

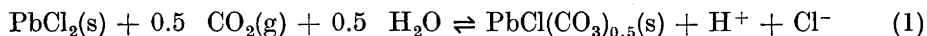
Potentiometric Study of a Synthesis of Phosgenite

R. NÄSÄNEN, P. MERILÄINEN and R. HAVANKA

Department of Chemistry, University of Helsinki, Helsinki, Finland

The stability of phosgenite in contact with an aqueous solution of carbon dioxide was investigated. With this purpose the equilibria $\text{PbCl}_2(\text{s}) + 0.5 \text{CO}_2(\text{g}) + 0.5 \text{H}_2\text{O} \rightleftharpoons \text{PbCl}(\text{CO}_3)_{0.5}(\text{s}) + \text{H}^+ + \text{Cl}^-$ and $\text{PbCl}(\text{CO}_3)_{0.5}(\text{s}) + 0.5 \text{CO}_2(\text{g}) + 0.5 \text{H}_2\text{O} \rightleftharpoons \text{PbCO}_3(\text{s}) + \text{H}^+ + \text{Cl}^-$ at 25°C were studied. The respective equilibrium constants were determined by the pH method. The value $10^{-9.99}$ ($I = 0$; 25°C) was calculated for the solubility product of phosgenite, $\text{PbCl}(\text{CO}_3)_{0.5}$, from the equilibrium constant of the first reaction and known data for lead chloride and carbonic acid. The value $10^{-9.84}$ ($I = 0$, 25°C) was obtained for this constant from the equilibrium constant of the second reaction and data for lead carbonate and carbonic acid.

The equilibria of phosgenite, $\text{PbCl}(\text{CO}_3)_{0.5}$, and lead chloride or lead carbonate in contact with an aqueous solution of carbon dioxide have apparently not been studied before although methods for the preparation of phosgenite were presented long ago¹. The reaction in question are



and



We have investigated these systems proceeding, for the present, from lead chloride only. The method was as follows. A weighed amount of lead chloride was allowed to stand in water to which a given amount of sodium hydroxide had been added and through which carbon dioxide was passed. The pH of the solution was measured and the solid phase was analyzed after equilibrium was reached. The results of one series of such experiments are shown in Fig. 1 where the logarithm of hydrogen ion concentration is plotted as a function of the mole ratio of sodium hydroxide and lead chloride added to the solution. The curve has two buffer ranges of which the lower one is due to reaction (1) and the higher one to reaction (2). When equimolar amounts of lead chloride and sodium hydroxide were used, the solid phase consisted only of well-formed crystals of phosgenite.

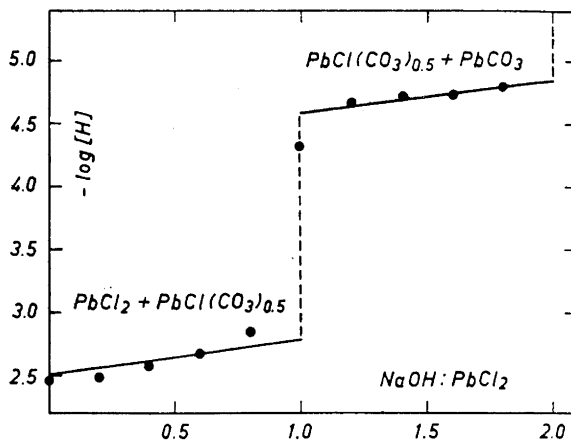


Fig. 1. A plot of $-\log[\text{H}]$ against the mole ratio of sodium hydroxide and lead chloride. $p_{\text{CO}_2} = \text{about } 1 \text{ atm.}$

The equilibrium constant of reaction (1)

$$K_p = [\text{H}] [\text{Cl}]/p_{\text{CO}_2} \quad (3)$$

can be calculated from experimental values of $\log [\text{H}]$ and p_{CO_2} , referring to the lower buffer range and the calculated value of $[\text{Cl}]$. The last quantity was calculated by iteration from the equation

$$[\text{Cl}] = \{2 K_{\text{sp}} + K_{\text{sp}}\beta_1 [\text{Cl}] + (c_{\text{B}} + [\text{H}])([\text{Cl}]^2)^{1/2}\} \quad (4)$$

where c_{B} is the total concentration of added sodium hydroxide, K_{sp} the solubility product of lead chloride and $\beta_1 = [\text{PbCl}]/[\text{Pb}][\text{Cl}]$. The value of K_{sp} for the ionic strength in question was calculated from the equation

$$pK_{\text{sp}} = pK_{\text{sp}}^{\circ} - \frac{3.054 \sqrt{I}}{1 + \alpha \sqrt{I}} \quad (5)$$

and the stability constant β_1 from

$$\log \beta_1 = \log \beta_1^{\circ} - \frac{2.036 \sqrt{I}}{1 + \alpha \sqrt{I}} \quad (6)$$

Table 1. Computation of the equilibrium constant of reaction (1) at 25°C. $p_{\text{CO}_2} = 0.976 \text{ atm.}$

$c_{\text{B}} \cdot 10^2$	$-\log[\text{H}]$	\sqrt{I}	pK_{sp}	$\log \beta_1$	$[\text{Cl}] \cdot 10^2$	$[\text{Pb}] \cdot 10^2$	$[\text{PbCl}] \cdot 10^2$	pK_p	pK_p°
1.920	2.49	0.288	4.17	1.22	6.81	1.46	1.65	3.65	3.84
3.840	2.59	0.298	4.16	1.21	7.81	1.14	1.44	3.68	3.87
5.747	2.68	0.315	4.14	1.20	9.01	0.893	1.27	3.71	3.91
7.667	2.85	0.332	4.12	1.18	10.33	0.711	1.11	3.83	4.03
								Mean	3.91

Table 2. Computation of the equilibrium constant of reaction (2) at 25°C. $p_{\text{CO}_2} = 0.967$ atm.; $pS^\circ = 1.464$.

c_B	\sqrt{I}	pK_1	pK_2	$-\log[H]$	$[HCO_3^-]$	$[Cl^-]$	pK'_p	pK_p°
0.115	0.339	6.12	9.88	4.66	0.0011	0.114	5.59	5.79
0.134	0.366	6.11	9.86	4.73	0.0014	0.133	5.59	5.80
0.154	0.392	6.10	9.83	4.73	0.0014	0.153	5.53	5.75
0.173	0.416	6.09	9.82	4.79	0.0017	0.171	5.54	5.78
							Mean	5.78

For pK_{sp}° the value 4.73 (at 25°C) was used. It is the mean of Fromherz's value² 4.67 and Nobel and Garrett's value² 4.79. For $\log \beta_1^\circ$ the value 1.59 was used. It is the mean of several values ranging from 1.42 to 1.75 taken from the literature². The higher chlorocomplexes were neglected. For the parameter α the value 2 was chosen somewhat arbitrarily. The results relating to the first buffer range are given in Table 1. The ionic strength given in the table was calculated from $I = \frac{1}{2} \sum c_i z_i^2$. The values of pK_p were extrapolated to zero ionic strength with the aid of the equation

$$pK_p^\circ = pK_p + \frac{1.018 \sqrt{I}}{1 + \alpha \sqrt{I}} \quad (7)$$

For the parameter α the value 2 was again used.

The equilibrium constant of reaction (2)

$$K'_p = [H] [Cl^-] / p_{\text{CO}_2} \quad (8)$$

was computed from experimental values of $[H]$ and p_{CO_2} , referring to the higher buffer range of the curve in Fig. 1 and the calculated value of $[Cl^-]$. For the calculation of $[Cl^-]$, the equation

$$[Cl^-] = c_B - [HCO_3^-] + 2 [Pb] + [PbCl] \quad (9)$$

was derived. However, the last two terms on the right-hand side of eqn. (9) can be neglected and also $[HCO_3^-]$ is only about one per cent of c_B . The values of these terms were calculated from the equations

$$[CO_2] = Sp_{\text{CO}_2} \quad (10)$$

$$[HCO_3^-] = K_1 [CO_2] / [H] \quad (11)$$

$$[CO_3^{2-}] = K_2 [HCO_3^-] / [H] \quad (12)$$

$$[Pb] = K'_{sp} / [CO_3^{2-}] \quad (13)$$

$$[PbCl] = \beta_1 [Pb] [Cl^-] \quad (14)$$

where S is the Henry's law constant, K_1 and K_2 the first and second acid dissociation constants of carbonic acid, K'_{sp} the solubility product of lead carbonate and $\beta_1 = [PbCl] / [Pb] [Cl^-]$. The values of the equilibrium constants of carbonic acid were obtained from

$$pK_1 = 6.35 - \frac{1.018 \sqrt{I}}{1 + 1.40 \sqrt{I}} + 0.055 I \quad (15)$$

$$pK_2 = 10.33 - \frac{2.036 \sqrt{I}}{1 + 1.49 \sqrt{I}} + 0.055 I \quad (16)$$

For the Henry's law constant, the value $S^\circ = 3.44 \times 10^{-2}$ for pure water was used³. The value $pK_1^\circ = 6.35$ at zero ionic strength stems from measurements of Harned and Bonner⁴ (6.352) and Näsänen⁴ (6.349) and the value $pK_2^\circ = 10.33$ from measurements of Harned and Scholes⁵. Näsänen⁵ obtained the value 10.32 for the latter constant. The other coefficients in eqns. (15) and (16) were taken from investigations of Näsänen and co-workers^{5,6} and the values of the solubility product of lead carbonate from a paper of Näsänen and Meriläinen⁶.

The solubility product of phosgenite

$$K_{sp} = [\text{Pb}] [\text{Cl}] [\text{CO}_3]^{1/2} \quad (17)$$

can be evaluated from the expression

$$pK_{sp}^\circ = pK_{sp}^\circ(\text{PbCl}_2) + 0.5 pS^\circ + 0.5 pK_1^\circ + 0.5 pK_2^\circ - pK_p^\circ \quad (18)$$

as well as from

$$pK_{sp}^\circ = pK_{sp}^\circ(\text{PbCO}_3) + pK_p'^\circ - 0.5 pS^\circ - 0.5 pK_1^\circ - 0.5 pK_2^\circ \quad (19)$$

Using the values given above for the constants, we obtained in the first case

$$pK_{sp}^\circ = 4.73 + 0.73 + 3.18 + 5.16 - 3.91 = 9.89.$$

and in the second case

$$pK_{sp}^\circ = 13.13 + 5.78 - 0.73 - 3.18 - 5.16 = 9.84.$$

The agreement between these two independent results is thus very good considering the uncertainty of the values of the solubility products of lead chloride and lead carbonate as well as of the values of K_p and K_p' . The extrapolation of K_p and K_p' to zero ionic strength is also somewhat arbitrary. For example, if we use the value 1 instead of 2 for α in eqn. (7), we obtain in the first case $pK_{sp}^\circ = 9.85$ and in the second case $pK_{sp}^\circ = 9.90$. It is obvious that the values originating from the higher buffer range are more accurate. A more thorough study of the equilibrium in this buffer range is in progress.

REFERENCES

1. Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London 1930, Vol. 7, p. 852.
2. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Stability Constants of Metal-ion Complexes. Part II: Inorganic Ligands*. London 1958, p. 108.
3. Harned, H. S. and Davis, R. *J. Am. Chem. Soc.* **65** (1943) 2030.
4. Harned, H. S. and Bonner, T. *J. Am. Chem. Soc.* **67** (1945) 1026; Näsänen, R. *Acta Chem. Scand.* **1** (1947) 204.
5. Harned, H. S. and Scholes, S. R. *J. Am. Chem. Soc.* **63** (1941) 1706. Näsänen, R. *Suomen Kemistilehti* **B 19** (1946) 90.
6. Näsänen, R., Meriläinen, P. and Leppänen, K. *Acta Chem. Scand.* **15** (1961) 913.

Received March 8, 1962.