

would be of the order of magnitude of  $10^{-15}$  mm. The largest value which one could obtain from the above limits would be  $10^{-10}$  mm. This is of the order of magnitude of the vapor pressure of sodium. Hence one can conclude that in all probability the vapor pressure of mercury is less from this amalgam than that of sodium.

### Conclusions

1. The activity of sodium in concentrated

liquid sodium amalgam is approximately the same as that of the solid metal.

2. Sodium amalgams cannot be well represented by the equation  $\log a_2/N_2 = 1/2 \beta N_1^2$ , which has been used successfully in treating so many solutions.

3. The vapor pressure of mercury from concentrated liquid sodium amalgam is probably much less than  $10^{-10}$  mm.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ADRIAN COLLEGE]

## The System Zinc Oxalate, Potassium Oxalate, Water. II. At 35°

By V. METLER

It has been shown<sup>1</sup> that the complex compound  $K_2Zn(C_2O_4)_2 \cdot 7H_2O$  exists in stable equilibrium with solutions of potassium oxalate saturated with zinc oxalate at 25°. The hydrate was observed to be unstable, becoming anhydrous when exposed to the air. Scholder and Linstrom<sup>2</sup> prepared the anhydrous compound.

In the present investigation the solubility of zinc oxalate and potassium oxalato-zincate in solutions of various concentrations of potassium oxalate has been determined at 35°, and the existence of the hydrated complex compound  $K_2Zn_2(C_2O_4)_3 \cdot xH_2O$  is demonstrated.

Other complex compounds of the type  $K_2M_2''(C_2O_4)_3$  have been prepared by Scholder and co-workers.<sup>3</sup>

### Experimental

Materials used in this work were from the same lot or of the same general purity as those described in Part I.

A small thermostat regulated at  $35 \pm 0.02^\circ$  was used, with a device for rotating small saturation bottles. The glass stoppers of the bottles were covered with wax while in the thermostat.

The same methods of analysis were used as before.

**Preparation of the Complex Salts.**—A description of the method of preparing the potassium oxalato-zincate already has been given.<sup>1</sup> Well-formed crystals of the anhydrous salt  $K_2Zn(C_2O_4)_2$  form from the heptahydrate, or from the compound  $K_2Zn_2(C_2O_4)_3$  described below, when they are shaken at 35° with a saturated solution of potassium and zinc oxalates. This preparation is preferable to that formed when the heptahydrate is dehydrated in air since the latter tends to form colloidal solutions.

(1) Metler and Vosburgh, *THIS JOURNAL*, **55**, 2625 (1933).

(2) Scholder and Linstrom, *Ber.*, **63**, 2831 (1930).

(3) Scholder, Gadenne and Niemann, *ibid.*, **60**, 1496 (1927).

### Solubility Determinations

**Stable Systems.**—Solutions of various concentrations of potassium oxalate were saturated with zinc oxalate (solutions 12-29), or the hydrated complex salt,  $K_2Zn(C_2O_4)_2 \cdot 7H_2O$  (solutions 1-11). After allowing time for saturation, samples of the solution were withdrawn and analyzed. The wet solid phase was dissolved and analyzed as described in Part I.

The analytical results are summarized in Table I and presented graphically in Fig. 1.

Triple points A and B are the average of two separate saturations in which both solid components were shown to be present by analysis of the wet solid phases.

It may be seen that zinc oxalate is the stable solid phase in equilibrium with solutions up to 25.28%  $K_2C_2O_4$  (and saturated with zinc oxalate). From this concentration to saturation with both potassium oxalate and the oxalato-zincate the solutions are in equilibrium with anhydrous  $K_2Zn(C_2O_4)_2$ . Algebraic extrapolation on the assumption of this latter formula is in agreement with the graph.

The portion of the curve representing solutions in equilibrium with  $ZnC_2O_4 \cdot 2H_2O$  coincides with the corresponding portion of the curve determined at 25°.

**Metastable System.**—In the preparation of the heptahydrate, thin, hexagonal crystals of another complex compound form. Its composition when dried in air is  $K_2Zn_2(C_2O_4)_3 \cdot 5H_2O$ .<sup>4</sup>

Solutions of potassium oxalate were saturated with this compound at 35°. Several solutions with their corresponding solid phases are indicated by squares in Fig. 1. All tie-lines cross the  $K_2Zn_2(C_2O_4)_3$ - $H_2O$  axis. Since the tie-lines lie very nearly parallel to this axis, the water content of the metastable complex is indefinite. By algebraic extrapolation the formula of the complex salt appears to be  $K_2Zn_2(C_2O_4)_3 \cdot 12H_2O$ .

Solutions in contact with both zinc oxalate and the trioxalato salt when sampled at intervals of twelve to twenty-four hours showed a very slow increase in oxalate

(4) *Anal.* Calcd. for  $K_2Zn_2(C_2O_4)_3 \cdot 5H_2O$ : Zn, 23.22;  $C_2O_4$ , 46.89. Found: Zn, 23.38;  $C_2O_4$ , 46.70.

content. The compositions fell on the metastable curve until the trioxalato salt had disappeared.

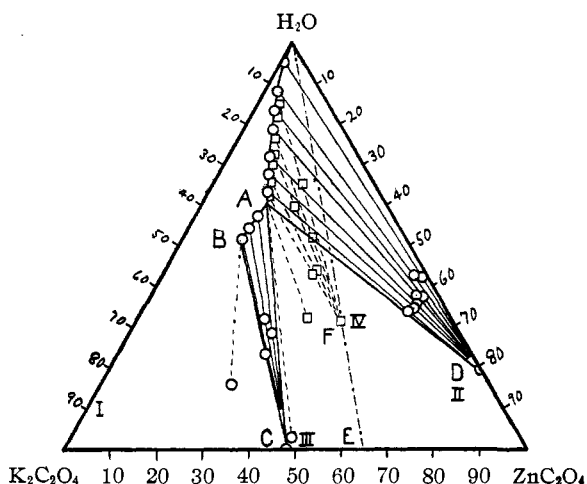


Fig. 1.—The system zinc oxalate, potassium oxalate, water, at 35°. Line A-H<sub>2</sub>O represents saturated solutions in equilibrium with ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, the line A-B, solutions in equilibrium with K<sub>2</sub>Zn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> (anh.); point C, the theoretical composition of K<sub>2</sub>Zn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(anh.); point D, that of ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O; point E, that of K<sub>2</sub>Zn<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>(anh.); and point F, that of K<sub>2</sub>Zn<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·12H<sub>2</sub>O. Line E-H<sub>2</sub>O represents hydrates of the compound K<sub>2</sub>Zn<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>. O, Composition of solutions and solid phases in stable equilibrium; □, composition of solutions and solid phases in metastable equilibrium.

Several solutions were sampled at least twice at twelve-hour intervals and showed no appreciable change in concentration, evidence that no free zinc oxalate was present in the solid phase. The solid phases in contact with these solutions were analyzed. Without seeding, the metastable systems existed indefinitely.

Further work on the potassium trioxalatozincate is being done by the author.

TABLE I

COMPOSITIONS OF SATURATED SOLUTIONS AND CORRESPONDING WET SOLID PHASES

No.	Solution wt. %		Wet solid wt. %		Solid phase ZnC <sub>2</sub> O <sub>4</sub> <sup>a</sup> wt. %	Formula <sup>c</sup>
	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	ZnC <sub>2</sub> O <sub>4</sub>	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	ZnC <sub>2</sub> O <sub>4</sub>		
1	35.96	12.66	55.47	28.32		I and III
2	35.66	12.78	44.76	31.97	47.75	III
3	34.56	12.77	46.35	37.65	48.51	III
4	32.54	13.02	40.34	27.52	48.42	III
5	30.47	13.22	39.06	27.47	48.35	III
6	30.07	13.17	41.89	32.36	49.30	III
7	29.14	13.30	40.55	30.94	48.25	III
8	28.33	13.41	38.80	30.06	49.18	III
9	26.91	13.68	36.64	27.14	48.16	III
10	25.82	13.61	38.78	30.62	47.99	III
11	25.28	13.70	49.07	47.75		II and III
12	24.78	13.26				II
13	23.99	12.65	8.46	57.85	17.53 <sup>b</sup>	II
14	21.48	10.69	6.84	58.82	18.69	II
15	20.29	9.88	6.84	57.70	17.98	II
16	19.11	8.94	5.87	58.56	19.44	II

17	17.72	7.84	6.91	56.31	12.77	II
18	16.49	7.12				II
19	15.11	6.10	4.87	57.42	18.17	II
20	13.83	5.31	4.93	54.13	18.83	II
21	13.13	4.82				II
22	12.27	4.26	3.42	59.03	19.87	II
23	10.62	3.32				II
24	9.41	2.60	2.78	54.52	23.71	II
25	8.14	2.08				II
26	6.33	1.39				II
27	5.38	0.96				II
28	4.02	.57	1.13	56.73	21.31	II
29	2.14	.17				II

<sup>a</sup> Calculated by algebraic extrapolation. The theoretical value for K<sub>2</sub>Zn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> is 48.00% ZnC<sub>2</sub>O<sub>4</sub>. <sup>b</sup> For solutions 13-28 the water content of the solid phase is calculated by algebraic extrapolation. The theoretical value for ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O is 19.02% water. <sup>c</sup> The compound K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O is designated by I, ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O by II, and K<sub>2</sub>Zn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(anh.) by III.

TABLE II

COMPOSITIONS OF METASTABLE SOLUTIONS AND WET SOLID PHASES

No.	Solution wt. %		Wet solid wt. %		Solid phase ZnC <sub>2</sub> O <sub>4</sub> <sup>a</sup> wt. %	Formula <sup>b</sup>
	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	ZnC <sub>2</sub> O <sub>4</sub>	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	ZnC <sub>2</sub> O <sub>4</sub>		
30	25.05	13.73	31.04	36.81		III and IV
31	24.67	13.57				II and IV
32	24.29	13.29				II and IV
33	24.16	13.18	24.89	32.38	43.80	IV
34	23.52	12.64				II and IV
35	23.01	12.44	23.74	25.88	44.15	IV
36	22.27	11.95	23.08	32.98	44.85	IV
37	21.04	11.05	23.31	31.36	44.15	IV
38	20.27	10.50	23.04	33.36	44.36	IV
39	19.70	10.30				II and IV
40	18.09	9.17	20.04	20.68	44.54	IV
41	15.81	7.76	20.04	27.92	44.82	IV
42	12.73	5.94	19.55	29.60	44.66	IV
43	11.29	5.23				II and IV
44	10.58	4.84	15.45	19.08	44.92	IV
45	10.46	4.71				II and IV

<sup>a</sup> Calculated by algebraic extrapolation. The theoretical value for K<sub>2</sub>Zn<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·12H<sub>2</sub>O is 44.52% ZnC<sub>2</sub>O<sub>4</sub>.

<sup>b</sup> The compound ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O is designated by II, K<sub>2</sub>Zn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> (anh.) by III, and K<sub>2</sub>Zn<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O by IV.

### Summary

1. The solubility of zinc oxalate and the anhydrous complex salt, K<sub>2</sub>Zn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>, in potassium oxalate solutions has been determined at 35°. The compound existing in stable equilibrium with dilute solutions was zinc oxalate, that with concentrated solutions was the anhydrous complex salt.

2. The complex K<sub>2</sub>Zn<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·12H<sub>2</sub>O has been shown to exist in metastable equilibrium with dilute solutions of potassium oxalate at 35°.

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