alcohol and ether indicated the formula $K_2Zn(C_2O_4)_2 \cdot 6H_2O$, in which, however, the degree of hydration is not well established.

Anal. Calcd. for $K_2Zn(C_2O_4)_2 \cdot 6H_2O$: Zn, 15.29; C_2O_4 , 41.15. Found: Zn, 15.30, 15.29, 15.35; C_2O_4 , 41.66, 41.68.

The compound is efflorescent and becomes anhydrous when exposed to the air. A sample was exposed to the air for a week and analyzed.

Anal. Calcd. for $K_2Zn(C_2O_4)_2$: Zn, 20.46; C_2O_4 , 55.07. Found: Zn, 20.82, 20.87, 20.82; C_2O_4 , 54.82, 54.80, 54.84.

In washing the crystals free from mother liquor there was probably some decom-

(6) See Lundell and Bee, *Trans. Am. Inst. Mining Met. Engrs.*, **8**, 146 (1914). The authors are indebted to Dr. Lundell for the loan of an unpublished manuscript on this method.

(7) Analysis of this solution gave 25.9% $K_2C_2O_4 \cdot H_2O$, 17.9% $ZnC_2O_4 \cdot 2H_2O$ and 56.2% H_2O .

position, resulting in the contamination of the material with zinc oxalate. This would account for the high results for the zinc content.

Solubility Determinations

A number of potassium oxalate solutions of varying concentration were saturated at 25° with either zinc oxalate (solutions 16-24) or the hydrated complex salt, $K_2Zn(C_2O_4)_2 \cdot xH_2O$ (solutions 1-15). Equilibrium was attained in less than eight hours. Samples were withdrawn for analysis by the use of a filter pipet and weighed. They were analyzed by the methods described above. After taking the samples of the saturated solutions, as much as possible of the liquid was removed and the wet solid residue with its container was weighed. The solid was dissolved by an excess of sulfuric acid, and solution and container were again weighed. Samples of this solution were then weighed and analyzed. The container was cleaned, dried and weighed.

The results are given in Table I and graphically in Fig. 1. It was found that for solutions up to 1.14 molal with respect to potassium oxalate (and saturated with zinc oxalate) the solid phase in equilibrium was zinc oxalate. Solutions somewhat less concentrated than this are capable of existing temporarily in metastable equilibrium with the oxalato-zincate. Solutions from 1.14 molal to saturation with respect to both potassium oxalate and oxalato-zincate were in equilibrium with the complex, $K_2Zn(C_2O_4)_2$.

TABLE I

COMPOSITIONS OF SATURATED SOLUTIONS AND CORRESPONDING WET SOLID PHASES

No.	Solution		Wet solid		Solid phase	
	$K_2C_2O_4$, wt.-%	ZnC_2O_4 , wt.-%	$K_2C_2O_4$, wt.-%	ZnC_2O_4 , wt.-%	H_2O^a , wt.-%	Formula ^b
1	34.09	11.11	40.85	24.02		I and III
2	29.07	9.70	34.07	23.63	26.41	III
3	23.74	8.36	29.56	19.59	28.26	III
4	22.76	8.00	33.13	26.92	28.50	III
5	21.17	7.63	24.06	12.38	27.40	III
6	16.71	6.46				III
7	16.09	6.32	31.98	27.39	28.38	III
8	15.64	6.20				III
9	15.19	6.06				II and III
10	14.26	5.80				III ^c
13	10.28	4.42				III ^c
15	6.01	1.17				II
16	13.71	4.86	6.30	48.22	17.7	II
17	11.73	3.85				II
18	10.45	3.11	3.99	50.37	20.4	II
19	9.44	2.59				II
20	7.73	1.76	5.83	44.51		II
21	5.72	1.01				II
22	4.57	0.69	1.72	50.35	19.7	II
23	3.80	.38				II
24	3.31	.29				II

^a Calculated by algebraic extrapolation. The theoretical value for $K_2Zn(C_2O_4)_2 \cdot 7H_2O$ is 28.29% water. ^b The compound $K_2C_2O_4 \cdot H_2O$ is designated by I, $ZnC_2O_4 \cdot 2H_2O$ by II and $K_2Zn(C_2O_4)_2 \cdot 7H_2O$ by III. ^c The solid phase was metastable. In the similar solutions 11, 12 and 14 the solid complex salt first introduced partly changed to zinc oxalate and the results are omitted from the table. In 15 the change seemed to have been complete.

$7\text{H}_2\text{O}$. In the latter case an algebraic extrapolation⁸ was made on the assumption that the formula for the anhydrous compound was $\text{K}_2\text{Zn}(\text{C}_2\text{O}_4)_2$. This assumption is in agreement with the graph and with the direct analysis after dehydration of the compound obtained by crystallization at 20 to 25°.

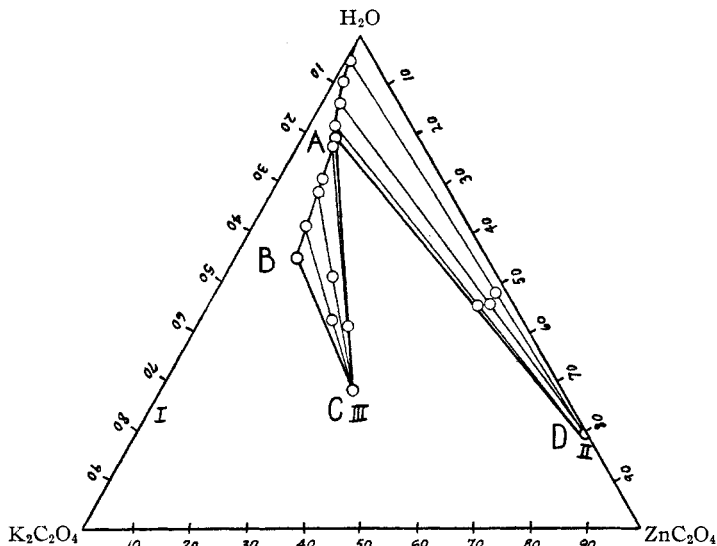


Fig. 1.—The system zinc oxalate, potassium oxalate, water at 25°. Line A-H₂O represents saturated solutions in equilibrium with $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; line A-B solutions in equilibrium with $\text{K}_2\text{Zn}(\text{C}_2\text{O}_4)_2 \cdot 7\text{H}_2\text{O}$; point B, solution equilibrium with both $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and the complex salt; point C the theoretical composition of $\text{K}_2\text{Zn}(\text{C}_2\text{O}_4)_2 \cdot 7\text{H}_2\text{O}$; and point D that of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Transition Temperature.—The methods of preparation of the two complex salts suggested that the compound crystallizing above 40° might be the stable form at temperatures somewhat higher than 25°. A voltaic cell was set up with zinc amalgam electrodes in equilibrium with saturated solutions of the two complex salts, respectively, and the electromotive force measured at various temperatures. The electromotive force became zero at about 34°, below which temperature the compound $\text{K}_2\text{Zn}(\text{C}_2\text{O}_4)_2 \cdot 7\text{H}_2\text{O}$ was stable. Subsequent solubility determinations at 35° were in agreement with this.

Solubility of Zinc Oxalate in Dilute Oxalate Solutions.—Some measurements were made of the solubility of zinc oxalate in dilute solutions of sodium oxalate in order to check Kunschert's results and extend them to more dilute solutions. Kunschert has shown that if the formula for the complex ion in solution is $\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}$, the ratio $[\text{C}_2\text{O}_4^{2-}]/[\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}]$ should be constant, where the brackets indicate molality. Since the two

(8) See Hill and Ricci, *THIS JOURNAL*, **53**, 4306 (1931).

ions are of the same valence type, the activity coefficients should approximately cancel. Table III gives the results.

TABLE II

SOLUBILITY OF ZINC OXALATE IN DILUTE SODIUM OXALATE SOLUTION

Total oxalate <i>m</i>	Complex <i>m</i>	$\frac{[\text{C}_2\text{O}_4^-]}{[\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}]}$	Total oxalate <i>m</i>	Complex <i>m</i>	$\frac{[\text{C}_2\text{O}_4^-]}{[\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}]}$
0.2620	0.0254	8.3	0.0521 ^a	0.0019	25
.2247	.0194	9.6	.0259	.00085	28
.1087	.0058	17	.0127	.00045	26
.0516	.0018	27	.0122 ^a	.00043	27

^a Potassium oxalate was used instead of sodium oxalate.

For total oxalate molalities of not more than 0.05 the ratio in the last column is fairly constant. From 0.1 to 0.26 *m* it decreases, in agreement with Kunschert. If the constancy in the more dilute solutions is interpreted as indicating the correctness of the formula $\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}$, another complex must be present in the more concentrated solutions. It is impossible properly to test the applicability of the formula $\text{Zn}(\text{C}_2\text{O}_4)_3^{3-}$ in this way as Kunschert attempted, because of lack of activity data. At present there is no evidence that such a compound exists.

Summary

1. The compounds $\text{K}_2\text{Zn}(\text{C}_2\text{O}_4)_2 \cdot 7\text{H}_2\text{O}$ and $\text{K}_2\text{Zn}(\text{C}_2\text{O}_4)_2$ have been prepared.

2. The solubility of zinc oxalate and the hydrated complex salt in potassium oxalate solutions has been determined. The compound in equilibrium with the more concentrated solutions at 25° was the complex salt. Above 34° this compound becomes metastable and another complex salt is stable in equilibrium with saturated solutions.

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