of diffusion of colored solutions into gels, with and without adsorption, are described. The rate of diffusion follows a simple mathematical law.

2. The rate of diffusion is a simple function of the concentration of the solution. The influence of temperature upon both types of diffusion is discussed.

3. Considerable differences between the rates of diffusion in upward and in downward direction can be observed under certain conditions. The application of the term "barophoresis" is suggested for this phenomenon. For a given system consisting of a gel and a diffusing substance, a critical concentration of the latter is found at which the sense of barophoresis is reversed.

4. The specific gravities of the intermicellular fluids of various gels are indirectly determined. They coincide with the specific gravities of the corresponding critical concentrations.

NEW YORK, N. Y.

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SOLUBILITY OF LEAD MONOXIDE AND BASIC LEAD CARBONATE IN ALKALINE SOLUTIONS

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Heretofore no attempt has been made to prepare a comprehensive table of the free energies of formation of the compounds of the metallic elements. From a cursory search of the literature it was seen that data were available from which the free energies of formation of a large number of compounds of lead could be calculated. These values are particularly interesting because of the technical importance of lead, its amphoteric character and its marked tendency to form "basic" compounds. We have therefore undertaken a systematic investigation of the free energy of the lead compounds. The new equilibria measured are those between the basic carbonate, the hydrated monoxide, the red and yellow monoxides and the plumbite ion. The results of these measurements will be given in the present paper.

Berl and Austerweil[1] measured the solubility in sodium hydroxide solutions of lead monoxide prepared by heating pure basic lead carbonate. Their results appeared untrustworthy since the value of the solubility in pure water was much higher than that obtained by other investigators. Their oxide was evidently neither the most stable form[2] nor the most important. Only the dissolved lead was determined, and the amount of sodium hydroxide in the solutions was calculated according to assumptions which we shall show to be erroneous.

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[1] Berl and Austerweil, *Z. Elektrochem.*, **13**, 165 (1907).

[2] A discussion of the allotropy of lead monoxides will be given in a later paper.

Glasstone[3] measured the solubility of the red form in sodium hydroxide solutions of varying concentration and found the solubility, in normal solutions, only slightly different from that of the yellow form. The measurements with normal solutions were carried out at room temperature. The liquid was gently stirred over the surface of the solid, without disturbing the latter, by means of a current of air free from carbon dioxide. In the series of determinations using the red form, solutions which were considered supersaturated were merely placed in contact with the solid phase, without stirring, in a thermostat at 25°. He concluded that the two forms were identical, and attributed his observed differences[4] to a variation in the size of the particles. Applebey and Reid[5] repeated the measurements in normal solutions. They used carefully prepared oxides and qualitatively confirmed the measurements of Ruer[6] who had found different solubilities for the two forms in water. Berl and Austerweil[1] have also shown that in hydroxide solutions below one molal or thereabouts, the lead monoxide forms the monoplumbite ion in accordance with the reaction

$$\mathrm{PbO(s)} + \mathrm{KOH(aq)} = \mathrm{KHPbO_2(aq)} \qquad (1)$$

but from their data it was impossible to evaluate accurately the constant of the reaction, and it was decided to redetermine the solubility of the red and yellow forms of the monoxide.

Rubenbauer,[7] Wood[8] and Glasstone[9] determined the solubilities of the hydrated lead monoxide at 18 and 25°. These investigators assumed the concentration of the sodium hydroxide in the final solution to be that of the original solution, less the concentration of the lead hydroxide dissolved in excess of its solubility in water. Rubenbauer and Wood shook their mixtures continuously but only for short periods. Apparently equilibrium was not attained in any case, as our experiments show concentrations of lead about 50% higher. Because of the uncertainty respecting the composition of the solid phase and the lack of sufficient analytical data, these experiments have been repeated.

The solubility of the basic lead carbonate,[10] in potassium hydroxide solutions was also studied. This is a condensed system of four components two phases and therefore three degrees of freedom. Starting with carbon

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[3] Glasstone, *J. Chem. Soc.*, **119**, 1689 (1921).

[4] Larger differences were obtained in shaking experiments, but these were not considered equilibrium values.

[5] Applebey and Reid, *J. Chem. Soc.*, **121**, 2129 (1922).

[6] Ruer, *Z. anorg. Chem.*, **50**, 265 (1906).

[7] Rubenbauer, *Z. anorg. Chem.*, **30**, 336 (1902).

[8] Wood, *J. Chem. Soc.*, **97**, 884 (1910).

[9] Glasstone, *J. Chem. Soc.*, **121**, 58 (1921).

[10] The individuality of the basic lead carbonate, $\mathrm{Pb_3(CO_3)_2(OH)_2}$, has been established by the work of Pleissner, *Arb. kais. Gesundh.*, **26**, 384 (1907).

dioxide free solutions only one degree remains if the temperature is fixed, and the analysis for total alkalinity and lead is sufficient to determine the system. The equilibrium involved may be represented by

$$Pb_3(CO_3)_2(OH)_2(s) + 7KOH(aq) = 3KHPbO_2(aq) + 2K_2CO_3(aq) + 3H_2O(l) \quad (2)$$

Preparation of Materials.—The red and yellow forms of lead monoxide were prepared by dehydrating the hydrated monoxides by a modification of the method described by Geuther[11] and by Ruer.[6] At temperatures just below the boiling point the red modification was obtained when the concentration of the hydroxide was about 12 *M* and the yellow form when it was about 5 *M*. Hydrated lead monoxide prepared and purified as described below was heated[12] with the sodium hydroxide solution in a flask provided with an air condenser and a soda lime tube to prevent the access of carbon dioxide. The products in each case were of uniform color. The solids were washed by decantation with boiling water a large number of times. They were stored under conductivity water.

The hydrated lead monoxide was prepared according to the method of Pleissner.[10] It was washed thoroughly by decantation with conductivity water. Some of the solid thus obtained was dried to constant weight in a vacuum desiccator over sulfuric acid. On analysis we found 89.8% of lead, compared with 90.39% calculated for $3PbO \cdot H_2O$ and 89.22% calculated for $2PbO \cdot H_2O$.[13] This was considered satisfactory owing to the difficulty of removing the last traces of water. The composition of this hydrated lead monoxide is to be further discussed in a later paper.

The basic lead carbonate was prepared by the method of Auerbach and Pick.[14] Lead sulfate was shaken with successive portions of dilute sodium carbonate solutions. It was washed and stored as were the above solids. Analyses for lead were made on samples dried in a vacuum desiccator. The agreement between the values found, 80.0, 80.9 and 80.8% of lead and 80.13 % calculated from the formula was considered quite satisfactory.

Procedure.—Samples of the solid phases, usually between 15 and 25 g., were transferred with some of the water under which they were kept to long-necked, round-bottomed flasks kept free from air by a slow stream of nitrogen. This precaution was not taken in a few experiments, but the results did not differ appreciably. The solids were then washed several times with portions of the solution with which they were to be shaken. Finally, the flask was filled almost to the neck and the end of the neck sealed off.

The flasks were rotated in a thermostat at 25 ± 0.05°, according to the method described by Randall and Vietti.[15] When the equilibrium was to be approached from

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[11] Geuther, *Ann.*, **219**, 56 (1883).

[12] This method is similar to the one employed by Applebey and Reid.

[13] Müller, *Z. physik. Chem.*, **114**, 129 (1924), found 89.75 % of Pb.

[14] Auerbach and Pick, *Arb. kais. Gesundh.*, **45**, 113 (1913).

[15] Randall and Vietti, This Journal, **50**, 1526 (1928).

supersaturation, the flasks were first shaken for several weeks in a thermostat at 32°, the shaker of which was governed by an eccentric rod and gave a jerking vertical motion to the flasks. The period of rotation varied from one week to several months. In general, four to six weeks were allowed for the attainment of equilibria in experiments which were to be considered final.

Analysis of Liquid Phase.—The method of sampling was similar to that described by Randall and Vietti.[15] The total alkalinity was determined by weight titrations using methyl orange as an indicator. Standardized hydrochloric acid solution was added in slight excess and final adjustment to the first appearance of orange from the yellow side was made by alternate additions of hydrochloric acid and sodium hydroxide. The lead was first precipitated as the hydrated oxide but the precipitate dissolved completely before the end-point was reached. The hydroxide was neutralized and the carbonate in the solutions from basic carbonate was changed to carbon dioxide.

Lead was determined by the precipitation of lead chromate. The neutralized solutions were heated to boiling and transferred to Pyrex beakers. Each flask was rinsed first with boiling water to which a few drops of glacial acetic acid had been added, then with two small portions of boiling water. A few cc. of 1*M* sodium acetate were added. After the solution had been heated to boiling, the addition of potassium chromate was made a little at a time. Gentle boiling was continued until the precipitate had taken on a shade of orange and settled completely, leaving a clear solution. The precipitate was collected and washed on Gooch crucibles which had been alternately washed and dried to constant weight. The oven used was kept at 135°.

Analysis of the Solid Phase.—The solid phase left after sampling was transferred along with some of the equilibrium solution to a weighed beaker and immediately weighed. The beakers were then put in a vacuum desiccator and were dried to constant weight. From the loss of weight the amount of water and thence the amount of dissolved salts and other solutes associated with it were calculated. The solid was analyzed for lead, corrections being made for the solutes from the liquid phase.

The Equilibrium Constants.—As a first approximation, we may assume that the total lead in the equilibrium solution is in the form of $HPbO_2^-$ and that this is completely converted to Pb^{++} in the titration

$$HPbO_2^- + 3H^+ = 2H_2O + Pb^{++} \qquad (3)$$

Three moles of hydrochloric acid are thus used to change each mole of dissolved lead. Since in the solutions from the basic carbonate equilibria (Equation 2) the concentration of the carbonate ion is two-thirds that of the dissolved lead, the number of moles of hydrochloric acid required to decompose the carbonate ion is four-thirds the number of moles of dissolved lead present. The total amount of hydrochloric acid used, less the sum of the amounts necessary to change $HPbO_2^-$ to Pb^{++} and CO_3^{--} to H_2CO_3, gives the approximate concentration of the hydroxide ion. All concentrations are given in moles per 1000 g. of water and vacuum corrections are used throughout.

While the principle of the ionic strength as enunciated by Lewis and Randall[16] has not been experimentally studied in the case of these compounds we may as an approximation assume that the activity coefficient of a given

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[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, pp. 373, 380 and 382.

salt is the same in all solutions of the same ionic strength. Since the potassium ion does not take part in the reactions, no further error is introduced by utilizing the principle of the independent activity coefficient of the ions. We shall assume that the activity coefficient of $HPbO_2^-$ is the same as that of NO_3^-, and use the preliminary revised values of the activity coefficients which are now being compiled in this Laboratory. We shall find that the values of the equilibrium constants on these assumptions vary somewhat with the ionic strength, owing to experimental errors and to the fact that the above assumptions are not exact. These differences become smaller at the lower ionic strengths.

As a first approximation we may assume the ionic strength to be given by the following equation,

$$\mu = m'(\mathrm{KOH}) + m'(\mathrm{KHPbO_2}) + 3m'(\mathrm{K_2CO_3}) \qquad (4)$$

where values of $m'(\mathrm{KOH})$, etc., are the approximate molalities obtained as above and we shall find that the values of the ionic strength thus calculated are the same as the final value.

The assumption that the lead is converted completely to lead ion in the titration is justified by the following considerations. Pleissner[10] measured the conductivity of solutions of the hydrated lead monoxide at 18° and found 4×10^{-5} for the first dissociation constant as a base and approximately 2×10^{-9} for complete dissociation. Using the dissociation constant of water, $K_{291} = 0.58 \times 10^{-14}$, we have

$$\mathrm{Pb(OH)_2 + H^+ = PbOH^+ + H_2O};\; K_{291} = 6.9 \times 10^{9} \qquad (5)$$

$$\mathrm{PbOH^+ = Pb^{++} + OH^-};\; K_{291} = 5 \times 10^{-5} \qquad (6)$$

At the end-point in the methyl orange titration the hydrogen-ion concentration is approximately 10^{-4}. Therefore $m(\mathrm{PbOH^+}) = 2 \times 10^{-6} m(\mathrm{Pb^{++}})$ and $m(\mathrm{Pb(OH)_2}) = 3 \times 10^{-12} m(\mathrm{Pb^{++}})$.

We may now consider the distribution of the dissolved lead in the equilibrium solutions among its possible forms. Berl and Austerweil[1] have shown the dissociation constant of lead hydroxide as a monobasic acid to be about 10^{-12}. In a later paper we shall find

$$\mathrm{Pb(OH)_2(aq) = H^+ + HPbO_2^-};\; K_{298} = a(\mathrm{H^+}) \times a(\mathrm{HPbO_2^-})/a(\mathrm{Pb(OH)_2}) = 1.2 \times 10^{-12} \qquad (7)$$

or, combining with the dissociation constant of water

$$\mathrm{Pb(OH)_2(aq) + OH^- = HPbO_2^- + H_2O};\; K_{298} = a(\mathrm{HPbO_2^-})/a(\mathrm{Pb(OH)_2}) \times a(\mathrm{OH^-}) = 120 \qquad (8)$$

Taking the activity of the dissolved lead hydroxide equal to its molality, we find

$$m(\mathrm{Pb(OH)_2}) = m\gamma\,(\mathrm{HPbO_2^-})/120m\,\gamma\,(\mathrm{OH^-}) \qquad (9)$$

In a similar way the ratio $m(\mathrm{PbOH^+})/m(\mathrm{HPbO_2^-})$ was calculated from the above ratio and the first dissociation of lead hydroxide as a base. In this calculation it was assumed that $a(\mathrm{PbOH^+}) = m(\mathrm{PbOH^+})$. Thus

$$m(\mathrm{PbOH^+}) = m\gamma(\mathrm{HPbO_2^-}) \times 4 \times 10^{-5}/120m^2\,\gamma^2(\mathrm{OH^-}) \qquad (10)$$

The sum of the molalities of the three forms of dissolved lead is equal to the total molality obtained by analysis.

$$\text{Pb} = m(\text{HPbO}_2^-) + m(\text{Pb(OH)}_2) + m(\text{PbOH}^+) \qquad (11)$$

Using values of $m'(\text{OH}^-)$ obtained as a first approximation and Equations 9, 10 and 11, preliminary values of $m(\text{HPbO}_2^-)$, $m(\text{Pb(OH)}_2)$ and $m(\text{PbOH}^+)$ were calculated.

Since the hydroxide ion concentration used in the above calculation might have been too low, the distribution among the various forms of lead so obtained would not be exact. Therefore we make a third approximation in which the hydroxide ion concentration used is calculated from the total alkalinity and the values of $m(\text{HPbO}_2^-)$, $m(\text{Pb(OH)}_2)$ and $m(\text{PbOH}^+)$ found above and $m(\text{CO}_3^{--})$ when the basic lead carbonate solutions are considered. Even in the solutions of lowest hydroxide concentration, where values of $m(\text{PbOH}^+)$ should be the greatest, they were found to be negligible (of the order $10^{-6}M$) and were therefore neglected. The third approximation yielded values of $m(\text{OH}^-)$ which did not differ from the values found by the second approximation, and values of $m(\text{HPbO}_2^-)$ and $m(\text{Pb(OH)}_2)$ which differed only slightly from those of the second approximation.

The results of the measurements with red lead monoxide are given in Table I. In the first column the letter U indicates that equilibrium was approached from undersaturation, and the letter S from supersaturation.

TABLE I

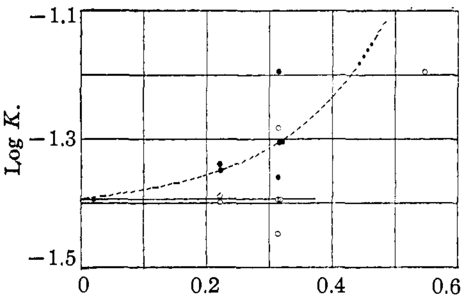
SOLUBILITY OF RED LEAD MONOXIDE (TETRAGONAL) IN POTASSIUM HYDROXIDE SOLUTIONS AT 25°. $\text{PbO (red)} + \text{OH}^- = \text{HPbO}_2^-$

No. of expt.	Days of rotation	0.5023 *M* HCl to 1 g. of soln., g.	PbCrO_4 to 1 g. of soln., g.	Pb in solid phase, %	$m'(\text{OH}^-)$ 1st approx.	$m'(\text{HPbO}_2^-)$ 1st approx.
1U	28	0.1100	0.0008085	92.8	0.04665	0.002516
2S[a]	20	.1090	.0008105	...	.04615	.002516
3S[a]	20	.2258	.002077	92.7	.09229	.006468
4U	24	.2222	.001644	92.72	.09448	.005121
5S[a]	38	.2268	.001679	...	.09645	.005231
6U	28	.2176	.001443	...	.09409	.004493
7U	50	.7043	.009157	...	.2687	.02899

No. of expt.	$\mu^{1/2}$	$-\log \gamma$ (OH^-)	$-\log \gamma$ (HPbO_2^-)	$m(\text{OH}^-)$ final	$m(\text{HPbO}_2^-)$ final	$\log K_m$	$\log K$
1U	0.222	0.0800	0.1311	0.04705	0.002110	−1.3483	−1.3994
2S[a]	.221	.0800	.1311	.04587	.002102	−1.3388	−1.3890
3S[a]	.314	.0980	.1865	.09278	.005933	−1.1942	−1.2827
4U	.316	.0982	.1880	.09490	.004703	−1.3048	−1.3946
5S[a]	.319	.0986	.1895	.09686	.004808	−1.3042	−1.3951
6U	.314	.0980	.1865	.09433	.004125	−1.3592	−1.4477
7U	.546	.110	.325	.2694	.02823	−0.9799	−1.1949

[a] In Expts. 2 and 3 the solutions were rotated for fifteen days at 32° and in Expt. 5, twenty-one days at 32°, and were then transferred to a thermostat at 25° and rotated for the time indicated in Col. 2.

The second column gives the number of days of rotation, the third the number of grams of $0.5023M$ hydrochloric acid required to neutralize one gram of the solution, the fourth the number of grams of lead chromate precipitated from one gram of the solution and the fifth the percentage of lead in the solid phase (PbO; Pb = 92.8%). Columns 6 to 12 give, respectively, the molality of the OH^- (first approx.); the molality of $HPbO_2^-$ (1st approx.); $\mu^{1/2}$; the logarithm of the activity coefficient of the OH^-, and that of the $HPbO_2^-$; the final value of the molality of the OH^-, and that of the $HPbO_2^-$. Column 13 gives the value of log $K_m = \log\,[m(HPbO_2^-)/m(OH^-)]$, and the last column gives the logarithm of the equilibrium constant, $K_{298} = (HPbO_2^-)/(OH^-)$.



Square root of ionic strength.

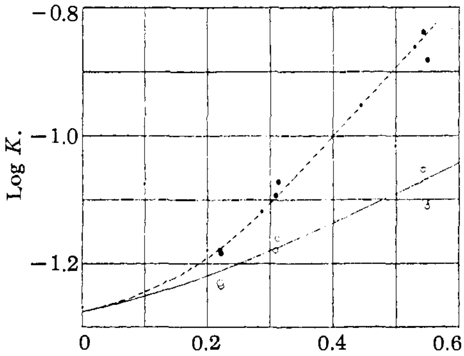
○, Log K; ●, Log K_m.

Fig. 1.—Solubility of red lead monoxide in aqueous potassium hydroxide.

The values of log K are plotted as circles in Fig. 1, and those of log K_m as dots. If the assumption that $\gamma\ (HPbO_2^-) = \gamma\ (NO_3^-)$ is correct, then the values of log K should not change with the ionic strength. If the activity coefficient of potassium hydroxide is the same as that of potassium plumbite, then K_m should equal K. In either case the values should approach the same constant value as the concentration diminishes. The agreement of the results is excellent and we shall choose log $K_{298} = -1.394$, $K = 0.0402$, whence

$$PbO(red) + OH^- = HPbO_2^-;\quad \Delta F^\circ_{298} = 1903 \text{ cal.} \quad (12)$$

The solubility of the yellow form is given in Table II, in which the column headings are the same as those of Table I. The values of log K_m and log K are plotted in Fig. 2 as in the previous plot.



Square root of ionic strength.

○, Log K; ●, Log K_m.

Fig. 2.—Solubility of yellow lead monoxide in aqueous potassium hydroxide.

The results of these measurements are not as satisfactory as those obtained with the red form and we can offer no explanation of the reason why the values of K are not constant. No change in the appearance of

TABLE II

SOLUBILITY OF YELLOW LEAD MONOXIDE (ORTHORHOMBIC) IN POTASSIUM HYDROXIDE SOLUTIONS AT 25°. $PbO\ (yellow) + OH^- = HPbO_2^-$

No. of expt.	Days of rotation	0.5023 M HCl to 1 g. of soln., g.	$PbCrO_4$ to 1 g. of soln., g.	Pb in solid phase, %	$m'(OH^-)$ 1st approx.	$m(HPbO_2^-)$ 1st approx.
1U	30	0.1143	0.001134	...	0.04577	0.003522
2S[a]	20	.1130	.001132	92.76	.04515	.003516
3S[a]	20	.2306	.002632	92.7	.08946	.008203
4U	28	.2253	.002483	92.7	.08820	.007738
5U	50	.7247	.01112	...	.2662	.03599
6S	50	.7369	.01207	...	.2560	.03827

No. of expt.	$\mu^{1/2}$	$-\log \gamma$ (OH^-)	$-\log \gamma$ $(HPbO_2^-)$	$m(OH^-)$ final	$m(HPbO_2^-)$ final	Log K_m	Log K
1U	0.222	0.0802	0.1314	0.04627	0.003031	−1.1838	−1.2349
2S[a]	.221	.0802	.1313	.04565	.003020	−1.1794	−1.2305
3S[a]	.313	.0978	.1840	.09004	.007611	−1.0730	−1.1612
4U	.310	.0975	.1840	.08877	.007171	−1.0927	−1.1792
5U	.550	.1080	.327	.2671	.03503	−0.8823	−1.1013
6S	.543	.1081	.323	.2569	.03725	−0.8387	−1.0536

[a] In Expt. 2 the solution was rotated for fifteen days at 32°; in Expt. 3, seventeen days at 32°, and then transferred to a thermostat at 25° and rotated for the time indicated in Col. 1.

the solid phase was evident, although it is possible that some change may have taken place since a trend in the value of K with changing values of μ is clearly shown. We shall choose the value $\log K_{298} = -1.275$, $K_{298} = 0.0531$, whence

$$PbO(yellow) + OH^- = HPbO_2^-;\ \Delta F^\circ_{298} = 1740 \text{ cal.} \tag{13}$$

The solubility of the hydrated lead monoxide is given in Table III and Fig. 3. The column headings are again the same as those of Table I.

TABLE III

SOLUBILITY OF HYDRATED LEAD MONOXIDE IN POTASSIUM HYDROXIDE SOLUTIONS AT 25°. $PbO\cdot{}^1/_3H_2O(s) + OH^- = HPbO_2^- + {}^1/_3H_2O(1)$

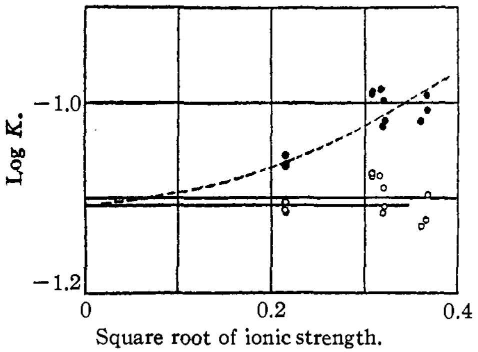
No. of expt.	Days of rotation	0.5023 M HCl to 1 g. of soln., g.	$PbCrO_4$ to 1 g. of soln., g.	Pb in solid phase, %	$m'(OH^-)$ 1st approx.	$m'(HPbO_2^-)$ 1st approx.
1S[a]	5	0.1115	0.001392	...	0.04197	0.004323
2S[a]	20	.1115	.001418	87.61	.04174	.004403
3U	30	.1114	.001385	...	.04265	.004301
4S[a]	37	.2305	.003059	85.80	.08543	.009535
5S[a]	21	.2298	.003060	...	.08507	.009538
6U	16	.2408	.003242	85.99	.09022	.01011
7S[a]	26	.2468	.003211	...	.09211	.01001
8U	31	.2472	.003102	85.69	.09411	.009674
9S[a]	30	.2438	.003031	...	.09310	.009451
10U	18	.3098	.003833	85.60	.1177	.01198
11U	33	.3221	.004060	...	.1277	.01269
12S[a]	30	.3195	.003974	...	.1212	.01242

TABLE III (*Concluded*)

No. of expt.	$\mu^{1/2}$	$-\log \gamma$ (OH^-)	$-\log \gamma$ ($HPbO_2^-$)	$m(OH^-)$ final	$m(HPbO_2^-)$ final	$\log K_m$	$\log K$
1S[a]	0.215	0.0784	0.1270	0.04262	0.003672	−1.0647	−1.1133
2S[a]	.215	.0784	.1270	.04242	.003729	−1.0560	−1.1046
3U	.215	.0784	.1270	.04262	.003654	−1.0668	−1.1154
4S[a]	.308	.0971	.1830	.08614	.008815	−0.9900	−1.0759
5S[a]	.308	.0971	.1830	.08579	.008816	−0.9881	−1.0740
6U	.317	.0982	.1885	.09094	.009389	−0.9861	−1.0764
7S[a]	.320	.0989	.1902	.09282	.009314	−0.9985	−1.0898
8U	.321	.0990	.1904	.09398	.009006	−1.0185	−1.1099
9S[a]	.319	.0988	.1900	.09296	.008791	−1.0243	−1.1158
10U	.360	.1034	.2150	.1183	.011324	−1.0189	−1.1305
11U	.367	.1040	.2196	.1224	.01202	−1.0079	−1.1235
12S[a]	.366	.1040	.2190	.1219	.01242	−0.9919	−1.0969

[a] In Expts. 1 and 2 the solutions were shaken for six days at 32°; in Expts. 4 and 5, eighteen days at 32°; in Expt. 7, thirty-seven days at 32°, in Expt. 9, thirty days at 32° and in Expt. 12, twenty-seven days at 32°. The flasks were then transferred to a thermostat at 25° and rotated for the time indicated in Col. 2.

From the analyses of the solid phase after rotation one might assume that the formula of the hydrated lead monoxide was $PbO \cdot H_2O$ (85.89%Pb) although the results are irregular. However, some solution is removed with the solid phase. This solution contains potassium hydroxide from which it is difficult to remove the water by desiccation. The appearance of the solid phase does not change and we prefer to consider that the composition of the solid phase in equilibrium with the dilute potassium hydroxide solution is expressed by the formula $3PbO \cdot H_2O$ (90.30%Pb), as was found in the previous section. Referring to Equation 14 we note that this uncertainty affects merely the exponent of the activity of the water in the equilibrium constant, and since the activity of the water in the dilute solutions is nearly unity it does not seriously affect Equation 14. But if we wish to calculate the free energy of formation of hydrated lead monoxide, it is important to choose permanently (even if the choice is quite arbitrary) some one formula. Anomalous results which we were unable to explain were obtained in the case of Expts. 4, 5 and 6. For the most part the results are quite satisfactory and we shall choose $\log K = \log (HPbO_2^-)(H_2O)/(OH^-) = -1.108$; $K = 0.0780$, whence



○, Log K; ●, Log K_m.

Fig. 3.—Solubility of hydrated lead hydroxide in aqueous potassium hydroxide.

$$PbO\cdot 1/3H_2O(s) + OH^- = HPbO_2^- + 1/3H_2O(l);\ \Delta F^\circ_{298} = 1512 \text{ cal.} \quad (14)$$

The measurements of the solubility of basic lead carbonate in potassium hydroxide solutions are given in Table IV and Fig. 4. The headings of Cols. 1 to 4 are the same as those of Table I. Col. 5 gives the molality of CO_3^{--}. Cols. 6 to 10 are the same as those of Table I. Cols. 11 to 13 give, respectively, $^1/_4$ the logarithm of the activity coefficient of CO_3^{--}, the final molality of OH^- and the final molality of the $HPbO_2^-$. Col. 14 gives the logarithm of the ratio of molalities $m^3(HPbO_2^-) = m^2(CO_3^{--})/m^7(OH)^-$, and Col. 15 the value of log K. The percentage of lead in the solid phase, in equilibrium in Expt. 4 was 80.08, in Expt. 14 it was 80.21 and in Expt. 17 it was 80.18%, while the percentage of lead corresponding to $Pb_3(CO_3)_2(OH)_2$ is 80.12%.

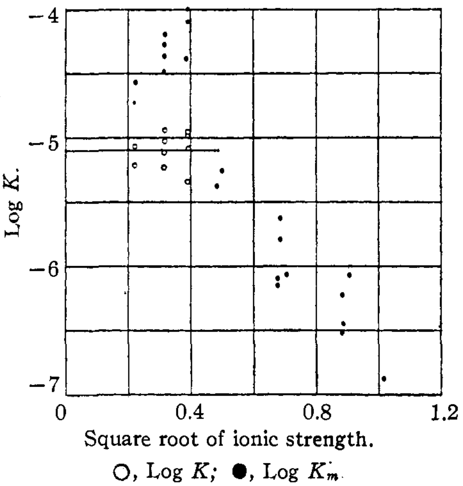


Fig. 4.—Solubility of basic lead carbonate in aqueous potassium hydroxide.

TABLE IV

SOLUBILITY OF BASIC LEAD CARBONATE IN POTASSIUM HYDROXIDE SOLUTIONS AT 25°

$$Pb_3(CO_3)_2(OH)_2(s) + 7OH^- = 3HPbO_2^- + 2CO_3^{--} + 3H_2O(l)$$

No. of expt.	Days of rotation	0.5023 *M* HCl to 1 g. of soln., g.	$PbCrO_4$ to 1 g. of soln., g.	$m(CO_3^{--})$ final	$m'(OH^-)$ 1st approx.	$m'(HPbO_2^-)$ 1st approx.
1U	39	0.1059	0.000637	0.001318	0.04360	0.001977
2	19	.1054	.000600	.001240	.04385	.001862
3U	19	.1077	.000651	.001348	.04432	.002020
4S[a]	30	.2156	.001667	.003462	.08407	.005192
5S[a]	30	.2149	.001595	.003312	.08469	.004968
6U	34	.2184	.001745	.003619	.08429	.005428
7U	35	.2200	.002075	.003556	.08415	.005838
8U	58	.3257	.002784	.005802	.1239	.008702
9U	44	.3244	.003280	.006842	.1215	.01026
10U	44	.3344	.003251	.006823	.1225	.01021
11S[a]	33	.3380	.003203	.006681	.1244	.01002
12U	15	.5129	.003694	.007769	.2074	.01165
13	24	.4967	.003403	.007101	.2006	.01065
14U	24	.9676	.006284	.01335	.4026	.02003
15U	16	.9939	.006382	.01349	.4127	.02023
16U	12	1.0013	.007302	.01544	.4037	.02317
17U	12	1.0013	.007736	.01146	.4001	.02469
18S[a]	24	1.0392	.007047	.01501	.4293	.02251
19	22	1.6020	.01169	.02536	.4659	.03804

TABLE IV (*Concluded*)

No. of expt.	Days of rotation	0.5023 *M* HCl to 1 g. of soln., g.	$PbCrO_4$ to 1 g. of soln., g.	$m(CO_3^{--})$ final	$m'(OH^-)$ 1st approx.	$m'(HPbO_2^-)$ 1st approx.
20	12	1.6127	.01055	.02278	.6807	.03416
21	39	1.6266	.01060	.02297	.6854	.03445
22	11	1.7111	.01331	.02868	.6910	.04300
23	22	1.339	.01529	.03341	1.0075	.05012

No. of expt.	$\mu^{1/2}$	$-\log \gamma$ (OH^-)	$-\log \gamma$ (HPO_2^-)	$-1/4 \log \gamma$ (CO_3^{--})	$m(OH^-)$ final	$m(HPbO_2^-)$ final	Log K_m	Log K
1U	0.222	0.0801	0.1310	0.0830	0.04389	0.001689	−4.574	−5.070
2	.222	.0801	.1310	.0830	.04412	.001588	−4.723	−5.219
3U	.224	.0809	.1320	.0835	.04459	.001731	−4.570	−5.068
4S[a]	.316	.0981	.1880	.1091	.08447	.004792	−4.387	−5.117
5S[a]	.316	.0981	.1880	.1091	.08507	.004590	−4.483	−5.233
6U	.317	.0984	.1885	.1095	.08471	.005015	−4.277	−5.030
7U	.317	.0984	.1885	.1095	.08459	.005392	−4.191	−4.943
8U	.386	.1055	.2318	.1260	.1243	.008255	−4.384	−5.348
9U	.390	.1060	.2340	.1270	.1220	.009714	−3.977	−4.953
10U	.391	.1061	.2345	.1274	.1230	.009682	−4.003	−4.983
11S[a]	.392	.1061	.2350	.1278	.1250	.009505	−4.095	−5.079
12U	.500	.1100	.3000	.149	.2058	.011305	−5.253	−6.575
13	.482	.1100	.2900	.146	.2009	.01032	−5.377	−6.645
14U	.676	....	....	....	.4029	.01977	−6.097	.....
15U	.678	....	....	....	.4131	.01997	−6.151	.....
16U	.687	....	....	....	.4040	.02288	−5.789	.....
17U	.689	....	....	....	.4004	.02438	−5.624	.....
18S[a]	.706	....	....	....	.4340	.02225	−6.068	.....
19	.883	....	....	....	.6661	.03781	−6.222	.....
20	.885	....	....	....	.6809	.03396	−6.524	.....
21	.888	....	....	....	.6900	.03426	−6.545	.....
22	.906	....	....	....	.6913	.04276	−6.069	.....
23	1.076	....	....	....	1.0077	.04994	−6.879	.....

[a] In Expts. 4 and 5 the solutions were rotated for fifteen days at 32°; in Expt. 11, fourteen days at 32°; and in Expt. 18, eleven days at 32°, and then transferred to a thermostat at 25° and rotated for the time indicated in Col. 2.

In Tables I–IV are included all the experiments in which check results were obtained. The agreement is satisfactory, except in Expts. 9, 10 and 11, in which the results are anomalous. The variations of the values of the equilibrium constant appear to be of considerable magnitude owing to the smaller proportion of lead, and therefore of CO_3^{--}. The difficulties of analysis are very great and the principle of the ionic strength is probably not as exact under these conditions as in the other experiments. There is a large multiplication of errors in obtaining log K, but the final value of the free energy change is probably not in error by more than 130 cal. per mole of lead. We shall choose as a final value

$$\log K_{298} = \log (HPbO_2^-)^3(CO_3^{--})^2(H_2O)^3/(OH^-)^7 = -5.10;\ K_{298} = 8 \times 10^{-6}$$

$$Pb_3(CO_3)_2(OH)_2(s) + 7OH^- = 3HPbO_2^- + 2CO_3^{--} + 3H_2O;\ \Delta F^\circ_{298} = 6961 \text{ cal.} \quad (15)$$

Summary

The solubilities of the red and yellow forms of lead monoxide, of hydrated lead monoxide and of basic lead carbonate in dilute aqueous potassium hydroxide solutions at 25° have been determined.

The change of the stoichiometrical equilibrium constant with concentration shows that the activity coefficient of the plumbite ion is about the same as that of the nitrate ion in dilute solutions.

From the extrapolated values of the equilibrium constants, the free energies of solution have been calculated.

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[CONTRIBUTION FROM THE PHYSICAL AND CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE ATOMIC ARRANGEMENT IN THE CRYSTAL OF ORTHORHOMBIC IODINE

BY PRESTON M. HARRIS, EDWARD MACK, JR., AND F. C. BLAKE

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The crystal structures of few of the non-metallic elements have been fully analyzed by the use of x-rays. Iodine has been studied recently by Ferrari[1] who has determined only the size of the unit cell, nothing being published concerning the arrangement of the atoms in the cell. A complete solution of the iodine structure is of special interest in connection with the question of the existence of molecules in crystals of non-polar substances and of the relationship of atomic to ionic radius.

The results presented by Ferrari were also obtained by the authors and presented in an unpublished thesis[2] at The Ohio State University in August, 1925. The methods used in this work were the same as those of Ferrari.[1] However, the results of the powder photographs obtained cannot be reconciled with those of Ferrari. These will be discussed in detail in the latter part of the present paper.

An extended study of the iodine symmetry was made by means of Laue photographs prepared with various crystal orientations and what is believed to be a unique solution of its structure was obtained in May, 1926. The definition of the structure involves two parameters which must be wholly evaluated from measurements of the intensities of reflection alone. Since the data obtained by the Laue and powder methods were not sufficient for as accurate a parameter determination as was desired, the crystal has since been re-analyzed by the oscillated crystal method.

The parameters have been evaluated from the intensity data in two ways, one being the well-known structure factor method[3] and the other the Four-

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[1] Ferrari, *Atti. Accad. Lincei*, [6] 5, 582 (1927).

[2] Thesis for the Master of Arts Degree by P. M. Harris.

[3] Wyckoff, "Structure of Crystals," Chemical Catalog Co., Easton, Pa., **1924.**