Summary

The technique and apparatus have been described for making qualitative or quantitative determinations of the adsorption of dissolved salts from aqueous solutions by a surface monolayer of an insoluble substance.

The absolute viscosities of stearic acid and barium stearate monolayers on water having various *p*H values have been listed. These show progressive changes due to adsorption of impurities. The equations and the apparatus used for measuring the viscosity or elasticity of insoluble monolayers have been given.

The modification of a crystallized monoskim of pure stearic acid by the adsorption of aluminum from water containing one part of aluminum in two billion parts of water has been shown by photographs. A melted monoskim of stearic acid colored by copper adsorbed from water containing one part of copper in three hundred million parts of water was described.

Simple methods for the visual observation of the modification of pure stearic acid monolayers caused by minute concentrations of impurities in water which produce a change in the crumple pattern and crystallized monoskim have been described, together with the detection in a similar way of non-volatile impurities in volatile substances such as benzene.

Equations have been given for the rate of diffusion of dissolved substances through water to an insoluble monolayer on the surface and a method described for greatly accelerating the rate of arrival at the surface.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Equilibria in Solutions of Cadmium and Zinc Oxalates[1]

BY WILLIAM J. CLAYTON AND WARREN C. VOSBURGH

The conductivity data of Scholder[2] for a number of oxalates in water solution have been interpreted by Money and Davies[3] in terms of simple ionization. Scholder had explained the abnormally small conductivities entirely on the basis of complex ion formation, but Money and Davies consider this to play only a small part. Among the oxalates in question were those of cadmium and zinc, for which the simple ionization constants are given as 1.3×10^{-4} and 1.3×10^{-5}, respectively, at 18°.

This paper presents the results of a further investigation of equilibria in solutions of cadmium and zinc oxalates by electromotive force and solubility methods. The solubility products at 25° were determined by an electromotive force method, and the solubilities of the two oxalates were determined in cadmium and zinc sulfate solutions, respectively, and in potassium oxalate solutions. From the experimental data, the concentrations of simple ions, undissociated molecules and complex ions in the various solutions have been calculated. The results are in agreement with the conclusions of Money and Davies.

Materials.—Cadmium and zinc oxalates were prepared by slow addition of 0.1 *M* cadmium or zinc sulfate solution to an equal volume of 0.11 *M* oxalic acid solution. In the preparation of the zinc oxalate, the oxalic acid solution was seeded with crystals formed by mixing a small portion of the two solutions.

All other salts used were recrystallized at least once from water.

Mercury was purified by treatment with mercurous nitrate solution and distillation.

Cadmium and zinc amalgams were prepared by electrolysis of cadmium or zinc sulfate solution with a mercury cathode and with a C. P. stick of cadmium or zinc, as anode. The cadmium amalgam contained about 10% cadmium and the zinc amalgam about 5% zinc.

One sample of quinhydrone was obtained from the Eastman Kodak Company and others were prepared by the method of Biilmann and Lund.[4] Further treatment of the quinhydrone is described below.

Apparatus.—A Leeds and Northrup Type K potentiometer was used for the electromotive force measurements. A group of five saturated Weston cells was used as a reference standard.[5] These cells were compared with a similar set of cells that had been checked by the National Bureau of Standards, and the value assigned in this way agreed within 0.01 mv. with the value that had been assigned previously by comparison with newly made cells. The standard cells were kept in an oil-bath at 25 ± 0.02°.

For the temperature control of the experimental cells

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[1] A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, June, 1937.

[2] Scholder, *Ber.*, **60**, 1527 (1927).

[3] Money and Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).

[4] Biilmann and Lund, *Ann. chim.*, [9] **16**, 339 (1921).

[5] The standards were cells 353–356 and 496 which have been used as standards for several years. See Vosburgh and Elmore, THIS JOURNAL, **53**, 2822 (1931).

and in the solubility measurements, a constant-temperature air-bath was used. The temperature (25°) as measured by a thermometer with its bulb covered with mercury in a test-tube fluctuated over a range of about 0.05°.

Analytical Methods.—Analysis of the cell electrolytes involved determinations of total oxalate, acid, and total cadmium or zinc. In the solubility determinations, total oxalate and total cadmium or zinc were determined. Total oxalate was determined by titration with permanganate. The acid was determined by titration with standard sodium hydroxide solution using phenolphthalein as the indicator. It is believed that no appreciable error was caused by carbon dioxide. Cadmium was determined electrolytically[6] after the addition of sulfuric acid and the concentration of the sample (of 200 g. or more) to about 100 ml. Check analyses of cadmium metal of reagent quality under the same conditions showed that the method was satisfactory. For the determination of zinc, the gravimetric mercuric thiocyanate method[7] was used. The sample was acidified with sulfuric acid and evaporated to fumes to decompose the oxalic acid. Dilution gave a solution free from interfering substances.

Electromotive Force Measurements

For the determination of the solubility products of cadmium and zinc oxalates, measurements were made of the electromotive force of the cell

$$\mathrm{Cd(Hg)/CdC_2O_4(sat.),\ K_2C_2O_4,\ KHC_2O_4,\ Quinhydrone/(Pt)}$$

and of the corresponding zinc cell. Hydrogen electrodes were not satisfactory in solutions containing cadmium and zinc oxalates.

Quinhydrone Half-Cells.—In the preparation of the quinhydrone half-cells the platinum electrodes were cleaned with hot chromic acid and washed with water and absolute alcohol as recommended by Morgan, Lammert and Campbell[8] but a different method of drying was used. The electrodes while still wet with alcohol were put in place in the cell vessel (a four-necked 50-ml. flask) and the vessel evacuated to a low pressure by means of a vacuum pump. The evacuation was continued for at least five minutes. Then dry nitrogen was allowed to enter, and as soon as possible thereafter the air-free electrolyte, saturated with quinhydrone and containing an excess of the solid, was introduced. A slow stream of purified nitrogen was passed through the electrolyte in the cell vessel, but the exclusion of all traces of air was not attempted. Two electrodes in the same vessel always agreed to within 0.005 mv. and came to agreement within one minute after the introduction of the electrolyte, provided the cell was at temperature equilibrium. Electrodes in different vessels with the same electrolyte agreed equally well. If the evacuation treatment was omitted and the platinum electrodes were dried in air after washing, about an hour was required for the electrodes to come to agreement within 0.01 mv.

A study was made of different methods of preparing and treating quinhydrone, the different samples being compared in cells set up by the above procedure with potassium tetroxalate solution as the electrolyte. Seven samples of quinhydrone were tried: (1) quinhydrone from the Eastman Kodak Company; (2) sample 1 recrystallized from water in an atmosphere of nitrogen; (3) like sample 2, but recrystallized from 0.001 *M* hydrochloric acid solution; (4) sample 1 recrystallized from water saturated with carbon dioxide in an atmosphere of carbon dioxide; (5, 6) two preparations by the ferric alum method of Biilmann and Lund;[4] (7) sample 5 recrystallized from 0.001 *M* hydrochloric acid solution in an atmosphere of nitrogen. Differences of as much as 0.2 mv. were found on comparison of quinhydrone electrodes made with these preparations. However, when the quinhydrone to be used was washed three times in an atmosphere of nitrogen with the cell electrolyte before bringing into the cell, the electrodes made with samples 2–7 agreed within 0.005 mv.[9]

In making the quinhydrone half-cells for the cells described below, the platinum electrodes were dried by the evacuation procedure and the quinhydrone was well washed with the cell electrolyte. Quinhydrone samples 5 and 6 were used. The cell electrolytes were saturated throughout with cadmium or zinc oxalate.

Oxalate Half-Cells.—Vessels were made for the cadmium and zinc half-cells from 18 × 150 mm. Pyrex test-tubes. A stopcock tube was sealed on as a side-arm and the outer end bent downward parallel to the test-tube. A tungsten wire was sealed in at the bottom of the test-tube.

The amalgam (cadmium or zinc) to be used in the half-cell was washed in a test-tube with 0.1 *M* hydrochloric acid solution and water, and was then heated until the water had evaporated and

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[6] Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, 1930, p. 189.

[7] (a) Lundell and Bee, *Trans. Am. Inst. Mining Met. Engrs.*, **8**, 146 (1914); *C. A.*, **8**, 3404 (1914); (b) Jamieson, THIS JOURNAL, **40**, 1036 (1918); (c) unpublished experiments in this Laboratory.

[8] Morgan, Lammert and Campbell, *Trans. Electrochem. Soc.*, **61**, 409 (1932).

[9] Biilmann and Jensen, *Bull. soc. chim.*, **41**, 158 (1927), have pointed out the desirability of washing the quinhydrone with the cell electrolyte.

the amalgam began to boil. The hot amalgam was passed through a small hole in a filter paper into the cell vessel, which previously had been filled with nitrogen and into which nitrogen was being passed by way of the side-arm. The tube was stoppered quickly with a one-hole rubber stopper bearing a glass tube connected with the vacuum pump, and the vessel was evacuated for forty minutes. Dry nitrogen was then allowed to flow into the vessel, and as soon as possible the cell electrolyte was introduced along with an excess of cadmium or zinc oxalate crystals.

Cadmium oxalate half-cells made by this procedure came to agreement within 0.01 mv. practically immediately, and could be reproduced within 0.01 mv. after four days. Zinc oxalate half-cells agreed equally well at first, but began to deteriorate about five hours after preparation, and all measurements involving them were completed within this time.

Cells.—An oxalate half-cell was joined to a quinhydrone half-cell made with the same electrolyte solution by the insertion of the open end of the side-arm of the oxalate half-cell vessel into one of the necks of the small flask containing the quinhydrone half-cell. The cell was transferred to the air-bath at 25° and the electromotive force measured at ten-minute intervals for about two hours.

The results are given in Tables I and II. The composition of the solution is expressed in millimoles per 1000 g. of water ($m \times 10^3$). Each electromotive force is the mean value for at least three cells that agreed within 0.01 mv. for the more concentrated solutions or 0.03 mv. for the more dilute. The cells made from solutions 1–7 were constant within 0.01 mv. for about two hours. Solutions 8 and 9 were made from potassium tetroxalate and water and were more acid than the others. The cells made from these solutions were constant over a period of three hours. The cadmium electrodes made with this solution became variable after about five hours.

TABLE I

THE CELL: $Cd(Hg)/CdC_2O_4 \cdot 3H_2O(s),\ H_2C_2O_4(m)/CdC_2O_4 \cdot 3H_2O(s),\ H_2C_2O_4(m)$, Quinhydrone/(Pt)

Solution	Oxalate total $m \times 10^3$	$H_2C_2O_4$ total $m \times 10^3$	CdC_2O_4 total $m \times 10^3$	E, v.
1	12.42	3.103	0.261	0.96718
2	12.11	2.406	.238	.95883
3	31.58	7.840	.330	.97996
4	61.66	15.37	.477	.98969
5	62.02	12.35	.518	.98190
6	123.4	25.00	.930	.99244
7	138.1	21.46	1.110	.98507
8	26.57	19.60	0.467	1.04149
9	58.71	43.53	.578	1.05778

Results from the zinc cells are given in Table II. Each electromotive force is the mean value for three cells that agreed within 0.1 mv. The constancy was about the same as for the corresponding cadmium cells.

TABLE II

THE CELL: $Zn(Hg)/ZnC_2O_4 \cdot 2H_2O(s),\ H_2C_2O_4(m)/ZnC_2O_4 \cdot 2H_2O(s);\ H_2C_2O_4(m)$, Quinhydrone/(Pt)

Solution	Oxalate total $m \times 10^3$	$H_2C_2O_4$ total $m \times 10^3$	ZnC_2O_4 total $m \times 10^3$	E, v.
10	12.52	3.103	0.360	1.40764
11	32.07	7.84	.820	1.42035
12	62.48	15.37	1.300	1.42981
13	143.14	21.46	6.12	1.42584

A few cells were made by combining zinc oxalate half-cells with cadmium oxalate half-cells. The cadmium oxalate half-cells for these cells were prepared with solutions saturated with zinc oxalate, and some solid zinc oxalate was included. These cells came to agreement within 0.1 mv. in about thirty minutes and remained constant for about seven hours. Subsequently small differences developed. The results are given in Table III. To obtain the values of E^0 in the last column of the table a small calculated correction for the water activity was applied; E^0, therefore, is the electromotive force of the cell with amalgam electrodes, with unit water activity and with cadmium and zinc oxalates present as the pure hydrated crystals.

TABLE III

THE CELL: $Zn(Hg)/ZnC_2O_4 \cdot 2H_2O(s),\ K_2C_2O_4/K_2C_2O_4,\ ZnC_2O_4 \cdot 2H_2O(s),\ CdC_2O_4 \cdot 3H_2O(s)/Cd(Hg)$

Solution	Oxalate total $m \times 10^3$	Zinc total $m \times 10^3$	No. of cells	E, v.	E^0, v.
14	27.45	1.03	2	0.44064	0.44062
15	48.44	1.80	2	.44065$_5$	.44062

Solubility Measurements

Saturated solutions for the solubility measurements were prepared by stirring suspensions of cadmium or zinc oxalate in the solvent solutions at 25° in the air-bath. Preliminary experiments showed that vigorous stirring for an hour was sufficient. In the final experiments the suspensions were stirred for at least ninety minutes before samples were taken. Samples were taken by allowing the excess solid to settle and siphoning the solution through a tube containing a plug of cotton which previously had been soaked in some of the solution. The filtered solution was kept at 25° or above until samples were taken for analysis. All analyses were made in duplicate. Repetition of some of the measurements showed that the results were reproducible within the limits specified.

Solubility of Cadmium and Zinc Oxalates in Cadmium and Zinc Sulfate Solutions.—Cadmium sulfate solutions of known molality were prepared by weighing selected crystals of hydrated cadmium sulfate and redistilled water.[10] These solutions were saturated with cadmium oxalate and the oxalate content determined in weighed samples of about 200 or 400 g. by titration with 0.01 *N* permanganate solution.[11] Zinc sulfate solutions were prepared by weighing selected crystals of hydrated zinc sulfate and water, and the solubility of zinc oxalate in them determined similarly. The 0.01 *N* permanganate solution was standardized against sodium oxalate dissolved in a solution of cadmium or zinc sulfate made up to imitate the unknown solutions as closely as possible. The solubilities, expressed in millimoles per 1000 g. of water, are given in Table IV. It is believed that the results for cadmium oxalate in cadmium sulfate solutions are not in error by more than 1.5% and that the results for zinc oxalate in zinc sulfate solutions are not in error by more than 2%.

TABLE IV

SOLUBILITY OF CADMIUM AND ZINC OXALATES IN SOLUTIONS OF CADMIUM AND ZINC SULFATES

$CdSO_4$ or $ZnSO_4$, *m*	CdC_2O_4 total $m \times 10^3$	ZnC_2O_4 total $m \times 10^3$
...	0.300[a]	0.1685[b]
...	.297	.167
0.005	.171	.145
.010	.188	.202
.020	.226	.226
.040	.294	.386
.080	.410	.645

[a] Cadmium was determined electrolytically in an 800-g. sample. [b] Zinc was determined gravimetrically in a 2200-g. sample.

Solubility of Cadmium and Zinc Oxalates in Potassium Oxalate Solutions.—For the determination of the solubility of cadmium and zinc oxalates in potassium oxalate solutions, the solutions of approximately known concentration were saturated with cadmium or zinc oxalate, and both total oxalate and cadmium or zinc determined. For the oxalate determinations, samples of 15 to 200 g. were taken, depending on the concentration. For the cadmium and zinc determinations, samples of 100 to 800 g. were taken, depending on the solubility. The results are given in Table V. The values for the solubility of cadmium oxalate probably are not in error by more than 1% and those for zinc oxalate not more than 0.4%. The values for the total oxalate are probably not in error by much more than 0.1%.

TABLE V

SOLUBILITY OF CADMIUM AND ZINC OXALATES IN POTASSIUM OXALATE SOLUTIONS

Oxalate total *m*	CdC_2O_4 total $m \times 10^3$	Oxalate total *m*	ZnC_2O_4 total $m \times 10^3$
0.00576	0.194	...	...
.009485	.230	0.01000	0.460
.02456	.374	...	...
.02700	.396	.02745	1.030
.02866	.412	...	...
.04863	.627	.04844	1.803
.09751	1.077	.1116	6.480

Discussion

Solubility Products of Cadmium and Zinc Oxalates.—For the cell

$H_2(Pt)/HCl\ (0.01\ m)(HCl\ (0.01\ m),\ Quinhydrone/(Pt)$

Harned and Wright[12] found an electromotive force of 0.69969 v. at 25° and a value at 18° agreeing closely with the value of Biilmann and Jensen.[13] Hovorka and Dearing[14] found a value about 0.3 mv. lower. The difference is unimportant for present purposes, and the value of Harned and Wright was adopted. Subtraction of 0.69969 v. from the electromotive force values in Table I gives a series of values for the electromotive force of the cell

$$Cd(Hg)/CdC_2O_4{\cdot}3H_2O(s),\quad H_2C_2O_4(m)/H_2(Pt)$$

For this cell

$$E = E^0 - k \log (Cd^{++})(C_2O_4^{=}) + k \log (H^+)^2(C_2O_4^{=}) \quad (1)$$

in which parentheses indicate activities, *k* stands for 2.303 RT/nF and E^0 is the standard electrode potential of the cadmium amalgam electrode, for which the value 0.3519 v. at 25° was adopted.[15]

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(10) That selected crystals of cadmium sulfate have a definite composition was shown by Perdue and Hulett, *J. Phys. Chem.*, **15**, 155 (1911).

(11) Ceric sulfate solution did not give good results.

(12) Harned and Wright, THIS JOURNAL, **55**, 4849 (1933).

(13) (a) Biilmann and Jensen, *Bull. soc. chim.*, **41**, 151 (1927). See also (b) La Mer and Armbruster, THIS JOURNAL, **57**, 1511 (1935).

(14) Hovorka and Dearing, *ibid.*, **56**, 243 (1934).

(15) (a) Shrawder, Cowperthwaite and La Mer, *ibid.*, **56**, 2348 (1934). A slightly lower value, 0.3515 v., has been given by (b) Harned and Fitzgerald, *ibid.*, **58**, 2627 (1936), and a slightly higher one, 0.3521 v., by Quintin, *Compt. rend.*, **200**, 1754 (1935).

Since the solutions were saturated with cadmium oxalate

$$(Cd^{++})\,(C_2O_4^{=})\,(H_2O)^3 = K_{S.P.} \qquad (2)$$

The activity of water may be considered practically unity and Equations 1 and 2 combined.

$$\log K_{S.P.} = 11.893 - 33.795\,E + \log\,(H^+)^2\,(C_2O_4^{=}) \qquad (3)$$

Solutions 1–7 of Table I may be considered to have contained potassium oxalate, potassium acid oxalate and cadmium oxalate. The total molality of the acid oxalate ion is practically twice the oxalic acid molality given in Table I, and the molality of the oxalate ion is the difference between the total oxalate and the sum of twice the acid molality and the cadmium oxalate molality. The molalities so obtained are given in Table VI. It is assumed as a first approximation that the contribution of oxalate ions from the cadmium oxalate and the formation of complex ions are both negligible compared with the total oxalate ion concentration. This assumption is shown to be valid within the limits of error by the results of the solubility determinations.

The hydrogen and oxalate ion activities needed for Equation 3 can be calculated from the data in Table VI with the help of the second ionization constant of oxalic acid.[16]

$$[H^+][C_2O_4^{=}]\,f(\gamma) = 7.2 \times 10^{-5}[HC_2O_4^-]$$

The activity coefficient function, $f(\gamma)$, may be taken as approximately equal to $\gamma^3/(\gamma')^2$ in which γ is the mean activity coefficient for a typical 1–2 electrolyte and γ' the mean activity coefficient for a 1–1 electrolyte.[17] On the basis of the Debye–Hückel limiting law, γ should be equal to $(\gamma')^2$, as pointed out by McDowell and Johnston.[18] This can be shown to hold very closely up to an ionic strength of 0.3 for sodium sulfate and potassium chloride if activity coefficients interpolated from the results of Randall and Scott[19] for the former and Harned[20] for the latter are compared at the same ionic strengths. Substituting γ for $(\gamma')^2$

$$[H^+][C_2O_4^{=}]\gamma^2 = [HC_2O_4^-]\,(7.2 \times 10^{-5}) \qquad (4)$$

Squaring and rearranging

$$[H^+][C_2O_4^{=}]\gamma^3 = (H^+)^2(C_2O_4^{=}) = \frac{[HC_2O_4^-]^2\,(7.2 \times 10^{-5})^2}{[C_2O_4^{=}]\gamma} \qquad (5)$$

The values for the solubility product calculated by means of Equations 3 and 5 are given in Table VI. For γ in Equations 4 and 5 the activity coefficients for sodium sulfate[19] were used. From Equation 4 by an approximation method, a better ionic strength and better acid oxalate and oxalate ion concentrations were found, then Equation 5 was solved, and finally Equation 3.

TABLE VI

THE SOLUBILITY PRODUCT OF CADMIUM OXALATE

Solution	CdC_2O_4 $m \times 10^3$	KHC_2O_4 $m \times 10^3$	$K_2C_2O_4$ $m \times 10^3$	$\mu^{1/2}$	$-\log K_{S.P.}$
1	0.261	6.206	5.95	0.156	7.519
2	.238	4.812	7.06	.162	7.520
3	.330	15.68	15.57	.250	7.487
4	.477	30.74	30.44	.350	7.461
5	.518	24.70	36.82	.368	7.457
6	.930	50.00	72.50	.518	7.416
7	1.110	42.92	94.10	.571	7.385

The values for $-\log K_{S.P.}$ were plotted against $\mu^{1/2}$ giving Curve I of Fig. 1. Extrapolation to zero ionic strength gave $-\log K_{S.P.} = 7.556$ and $K_{S.P.} = 2.78 \times 10^{-8}$.

For solutions 8 and 9 the calculation was a little different, because these solutions contained free oxalic acid and potassium acid oxalate. The hydrogen ion molality was obtained from the equation

$$[H^+][HC_2O_4^-]\gamma^2 = 0.057\,[H_2C_2O_4] \qquad (6)$$

in which for a first approximation $[H_2C_2O_4]$ can be set equal to the total free acid minus the hydrogen ion molality. For γ, the activity coefficient of hydrochloric acid was used, and an approximation method was used for finding the ionic strength. It was found that a correction for the ionization of the acid oxalate ion had little effect on the final result. From the hydrogen ion molality and the total oxalic acid molality, the molality of undissociated oxalic acid was calculated. This was substituted in the equation

$$(H^+)^2(C_2O_4^{=}) = (4.1 \times 10^{-6})\,[H_2C_2O_4] \qquad (7)$$

and from Equations 7 and 3 the solubility product was calculated. The results are given in Table VII and graphically in Fig. 1. Extrapolation to zero ionic strength gave $-\log K_{S.P.} = 7.497$ and $K_{S.P.} = 3.2 \times 10^{-8}$. This value is not as reliable as the value from the data of Table VI.

The calculations for zinc oxalate were like the

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(16) The ionization constants found by (a) Dawson, Hoskins and Smith, *J. Chem. Soc.*, 1889 (1929), and (b) Dawson and Smith, *ibid.*, 2539 (1929), namely, $K_1 = 0.057$ and $K_2 \times 7.2 \times 10^{-5}$, were adopted. Comparison with other values in the literature indicates that the uncertainty of the ionization constant is the largest uncertainty in the determination of the solubility products.

(17) This will be evident if the equation is written

$$[K^+][H^+][C_2O_4^{=}]f(\gamma) = 7.2 \times 10^{-5}[K^+][HC_2O_4^-]$$

(18) McDowell and Johnston, THIS JOURNAL, **58**, 2013 (1936).

(19) Randall and Scott, *ibid.*, **49**, 654 (1927).

(20) Harned, *ibid.*, **51**, 424 (1929).

TABLE VII

THE SOLUBILITY PRODUCT OF CADMIUM OXALATE

Solution	CdC_2O_4 $m \times 10^3$	$H_2C_2O_4$ $m \times 10^3$	KHC_2O_4 $m \times 10^3$	$\mu^{1/2}$	$-\log K_{S.P.}$
8	0.467	13.10	13.00	0.151	7.554
9	.578	28.93	29.20	.218	7.579

first calculations for cadmium oxalate except that in the calculation of the oxalate ion molality the zinc oxalate was assumed, in accordance with the data of Table XII, to have reacted with oxalate ion to give a concentration of the ion $Zn(C_2O_4)_2^{=}$ that was one thirty-third of the oxalate molality, for solutions 10–12 and one seventeenth for solution 13. For E^0 the value 0.7614 v.[15a] was used. The results are given in Table VIII and Fig. 1.

TABLE VIII

Solution	Zn (total) $m \times 10^3$	KHC_2O_4 $m \times 10^3$	$K_2C_2O_4$ $m \times 10^3$	$\mu^{1/2}$	$-\log K'_{S.P.}$
10	0.360	6.206	5.78	0.156	8.555
11	.820	15.68	15.11	.250	8.519
12	1.30	30.74	29.58	.350	8.485
13	6.12	42.92	89.0	.572	8.424

The cells of Table III allow a direct comparison of the solubility products of zinc and cadmium oxalates.

$$E^0 = E^0_{Zn(Hg),Zn^{++}} - E^0_{Cd(Hg),Cd^{++}} - k \log K'_{S.P.} + k \log K_{S.P.}$$

Substituting the values of the electromotive forces and the solubility product of cadmium oxalate

$$-k \log K'_{S.P} = 0.44062 + 0.3519 - 0.7614 + 7.556\,k \quad (9)$$

Solving gives for zinc oxalate, $-\log K'_{S.P.} = 8.608$ as compared with the value 8.606 resulting from extrapolation of the data of Table VIII. Therefore for zinc oxalate, $K_{S.P.} = 2.47 \times 10^{-9}$.

Simple Ionization Constants.—Comparison of the solubility products with the solubilities of the oxalates in water shows that only 56% of the cadmium oxalate and 30% of the zinc oxalate is in the form of simple ions. It is assumed that in solution in water, or in the presence of excess cadmium or zinc ion, the part of the total oxalate not dissociated into simple ions is in the form of the undissociated compound, CdC_2O_4 or ZnC_2O_4. Money and Davies[8] have presented evidence from conductivity data in favor of this assumption. The exclusion of the complex anions $Cd(C_2O_4)_2^{=}$ and $Zn(C_2O_4)_2^{=}$ will be shown later to be reasonable.

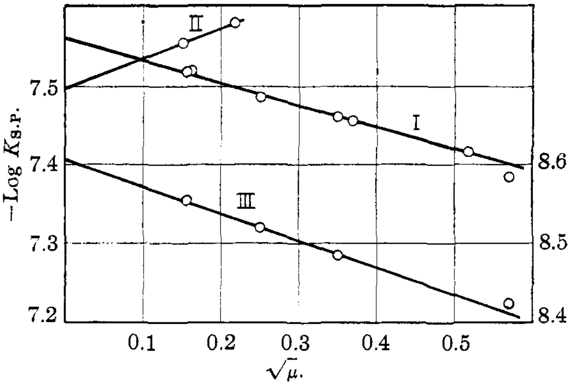

Fig. 1.—Extrapolation of $K_{S.P.}$ and $K'_{S.P}$ to zero ionic strength: I, CdC_2O_4 in solutions of oxalate and acid oxalate; II, CdC_2O_4 in solutions of acid oxalate and oxalic acid; III, ZnC_2O_4. The left-hand scale of ordinates is for Curves I and II and the right-hand scale for Curve III.

With this assumption, the ionization constants of cadmium and zinc oxalates have been calculated. By means of the equation

$$[Cd^{++}][C_2O_4^{=}]\,(\gamma_{2-2})^2 = 2.78 \times 10^{-8} \quad (10)$$

the oxalate ion molalities in the solutions of Table IV were calculated. The ionic strength, μ, was calculated by successive approximations for the solution containing no cadmium sulfate, and in the other solutions it was calculated from the cadmium sulfate molality alone, on the assumption of complete ionization of cadmium sulfate. The activity coefficients were interpolated from the cadmium sulfate activity coefficients of La Mer and Parks.[21] The results are shown in Table IX.

TABLE IX

MOLALITY OF UNDISSOCIATED CADMIUM OXALATE IN SATURATED SOLUTIONS CONTAINING CADMIUM SULFATE

$CdSO_4$ m	$\mu^{1/2}$	γ_{2-2}	$[C_2O_4^{=}]$ $m \times 10^5$	$[CdC_2O_4]$ $m \times 10^4$
...	0.0280	0.853	19.7	1.03
0.005	.141	.476	2.50	1.46
.010	.200	.383	1.93	1.68
.020	.283	.302	1.55	2.10
.040	.400	.223	1.42	2.80
.080	.566	.157	1.43	3.96

Subtraction of the oxalate ion molality from the total oxalate molality gave the molality of undissociated cadmium oxalate, $[CdC_2O_4]$. If the latter molality is plotted against the square root of the ionic strength, the points lie on a smooth curve, as shown in Fig. 2. Extrapolation to zero ionic strength gives for the hypothetical solubility of undissociated cadmium oxalate in pure water, 9.2×10^{-5} m. This was taken as the activity

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[21] La Mer and Parks, THIS JOURNAL, **53**, 2055 (1931).

of undissociated cadmium oxalate in a saturated solution. Then, in the equation

$$(Cd^{++})\,(C_2O_4^{=}) = K_D\,(CdC_2O_4) \qquad (11)$$

$K_D = K_{S.P.}/9.2 \times 10^{-5} = 3.0 \times 10^{-4}$. Money and Davies[3] calculated $K_D = 1.3 \times 10^{-4}$ at 18° from the conductivity data of Scholder.[2]

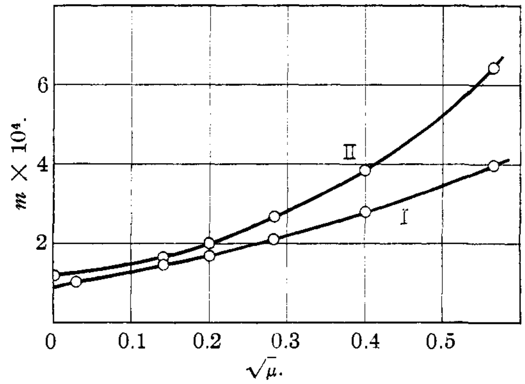

Fig. 2.—Concentration of undissociated cadmium and zinc oxalates in solutions of cadmium and zinc sulfates, respectively, as a function of ionic strength; Curve I, cadmium oxalate, Curve II, zinc oxalate.

A similar calculation for zinc oxalate gave the data in Table X. The activity coefficients for cadmium sulfate were assumed to hold for zinc oxalate, but little error is involved, because the ions are only a small part of the total. The variation of the molality of undissociated zinc oxalate with the square root of the ionic strength is shown in Fig. 2. The activity of undissociated zinc oxalate in a saturated solution is 1.19×10^{-4}, and the ionization constant of zinc oxalate is 2.1×10^{-5} as compared with 1.3×10^{-5} at 18° calculated by Money and Davies.

TABLE X

MOLALITY OF UNDISSOCIATED ZINC OXALATE IN SATURATED SOLUTIONS CONTAINING ZINC OXALATE

$ZnSO_4$ m	$\mu^{1/2}$	γ_{2-2}	$[C_2O_4^{=}]$ $m \times 10^5$	ZnC_2O_4 $m \times 10^4$
...	0.00141	0.996	4.99	1.19
0.005	.141	.476	0.218	1.65
.010	.200	.383	.168	2.00
.020	.283	.302	.137	2.68
.040	.400	.223	.128	3.85
.080	.566	.157	.125	6.44

Stability of the Complex Anions.—Tables IV and V show that addition of potassium oxalate to a saturated solution of cadmium oxalate causes first a decrease in the solubility and then an increase. The increase is more pronounced than when cadmium sulfate is added, and probably cannot be explained entirely on the basis of a decrease in the activity coefficient of undissociated cadmium oxalate. Only an increase in solubility is shown by zinc oxalate. The assumption of the presence of the anions $Cd(C_2O_4)_2^{=}$ and $Zn(C_2O_4)_2^{=}$ is in harmony with the experimental data.

From the data for cadmium oxalate in Table V, the approximate oxalate ion molalities were calculated by the subtraction of the total cadmium oxalate molality from the total oxalate. This involves the assumption that the cadmium is all present as undissociated cadmium oxalate, but this can be shown later to involve an error of less than 1%. From the oxalate ion molality, the cadmium ion molality was calculated by means of Equation 10. The ionic strength was calculated from the potassium oxalate concentration. Then, the concentration of undissociated cadmium oxalate corresponding to each ionic strength was read from Curve I of Fig. 2. This involves the assumption that the activity coefficient of the undissociated cadmium oxalate is a function of ionic strength alone and not of the specific nature of the ions present. The results of these calculations are given in Table XI. Subtraction of the cadmium ion molality and the molality of undissociated cadmium oxalate from the total molality of cadmium oxalate (Table V) gave the molality of the complex anion.

TABLE XI

CALCULATION OF MOLALITY OF THE OXALATOCADMIATE ION

$[C_2O_4^{=}]$ $m \times 10^3$	$\mu^{1/2}$	$[Cd^{++}]$ $m \times 10^3$	$[CdC_2O_4]$ $m \times 10^3$	$[Cd(C_2O_4)_2^{=}]$ $m \times 10^3$	Ratio
5.57	0.129	0.014	0.141	0.039	143
9.26	.167	.011	.156	.063	147
24.19	.269	.008	.203	.163	148
26.60	.283	.007	.210	.179	148
28.25	.292	.007	.215	.190	148
48.00	.380	.007	.268	.352	136
96.43	.538	.007	.375	.695	139

The ratio in the last column of Table XI is the ratio of the oxalate ion molality to the molality of the complex ion. Multiplication of this by the activity of undissociated cadmium oxalate gives an instability constant for the oxalatocadmiate ion, the value being 0.014 if 148 is taken as the best value of the ratio. The constant 0.014 is quite uncertain because of the assumptions involved in its calculation. If instead of considering cadmium sulfate completely dissociated in solution, the ionization constant of Money and Davies[3] is accepted, the instability constant becomes 0.017. The largest uncertainty is probably the assumption that the activity coefficient of undissociated cadmium oxalate depends only on the ionic strength.

A similar calculation for zinc oxalate gave the results in Table XII. Because of the larger concentration of complex ion, a second approximation was made in the calculation of the oxalate ion molality.

TABLE XII

CALCULATION OF THE MOLALITY OF THE OXALATOZINCATE ION

$[C_2O_4^=]$ $m \times 10^3$	$\mu^{1/2}$	$[Zn^{++}]$ $m \times 10^3$	$[ZnC_2O_4]$ $m \times 10^3$	$[Zn(C_2O_4)_2^=]$ $m \times 10^3$	Ratio
9.26	0.169	0.001	0.182	0.277	33.4
25.66	.282	.001	.267	.762	33.7
45.20	.374	.001	.360	1.442	31.4
99.28	.562	.001	.640	5.84	17.0

Taking 33.6 as the best value of the ratio, the instability constant is $1.19 \times 10^{-4} \times 33.6 = 4.0 \times 10^{-3}$. If zinc sulfate is regarded as incompletely dissociated, and the ionization constant of Money and Davies used, the instability constant is 4.4×10^{-3}.

The decrease in the ratio shown in Table XII is probably real, and not the result of experimental error. A similar but more pronounced decrease is apparent in the solubility data of Kunschert[22] and Metler and Vosburgh,[23] which extend to higher oxalate concentrations. These measurements cannot be interpreted quantitatively for lack of data as to the concentration of undissociated zinc oxalate.

Brintzinger and Eckardt[24] by the dialysis coefficient method have found that the molecular weights of cadmium and zinc oxalates dissolved in 1 molar potassium oxalate solution correspond to the formulas

$$Cd_2(C_2O_4)_4^= \text{ and } Zn_2(C_2O_4)_4^=$$

The results of this investigation are in agreement with the simpler formulas $Cd(C_2O_4)_2^=$ and $Zn(C_2O_4)_2^=$ for the complex ions. It is possible that in the more concentrated oxalate solutions the simple ions polymerize. This hypothesis is in accord with the decrease in the ratio in Table XII.

From the solubility products and the ratios in Tables XI and XII, the compositions of saturated solutions of cadmium and zinc oxalates can be calculated. In Table XIII the ion molalities were calculated from the constants, and the molality of undissociated oxalate was calculated by difference.

TABLE XIII

COMPOSITION OF CADMIUM AND ZINC OXALATE SOLUTIONS

	$[M^{++}]$ $m \times 10^3$	$[C_2O_4^=]$ $m \times 10^3$	$[M(C_2O_4)_2^=]$ $m \times 10^3$	$[MC_2O_4]$ $m \times 10^3$
CdC_2O_4	0.196	0.195	0.0013	0.101
ZnC_2O_4	.051	.049	.0015	.116

Summary

An improvement in the technique of preparing quinhydrone electrodes has been made.

The solubility products of cadmium and zinc oxalates have been found by an electromotive force method to be 2.78×10^{-8} and 2.47×10^{-9}, respectively, at 25°.

The solubilities of cadmium and zinc oxalates in water, in solutions of cadmium or zinc sulfate and in potassium oxalate solutions, at 25° have been determined.

From the data obtained, the ionization constants of cadmium and zinc oxalates have been found to be 3.0×10^{-4} and 2.1×10^{-5}, respectively, at 25°. Only a small part of the solute in cadmium and zinc oxalate solutions is in the form of the complex ions $Cd(C_2O_4)_2^=$ and $Zn(C_2O_4)_2^=$. With certain assumptions, the instability constants of these complex ions were calculated.

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[22] Kunschert, *Z. anorg. Chem.*, **40**, 337 (1904).

[23] Metler and Vosburgh, THIS JOURNAL, **55**, 2625 (1933).

[24] Brintzinger and Eckardt, *Z. anorg. allgem. Chem.*, **224**, 93 (1935).