Summary

The catalytic efficiency of HCO_3^- confirms the statements found in various published articles that the first ionization constant for carbonic acid is about 2×10^{-4}.

From the rates of the reaction $CO_2 + H_2O = H_2CO_3$ at various temperatures, the heat of activation is found to be 19 kcal./mole.

For the reaction $CO_2 + OH^- = HCO_3^-$ the heat of activation is found to be from 10 to 13 kcal./mole.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Solubility of Cadmium and Zinc Oxalates in Salt Solutions

BY WARREN C. VOSBURGH AND J. FINK BECKMAN

In the determination of the ionization constants of cadmium and zinc oxalates by Clayton and Vosburgh[1] there were two sources of uncertainty. One was the value used for the second ionization constant of oxalic acid and the other the interpretation of the solubility data for cadmium oxalate in cadmium sulfate solutions. The redetermination of the second ionization constant of oxalic acid by Harned and Fallon[2] has made it advisable to recalculate some of the data of Clayton and Vosburgh,[1] and some new experiments have led to a better interpretation of the solubility data.

Materials.—Cadmium oxalate was prepared by precipitation as described by Clayton and Vosburgh.[1]

Potassium perchlorate was prepared from potassium hydroxide and perchloric acid. It was recrystallized three times and dried at 100°.

Cadmium perchlorate was prepared by addition of an excess of cadmium oxide to a known quantity of 60% perchloric acid solution. The solution was separated from the excess oxide and heated, whereupon some cadmium hydroxide precipitated. Filtration and dilution gave a stock solution with a *p*H of about 7 as measured by a glass electrode. The concentration determined by an electrolytic cadmium determination agreed with the concentration as calculated from the original quantity of perchloric acid. Dilution of the cadmium perchlorate solution caused a decrease in *p*H, the largest decrease observed being about one unit.

Potassium sulfate was recrystallized twice. Solutions of this and of potassium perchlorate were prepared by weight, and analysis was considered unnecessary.

Solubility Determinations.—Solutions of potassium and cadmium perchlorates and potassium sulfate were saturated with cadmium oxalate at 25 ± 0.02° (in an oil-bath) by stirring mechanically for at least two hours. Experiments showed that saturation could be attained in one hour. A large sample was drawn through a filter of Pyrex glass wool and portions of 200 ml. each were taken for analysis, without allowing the temperature to fall appreciably below 25°. The oxalate was titrated with 0.05 *N* permanganate solution by the use of a 5-ml. semimicro buret. The permanganate solution was standardized frequently against sodium oxalate from the National Bureau of Standards under conditions similar to those used in the oxalate determinations. Experiments showed that the solvent salts did not interfere with the analyses. The results of the solubility determinations are given in Tables I–IV in the columns headed "total oxalate." It is believed that errors were within 1.5%.

The values reported for the solubility of cadmium oxalate in water by Clayton and Vosburgh[1] differ from the one in this paper by more than 1.5%, but it is believed that the latter is the more reliable and is accurate within the limit claimed.

Discussion

For the interpretation of the solubility data it is necessary to recalculate the solubility product of cadmium oxalate. Use of the value 5.18×10^{-5} for the second ionization constant of oxalic acid[2] and the experimental data of Clayton and Vosburgh[1] gives 1.44×10^{-8} for the activity solubility product.

By means of the solubility product and the activity coefficients of Kielland[3] the concentration of oxalate ion in the salt solutions was calculated. In potassium perchlorate and potassium sulfate solutions allowance was made for a small amount of autocomplex formation. For potassium perchlorate solutions the data in Table I were obtained.

TABLE I

SOLUBILITY OF CADMIUM OXALATE IN POTASSIUM PERCHLORATE SOLUTIONS

$KClO_4$ $m \times 10^3$	Total oxalate $m \times 10^3$	$\sqrt{\mu}$	$C_2O_4^=$ $m \times 10^3$	CdC_2O_4 un-ionized $m \times 10^3$
None	0.289	0.0232	0.133	0.154
5	.316	.0752	.163	.150
10	.341	.104	.179	.159
20	.365	.144	.208	.153
40	.413	.203	.247	.161
80	.475	.285	.303	.166

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[1] Clayton and Vosburgh, THIS JOURNAL, **59**, 2414 (1937).

[2] Harned and Fallon, *ibid.*, **61**, 3111 (1939).

[3] Kielland, THIS JOURNAL, **59**, 1677 (1937).

The figures in the last column are the difference between the total oxalate and the concentration of oxalate ion plus twice the concentration of the complex ion $Cd(C_2O_4)_2^{=}$. The latter concentration was about 1% of the oxalate ion concentration, as will be shown later. The difference so calculated is assumed to represent undissociated cadmium oxalate and in Table I is as nearly constant as could be expected. The corresponding differences for the solutions of the other salts increased considerably with the concentration of the solvent salt. This is shown in Fig. 1, in which are represented also the data of Clayton and Vosburgh for cadmium sulfate solutions recalculated with the use of the new solubility product.

Clayton and Vosburgh assumed that the cadmium sulfate curve of Fig. 1 represented the solubility of undissociated cadmium oxalate in cadmium sulfate solutions. They also assumed that cadmium oxalate would behave similarly in other salt solutions. In view of the practically constant concentration of the undissociated oxalate in potassium perchlorate solutions, it now seems preferable to consider that small concentrations of electrolytes have no appreciable effect on the concentration of undissociated cadmium oxalate in saturated solutions.

The abnormal solubility in the cadmium perchlorate solutions cannot be ascribed to the perchlorate ion. Therefore it must be caused by the cadmium ion. The assumption of the existence of the ion $CdC_2O_4 \cdot Cd^{++}$ allows an explanation. This ion can be considered to be formed according to the equation

$$CdC_2O_4 + Cd^{++} \rightleftarrows CdC_2O_4 \cdot Cd^{++}$$

and its instability constant calculated by the equation

$$(CdC_2O_4)[Cd^{++}]/[CdC_2O_4 \cdot Cd^{++}] = K_1$$

in which parentheses indicate activity and square brackets concentration. The activity coefficients for the ions should cancel approximately.

The activity of undissociated cadmium oxalate was found by extrapolation of the curve for cadmium perchlorate in Fig. 1. This gives the value $1.44 \times 10^{-4}\ m$, as compared with $1.54 \times 10^{-4}\ m$, in Table I for the solubility in water. Since the extrapolated values for solutions of the two cadmium salts agreed well, 1.44×10^{-4} was accepted as the activity. The higher value for the potassium perchlorate and sulfate solutions involves a much larger correction for ionized cadmium oxalate, and appreciable hydrolysis may have taken place in these solutions and in water.

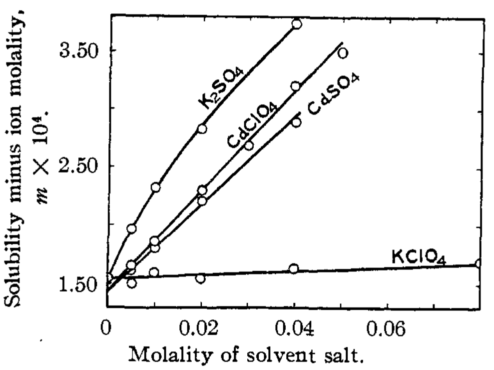

Fig. 1.—Variation of the solubility of cadmium oxalate with salt concentration. From the total solubility has been subtracted the concentration of the ionized cadmium oxalate as calculated from the solubility product.

The concentration of the ion $CdC_2O_4 \cdot Cd^{++}$ was taken as the difference between the total oxalate concentration and the sum of the oxalate ion and undissociated cadmium oxalate concentrations. The latter was assumed constant and equal to $1.44 \times 10^{-4}\ m$. Table II shows that K_1 is constant.

TABLE II

COMPOSITION OF CADMIUM PERCHLORATE SOLUTIONS SATURATED WITH CADMIUM OXALATE

$Cd(ClO_4)_2$ or Cd^{++} $m \times 10^3$	Total oxalate $m \times 10^3$	CdC_2O_4 $m \times 10^3$	$C_2O_4^{=}$ $m \times 10^3$	$CdC_2O_4 \cdot Cd^{++}$ $m \times 10^3$	K_1
5	0.173	0.144	0.008	0.021	0.034
10	.191	.144	.005	.042	.034
20	.234	.144	.004	.086	.034
30	.272	.144	.003	.125	.035
40	.323	.144	.003	.176	.033
50	.353	.144	.003	.206	.035

A similar calculation was made for cadmium sulfate solutions with the assumption that cadmium sulfate is only partially dissociated and the dissociation constant is 0.0050 as calculated by Davies.[4] The values for K_1 so calculated were not constant. If the concentration of the ion $CdC_2O_4 \cdot Cd^{++}$ is calculated by the use of the value 0.034 for K_1, an appreciable amount of the oxalate in the more concentrated cadmium sulfate solutions is left unaccounted for, as shown in the column headed "difference" in Table III. As a possible explanation for this difference the ion $CdC_2O_4 \cdot SO_4^{=}$ was assumed, and its equilibrium constant calculated by the expression

$$(CdC_2O_4)[SO_4^{=}]/[CdC_2O_4 \cdot SO_4^{=}] = K_2$$

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[4] Davies, *J. Chem. Soc.*, 2093 (1938).

The results of this calculation, based on the experimental data of Clayton and Vosburgh, are given in Table III.

TABLE III

COMPOSITION OF CADMIUM SULFATE SOLUTIONS SATURATED WITH CADMIUM OXALATE

Total $CdSO_4$ $m \times 10^3$	Total oxalate $m \times 10^3$	Cd^{++} and $SO_4^=$ $m \times 10^3$	$CdC_2O_4 \cdot Cd^{++}$ $m \times 10^3$	Difference $m \times 10^3$	K_2
5	0.171	3.88	0.016	0.001	..
10	.188	7.12	.030	.006	0.17
20	.226	13.1	.056	.020	.09
40	.294	24.0	.102	.043	.08

For solutions of potassium sulfate it is necessary to assume the formation of both undissociated cadmium sulfate and the ion $CdC_2O_4 \cdot SO_4^=$. Because of the formation of cadmium sulfate, the oxalate ion molality is not equal to the cadmium ion molality. The values of K_2 for the ion $CdC_2O_4 \cdot SO_4^=$ agreed with those in Table III as well as could be expected. The data for potassium sulfate solutions are given in Table IV. The figures in the column headed "difference" were obtained by the subtraction of 1.54×10^{-4}, and the oxalate ion molality, and twice the concentration of the ion $Cd(C_2O_4)_2^=$ from the total oxalate molality. For the undissociated cadmium sulfate the molality 1.54×10^{-4} was used instead of 1.44×10^{-4} because the former is the extrapolated value in Fig. 1 for potassium sulfate and potassium perchlorate solutions. On account of the large activity of cadmium and oxalate ions, hydrolysis might be appreciable in these solutions and the larger figure would include a correction for this. The values for the "difference" in Table IV were taken as the molalities of the ion $CdC_2O_4 \cdot SO_4^=$.

TABLE IV

COMPOSITION OF POTASSIUM SULFATE SOLUTIONS SATURATED WITH CADMIUM OXALATE

K_2SO_4 $m \times 10^3$	Total oxalate $m \times 10^3$	$C_2O_4^=$ $m \times 10^3$	$Cd(C_2O_4)_2^=$ $m \times 10^3$	Difference $m \times 10^3$	K_2
5	0.390	0.230	0.002	0.002	...
10	.463	.285	.003	.018	0.079
20	.564	.368	.0035	.035	.082
40	.719	.481	.0045	.075	.076

It has been shown that the solubility of cadmium oxalate in dilute salt solutions can be explained on the assumption that the concentration of the undissociated portion is constant. This should apply to potassium oxalate solutions, and it is necessary to recalculate the data of Clayton and Vosburgh on the oxalatocadmiate ion. The results of such a recalculation are given in Table V. The concentration of the oxalatocadmiate ion, $Cd(C_2O_4)_2^=$, was taken as the difference between the total cadmium oxalate dissolved and the sum of the cadmium ion molality and the molality of undissociated cadmium oxalate. The instability constant was calculated by means of the equation.

$$(CdC_2O_4)[C_2O_4^=]/[Cd(C_2O_4)_2^=] = K_3$$

and the activity coefficients for the ions were assumed to cancel.

TABLE V

INSTABILITY CONSTANT OF THE OXALATOCADMIATE ION

Oxalate total $m \times 10^3$	CdC_2O_4 total $m \times 10^3$	$C_2O_4^=$ $m \times 10^3$	Cd^{++} $m \times 10^3$	$Cd(C_2O_4)_2^=$ $m \times 10^3$	K_3
5.76	0.194	5.53	0.007	0.043	0.019
9.49	.230	9.18	.005	.081	.016
24.56	.374	23.96	.004	.226	.015
27.00	.394	26.38	.003	.237	.016
28.66	.412	27.98	.003	.265	.015
48.6	.627	47.5	.003	.480	.014
97.5	1.077	95.5	.002	.931	.015

The ionization constant of cadmium oxalate at 25° can be calculated from the solubility product (1.44×10^{-8}) and the activity of the undissociated oxalate (1.44×10^{-4}), to be 1.00×10^{-4}. Money and Davies[5] found 1.3×10^{-4} at 18° by calculation from the conductivity data of Scholder.[6]

Recalculations for Zinc Oxalate.—Recalculation of the solubility product for zinc oxalate gives $K_{S.P.} = 1.28 \times 10^{-9}$. The solubility in water is 1.68×10^{-4} and if hydrolysis is neglected the concentration of undissociated oxalate is 1.29×10^{-4}. The ionization constant is 0.99×10^{-5} at 25° as compared with 1.3×10^{-5} at 18° calculated by Money and Davies.[5]

The effect of zinc sulfate on the solubility of zinc oxalate can be explained by the assumption of the ion $ZnC_2O_4 \cdot Zn^{++}$. In Table VI it is assumed that the concentration of this ion is equal to the total oxalate minus 1.29×10^{-4} m, with a further correction of 0.01×10^{-4} m in two cases for

TABLE VI

COMPOSITION OF ZINC SULFATE SOLUTIONS SATURATED WITH ZINC OXALATE

Total $ZnSO_4$ $m \times 10^3$	Total oxalate $m \times 10^3$	Zn^{++} $m \times 10^3$	$ZnC_2O_4 \cdot Zn^{++}$ $m \times 10^3$	K_4
..	0.168	0.039	...	...
5	.167	4.0	0.037	0.014
10	.202	7.5	.072	.013
20	.269	15.4	.140	.014
40	.386	26.0	.257	.013

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(5) Money and Davies, *Trans. Faraday Soc.*, **28**, 613 (1932).

(6) Scholder, *Ber.*, **60**, 1527 (1927).

oxalate ion. The K_4 in the table is the instability constant of this ion calculated from the solubility data, with the assumption that zinc sulfate is incompletely dissociated and its ionization constant[4] is 0.0054.

Recalculation of the data on the oxalatozincate ion $Zn(C_2O_4)_2^=$ in the same manner as for the oxalatocadmiate ion gives the results in Table VII. To the data of Clayton and Vosburgh have been added some experimental data of Metler and Vosburgh[7] and some of Kunschert.[8] The first three values for K_5 from the data of Metler and Vosburgh are probably too high; the analysis for zinc gave somewhat low results and the error was probably largest in the most dilute solutions. It may be concluded that in the more dilute solutions the complex ion $Zn(C_2O_4)_2^=$ is formed, but all three sets of results are in agreement in showing that at a molality of between 0.05 and 0.1 the value of K_5 begins a rapid decrease. The significance of this is discussed by Clayton and Vosburgh.

TABLE VII

INSTABILITY CONSTANT OF THE OXALATOZINCATE ION

Oxalate total $m \times 10^3$	ZnC_2O_4 total $m \times 10^3$	$C_2O_4^=$ $m \times 10^3$	$Zn(C_2O_4)_2^=$ $m \times 10^3$	K_5
	A. Clayton and Vosburgh			
10.00	0.460	9.21	0.331	0.0036
27.45	1.030	25.52	.901	.0037
48.44	1.803	44.97	1.674	.0035
111.6	6.48	98.77	6.35	.0020
	B. Metler and Vosburgh			
12.2	0.43	11.5	0.30	0.0049
12.7	.45	11.9	.32	.0048
25.9	.85	24.3	.72	.0043
52.1	1.9	48.4	1.77	.0035
51.6	1.8	48.1	1.67	.0037
108.7	5.8	98.2	5.67	.0022
224.7	19.4	186.0	19.3	.0012
262.0	25.4	211.3	25.3	.0011
C. Kunschert (concentrations in moles per liter)				
52.2	2.2	47.9	2.1	0.0029
105.5	5.5	94.6	5.4	.0023
160.6	10.55	140	10.4	.0017
217.3	17.4	183	17.3	.0014
275.7	25.7	224	25.6	.0011

Summary

The solubility of cadmium oxalate in solutions of potassium and cadmium perchlorates and potassium sulfate has been measured.

The increase in solubility with concentration in solutions of potassium and cadmium sulfates and cadmium perchlorate, and the constancy in potassium perchlorate solutions, can be explained if the existence of the ions $CdC_2O_4{\cdot}Cd^{++}$ and $CdC_2O_4{\cdot}SO_4^=$ is postulated and cadmium sulfate regarded as incompletely dissociated.

The solubility of zinc oxalate in zinc sulfate solutions can be explained similarly if the ion $ZnC_2O_4{\cdot}Zn^{++}$ is postulated.

The instability constants of the ions $Cd(C_2O_4)_2^=$ and $Zn(C_2O_4)_2^=$ have been recalculated.

[7] Metler and Vosburgh, THIS JOURNAL, **59**, 2421 (1937).

[8] Kunschert, *Z. anorg. Chem.*, **41**, 339 (1904).

DURHAM, NORTH CAROLINA RECEIVED JANUARY 19, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

Ternary Systems. XXV. Solid Solutions of Some Picromerites at 25°

BY ARTHUR E. HILL,* GEORGE S. DURHAM** AND JOHN E. RICCI

In continuation of the project undertaken in this Laboratory, of collecting reliable equilibrium data on the distribution of isomorphous salts between liquid and conjugate solid solutions, a series of ternary systems consisting of water and a pair of double sulfates of the picromerite series, has been investigated, at the temperature of 25°. The purpose of these measurements is ultimately to relate if possible the distribution ratio of these salts between liquid and solid phases, with certain properties of the individual salts such as their aqueous solubilities. With the necessity in mind of having as nearly as possible ideal conditions for the interpretation of solution relationships, pairs of salts were chosen for this work which because of their very close similarity in formula and in other properties would be expected to form very nearly ideal solid solutions in their mixed crystals. Reports already have been published on a number of alum pairs,[1,2] as also on some picromerite systems.[3] The present report covers

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* This paper is being published, following the death of Professor Hill, by his collaborators.

** The material of this article is taken from a thesis presented by G. S. Durham for the Degree of Doctor of Philosophy at New York University, June, 1939.

[1] Hill and Kaplan, THIS JOURNAL, **60**, 550 (1938).

[2] Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).

[3] Hill and Taylor, *ibid.*, **60**, 1099 (1938).