

## 20. *Equilibria in Ternary Systems containing Oxalates.*

By L. M. HILL, T. P. GOULDEN, and E. HATTON.

Data are given for a number of isotherms in the systems: (1) oxalic acid–sodium oxalate–water at 0°, 25°, 60°, and 80°; (2) oxalic acid–sulphuric acid–water at 25° and 60°; (3) sodium sulphate–sodium oxalate–water at 25° and 60°. The results obtained at 25° agree in the main with those already published, but in some cases they are more complete.

In system (1) the hydrated double salt  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , which was known to exist at 25°, has been found to exist throughout the temperature range 0–80°. In system (2) the dehydration of hydrated oxalic acid by sulphuric acid is again a feature of the 60° isotherm.

The data include some additional determinations in the binary systems oxalic acid–water and sodium oxalate–water.

*System Oxalic Acid–Sodium Oxalate–Water.*—Data at 25° have been reported by Foote and Andrew (*Amer. Chem. J.*, 1905, **34**, 153, 165). The interesting feature of the system is the formation of the hydrated double

salt  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Our work at  $25^\circ$  is in fair agreement with that already reported, and the additional isotherms at  $0^\circ$ ,  $60^\circ$ , and  $80^\circ$  also show that the same compound is stable at these temperatures. The region of unsaturated solutions shows a considerable expansion as the temperature is raised from  $0^\circ$  to  $80^\circ$ ; this is due to the rapid increase in the solubility of hydrated oxalic acid with rising temperature. It should be noted that the amount of sodium oxalate dissolved at  $80^\circ$  is insufficient to dehydrate the oxalic acid.

*System Oxalic Acid-Sulphuric Acid-Water.*—The main characteristic of this system is that we have two liquid components at the temperatures under investigation. Since oxalic acid is normally hydrated, the isotherm must contain at least two solubility curves, one starting from the solubility of hydrated oxalic acid in water and the other from the solubility of anhydrous oxalic acid in sulphuric acid. This system was studied at  $25^\circ$  by Elöd and Acker (*Z. anorg. Chem.*, 1928, **176**, 305), who gave data for the hydrate curve extending to the point of dehydration in a solution containing approximately 59% of sulphuric acid and 8% of oxalic acid. Our work at  $25^\circ$  agrees with their results and supplements it by data for the anhydrous oxalic acid curve over a large part of its course. Our isotherm at  $60^\circ$  is similar in character to that at  $25^\circ$  and shows that the dehydration of hydrated oxalic acid occurs at a lower concentration of sulphuric acid (45%). The solubility of anhydrous oxalic acid in sulphuric acid was not determined at  $25^\circ$  or  $60^\circ$  and no new solid phase has been observed.

*System Sodium Sulphate-Sodium Oxalate-Water.*—The published information on this system consists of the compositions of invariant solutions in equilibrium with sodium oxalate and sodium sulphate at  $25^\circ$  (Elöd and Acker, *loc. cit.*) and at  $15^\circ$  and  $50^\circ$  (Colani, *Bull. Soc. chim.*, 1916, **19**, 405). At  $15^\circ$  and  $25^\circ$  the sodium sulphate is hydrated ( $10 \text{ H}_2\text{O}$ ) and at  $50^\circ$  it is anhydrous. The system is characterised by the low solubility of sodium oxalate in a solution saturated with sodium sulphate. This was found to be true at  $60^\circ$  as well as at the lower temperatures. No intermolecular compounds or other complications were noted.

## EXPERIMENTAL.

The solubility mixtures were prepared from B.D.H. reagents of A.R. quality. In most cases it was possible to dissolve all the solids by a preliminary heating to a temperature above that of the required isotherm. This assisted the formation of the correct solid phase and helped to avoid inclusions of another solid within the newly formed crystals. Each mixture was put in a glass bottle fitted with a glass stirrer; the bottle and contents were then clamped in a bath of water and the temperature controlled within  $\pm 0.02^\circ$  of that required. At  $0^\circ$  a stirred mixture of ice and water was used for the bath.

After stirring had proceeded long enough for the attainment of equilibrium (usually overnight), the solid was allowed to settle, and samples of the clear solution and moist solid were then withdrawn and analysed by means of methods selected from the following: (a) Total acidity by titration with *N*-sodium hydroxide solution (free from sodium carbonate) with phenolphthalein as indicator. (b) Oxalate by titration with 0.1*N*-potassium permanganate solution in the presence of sulphuric acid. (c) Sulphate gravimetrically as barium salt in the presence of hydrochloric acid. (d) Sodium by conversion into sulphate by sulphuric acid, and ignition to expel excess of acid. The methods used in each system are indicated at the foot of the tables: where the common ion was determined, the concentration of one component was obtained by difference.

The identity of each solid phase was determined graphically by the method of residues. Some of the tie lines are a little wide of the point representing possible solid phases, and these deviations may be emphasised by small analytical errors where one component has been determined by difference. As far as can be seen they have no special significance. In a few cases the identification of the solid phase was made by microscopic examination and these are indicated in the tables.

System  $\text{H}_2\text{C}_2\text{O}_4$ - $\text{Na}_2\text{C}_2\text{O}_4$ - $\text{H}_2\text{O}$ .

Solid phase.*	$d_{15}^\circ$ .	Solution, g. per 100 g.		Moist solid, g. per 100 g.		Solid phase.	$d_{15}^\circ$ .	Solution, g. per 100 g.		Moist solid, g. per 100 g.	
		$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{Na}_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{Na}_2\text{C}_2\text{O}_4$ .			$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{Na}_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{Na}_2\text{C}_2\text{O}_4$ .
Temperature = $0^\circ$ .											
H	1.013	3.4	—	—	—	H	1.043	10.2	—	—	—
H + DS	1.012	3.5	0.3	40.3	3.7	H + DS	1.046	10.3	1.0	34.7	3.10
DS	1.015	3.3	0.3	21.0	29.5	H + DS	1.049	10.3	1.0	27.9	25.3
DS	—	0.3	0.8	16.4	24.7	DS	1.044	8.8	0.9	24.0	31.3
DS	1.007	0.2	1.3	17.3	25.9	DS	1.027	5.3	1.0	21.7	30.7
DS + N†	—	0.1	2.9	—	—	DS	1.022	4.3	1.1	21.3	30.1
N †	—	—	2.8	—	—	DS + N	1.025	0.4	3.7	2.7	31.8
			2.71	—	—	N	1.023	—	3.6	—	—
Temperature = $80^\circ$ .											
H	—	47.4	—	—	—	H	1.129	31.6	—	—	—
H	—	48.1	3.7	61.4	2.2	H	1.138	31.5	1.7	51.3	1.4
H	—	47.4	1.3	60.9	0.5	H	1.148	31.8	2.8	53.7	2.2
H + DS	—	48.2	4.9	56.7	9.1	H + DS	1.151	31.6	3.3	51.4	8.7
DS	—	47.3	4.5	41.2	29.3	DS	1.144	30.7	3.1	33.2	33.0
DS	—	37.5	5.2	36.3	32.0	DS	1.091	19.3	3.0	28.0	32.1
DS	—	29.6	5.2	32.7	29.4	DS	1.044	9.4	3.5	25.1	33.9
DS	—	22.2	5.4	29.4	30.1	DS + N	1.034	1.7	5.8	17.0	40.9
DS	—	10.0	5.4	25.0	34.2	N	1.028	1.1	5.3	0.5	54.9
DS + N	—	3.3	7.8	8.9	45.2	N	1.020	—	4.6	—	—
N	—	2.4	6.9	0.9	70.9						
N	—	0.9	5.9	0.4	63.8						
N	—	—	5.3	—	—						

Analytical methods (a) and (b) were used.

\* H =  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ; DS =  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{Na}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ; N =  $\text{Na}_2\text{C}_2\text{O}_4$ .

† Solid phases identified by the microscope.

System $\text{H}_2\text{C}_2\text{O}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ .											
Solid phase.*	$d_{15}^{25^\circ}$	Solution, g. per 100 g.		Moist solid, g. per 100 g.		Solid phase.	$d_{15}^{60^\circ}$	Solution, g. per 100 g.		Moist solid, g. per 100 g.	
		$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{SO}_4$ .	$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{SO}_4$ .			$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{SO}_4$ .	$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{H}_2\text{SO}_4$ .
Temperature = 25°.											
H	1.043	10.2	—	—	—	H	1.129	31.6	—	—	—
H	1.078	6.6	9.6	54.4	2.2	H	1.150	25.2	7.2	57.4	1.8
H	1.119	4.7	15.4	54.8	3.6	H	—	20.2	14.2	53.4	4.4
H	1.165	3.6	21.5	47.6	7.1	H	—	16.6	20.2	52.9	6.4
H	1.174	2.9	29.5	49.8	8.7	H	1.294	12.3	33.2	50.3	11.2
H	1.272	2.3	38.6	41.6	16.5	H	1.334	12.1	38.5	51.1	13.1
H	—	2.6	47.1	24.2	32.0	H	1.387	13.1	43.5	50.4	14.9
H	1.469	4.6	55.1	25.2	37.9	H	—	15.1	44.9	51.2	15.2
H + A	1.516	7.8	59.6	48.3	31.9	H + A	—	20.5	44.6	64.6	12.6
A	1.600	5.2	67.4	39.9	42.0	A	1.469	19.4	46.4	69.9	16.9
A	1.662	4.0	74.4	34.9	50.4	A	1.493	16.5	50.5	63.4	21.7
A	1.771	4.1	85.9	39.9	53.6	A	1.514	13.9	55.6	65.7	21.6
A	1.788	4.6	89.9	32.7	63.5	A	1.583	9.5	65.0	61.1	27.6
A	—	4.6	91.6	32.8	64.2	A	1.610	8.6	67.7	57.6	31.5
						A	1.673	7.2	79.6	59.4	34.8
						A	—	8.3	84.0	34.5	59.9
						A	—	7.6	71.2	—	—
						A	1.704	8.7	86.5	51.9	45.4

Analytical methods (a) and (b) were used.

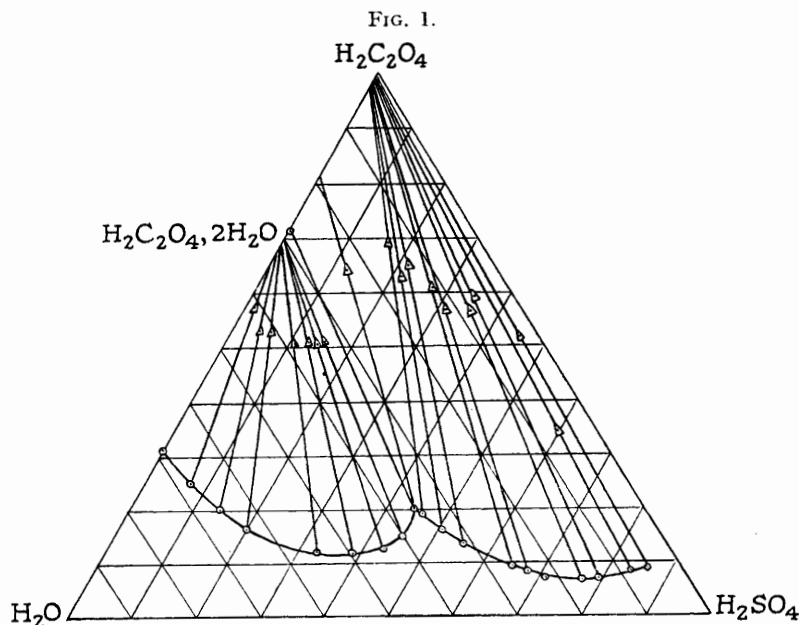
\* H =  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ; A =  $\text{H}_2\text{C}_2\text{O}_4$ .

System $\text{Na}_2\text{SO}_4\text{-Na}_2\text{C}_2\text{O}_4\text{-H}_2\text{O}$ .											
Solid phase.	$d_{15}^{25^\circ}$	Solution, g. per 100 g.		Moist solid, g. per 100 g.		Solid phase.	$d_{15}^{60^\circ}$	Solution, g. per 100 g.		Moist solid, g. per 100 g.	
		$\text{Na}_2\text{SO}_4$ .	$\text{Na}_2\text{C}_2\text{O}_4$ .	$\text{Na}_2\text{SO}_4$ .	$\text{Na}_2\text{C}_2\text{O}_4$ .			$\text{Na}_2\text{SO}_4$ .	$\text{Na}_2\text{C}_2\text{O}_4$ .	$\text{Na}_2\text{SO}_4$ .	$\text{Na}_2\text{C}_2\text{O}_4$ .
Temperature = 25°.											
S10	1.196	22.0	—	—	—	S	—	31.2*	—	—	—
S10 + S	1.200	22.0	0.5	33.0	4.9	S + N	1.289	30.7	0.3	57.7	30.0
S	1.182	19.7	0.5	10.9	46.5	N	1.269	28.6	0.4	9.0	62.6
S	1.155	14.7	0.8	7.5	54.6	N	1.177	20.2	0.7	6.4	70.0
S	1.060	5.9	1.7	2.7	55.8	N	1.088	10.1	1.7	3.5	66.8
S	1.023	—	3.6	—	—	N	1.020	—	4.6	—	—

Analytical methods (b), (c), and (d) were used.

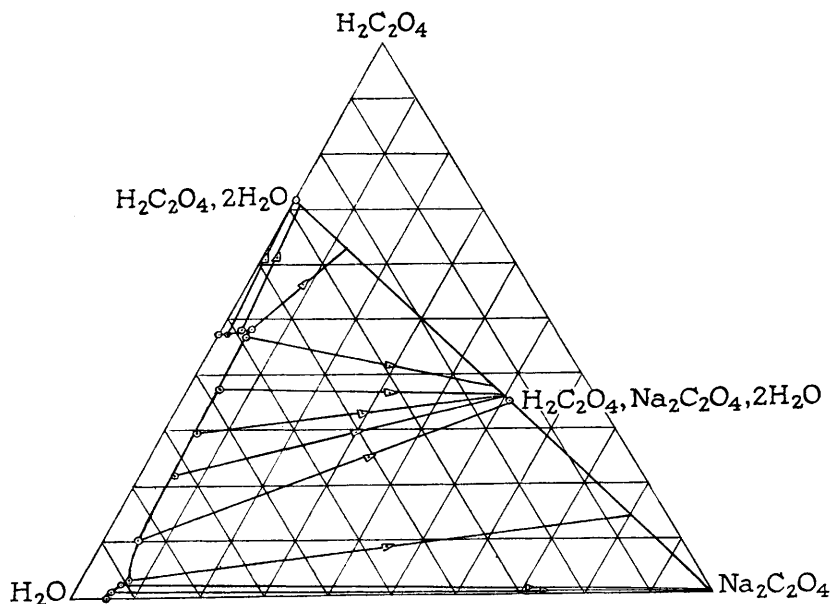
\* S10 =  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; S =  $\text{Na}_2\text{SO}_4$ ; N =  $\text{Na}_2\text{C}_2\text{O}_4$ .

† Seidell, "Solubilities of Inorganic and Metal Organic Salts," 1940, vol. 1, p. 1301.



The experimental results, expressed as g. per 100 g., are given in the tables, and representative triangular diagrams in Figs. 1 and 2.

FIG. 2.



The solution densities in the tables are approximate values only, determined in most cases by weighing the solution delivered at equilibrium temperature by a pipette which had been standardised with water at 15°.

IMPERIAL CHEMICAL INDUSTRIES RESEARCH DEPARTMENT,  
ALKALI DIVISION, NORTHWICH, CHESHIRE.

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