The Effect of pH on the Solubility of Calcium Oxalate

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The literature contains no accurate data on the effect of pH on the solubility of calcium oxalate. The purpose of our work was to supply such data and also to compare the observed effect of pH with theoretical predictions.

Theory

The solubility of calcium oxalate in any solution should follow the equation

$$[Ca^{++}]T = S' \frac{(H^+) + K_2'}{K_2'} \qquad (1)$$

where brackets denote the concentration of the enclosed species; parentheses denote activity; T is the total concentration of oxalate, $i.\ e.$, the sum of $[C_2O_4^=]$ and $[HC_2O_4^-]$; S' is the classical solubility product of calcium oxalate; and K_2' is the semiclassical second ionization constant of oxalic acid, defined by the equation

$$K_2' = \frac{(H^+)[C_2O_4^=]}{[HC_2O_4^-]} \qquad (2)$$

In the absence of excess calcium or oxalate

$$L = [Ca^{++}] = T \qquad (3)$$

where L is the solubility of calcium oxalate in moles per liter. Combination of these three equations yields

$$L = \sqrt{S' \frac{(H^+) + K_2'}{K_2'}} \qquad (4)$$

This equation can be used to predict the solubility of calcium oxalate in any given solution provided that values of S', (H^+), and K_2' are known. Data for S' are given in the previous paper. (H^+) may be calculated from pH measurements by the equation

$$p\text{H} = -\log (H^+) \qquad (5)$$

The non-thermodynamic assumptions implied in this equation do not introduce serious errors for our purpose.

Second Ionization Constant of Oxalic Acid

Solutions of the composition listed in Table I were prepared. Sodium hydrogen oxalate was not added as such, but sodium oxalate and oxalic acid were mixed to yield the indicated concentrations. The pH values of these solutions were

measured at 25° with a Beckman pH meter (previously standardized against 0.0500 molal potassium acid phthalate), and the pK_2' values were calculated with equation (2). No corrections were applied to the concentrations of primary or secondary oxalate ions for the progress of the reaction

$$HC_2O_4^- \longrightarrow H^+ + C_2O_4^=$$
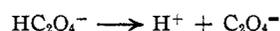
because these corrections would be smaller than the limit of error in measuring the pH, ± 0.03 unit.

Table I

DATA FOR pK_2' OF OXALIC ACID

All concentrations are expressed as molarities.

$Na_2C_2O_4$	$NaHC_2O_4$	NaCl	μ	pH	pK_2'
0.01875	0.0125	0.0000	0.0688	4.14	3.96
.0375	.0250	.0000	.1375	4.06	3.88
.01875	.0125	.150	.2188	3.96	3.78
.01875	.0125	.250	.3188	3.90	3.72
.01875	.0125	.350	.4188	3.83	3.65
.01875	.0125	.450	.5188	3.82	3.64
.01875	.0125	.550	.6188	3.76	3.58
.01875	.0125	.650	.7188	3.73	3.55
.01875	.0125	.750	.8188	3.70	3.52
.01875	.0125	.850	.9188	3.68	3.50
.01875	.0125	.950	1.0188	3.64	3.46
NH₄Cl					
.025	.025	.000	0.10	3.93	3.93
.025	.025	.100	.20	3.81	3.81
.025	.025	.200	.30	3.73	3.73
.025	.025	.300	.40	3.68	3.68
.025	.025	.400	.50	3.64	3.64
.025	.025	.500	.60	3.59	3.59
.025	.025	.540	.64	3.58	3.58
.025	.025	.600	.70	3.56	3.56
.025	.025	.700	.80	3.53	3.53
.025	.025	.800	.90	3.51	3.51
.025	.025	.900	1.00	3.49	3.49
.025	.025	1.80	1.90	3.36	3.36
KCl					
.01875	.0125	0.050	0.1188	4.07	3.89
.01875	.0125	.350	.4188	3.91	3.73
.01875	.0125	.540	.6088	3.87	3.69
.01875	.0125	.850	.9188	3.82	3.64

By combining the data of Harned and Fallon[2] for the e. m. f. of the cell

$$H_2 \mid NaHC_2O_4(xm_1), Na_2C_2O_4(xm_2), NaCl(xm_3) \mid AgCl + Ag$$

with the data of MacInnes[3] for the single activity coefficient of the chloride ion, values of the semi-

(1) This paper is taken from part of a thesis submitted by Wilbur H. McComas, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Harned and Fallon, This Journal, 61, 3111 (1939).

(3) MacInnes, ibid., 41, 1086 (1919).

classical second ionization constant of oxalic acid can also be computed. These values agree with ours within ±0.03 pK unit throughout the range of Harned and Fallon's measurements ($\mu = 0.03$ to 0.17).

From a large-scale graph of the foregoing pK_2' values against the square root of ionic strength, it can be seen that the effect of sodium and ammonium chlorides is the same, but that the graph for potassium chloride lies above the other, the divergence beginning at about $\sqrt{\mu} = 0.4$.

Solubility of Calcium Oxalate in Formate Buffers

Buffers of formic acid and ammonium formate were prepared. Each buffer was 0.36 M with ammonium formate, and therefore had an ionic strength of 0.36. The concentration of formic acid in the buffers was varied. The solubility of calcium oxalate monohydrate at 25° was determined in each of these buffers as described in the previous paper. The pH of each filtrate was also determined with the Beckman pH meter. The results are presented in Table II.

The values in the last column were calculated by equation (4) with $S' = 4.97 \times 10^{-8}$ and $K_2' = 1.97 \times 10^{-4}$. Good agreement is obtained between the observed and theoretical solubilities up to 0.5 M formic acid. Greater concentrations of formic acid not only increase the hydrogen-ion

TABLE II

SOLUBILITY OF CALCIUM OXALATE IN FORMATE BUFFERS

Molarity of HCOOH	pH	Solubility of CaC_2O_4, molarity $\times 10^4$ Observed	Calculated
0.0000	5.96	2.23	(2.23)
.0246	4.75	2.26	2.32
.0437	4.53	2.47	2.39
.0778	4.25	2.66	2.53
.138	4.02	2.86	2.73
.246	3.75	3.18	3.09
.437	3.50	3.48	3.60
.778	3.23	4.03	4.47
1.38	2.93	4.84	5.88
2.46	2.60	5.89	8.30

activity but also alter the solvent properties of the medium. Since equation (4) does not take the latter effect into account, it is not accurate in high concentrations of formic acid.

Summary

The semiclassical second ionization constant of oxalic acid has been determined at ionic strengths from 0 to 1 in the presence of sodium, potassium, and ammonium chlorides. The solubility of calcium oxalate monohydrate in formate buffers of constant ionic strength has been studied. Good agreement between observed and theoretical solubilities has been found.

The Specific Heats at Low Temperatures of Anhydrous Sulfates of Iron, Magnesium, Manganese, and Potassium.[1]

BY G. E. MOORE[2] AND K. K. KELLEY[3]

The Pacific Experiment Station of the Bureau of Mines for the past year has been engaged primarily in determining thermodynamic values of substances important in the metallurgy of strategic materials, particularly manganese and chromium. It is desirable to have these data not only for compounds of these metals themselves but also for the compounds of the metals associated with them in the ores and from which they must be separated. This paper deals with low-temperature specific heat measurements of anhydrous sulfates of iron, magnesium, manganese and potassium.

Materials.—Reagent quality ferrous sulfate heptahydrate was heated slowly for several days to 125°, while evacuating with an oil-pump. It was then transferred to a high-vacuum line (mercury diffusion pump) and the heating continued. It was found necessary to heat to 235° to remove the last of the water, and some decomposition was unavoidable at this temperature. Analysis gave 37.30% Fe and 63.1% SO_4 compared with the theoretical figures 36.77 and 63.23%. Ferric iron corresponding to 1.6% Fe_2O_3 also was determined. Upon the basis of the iron analyses, which are the more significant, the purity of the sample is 98.4%. Higher purity would be desirable, but tests conducted at various stages in the dehydration process indicated that it is not possible to dry completely without decomposition. A 124.02-g. sample of this material was used in the measurements.

Reagent quality magnesium sulfate heptahydrate was dehydrated by heating in air in large nickel crucibles, the final temperature (400°) being maintained for two hours.