325. *Physicochemical Studies of Complex Formation involving Weak Acids. Part XVI.* (a) *Isotherms at 18° of the Systems : Sodium Oxalate–Copper* (or *Zinc* or *Magnesium*) *Oxalate–Water.* (b) *The Solubility of Copper, Zinc, and Magnesium Oxalates in Solutions of Oxalic Acid and Sulphuric Acid.* (c) *A Potentiometric Investigation of the Complex Anion,* $Cu(C_2O_4)_2''$.

By H. T. S. BRITTON and MAURICE E. D. JARRETT.

THE sparingly soluble oxalates of copper, zinc, and magnesium are appreciably soluble in solutions of alkali and ammonium oxalates, the solutions of copper oxalate being deep blue and, as shown by Abegg and Schäfer (*Z. anorg. Chem.*, 1905, **45**, 293) by electrical migration experiments, the copper being in the anion. The salt $Na_2Cu(C_2O_4)_2,2H_2O$ has long been known (Vogel, *J. pr. Chem.*, 1835, **6**, 342), and Riley (J., 1929, 1307), assuming the existence of the complex anion suggested by this salt, and using a copper electrode, made a single determination of its instability constant. The analogous sodium salts of zinc and magnesium oxalates have not been prepared, but the potassium and ammonium salts have been described. The present work shows that it is highly improbable that they can be prepared at 18°, and attempts to crystallise them from solutions have been unsuccessful.

To establish the existence of the complex copper anion in sodium oxalate solutions, resort has been made to the $Ag|Ag_2C_2O_4$ electrode in order to measure the concentration of oxalate ions, from a knowledge of which it is possible to ascertain the amount of oxalate involved in the formation of the complex anion. A difficulty arose in the use of this electrode through the uncertainty of the exact solubility product of silver oxalate and the fact that the values obtained by potential measurements depend on the manner in which the silver oxalate is precipitated.

It is not yet possible to attribute the increased solubility of magnesium and zinc oxalates in sodium oxalate solutions to the formation of analogous complex anions. Kunshert (*Z. anorg. Chem.*, 1904, **41**, 337), however, states that in concentrated ammonium oxalate solutions $Zn(C_2O_4)_3''''$ ions are formed, whereas in dilute solutions $Zn(C_2O_4)_2''$ ions exist. We attempted to solve the problem in regard to sodium oxalate solutions by electrometric methods, but the data were inconclusive and are not recorded.

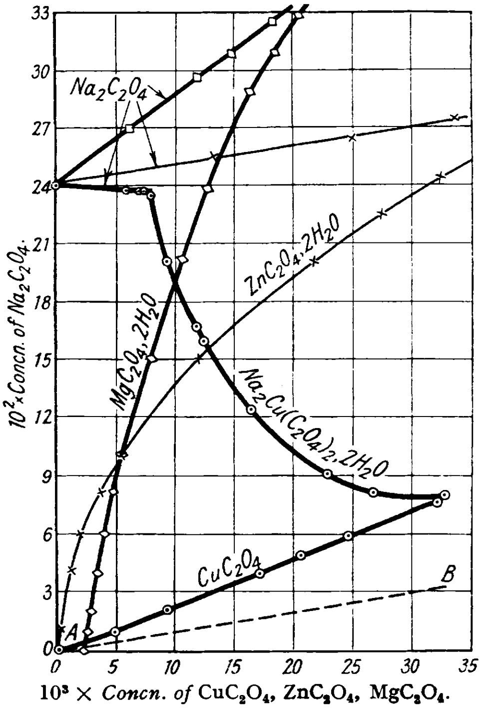
Neither copper nor zinc oxalate shows increased solubility in oxalic acid solutions as might be expected if complex acids were formed. On the other hand, magnesium oxalate increases in solubility. This increase, however, has been traced to the magnitude of its solubility product and to the diminishing secondary ionisation of oxalic acid with its increasing concentration. An attempt to calculate the solubility products of the three oxalates from their solubilities in sulphuric acid proved abortive.

EXPERIMENTAL.

(a) *Phase-rule Investigation.*—The precipitate of copper oxalate obtained by adding a small excess of ammonium or alkali oxalate to a solution of copper sulphate is fine and difficult to get free from adhering matter. It was prepared as a coarse powder by precipitating an ammoniacal solution of copper oxalate with dilute acetic acid, washing it thoroughly with water, and drying it either at 80° or by prolonged air-drying; the product was pure anhydrous copper oxalate (cf. Rauter, *Ber.*, 1892, **25**, 2823).

Suitable quantities of copper oxalate were shaken with solutions of A.R. sodium oxalate in glass-stoppered bottles at 18° for not less than one month, which was found necessary to ensure that equilibrium had been reached. The liquid phases were deep blue, and sodium cupric oxalate separated as a pale or dark blue voluminous mass of fine needles, the variation in the depth of colour being due to differences in the size of the crystals, since all products had the same analytical composition.

The liquid phases were separated from the solid phases by suction into a pipette, the lower end of which had been plugged with glass-wool. Owing to the low solubilities of the solid phases, Schreinemakers's residue method was unsatisfactory; hence these were filtered off by suction, pressed, dried between filter-papers, and air-dried. Wherever possible, the analyses were performed volumetrically; for copper it was necessary to oxidise the oxalate completely before an excess of potassium iodide was added. Sodium was estimated as sulphate after the copper had been removed as sulphide. The results are recorded in Table I and plotted in the figure.



In the figure the line *AB* refers to solutions containing sodium oxalate and cupric oxalate in equimolecular proportion. As this line does not intersect the section indicating liquid phases in equilibrium with sodium cuprioxalate, it follows that the complex salt is decomposed by water; in fact, it dissolves in water but such solutions rapidly deposit copper oxalate at 18°. Abegg and Schäfer (*loc. cit.*) made similar observations with the potassium salt.

The analogous isotherms for zinc and magnesium oxalates were investigated in a similar manner at 18°. The data are recorded in Table II and plotted in the figure. Despite the fact that in both cases the oxalate of the heavy metal becomes more soluble in sodium oxalate solutions of increasing concentration, probably owing to the formation of complex salts, no such

TABLE I.

CuC_2O_4–$Na_2C_2O_4$–H_2O *at* 18°.

Liquid phase. G.-mols./1000 l.		Dry solid phase.			
$Na_2C_2O_4$.	CuC_2O_4.	Na, %.	Cu, %.	C_2O_4, %.	Solid phase.*
0	0·15	0	41·61	57·80	A
10·1	4·90	0	41·54	57·70	
20·0	9·30	0	41·52	57·81	
40·0	17·1	0	41·41	57·68	
50·0	20·7	0	41·60	57·85	
60·0	24·7	0	41·20	57·40	
75·8	32·2	—	35·01	56·00	A + B
80·0	32·8	14·32	19·90	54·70	B
82·3	26·8	—	19·85	54·74	
91·9	23·0	14·38	19·91	54·60	
124·0	16·4	—	19·80	55·05	B
162·3	12·4	14·29	19·96	54·75	
167·0	11·9	—	19·76	54·91	
200·1	9·25	—	18·20	60·50	B + C
233·5	8·00	—	0·4	63·60	C
237·0	7·00	34·38	0	65·40	
237·0	6·00	—	0	64·60	
237·5	7·20	—	0	65·60	
240·0	0	—	—	—	

* A = CuC_2O_4; B = $Na_2C_2O_4,CuC_2O_4,2H_2O$; C = $Na_2C_2O_4$.

complex salt constitutes the solid phase in equilibrium with liquid phases at 18°. Attempts to obtain mother-liquors from which double oxalates separate at 18° were unsuccessful. This was also true of the liquid phases which enter into equilibrium with the two pairs of solid phases, $Na_2C_2O_4$–$ZnC_2O_4,2H_2O$ and $Na_2C_2O_4$–$MgC_2O_4,2H_2O$. The difficulty in the latter cases lies in the great ease with which solutions containing much sodium oxalate and either zinc or magnesium oxalate become supersaturated. The introduction of the appropriate solid phase into the liquid phases did not promote the attainment of equilibrium, even after the lapse of 3 months with frequent and vigorous agitation. It is significant that neither sodium zinc oxalate nor the analogous magnesium salt has yet been prepared, and the present work, as far as it goes, would suggest that such salts, if they are capable of existence, are not formed at 18°.

TABLE II.

ZnC_2O_4–$Na_2C_2O_4$–H_2O *at* 18°.

G.-mols./1000 l.		Solid phase.
$Na_2C_2O_4$.	ZnC_2O_4.	
0	—	$ZnC_2O_4,2H_2O$
10	0·26	,,
20	0·55	,,
40	1·10	,,
60	1·91	,,
80	3·26	$ZnC_2O_4,2H_2O$
100	5·29	,,
150	12·0	,,
200	21·7	,,
224	27·5	,,
245	32·5	,,
240	0	$Na_2C_2O_4$
254	13·3	,,
262	25·0	,,
273	33·7	,,

MgC_2O_4–$Na_2C_2O_4$–H_2O *at* 18°.

G.-mols./1000 l.		Solid phase.
$Na_2C_2O_4$.	MgC_2O_4.	
0	2·30	$MgC_2O_4,2H_2O$
10	2·46	,,
20	2·61	,,
40	3·25	,,
60	3·80	,,
80	4·39	,,
100	5·29	,,
150	7·94	$MgC_2O_4,2H_2O$
200	10·31	,,
238·4	12·6	,,
288·1	16·4	,,
309·3	18·8	,,
329·5	20·5	,,
240	0	$Na_2C_2O_4$
269·1	6·2	,,
296·0	11·7	,,
308	14·9	,,
324·9	18·5	,,

(b) *Solubility of Simple Oxalates in Oxalic and Sulphuric Acids at* 18°.—Although the solubility of copper and zinc oxalates in oxalic acid solutions is too small to be determined by analytical methods, that of magnesium oxalate is appreciable and increases with increasing concentration of acid as shown in Table III, where the p_H's of the solutions are also given.

TABLE III.

Solubility of MgC_2O_4 *in* $H_2C_2O_4$ *at* 18°.

$H_2C_2O_4$, g.-mols./l.	0	0·02	0·05	0·10	0·25	0·50
$[MgC_2O_4]$, g.-mols./1000 l.	2·30	9·97	15·5	21·7	32·2	51·3
p_H	4·07	2·11	1·72	1·50	1·23	1·04
$[C_2O_4''] \times 10^4$	2·30	2·57	2·24	1·48	1·02	0·76
$[Mg^{\cdot\cdot}][C_2O_4''] \times 10^6$	2·51	2·56	3·47	3·21	3·29	3·89

Mean $[Mg^{\cdot\cdot}][C_2O_4''] = 3{\cdot}1 \times 10^{-6}$.

If these simple oxalates were in any way comparable with chromium, aluminium, or tervalent iron as regards the formation of complex oxalates, it might have been expected that the simple oxalates would also dissolve in oxalic acid to give complex solutions. Instead, owing to their small solubility in water, both copper oxalate and zinc oxalate remain almost insoluble. The increased solubility of magnesium oxalate in oxalic acid is quite normal and is caused by the depressing effect on the concentration of oxalate ions of the relatively large concentration of hydrogen ions originating from the first stage of ionisation of oxalic acid, and this becomes more pronounced as the concentration of oxalic acid is increased. The magnesium oxalate dissolves in the form of the hydrogen oxalate, $Mg(HC_2O_4)_2$, and if it be assumed that this salt is completely ionised, the magnesium-ion concentrations are known. Also, knowing the p_H value of the solutions and by taking 1×10^{-2} and $1{\cdot}3 \times 10^{-4}$ as K_1 and K_2 respectively for oxalic acid, the oxalate-ion concentrations can be computed from the expression

$$[C_2O_4''] = K_1K_2\ [\text{concn. of oxalic acid}]/([H^\cdot]^2 + K_2[H^\cdot] + K_1K_2).$$

In this way, the values of the solubility product of magnesium oxalate were calculated, and in view of the approximations involved, especially in regard to the ionisation of oxalic acid in the fairly concentrated solutions employed, the agreement will be seen to be sufficient.

Table IV gives the solubilities of the three oxalates in sulphuric acid at 18°.

TABLE IV.

H_2SO_4, g.-mols./l.	0·05	0·125	0·25	0·50	1·00	1·50	1·875
$[MgC_2O_4] \times 10^3$	43·7	87·7	149·8	263·3	440·7	—	—
$[ZnC_2O_4] \times 10^3$	4·45	7·37	13·95	21·78	39·01	55·5	66·95
$[CuC_2O_4] \times 10^3$	0·39	0·83	1·80	3·36	6·58	9·69	12·4

(c) *Electrometric Investigation of Sodium Oxalate Solutions of Copper Oxalate.*—Hitherto the complex anion $Cu(C_2O_4)_2''$ has been tacitly assumed to exist in these solutions, but no experimental proof has been advanced. The first section of the work consists of a critical study of the behaviour of the $Ag|Ag_2C_2O_4$ electrode, and particularly of the solubility product of silver oxalate, for which, using conductivity methods, Böttger (*Z. physikal. Chem.*, 1902, **46**, 602) found $0{\cdot}696 \times 10^{-11}$, and Kohlrausch (*ibid.*, 1908, **64**, 194) $0{\cdot}562 \times 10^{-11}$. Potential measurements yielded $1{\cdot}03 \times 10^{-11}$ (Abegg and Schäfer, *loc. cit.*) and $0{\cdot}744 \times 10^{-11}$ (Thomas and Fraser, J., 1923, **123**, 2975). Determinations with the silver electrode may, however, lead to widely different values depending very largely upon the conditions under which the silver oxalate is precipitated. By carefully reproducing the conditions it is possible to get consistent results: the best results were obtained by precipitating the silver oxalate by adding 25 c.c. of 0·05*M*-sodium oxalate dropwise with constant stirring to 25 c.c. of 0·1*M*-silver nitrate and adding this to the solution it was desired to investigate. By using the cell,

$$Ag|Ag_2C_2O_4 + Na_2C_2O_4|\text{satd. } KNO_3|N\text{-Calomel},$$

at 18°, and taking different concentrations of sodium oxalate, *E.M.F.*'s were almost immediately set up which did not vary by more than a millivolt during 7—10 days. The electrode, which was a thin rod of pure silver, gave a normal potential of + 0·802 volt when tested in 0·1*M*- and 0·01*M*-silver nitrate solutions, the silver-ion concentrations of which were computed from the conductivity measurements of Noyes and Falk (*J. Amer. Chem. Soc.*, 1912, **34**, 454). The following table gives some typical determinations of $[Ag^\cdot]^2[C_2O_4'']$.

$Na_2C_2O_4$, millimols./l.	0	2·381	6·519	10·000
E_{Ag} (N-H = 0)	0·602	0·570	0·557	0·552
$-\log [Ag^\cdot]$	3·46	4·02	4·25	4·33
$[Ag^\cdot]^2[C_2O_4''] \times 10^{11}$	2·04	2·16	2·10	2·17

The values of the solubility product have not been corrected for the degree of ionisation of the sodium oxalate. When the silver oxalate is obtained by precipitation from more dilute solutions, much higher values are obtained; *e.g.*, if 25 c.c. of 0·005*M*-sodium oxalate are added to 25 c.c. of 0·01*M*-silver nitrate the values are about 50% higher than those given above, and incidentally, they vary with the length of time elapsing before the measurement is made. The ultimate attainment of equilibrium requires more than 14 days at 18°. These higher values appear, therefore, to be caused by supersaturation of the silver oxalate solution, probably owing to the fineness of the precipitate.

The precipitate obtained by the first method reaches equilibrium sufficiently quickly for titrimetric purposes. Thus calculations of the solubility product from the *E.M.F.*'s set up during the progressive addition of 0·05*M*-sodium oxalate to a mixture of 25 c.c. of 0·05*M*-sodium oxalate and 25 c.c. of 0·1*M*-silver nitrate yielded an average value of $1{\cdot}91 \times 10^{-11}$, the extreme values being $1{\cdot}73 \times 10^{-11}$ and $2{\cdot}02 \times 10^{-11}$.

The nature of the complex was investigated electrometrically by measuring the concentrations of hydrogen, copper, and oxalate ions existing in solutions of copper oxalate in sodium oxalate when the concentration of sodium oxalate was increased. The p_H values of the solutions were measured by means of the glass electrode, and the copper-ion concentrations were found by measuring the *P.D.*'s set up between a copper electrode immersed in the complex solution and a normal calomel electrode, the junction liquid being a saturated solution of potassium chloride. The electrode consisted of a small copper plate which had been covered with an electrodeposit of copper from a copper sulphate solution. When tested in copper sulphate solutions, Noyes and Falk's conductivity data being used, its normal electrode potential was found to be 0·341 volt. From the glass- and the copper-electrode potentials the values of the product $[Cu^{\cdot\cdot}][OH']^2$ were calculated (see Table V). They progressively diminish as the concentration of sodium oxalate increases. They are also a little smaller than the solubility product of copper hydroxide, which is of the order of 10^{-20}, showing that, despite the p_H of the solutions being appreciably higher than the normal precipitation p_H of copper hydroxide, the copper-ion concentration is correspondingly reduced. The oxalate-ion concentrations of a similar series of solutions were ascertained by suspending in them silver oxalate, precipitated as stated above, and finding the potentials which they set up at a silver electrode (N-H = 0). For the purpose of calculation, the value $2{\cdot}0 \times 10^{-11}$ was taken as the solubility product of silver oxalate. The oxalate-ion concentrations so found are given in Table V.

TABLE V.

$Na_2C_2O_4$.								$\overline{K}_{Cu(C_2O_4)_2''} \times 10^9$.	
C.c.	Excess concn., g.-mols./l. $\times 10^2$.	p_H.	E_{Ag} (N-H = 0).	E_{Cu} (N-H = 0).	$-\log [Cu^{\cdot\cdot}]$.	$[Cu^{\cdot\cdot}][OH']^2 \times 10^{22}$.	$[C_2O_4'']$ $\times 10^2$, obs.	(*a*).	(*b*).
0	1·00	6·53	0·555	0·155	6·41	2·34	0·73	2·07	3·89
10	1·36	6·57	0·548	0·152	6·53	2·14	1·27	5·21	5·94
20	1·67	6·60	0·546	0·146	6·72	1·69	1·49	5·07	6·38
30	1·92	6·64	0·544	0·142	6·87	1·35	1·75	5·37	6·46
40	2·14	6·66	0·543	0·138	7·00	1·10	1·89	5·01	6·35

The solutions used for the determination of p_H and copper-ion concentrations were prepared by adding 50 c.c. of water and the volume of 0·05*M*-sodium oxalate indicated in col. 1 to 50 c.c. of a solution 0·04*M* with respect to sodium oxalate and 0·02*M* with respect to the dissolved copper oxalate. For solutions employed for oxalate-ion concentration measurements, the 50 c.c. of water were replaced by 50 c.c. of a suspension of silver oxalate prepared by mixing 25 c.c. each of 0·1*M*-silver nitrate and 0·05*M*-sodium oxalate (see above). The data given in Table V refer to individual solutions that had reached a state of equilibrium with the various electrodes.

The concentrations of sodium oxalate (col. 2) are calculated on the assumption that all the copper oxalate had been converted into the complex anion, $Cu(C_2O_4)_2''$. The observed oxalate-ion concentrations range from 73 to 90% of the sodium oxalate thus assumed to be present. This is approximately the order of the degree of ionisation, or the mean activity coefficients, of sodium oxalate at the dilutions employed. These determinations thus furnish satisfactory evidence of the existence of the anion.

The instability constant, $\overline{K}_{Cu(C_2O_4)_2''}$, of the reaction $Cu(C_2O_4)'' \longrightarrow Cu^{\cdot\cdot} + 2C_2O_4''$ has therefore been evaluated from the observed [Cu] and $[C_2O_4'']$ values, that of $[Cu(C_2O_4)_2'']$ being taken as equal to the concentration of dissolved copper oxalate. These are recorded under (*a*) in col. 9. In computing the values given under (*b*) in col. 10, the oxalate-ion concentrations were assumed to be equal to the concentration of free sodium oxalate. The first value in (*b*) is almost identical with that obtained by Riley (*loc. cit.*) in a single determination by the same method. Except for this result, the values of $\overline{K}_{Cu(C_2O_4)''}$ are sensibly constant. Comparable results were obtained by carrying out potentiometric titrations in which sodium oxalate was added to the different electrode systems of solutions of sodium oxalate to which suitable quantities of copper sulphate had been added.

One of the authors (M. E. D. J.) thanks the Senate of the University of London for a Neil Arnott and a Postgraduate Studentship.

WASHINGTON SINGER LABORATORIES,
UNIVERSITY COLLEGE, EXETER.

[*Received, July* 14*th*, 1936.]