373. *The System Oxalic Acid–Sodium Hydroxide–Water.*

By William H. H. Norris.

The isotherms at 0°, 30°, 40°, and 50° are given for the system oxalic acid–sodium hydroxide–water, together with the cryohydric and boiling-point curves, solubility data for the acid and normal sodium oxalates, and a projection of the solid figure covering the fields in which compounds are capable of existence in equilibrium with saturated solutions of the two components. Oxalic acid and sodium hydrogen oxalate rapidly lose their water of crystallization at temperatures above 90° and 105°, respectively. Unlike potassium hydroxide, sodium hydroxide forms no other intermediate compounds with this acid radical.

Previous work on this system has been carried out at 25° by Foote and Andrews (*Amer. Chem. J.*, 1905, **34**, 153, 165), and at 0°, 25°, 60°, and 80° by Hill, Goulden, and Hatton (*J.*, 1946, 78), but data were only recorded by them up to the ordinate of normal sodium oxalate. The results now obtained agree well with those of the above authors at 0° and to a certain extent for the other isotherms, but the greater detail now obtained indicates considerable divergence from the approximated portions of their partial isotherms.

Data for the oxalic acid ordinate confirmed the figures of Alluard (*Compt. rend.*, 1864, **59**, 500), Koppel and Cahn (*Z. anorg. Chem.*, 1908, **60**, 110), Lamouroux (*Compt. rend.*, 1899, **128**, 998), and Flöttmann (*Z. anal. Chem.*, 1928, **73**, 32). Data for the solubility of sodium hydrogen oxalate have not been previously determined, but their values can be deduced from the isotherms, shown in Table I, and for 25° from that by Foote and Andrews. Work by Hill *et al.*

was not carried out in sufficient detail to afford reliable results by this method. The solubility of the normal sodium oxalate has been determined (Table IV), and confirmed Flöttmann's values at 15°, 20°, and 25°. It formed the limit of the isotherms of the other workers on this system. It was thought desirable to supplement the work of other authors by mapping the system over the complete concentration range from oxalic acid to sodium hydroxide, and over the whole temperature range from $-28°$ to 322°, with suitable isotherms in between. Thus the equilibrium conditions for all component mixtures could be obtained by interpolation.

The isotherms of 0°, 30°, 40°, and 50° (Figs. 4, 5, 6, and 7) showed a striking similarity of form, and exhibited the following unexpected features, best seen on the 50° isotherm in Fig. 1. (1) Upon addition of small quantities of sodium hydrogen oxalate, there was an increase in the solubility of $H_2C_2O_4,2H_2O$ from *A* until the first double point *B* was reached, corresponding to oxalic acid and sodium hydrogen oxalate in equilibrium, instead of the decrease usually observed when one salt is added to the saturated solution of another. (2) There was a rapid decline in the solubility of the acid oxalate on addition of minute quantities of the normal oxalate. (3) Then a rapid rise in solubility of the acid salt was shown until the double point *C* was obtained, corresponding to the acid and the normal oxalates in equilibrium. (4) A rapid fall followed on slight additions of sodium hydroxide, until the increase of the latter practically eliminated the oxalate radical from solution. (5) Finally, a non-variant point *D* (see Figs. 2 and 6) was reached, with both sodium oxalate and sodium hydroxide as solid phases. The solubility at this point was almost indistinguishable from that of sodium hydroxide, *E*.

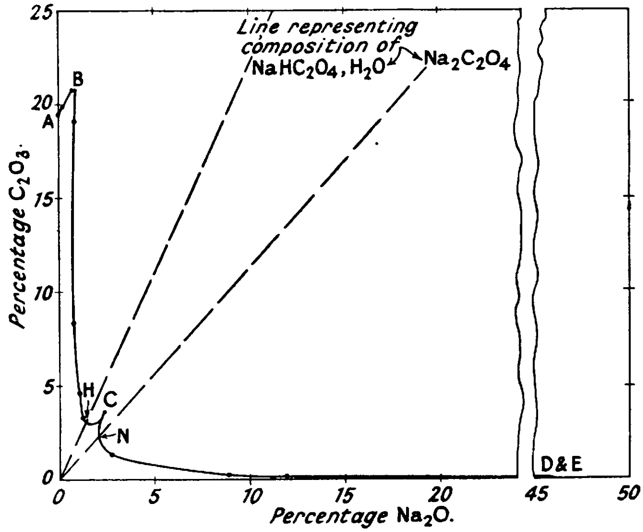


FIG. 1.

50° Isotherm showing " composition lines " of $NaHC_2O_4,H_2O$ *and* $Na_2C_2O_4$.

It has thus been found that the region of unsaturated solutions exhibited considerable expansion throughout the system with rise in temperature, owing not only to the presence of hydrated oxalic acid, the acid and normal oxalates, but in particular to that of sodium hydroxide. It will be noted from Fig. 2 that the quantity of sodium hydroxide was insufficient to dehydrate the oxalic acid up to 50°.

Solubilities of $H_2C_2O_4,2H_2O$ and $Na_2C_2O_4$ were experimentally determined, and those of $NaHC_2O_4,H_2O$ found graphically by intersection of the line representing the composition of $NaHC_2O_4,H_2O$ (*OH*) with the isothermal curve for each temperature at *H*, *e.g.*, values for 50° (Fig. 1) are shown in Table IV.

Proceeding from the above observations on rectangular isotherms, the interpolation of points between, and the extrapolation of points beyond, these isotherms were considered, and for this a solid figure was employed. Since the temperature range of the system extended between $-28°$ and 322°, this was plotted along a three-dimensional axis, on a scale proportional to $\log_{10}(t° + 100°)$ to include the extreme values without unduly condensing the portion between 0° and 50°.

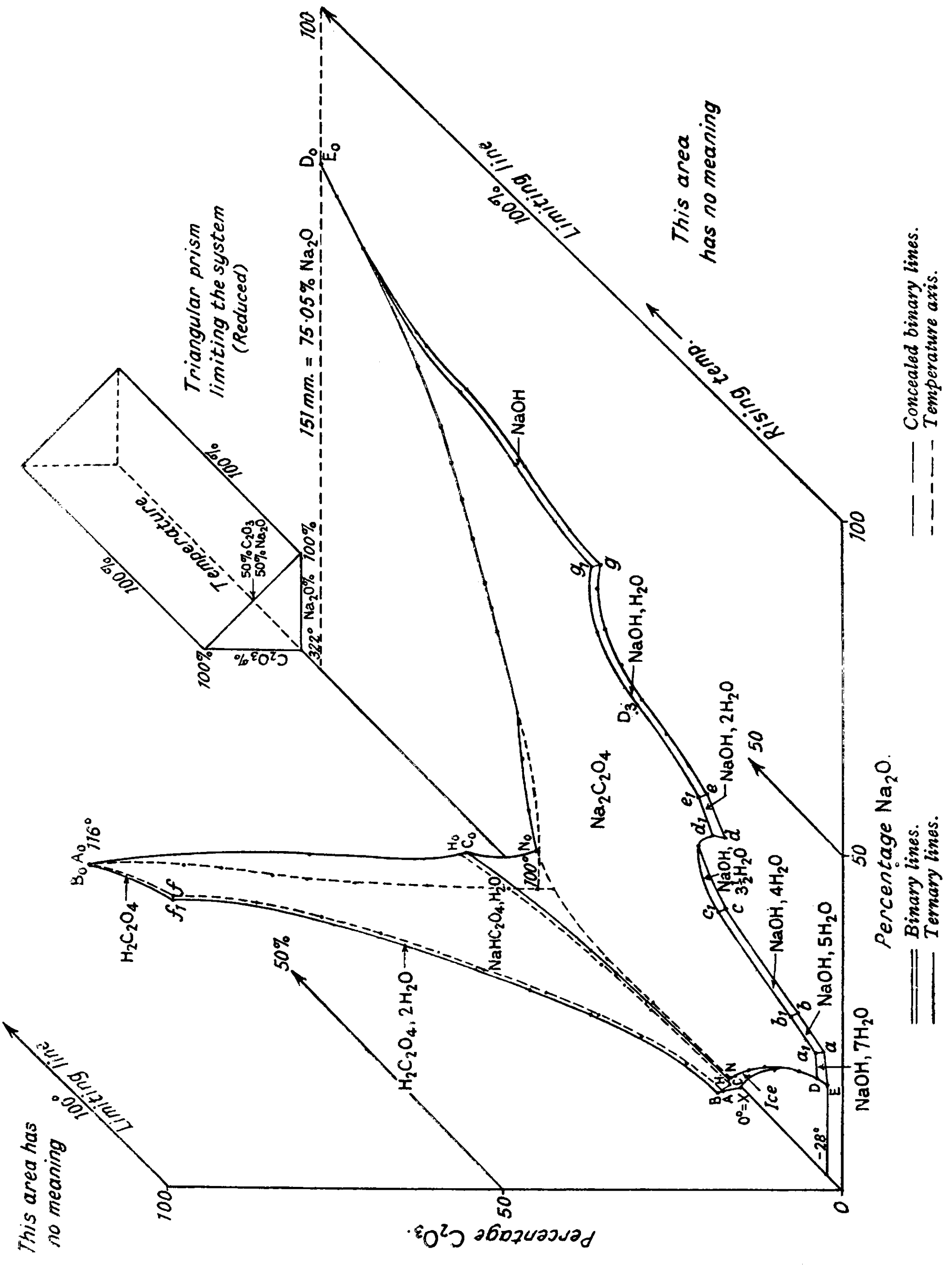


FIG. 2.

Isometric projection at 45° of space model, within a limiting prism, showing boundaries of the system and of the intermediate phases.

Fig. 2 represents a 45° oblique projection of this model Its sides are formed by an infinite number of isotherms, the front end by the cryohydric area, and the rear by the boiling-point area. The following notation with suitable suffixes has been used on all isotherms and the solid figure (Fig. 2) : A = Solubility of $H_2C_2O_4,2H_2O$; B = non-variant solubility point when $H_2C_2O_4,2H_2O$ and $NaHC_2O_4,H_2O$ are solid phases; C = non-variant solubility point when $NaHC_2O_4,H_2O$ and $Na_2C_2O_4$ are solid phases; D = non-variant solubility point when $Na_2C_2O_4$ and hydrates of Na_2O are solid phases: E = solubility of NaOH. These letters without suffixes define the cryohydric curve, to the curve bounding the boiling-point area A_0B_0 to E_0. The hydrates of NaOH are shown by small letters a, b—g, and their equilibrium points in presence of $Na_2C_2O_4$ by a_1, b_1—g_1.

Fig. 3.

Projection of the cryohydric curve on to the 0° *isotherm.*

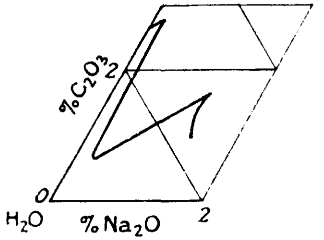
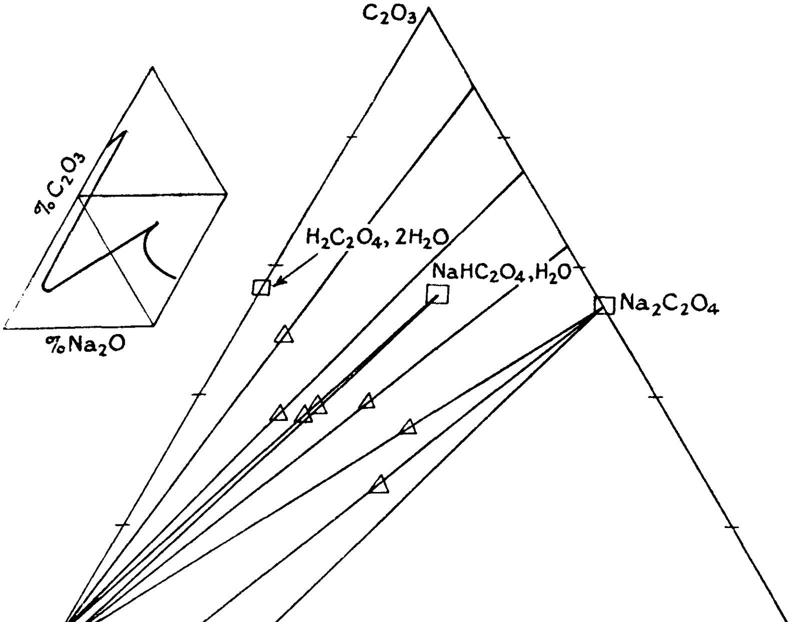


Fig. 4.

0° *Isotherm showing " convergence points."*



The ternary cryohydric curve, *ABCDEXA*, limiting the ice field, was determined, commencing at $X = 0°$, where ordinates for the solid components are zero (Table II), for saturated solutions of representative mixtures containing both solid components. This was incorporated with binary saturation curves for the single components in water, oxalic acid *XA*, by Raoult (*Z. physikal. Chem.*, 1882, **2**, 489) and sodium hydroxide, *XE*, by Pickering (*J.*, 1893, **63**, 890), to form the boundaries of the cryohydric area.

The ternary boiling-point curve $SA_0B_0C_0D_0E_0X_0$, for saturated solution in equilibrium with

FIG. 5.

30° Isotherm showing "convergence points."

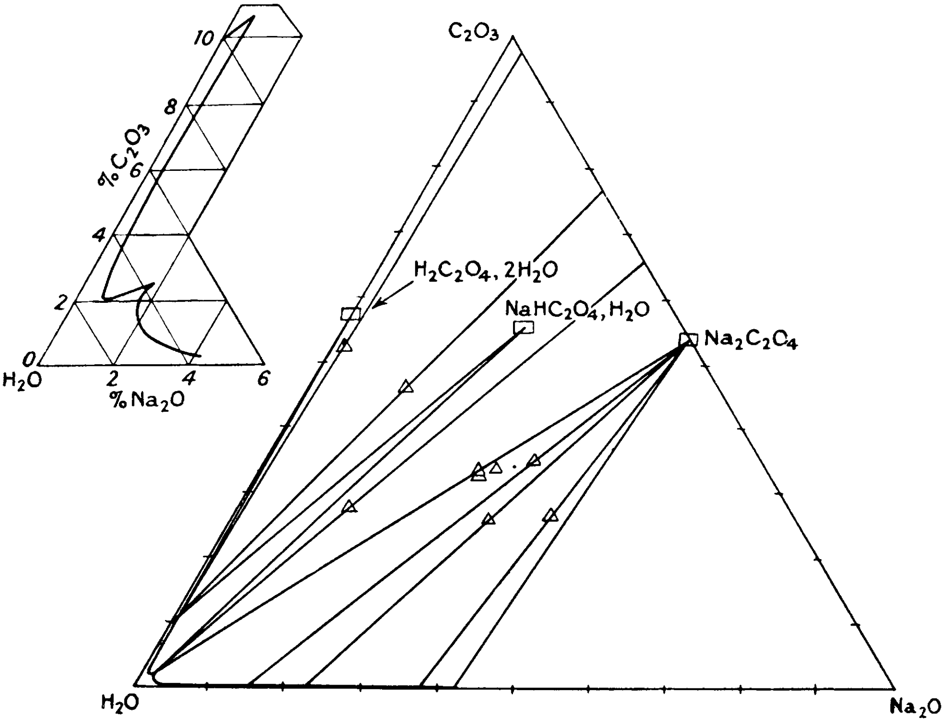
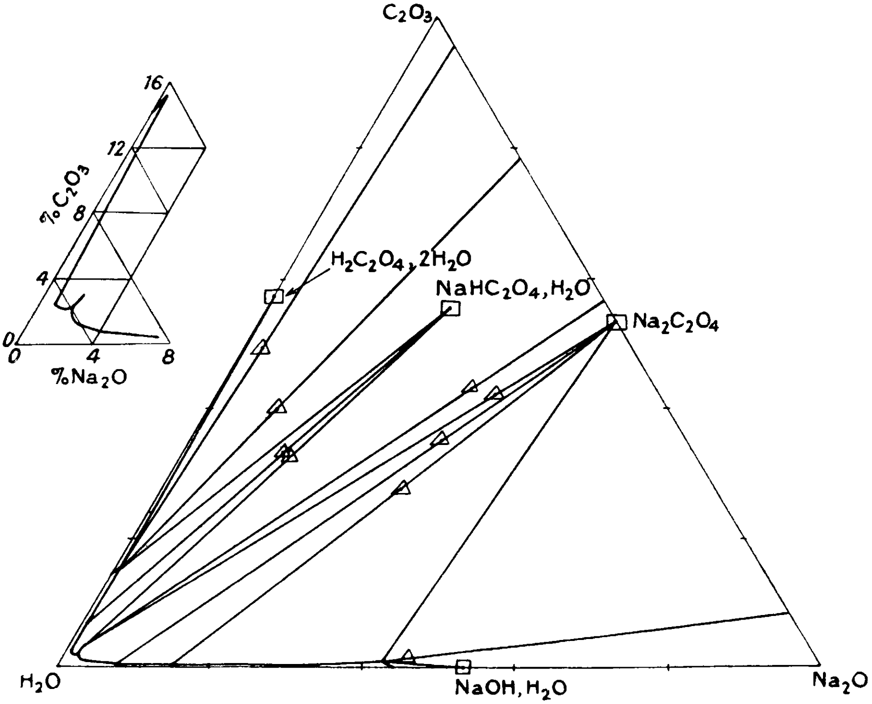


FIG. 6.

40° Isotherm showing "convergence points."

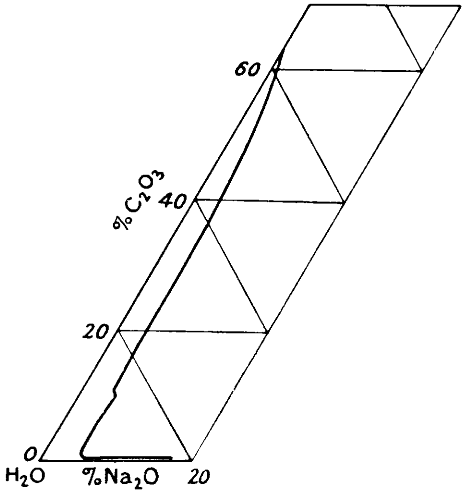


water vapour at 760 mm. pressure, was similarly determined, and incorporated with binary values of each component in water, by Gerlach (*Z. anal. Chem.*, 1887, **26**, 413) and by Antropoff and Sommer (*Z. physikal. Chem.*, 1926, **123**, 165) in the curves X_0A_0 and X_0E_0, which are concealed in the perspective shown, to form the limits of the boiling-point area at the back of the solid figure. It will be noticed that the line Bf_1B_0 joining the cusps of the isotherms in equilibrium with oxalic acid and sodium hydrogen oxalate conceals the solubility curve of oxalic acid, AfA_0, and the strip area ABf_1f associated with hydrated oxalic acid. The adjoining large area $Bf_1B_0C_0CB$ is in equilibrium with hydrated sodium hydrogen oxalate, and the largest concave area CC_0D_0DC is in equilibrium with the anhydrous normal oxalate. The solid figure is completed by a series of strips, forming " cliff " edges, each in equilibrium with the various hydrates of Na_2O. The height of the " cliff " is shown by point D_3 on Figs. 2 and 6.

When this figure is compared with that for the potassium compounds by Koppel and Cahn, it will be noted that there are no similar intermediate areas which would indicate compounds of the type $Na_4H_2(C_2O_4)_3$ and $NaH_3(C_2O_4)_2,2H_2O$ such as were found with the potassium compounds by the above authors. It is suggested that this work is sufficiently comprehensive to detect their presence if formed, and is conclusive proof that they do not exist.

FIG. 7.

Projection of the boiling-point curve on to the 100° *isotherm.*



EXPERIMENTAL.

The solubility mixtures were prepared by using materials of AnalaR quality. The thermostats were regulated to within ±0·05°. Starting from saturated solutions of oxalic acid, small known quantities of sodium oxalate were added and the new increased values for the solubility of oxalic acid were obtained.

The identity of the solid phase was determined graphically by joining the plotted position of the composition of the saturated solution with that of the moist solid (both expressed as weight percentages of C_2O_3 and Na_2O), and produced to convergence with other similar lines on triangular paper (Schreinemakers, *Z. physikal. Chem.*, 1892, **9**, 57). The co-ordinates of the convergence point represent very clearly the composition of the solid phase.

Experimental compositions of convergence points representing the solid phases are as follows: $H_2C_2O_4,2H_2O$ (Found: C_2O_3, 57·2; H_2O, 42·8. Calc.: C_2O_3, 57·14; H_2O, 42·86%); $NaHC_2O_4,H_2O$ (Found: C_2O_3, 55·6; Na_2O, 24·3; H_2O, 21·1. Calc.: C_2O_3, 55·39; Na_2O, 23·85; H_2O, 20·76%); $Na_2C_2O_4$ (Found: C_2O_3, 53·5; Na_2O, 46·4. Calc.: C_2O_3, 53·73; Na_2O, 46·27%).

From *A* to *B* convergence was upon $H_2C_2O_4,2H_2O$. From *B*, on further additions of normal oxalate, the composition of the solution remained the same whilst that of the moist solid varied progressively, until sufficient normal salt was added to convert all the original solid oxalic acid into sodium hydrogen oxalate. In Table I(i) (Fig. 4) determinations 2—6 indicated this continuous increase in Na_2O content of the moist solid and that the divergence passes from the ordinates of $H_2C_2O_4,2H_2O$ to those of $NaHC_2O_4,H_2O$, while the composition of the saturated solution remains constant, and the average of these values is shown as a " mean " at *B*. Continuing as above we arrive at *C*. Here also the moist solid varies progressively in Na_2O content while the composition of the saturated solution is taken as the " mean " of the determinations. Experimental values for isotherms (Table I), cryohydric and boiling-point curves (Tables II and III), and also solubilities of oxalic acid, and the acid and the normal sodium salt (Table IV) follow.

TABLE I.*

Solid phase.	Solution, %.		Moist solid, %.		Solid phase.	Solution, %.		Moist solid, %.	
	C_2O_3.	Na_2O.	C_2O_3.	Na_2O.		C_2O_3.	Na_2O.	C_2O_3.	Na_2O.
(i) 0° *Isotherm.*									
A	2·75	—	(1)57·1	—	*BC*	2·93	0·149	33·9	14·1
B	2·95	0·170	48·5	1·33		2·91	0·158	37·1	15·1
	3·07	0·175	52·0	4·09		2·26	0·188	38·3	16·3
	2·96	0·149	51·1	6·45		0·595	0·253	(2)55·4	(2)23·9
	3·03	0·170	37·5	13·7		0·598	0·240	49·7	22·1
	3·01	0·140	37·4	12·0		1·19	0·930	41·8	18·1
Mean	3·01	0·161	—	—					
C	1·54	1·26	40·3	21·2	*CD*	1·43	1·24	(3)53·7	(3)46·3
	1·65	1·36	39·1	22·7		0·717	1·94	35·1	30·3
	1·53	1·24	39·5	19·5		0·038	15·5	26·3	30·7
Mean	1·57	1·28	—	—	*E*	—	25·5	—	—
(ii) 30° *Isotherm.*									
A	9·94	—	(1)57·1	—	*C*	2·57	1·87	28·3	14·1
AB	10·3	0·22	46·0	0·12		2·50	1·85	33·3	28·1
					Mean	2·54	1·86	—	—
B	10·7	0·51	52·5	1·46	*CD*	2·02	1·74	(3)37·1	32·6
	10·6	0·47	46·6	12·7		0·665	3·13	37·1	33·9
Mean	10·6	0·49	—	—		0·185	7·08	35·3	35·7
						0·042	14·9	26·1	34·2
BC	6·3	0·57	38·4	15·9		0·190	22·9	26·8	41·3
	2·88	0·57	34·9	14·8		0·100	33·7	—	—
	2·15	0·63	35·8	15·4	*E*	—	42·1	—	—
(iii) 40° *Isotherm.*									
A	14·2	—	(1)57·1	—	*CD*	2·81	2·05	41·4	35·4
AB	15·0	0·52	49·0	0·38		2·17	1·88	(3)53·7	(3)46·3
B	15·2	0·53	49·7	2·62		1·57	2·24	36·2	31·7
	15·3	0·56	40·5	8·14		1·23	2·51	34·6	29·9
Mean	15·2	0·545	—	—		0·21	7·18	33·5	31·5
BC	11·7	0·65	30·0	10·6		0·21	7·41	28·2	27·7
	6·97	0·72	33·5	13·4		0·05	14·9	27·0	30·7
	2·37	0·90	32·8	14·0	*D*	0·99	42·1	1·07	44·0
C	3·09	2·13	(4)42·9	(4)32·1					
			(44·8)	(35·5)	*E*	—	43·6	—	—
(iv) 50° *Isotherm.*									
A	19·5	—	(1)57·1	—	*C*	3·69	2·38	37·1	17·0
						3·68	2·37	36·7	28·4
AB	19·9	0·21	41·9	0·26		3·64	2·34	31·1	25·8
	20·8	0·72	48·2	0·16	Mean	3·67	2·36	—	—
					CD	2·33	2·01	(3)53·7	(3)46·3
B	20·8	0·93	37·2	9·09		1·35	2·62	35·3	31·0
						0·23	8·84	28·1	28·4
						0·098	11·9	30·7	31·7
BC	19·1	0·91	42·6	15·8	*D*	0·027	21·2	(4)27·0	(4)34·1
	4·70	1·07	37·3	15·9				(31·5)	(35·9)
	3·32	1·20	36·5	15·8					
	2·97	1·50	43·3	18·6	*E*	—	45·9	—	—

* Solid phases : *A*, $H_2C_2O_4,2H_2O$; *B*, $H_2C_2O_4,2H_2O$ and $NaHC_2O_4,H_2O$; *BC*, $NaHC_2O_4,H_2O$; *C*, $NaHC_2O_4,H_2O$ and $Na_2C_2O_4$; *CD*, $Na_2C_2O_4$; *D*, $Na_2C_2O_4$ and NaOH; *E*, NaOH.

TABLE II.

Cryohydric curve.

Solid phase.	Ice separates at :	Solution, %.		Solid phase.	Ice separates at :	Solution, %.		Solid phase.	Ice separates at :	Solution, %.	
		C_2O_3.	Na_2O.			C_2O_3.	Na_2O.			C_2O_3.	Na_2O.
A	−0·93°	2·60	—	*BC*	−0·30°	0·640	0·276	*CD*	−0·90°	1·44	1·23
B	−0·96	2·76	0·124		−0·30	0·628	0·273		−4·20	0·285	4·27
	−0·96	2·78	0·132	Mean	−0·30	0·634	0·274		−8·00	0·189	7·04
Mean	−0·96	2·77	0·128								

The numbers in parentheses in these tables have the following significance : (1) Composition of $H_2C_2O_4,2H_2O$. (2) Composition of $NaHC_2O_4,H_2O$. (3) Composition of $Na_2C_2O_4$. (4) Analyses shown in pairs have a definite increase in Na_2O content.

It was not thought necessary to continue the readings further as the curve tapered to an almost unmeasurable quantity of C_2O_3 and followed the curve for sodium hydroxide and ice.

The Boiling-point Curve of the System.—The b. p. of a saturated solution of oxalic acid, as recorded by Koppel and Cahn (*loc. cit.*), is 116°, where it contains 63% of C_2O_3. The transition point of $H_2C_2O_4,2H_2O$ to $H_2C_2O_4$ was shown to be 98°, at *f*, in Fig. 2. Values for the b. p.s of saturated solutions containing varying amounts of C_2O_3 and Na_2O are shown in Table III.

TABLE III.

Boiling-point curve.

Solid phase.	B. p.	Solution, %. C_2O_3.	Solution, %. Na_2O.	Solid phase.	B. p.	Solution, %. C_2O_3.	Solution, %. Na_2O.
A	116·0°	63·0	—	*CD*	100·4°	0·12	5·70
BC	105·1	32·9	3·62		104·4	0·36	10·7
	102·4	17·8	3·96		109·6	0·15	17·3
	101·5	10·5	4·50				

It was not thought necessary to continue the determinations past point 8, as the curve tapered to an almost unmeasurable value of C_2O_3 and followed the curve for the boiling points of unsaturated solutions of sodium hydroxide.

TABLE IV.

Solubilities of single substances.

(G. of anhydrous substance per 100 g. of solution.)

Temp.	Solid phase in equilibrium. $H_2C_2O_4,2H_2O$.	$NaHC_2O_4,H_2O$.	$Na_2C_2O_4$.	Temp.	Solid phase in equilibrium. $H_2C_2O_4,2H_2O$.	$NaHC_2O_4,H_2O$.	$Na_2C_2O_4$.
0°	3·43	0·925	2·67	70°	—	8·58 *	4·91
10	6·40 *	1·20 *	3·01 *	80	—	11·0*	5·24
20	8·95 *	1·60 *	3·39	90	—	13·4 *	5·55
30	12·4	2·28	3·76	99·63	—	—	5·85
40	17·7	3·43	4·04	100	—	15·9 *	5·87 *
50	24·3	4·70	4·34	100·99	—	16·2	—
60	—	6·42 *	4·60				

* Interpolated values.

The principal points of the solid figure have been described. The lines and surfaces are lettered as follows.

Univariant Lines.—Binary lines. *XA* = dilute solutions of $H_2C_2O_4,2H_2O$ and ice; *Af* = solubility curve of $H_2C_2O_4,2H_2O$; fA_0 = solubility of $H_2C_2O_4$; ff_1 = increase in temperature and concentration of saturated solution with hydrated and anhydrous $H_2C_2O_4$, in presence of increasing quantities of $NaHC_2O_4,H_2O$ to saturation at f_1; A_0X_0 = boiling-point curve (760 mm.) at various dilutions of the above; E_0X_0 = boiling-point curve (760 mm.) at various dilutions of NaOH; $E_0gedcbaE$ = solubility of NaOH, $NaOH,H_2O$, $NaOH,2H_2O$, $NaOH,3\frac{1}{2}H_2O$, $NaOH,4H_2O$, $NaOH,5H_2O$, and $NaOH,7H_2O$, respectively; *EX* = dilute solutions of $NaOH,7H_2O$ and ice.

Ternary lines. *AB* = $H_2C_2O_4,2H_2O$ and ice; A_0 and B_0 are practically co-terminous = $H_2C_2O_4$ and water vapour at 760 mm. pressure; Bf_1 = $NaHC_2O_4,H_2O$ and $H_2C_2O_4,2H_2O$; *BC* = $NaHC_2O_4,H_2O$ and ice; B_0C_0 = $NaHC_2O_4$ and water vapour at 760 mm. pressure; f_1B_0 = $NaHC_2O_4$ and $H_2C_2O_4$; C_0 = $NaHC_2O_4,H_2O$ and $Na_2C_2O_4$; *CD* = $Na_2C_2O_4$ and ice; C_0D_0 = $Na_2C_2O_4$ and water vapour at 760 mm. pressure; D_0 and E_0 are practically coterminous = $Na_2C_2O_4$, NaOH, and water vapour at 760 mm. pressure; Da_1 = $NaOH,7H_2O$ and $Na_2C_2O_4$; a_1b_1 = $NaOH,5H_2O$ and $Na_2C_2O_4$; b_1c_1 = $NaOH,4H_2O$ and $Na_2C_2O_4$; c_1d_1 = $NaOH,3\frac{1}{2}H_2O$ and $Na_2C_2O_4$; d_1e_1 = $NaOH,2H_2O$ and $Na_2C_2O_4$; e_1g_1 = $NaOH,H_2O$ and $Na_2C_2O_4$; $g_1D_0 = g_1E_0$ = NaOH and $Na_2C_2O_4$; *HHo* = solubility curve of $NaHC_2O_4,H_2O$; *NNo* = solubility curve of $Na_2C_2O_4$.

Bivariant Surfaces.—ABf_1f = $H_2C_2O_4,2H_2O$; $ff_1B_0A_0$ = $H_2C_2O_4$; $Bf_1B_0C_0CB$ = $NaHC_2O_4,H_2O$; $CC_0D_0g_1e_1d_1c_1b_1a_1DC$ = $Na_2C_2O_4$; $DEaa_1$ = $NaOH,7H_2O$; aa_1b_1b = $NaOH,5H_2O$; bb_1c_1c = $NaOH,4H_2O$; cc_1d_1d = $NaOH,3\frac{1}{2}H_2O$; dd_1e_1e = $NaOH,2H_2O$; ee_1g_1g = $NaOH,H_2O$; $gg_1D_0E_0$ = NaOH to 322°; *ABCDEXA* = ice surface; $X_0A_0B_0C_0D_0E_0X_0$ = water vapour surface at 760 mm. pressure.

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