

Potentiometric Determination of the Solubility Product of Lead Carbonate

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A simple potentiometric pH method has been employed in the determination of the solubility product of lead carbonate. The method gave consistent values for the solubility product on both precipitation and dissolution of lead carbonate. The effect of added potassium nitrate on the solubility equilibrium was also investigated. The results are discussed on the assumption that the complex ion PbNO_3^+ is formed. Values of the first acid dissociation constant of carbonic acid in potassium nitrate solutions were determined. Extrapolation to zero ionic strength gave the value $10^{3.55}$ (25°C; $I = 0$) for the equilibrium constant of the reaction: $\text{PbCO}_3(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{CO}_2(\text{aq}) + \text{H}_2\text{O}$. Solubility product of lead carbonate was calculated to be $10^{-13.13}$ (25°C; $I = 0$).

The determinations of the solubility product of lead carbonate are relatively few in number and the conditions to which the results refer are mostly poorly specified¹. This concerns especially the partial pressure of carbon dioxide in equilibrium with the solution. A redetermination of the solubility product seemed therefore justified.

The reaction primarily studied is



Two methods were followed when carrying out the determinations. In the first method, a weighed amount of lead carbonate was allowed to stand in water through which carbon dioxide was passed. In some experiments, small amounts of strong acid were present in the solution. In the second method, carbon dioxide was passed through a lead nitrate solution to which some sodium hydroxide had been added. In both cases the pH of the solutions was measured after 2-4 days. The equilibrium constant of reaction (1)

$$K = [\text{Pb}^{2+}][\text{CO}_2]/[\text{H}^+]^2 \quad (2)$$

can be evaluated from the equations:

$$[\text{HCO}_3^-] = [\text{CO}_2]K_1/[\text{H}^+] \quad (3)$$

and

$$[\text{Pb}^{2+}] = \frac{1}{2}\{[\text{HCO}_3^-] + c_A + 2c_{\text{Pb}} - c_B - [\text{H}^+]\} \quad (4)$$

where K_1 is the apparent first acid dissociation constant of carbonic acid, c_A the total molarity of the added perchloric acid, c_{Pb} that of the added lead nitrate and c_B that of the added sodium hydroxide.

Some of the measurements were carried out without added neutral salt present and some with potassium nitrate present. This salt was chosen because the solubility of carbon dioxide in potassium nitrate solutions is known. Randall and Failey² have found that at 25°

$$\log \gamma = 0.0265 \mu \quad (5)$$

where γ is the activity coefficient of carbon dioxide and μ the ionic strength, both on the molality scale. Conversion to the molarity scale gives

$$\log y = 0.0458 I \quad (6)$$

As values of the apparent first acid dissociation constant of carbonic acid

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2] \quad (7)$$

in potassium nitrate solutions have not been determined previously, the values of the constant in 0.25, 1.00 and 2.00 molar solutions were determined. The method was as follows. Carbon dioxide was passed into a potassium nitrate solution and the solution was titrated with sodium hydroxide solution, the hydrogen ion concentration being measured after each addition of sodium hydroxide. The acid dissociation constant can be evaluated from

$$K_1 = [\text{H}^+](c_B + [\text{H}^+])/[\text{CO}_2] \quad (8)$$

where c_B is the total molarity of the added sodium hydroxide. The concentration $[\text{CO}_2]$ is obtained from

$$[\text{CO}_2] = p_{\text{CO}_2} S_o/y \quad (9)$$

where p_{CO_2} is the partial pressure of carbon dioxide in atm., S_o the Henry's law constant for carbon dioxide in pure water and y the activity coefficient. The value $3.44 \cdot 10^{-2}$ was used for the Henry's law constant S_o at 25°C³ and the value of y was computed from eqn. (6).

EXPERIMENTAL

Purified carbon dioxide gas was passed first through a spiral bubbling saturator into the solution in the titration vessel. The cover of the titration vessel had holes for tubes through which the gas entered and left the vessel, for the electrodes and for the buret. The partial pressure of carbon dioxide was obtained by subtracting the vapour pressure of the potassium nitrate solution⁴ from the barometric pressure.

The hydrogen ion concentration was measured with a Beckman 4990-83 glass electrode in combination with a calomel electrode. Two types of calomel electrode were used. When the solution under study contained no added neutral salt, the usual "saturated" electrode was used. When the solution contained potassium nitrate, the electrode vessel was filled with sodium chloride solution and the bridge with potassium nitrate solution, both equal in concentration to that of the salt in the test solution. In the former case, a 0.05 M solution of potassium hydrogen phthalate (pH = 4.01) served as the standard buffer solution. The conventional pH values obtained were converted to values

Table 1. Acetate buffers 0.005 M in acetic acid and sodium acetate at 25°C.

	$-\log [\text{H}^+]$
0.250 M KNO_3	4.535
1.000 » »	4.567
2.000 » »	4.688

of $-\log[\text{H}^+]$ by means of apparent $\text{p}f_{\text{H}^+}$ values⁵. When the test solutions contained potassium nitrate, acetate buffers 0.005 M in acetic acid and 0.005 M in sodium acetate served as standards. The three standard buffer solutions used are described in Table 1. The hydrogen ion concentrations of these buffers were determined by comparing them with the hydrogen ion concentrations of 0.005 M hydrochloric acid solutions containing the same concentrations of potassium nitrate. The values obtained were in good agreement with the values calculated from the acid dissociation constants of acetic acid determined by Ellilä⁶.

All chemicals used were of analytical grade. Several commercial preparations of lead carbonate were used and in addition a lead carbonate prepared by a method described by Centnerszwer, Falk and Awerbuch⁷. Identical results were obtained with all preparations. The analysis of the solid phase after equilibrium was reached showed it to be normal lead carbonate.

RESULTS

The accuracy obtained in the determination of the apparent first acid dissociation constant of carbonic acid in potassium nitrate solution is seen from Table 2 where data from an individual titration are shown. The values obtained for the constant K_1 are collected in Table 3. As seen from this table these values are satisfactorily represented by the equation

$$\text{p}K_1 = 6.35 - \frac{1.018 \sqrt{I}}{1 + 1.40 \sqrt{I}} + 0.055 I. \quad (10)$$

The value of $\text{p}K_1$ at zero ionic strength was taken to be 6.35. Harned and Bonner⁸ have obtained the value 6.352 and Näsänen⁹ the value 6.349, for this constant at 25°C.

The results of the determinations of the equilibrium constant of reaction (1) when no potassium nitrate was added are summarized in Table 4. The values given are means of several individual values. When dissolving lead carbonate, a small amount of perchloric acid was added since the pH measurement was then more accurate, probably because of the higher buffer capacity of the solution. The value of constant K at zero ionic strength given in Table 4 was calculated from the expression

$$\log K^\circ = \log K - 1.018 \sqrt{I}. \quad (11)$$

Table 2. Data from a titration for the determination of the apparent first acid dissociation constant of carbonic acid in a 2 M potassium nitrate solution at 25°C. $S_0 = 3.44 \times 10^{-2}$.

$c_B \times 10^3$	$-\log [\text{H}^+]$	p_{CO_2} (atm)	$1/y$	$\text{p}K_1$
5.00	5.232	0.982	0.810	5.976
7.00	5.381	0.982	0.810	5.973
10.00	5.537	0.982	0.810	5.974

Table 3. Values of the apparent first acid dissociation constant of carbonic acid in potassium nitrate solutions at 25°C.

I	$pK_1(\text{exptl.})$	$pK_1(\text{eqn. 10})$
0.257	6.059	6.064
1.007	5.991	5.982
2.007	5.973	5.979

The results of a series of measurements in a 2 M potassium nitrate solution are given in Table 5. In this case mineral acid was not added since the pH could be measured very well even without the addition. The results for potassium nitrate solutions are summarized in Table 6. The results are very satisfactorily represented by the expression

$$\log K = 3.55 + \frac{2.036 \sqrt{I}}{1 + \sqrt{I}} - \frac{1.018 \sqrt{I}}{1 + 2.20 \sqrt{I}} + 0.33 I \quad (12)$$

where the second term on the right is due to the activity coefficient of the lead ion and the third term to that of the hydrogen ion. The third term was taken somewhat arbitrarily from a previously reported equation for "the apparent activity coefficient" of the hydrogen ion⁵. The other parameters were adjusted so that eqn. (12) conformed to the experimental results as well as possible. The results could be represented satisfactorily by the following simple expression:

$$\log K = 3.55 + 1.018 \sqrt{I} + B I \quad (13)$$

but not quite so well as by expression (12).

DISCUSSION

The solubility product of lead carbonate

$$K_{sp} = [\text{Pb}^{2+}][\text{CO}_3^{2-}] \quad (14)$$

can be calculated from the expression

$$K_{sp} = K K_1 K_2 \quad (15)$$

where K is the equilibrium constant of reaction (1), K_1 the first and K_2 the second acid dissociation constant of carbonic acid. The value obtained for

Table 4. Equilibrium constant of reaction $\text{PbCO}_3(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{CO}_2(\text{aq}) + \text{H}_2\text{O}$ in dilute solutions at 25°C.

Conditions	Number of separate measurements	\sqrt{I}	$\log K$	$\log K^\circ$
185.4 mg PbCO_3 ; a small amount of strong acid added.	6	0.037	3.60	3.56
$\text{Pb}(\text{NO}_3)_2$ solution titrated with alkali hydroxide.	4	0.078	3.62	3.54
	5	0.102	3.64	3.54
	4	0.104	3.67	3.56
				mean 3.55

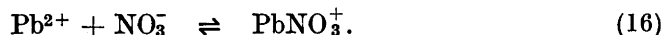
Table 5. Values of the equilibrium constant of reaction $\text{PbCO}_3(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{CO}_2(\text{aq.}) + \text{H}_2\text{O}$ in a 2 M potassium nitrate solution at 25°C.

PbCO ₃ , mg	Standing period, h	$-\log[\text{H}^+]$	p_{CO_2} , atm.	$1/\gamma$	$\log K$
140.2	23	4.820	0.989	0.810	5.063
135.2	52	4.825	0.965	0.810	5.055
101.7	26	4.825	0.968	0.810	5.059
130.0	23	4.823	0.968	0.810	5.053

the solubility product at zero ionic strength when the above value $\log K^0 = 3.55$, the value $^{8,9} pK_1^0 = 6.35$ and the value $pK_2^0 = 10.33$ determined by Harned and Scholes¹⁰ were substituted in (15) was $pK_{\text{sp}}^0 = 13.13$. ($I = 0$, 25°C). For the second acid dissociation constant pK_2^0 of carbonic acid, Näsänen¹¹ obtained the value 10.32 at 25°C.

Recently Uggla¹² determined the solubility product of lead carbonate conductometrically and obtained the value $pK_{\text{sp}}^0 = 13.23$ (25°C). From the data in a compilation of the National Bureau of Standards¹³ one can calculate the value $pK_{\text{sp}}^0 = 13.0$ (25°C). The partial pressure of carbon dioxide in equilibrium with the solution has not been specified in the earlier determinations and the older data for the solubility product must therefore be regarded as unreliable^{1,14}.

The effect of neutral salt additions on the solubility equilibrium of lead carbonate has not been studied before. In Fig. 1 the equilibrium constant K of reaction (1) is plotted as a function of ionic strength. The limiting slope according to the Debye-Hückel theory is also drawn in the figure. As is seen $\log K$ is always higher than expected from Debye's limiting law. This is not, however, at variance with the Debye-Hückel theory since $\log K$ is given very satisfactorily by eqn. (12). On the other hand, it is likely, as has been claimed¹⁵, that lead and nitrate ions form a complex as follows:



If this reaction is considered to take place, one obtains for the "true" constant of reaction (1) the expression

$$K' = K / (1 + \frac{1}{2}\beta_1[\text{NO}_3^-]) \quad (17)$$

where K is the above apparent equilibrium constant of reaction (1) and β_1 is defined by

$$\beta_1 = [\text{PbNO}_3^+] / [\text{Pb}^{2+}][\text{NO}_3^-] \quad (18)$$

Table 6. Values of the equilibrium constant of reaction $\text{PbCO}_3(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{CO}_2(\text{aq.}) + \text{H}_2\text{O}$ in potassium nitrate solutions at 25°C.

I	$\log K$ (exptl.)	$\log K$ (eqn. 12)
0.251	4.076	4.070
1.002	4.581	4.581
2.002	5.058	5.053

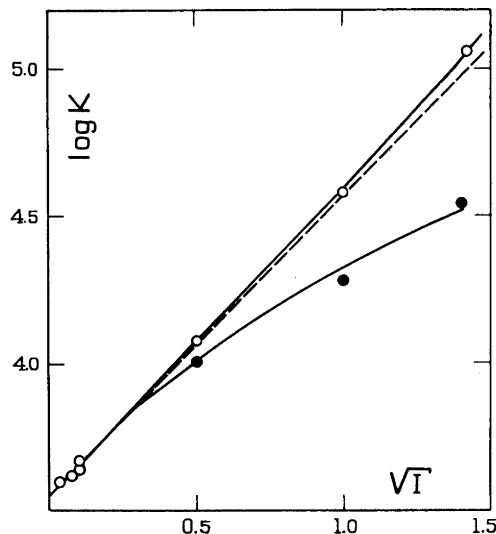


Fig. 1. Equilibrium constant of reaction (1) as a function of ionic strength. O, apparent constant; ●, "true" constant; — — —, limiting Debye-Hückel plot.

The "true" constant K' can be calculated from eqn. (17) if the stability constant β_1 is known. Using the values $\log \beta_1 = 0.25$ in 0.5 M, $\log \beta_1 = 0.31$ in 1 M, and $\log \beta_1 = 0.36$ in 2 M perchloric acid solution, determined by Biggs, Parton and Robinson¹⁶, the values plotted in Fig. 1 were obtained for the "true" constant. These values of the "true" constant are approximate and reveal only the direction of the effect of reaction (16).

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