

counts quantitatively for the apparent discrepancy, noted in Müller's<sup>2</sup> paper, between the "calculated" and observed values of the  $pH$ . The shift of the half-wave potential with a change in drop time, which is not to be expected on the basis of equations (5), (6) and (7), was not found by us as evidenced by curves b and c. It is possible that such an effect might exist at very small drop times, but in exact work small drop times should be avoided.

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### Summary

1. The oxidation potential of poorly poised systems can be determined with the dropping mercury electrode, if proper correction is made for the residual current. Neglecting this correction may lead to large errors.

2. When hydrogen ions are produced at the dropping mercury electrode during an electrolysis the surface concentration of hydrogen ions can be calculated by a proper consideration of the diffusion and current relations. Equations have been derived which were in excellent agreement with experimental results.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## The Solubility of Lead Iodide in Solutions of Potassium Iodide-Complex Lead Iodide Ions

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The solubility of lead iodide is increased by the addition of iodide ion after a certain definite minimum solubility has been reached. This fact has been demonstrated conclusively by Burrage,<sup>1</sup> by Van Klooster and Balon<sup>2</sup> and by Demassieux and Roger.<sup>3</sup> Furthermore, this behavior has been interpreted generally to be due to the formation of complex ions of lead and iodine, to which some authors,<sup>1,3,4</sup> although the data available are insufficient to establish composition, have ascribed the formula  $PbI_3^-$ ,—possibly because double salts of the type  $RI \cdot PbI_2 \cdot xH_2O$  have been identified as solid phases during equilibrium studies on such solutions while solid phases of double salts in which the molar ratio of alkali iodide to lead iodide is greater than one to one have not been encountered<sup>1,2,3,4</sup> in these investigations.

So to verify experimentally the formula of the ion,  $PbI_3^-$ , and to ascertain whether other complex lead iodide ions are formed in solutions of lead iodide and potassium iodide and to determine, if possible, their nature, a series of solubility measurements was made. Whereupon not only was evidence found for the existence of  $PbI_3^-$  but also for  $PbI_4^{2-}$  as well—both in significant amount. Moreover, their respective stability constants

and standard free energies of formation were evaluated.

### Materials and Procedure

Lead iodide and potassium iodide both of a high degree of purity were crystallized three times from water. All other reagents used in this investigation, although of the highest purity obtainable, were tested as an assurance that no other substances which would affect the results were present.

A colorimetric method was employed for the determination of lead. The sample containing between 0.4 and 1.0 mg. of lead was placed in a 100-ml. volumetric flask and 0.5 ml. of 3 *N* sodium acetate added. This operation was followed successively by the addition of 20 cc. of a 50% solution of sucrose, 4 ml. of 6 *N* hydrochloric acid, and 4 ml. of a saturated solution of hydrogen sulfide. The solution of hydrogen sulfide was freshly prepared from carefully washed commercially available gas. The resulting solution was thoroughly mixed, 5 ml. of 6 *N* ammonia added, and made to volume with constant agitation and intermixing. A brown color appeared after the addition of ammonia.

A Pulfrich photometer equipped with a violet ( $s_{43}$ ,  $\lambda = 4300$ ) filter was used to measure the extinction coefficient of the above solution contained in a three-centimeter cell. A blank solution containing all the reagents was present in the other side of the instrument.

To evaluate the solubility of lead iodide a calibration curve was made for the instrument by using standard solutions of lead nitrate and lead iodide. In making the curve the extinction coefficient was plotted against the lead content in the above solution. A straight line for solutions containing not more than 1.0 mg. of lead in 100 ml. of solution, which was the most concentrated solution

(1) L. J. Burrage, *J. Chem. Soc.*, 1703 (1926).

(2) H. S. Van Klooster and P. A. Balon, *THIS JOURNAL*, **56**, 591 (1934).

(3) N. Demassieux and Roger, *Compt. rend.*, **204**, 1818 (1937).

(4) L. J. Burrage, *Chem. News*, **134**, 85 (1937).

TABLE I  
 SOLUBILITY OF LEAD IODIDE IN SOLUTIONS OF POTASSIUM IODIDE,  $T = 25^\circ \pm 0.01$ . CONCENTRATIONS ARE EXPRESSED AS G./1000 G. H<sub>2</sub>O

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$M_{KI}$	$M_{PbI_2} \times 10^5$	$M(\text{Pb as complex ions}) \times 10^5$ $S_0(3.40 \times 10^{-5})$	$\gamma_{KI}^a$	$\gamma_{K_2PbI_4}^b$	$M_{PbI_3^-} \times 10^{3c}$	$M_{PbI_4^{2-}} \times 10^{3d}$	$S \times 10^5$ calculated
0.000	164.1						
.010	28.1						
.030	6.53						
.060	4.60						
.080	4.23						
.100	4.01	0.61	0.80	0.60	0.222	0.268	3.89
.125	4.06	.66	.79	.56	.278	.351	4.06
.150	4.42	1.02	.78	.53	.333	.798	4.53
.175	4.90	1.50	.77	.51	.389	1.16	4.95
.200	5.49	2.09	.76	.50	.444	1.54	5.38
.225	5.98	2.58	.76	.49	.500	2.03	5.93
.250	6.75	3.35	.75	.47	.555	2.80	6.75
.275	7.30	3.90	.75	.46	.611	3.44	7.45
.300	8.17	4.77	.74	.45	.666	4.26	8.33
.325	9.20	5.80	.74	.44	.722	5.06	9.18
.350	10.23	6.83	.73	.44	.775	5.85	10.03
.400	13.32	9.92	.73	.41	.888	9.10	13.38

<sup>a</sup> Taken from data of J. Wust and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925). <sup>b</sup> Taken from data from Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>. See references 9 and 10. <sup>c</sup> Calculated from  $K_1 \times M_1^-$ . <sup>d</sup> Calculated from  $K_2 \times \frac{(\gamma_{KI})^4}{(\gamma_{K_2PbI_4})^3} (M_1^-)^2$ .

investigated, was obtained. The line passes through the origin.

By preliminary experiments it was demonstrated that the presence of potassium iodide in amounts encountered in the course of this investigation did not affect the value of the extinction coefficient.

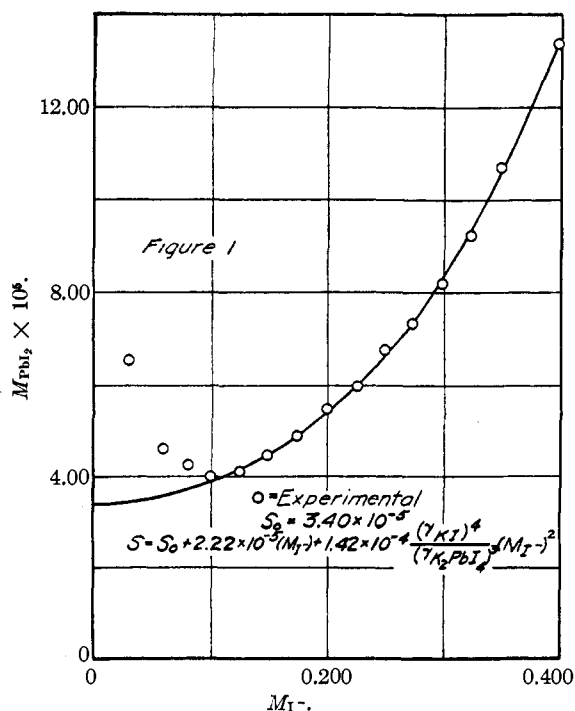


Fig. 1.

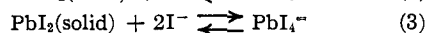
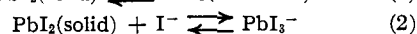
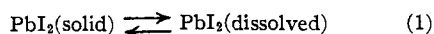
The experimental solutions prepared from standard potassium iodide solutions and solid lead iodide were put into 250-ml. "non-sol" bottles and stirred by end over end rotation for several days in a water-bath maintained at  $25 \pm 0.01^\circ$ . Then, after the solid lead iodide had settled, a sample of the solution was analyzed. The solubilities listed are in all cases the mean of values obtained, respectively, by starting with unsaturated solutions and with supersaturated solutions. In no case was the difference in lead content between such pairs greater than the experimental error of the analysis, which was less than five parts per thousand.

### Experimental Data

The data are presented in Table I. The molal concentration of iodide ion is given in column 1. Column 2 contains corresponding molal solubility of lead iodide, and column 3 the molal concentration of lead in the form of complex ions (column (2) minus the molal solubility of lead iodide in zero concentration of iodide ion obtained by extrapolation of the curve in Fig. 1 to zero concentration of iodide ion).

### Discussion

If one assumes that the increase in solubility beyond the point of minimum solubility of lead iodide caused by the presence of potassium iodide is due to the reactions



the solubility  $S$  may be expressed by the equation

$$S = S_0 + K_1 \frac{M_{I^-} - \gamma_{I^-}}{\gamma_{PbI_3^-}} + K_2 \frac{M_{I^-}^2 - (\gamma_{I^-})^2}{\gamma_{PbI_4^{2-}}} \quad (4)$$

In this equation

$$K_1 = a_{PbI_3^-} / a_{I^-} \quad (5)$$

$$K_2 = a_{PbI_4^{2-}} / (a_{I^-})^2 \quad (6)$$

$S_0 = 3.40 \times 10^{-5}$  molal = solubility of lead iodide from reaction (1), *i. e.*, lead other than complex ion. This value was determined by extrapolation of curve in Fig. 1 to zero concentration of iodide ion.

Again, if one assumes that at low ionic strengths  $\gamma_{I^-} = \gamma_{PbI_3^-}$ , the validity of which has been demonstrated on several occasions,<sup>5,6,7</sup> one may write

$$S = S_0 + K_1 M_{I^-} + K_2 (M_{I^-})^2 \frac{(\gamma_{KI})^4}{(\gamma_{K_2PbI_4})^3} \quad (7)$$

The values of the stability constants,  $K_1$  and  $K_2$ , in equation (7) were determined by the method of least squares from data in Columns (1), (2), (3) and (4) in Table I. In the calculations  $\gamma_{KI}$ , Column (4) was obtained from the data at the same ionic strength of Wüst and Lange.<sup>8</sup> For  $\gamma_{K_2PbI_4}$ , Column (5), the values of the activity coefficients of potassium sulfate<sup>9</sup> and sodium sulfate<sup>10</sup> at the same ionic strength were used because at low values for ionic strength, according to the Debye-Hückel theory, the activity coefficient of  $K_2PbI_4$  should differ but little from that of potassium sulfate or sodium sulfate. The sulfate was chosen because it resembles closely  $PbI_4^{2-}$  in symmetry. In evaluating the stability constants the molality of iodide ion was considered equal to the total concentration of the potassium iodide added because but a small amount of it was converted to complex ions.

Accordingly, up to an ionic strength of 0.4, the values for  $K_1$  and  $K_2$  are quite constant. Likewise, equation (7) expresses, rather faithfully, the solubility of lead iodide in solutions of potassium iodide as a comparison of the data in Columns (2) and (8) in Table I will disclose. Furthermore,

(5) Garrett, *THIS JOURNAL*, **61**, 2744 (1939).

(6) Johnston, Cuta and Garrett, *ibid.*, **55**, 2311 (1933).

(7) McDowell and Johnston, *ibid.*, **58**, 2009 (1936).

(8) Wüst and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925).

(9) Landolt-Börnstein, "Tabellen, III," p. 2147.

(10) H. S. Harned and J. C. Hecker, *THIS JOURNAL*, **56**, 650 (1934).

the fairly close agreement of the experimental with the calculated results tends to corroborate the validity of the two assumptions made in the evaluation of the constants, and to justify the claim that both  $PbI_3^-$  and  $PbI_4^{2-}$  are present in solutions of lead iodide with excess iodide ion and that they are the only complex lead iodide ions present in significant quantities. Their molal concentrations are given in Columns (6) and (7), respectively, of Table I. It is evident also from the form of the curve in Fig. 1 and their respective molal concentrations that the formation of  $PbI_4^{2-}$  exerts the preponderant effect upon the solubility of lead iodide in such solutions. If, however, the effect due to the formation of  $PbI_3^-$  were to predominate the solubility curve would in that case approach linearity instead of the experimental curve which falls short of a parabolic function. Moreover, we believe that  $PbI_3^-$  and  $PbI_4^{2-}$  are the only complex ions of lead ion and iodide ion present in significant quantities in such solutions.

The final values of the stability constants in equation (7) obtained by the method of least squares are

$$K_1 = 2.22 \times 10^{-5} \approx 0.28 \times 10^{-5}$$

$$K_2 = 1.42 \times 10^{-4} \approx 0.03 \times 10^{-4}$$

The standard free energy change for reaction (2) is

$$\Delta F_{298}^{\circ} = + 6346 \text{ calories}$$

and for reaction (3)

$$\Delta F_{298}^{\circ} = + 5247 \text{ calories}$$

### Summary

1. The solubility of lead iodide in solutions of potassium iodide at 25° has been measured to an iodide concentration of 0.4 molal.

2. The increase of solubility of lead iodide caused by the presence of iodide ion in concentration greater than 0.1 molal may be explained by the formation of the complex ions  $PbI_3^-$  and  $PbI_4^{2-}$ .

3. The stability constants and standard free energies of formation of the complex ions have been determined.

4. A colorimetric method for the determination of lead has been described.

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