

[CONTRIBUTION No. 629 OF THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

**THE SOLUBILITY OF LEAD IODATE IN WATER AND IN 0.1 N SALT SOLUTIONS**

BY VICTOR K. LA MER AND FREDERICK H. GOLDMAN

RECEIVED MAY 5, 1930

PUBLISHED JULY 3, 1930

In connection with our studies<sup>1</sup> on the solubilities of lanthanum and thalious iodates in salt solutions we also considered making similar measurements upon lead iodate as an example of a (2, -1) type saturating salt. Unfortunately experimental difficulties such as inability readily to reproduce the water solubility with the high precision desired (0.1%) for testing the principle of specific interaction, and the limited range of concentration for which sulfate solvents could be employed, led us to discontinue the more complete study in favor of  $TlIO_3$ . The final solubility value for  $Pb(IO_3)_2$  in water was  $3.61 \cdot 10^{-5}$  moles/liter at  $25^\circ$ , which is considerably lower than the value of  $5.51 \cdot 10^{-5}$  reported by Harkins and Winninghoff<sup>2</sup> or the value  $4.13 \cdot 10^{-5}$  moles/liter reported by Kohlrausch<sup>3</sup> for  $25.77^\circ$ .

**Preparation of Lead Iodate.**—One hundred and twenty grams (0.216 mole) of lead iodate was precipitated by simultaneous dropwise addition of equivalent solutions of c. p. lead nitrate and potassium iodate in a 23-liter jar filled with water under constant stirring at about  $60^\circ$ . The supernatant liquid was replaced with fresh water eight times during the precipitation process, which occupied several days' time. The potassium nitrate resulting from metathesis therefore did not exceed 0.002 *M* at any time. It has been our experience that higher solubilities are usually obtained when salts are precipitated from more concentrated solutions, due we believe to occlusion of metathetic products. Harkins and Winninghof gave no details other than that their salt was precipitated in very dilute solution in which the nitrate was constantly in excess. Our product was of a very light cream color and of a fineness resembling talcum powder.

**Results.**—The lead iodate was placed in the solubility tubes, described previously,<sup>4</sup> in January, 1927, and washed with water or salt solutions continuously until July, 1927, with the following results for  $S \cdot 10^5$ , 3.68, 3.63 and 3.66 on 1/21, 1/22 and 1/23, respectively. On 1/24,  $10^5S$  suddenly rose to 3.82 and the salt assumed a light yellow color, due we believe to the liberation of traces of iodine by some accidental impurity. By continuous washing the yellow color slowly disappeared until on 4/14,  $10^5S$  had fallen to 3.60, rising to 3.61 on 6/4. During this period equilibrium was ap-

<sup>1</sup> La Mer and Goldman, *THIS JOURNAL*, **51**, 2632 (1929).

<sup>2</sup> Harkins and Winninghoff, *ibid.*, **33**, 1830 (1911). Solubility determined by direct analysis.

<sup>3</sup> Kohlrausch, *Z. physik. Chem.*, **46**, 521-619 (1923). Solubility determined by conductivity method.

<sup>4</sup> La Mer and Mason, *THIS JOURNAL*, **49**, 363 (1927).

proached from supersaturation as well as undersaturation without producing significant differences in the results. Since both impurities and abnormally small crystals will produce a greater solubility, we feel justified in attributing more weight to our lower value than to the higher values of previous investigators. The analysis was carried out by adding 3 g. of potassium iodide to a 200-cc. aliquot of saturated solution in a 500-cc. iodine flask. Two cc. of 50% sulfuric acid was then added and the contents titrated after ten minutes with dilute thiosulfate from a weight buret. Although the precipitate formed interfered somewhat in the ease of reading the starch end-point, duplicate determinations usually checked to 0.2%.

The data in the table show that the solubilities in the potassium and sodium solvents with the same anion are almost identical, in agreement with the requirements of the principle of specific interaction since the osmotic properties (freezing-point lowerings) of potassium and sodium iodates are also almost identical<sup>5</sup> at 0.1 *N*. On the other hand, marked differences exist between the nitrates and chlorides, lead iodate like thallos iodate being more soluble in chlorides than in nitrates. This is opposite to what is usually observed and we attribute the greater solubility to the formation of complex chlorides. In the case of lead, complexes of the type  $PbCl_3^-$  have been isolated at high chloride concentrations.<sup>6</sup> The Debye-Hückel limit-

TABLE I  
SOLUBILITY AND ACTIVITY COEFFICIENTS OF LEAD IODATE AT 25°

Solvent	Date	Final detns. avgd.	$S \cdot 10^5$ mole/liter	$\log S/S_0$	$-\log f$	$\sqrt{\mu}$	$a_{1st} \text{ \AA. units}$
H <sub>2</sub> O	6/4	5	3.608	0.000	0.0105	0.0104	....
0.1 <i>M</i> NaNO <sub>3</sub>	5/16	3	6.99	.287	.297	.3165	+0.72
0.1 <i>M</i> KNO <sub>3</sub>	5/25	3	6.94	.284	.294	.3165	+0.82
0.1 <i>M</i> KCl	6/14	4	8.29	.361	.371	.3165	-1.34
0.1 <i>M</i> NaCl	7/8	4	8.30	.362	.372	.3165	-1.36

TABLE II  
RECALCULATIONS OF THE DATA OF HARKINS AND WINNINGHOF

Solvent	$S \cdot 10^5$ mole/liter	$\log S/S_0$	$-\log f$	$\sqrt{\mu}$
H <sub>2</sub> O	5.511	0.000	0.013	0.0128
KNO <sub>3</sub> 0.002 <i>M</i>	5.71	.015	.028	.0466
0.010 <i>M</i>	6.52	.073	.086	.102
0.050 <i>M</i>	10.18	.267	.280	.224
0.200 <i>M</i>	12.71	.363	.376	.477

$a_{1st}$  refers to the "a" value calculated using the first or Debye-Hückel approximation of the solution of the Poisson-Boltzmann equation. See Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928) for mathematical details regarding the higher approximations.  $\mu$  is the ionic strength, *i. e.*,  $1/2 \sum c_i z_i^2$ .

<sup>5</sup> See Ref. 1, p. 2642, for more details and for references to Brønsted's papers where this relation is developed.

<sup>6</sup> Kendall and Sloan, *THIS JOURNAL*, **47**, 2306 (1925).

ing law predicts a value of  $-\log f = 0.319$  in the 0.1 *M* solvents, and the last column gives the values of the parameter "a" in Å. units required by this theory. The values of "a" are absurdly small for the nitrates, which is frequently the case, but are actually negative in the case of chlorides, which is unusual for low valence chloride salts in water.

### Summary

The solubility of lead iodate is  $3.61 \cdot 10^{-5}$  mole/liter at 25°. The greater solubility in 0.1 *N* chlorides than in the nitrates of sodium and potassium is attributed to complex chloride formation.

NEW YORK, N. Y.

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]  
**THE EFFECT OF IODINE CHLORIDE ON THE PHOTOSYNTHESIS  
OF HYDROCHLORIC ACID**

BY G. K. ROLLEFSON AND F. E. LINDQUIST

RECEIVED MAY 5, 1930

PUBLISHED JULY 3, 1930

In recent discussions of the mechanism of the photosynthesis of hydrochloric acid it has been generally accepted that the action of the light which initiates the chain is to dissociate a chlorine molecule into a normal chlorine atom and one excited to the  $^2P_1$  state. A recent paper by Rollefson<sup>1</sup> discussed grounds for believing that it is the excited atoms which start the reaction, the normal ones having no effect. It is highly desirable, therefore, to carry out experiments in which only one of the two kinds of atoms is produced and to see if the reaction will start under such conditions. For such experiments to be of significance it is necessary that the atoms shall be produced with as little disturbance to the other molecules as possible. The most obvious way to do this is to dissociate some molecule by light. In this case it is possible to do it by introducing iodine monochloride into the mixture of hydrogen and chlorine and it is the purpose of this paper to present experiments dealing with the behavior of such a system.

The absorption spectrum of iodine chloride has been studied by Gibson and Ramsperger,<sup>2</sup> who found a series of bands converging at  $\nu = 17,410$   $\text{cm.}^{-1}$  ( $\lambda = 5744$  Å.) similar in character to the bands which have been observed in the halogens by Mecke<sup>3</sup> and Kuhn.<sup>4</sup> In the case of the halogens it was shown that the convergence corresponded to a dissociation into a normal and an excited atom. The thermal data available for iodine chloride are not sufficiently accurate to say definitely whether the observed convergence corresponds to a dissociation into two normal atoms or into a

<sup>1</sup> Rollefson, *THIS JOURNAL*, **51**, 770 (1929).

<sup>2</sup> Gibson and Ramsperger, *Phys. Rev.*, **30**, 598 (1927).

<sup>3</sup> Mecke, *Ann. Physik*, **71**, 104 (1923).

<sup>4</sup> Kuhn, *Z. Physik*, **39**, 77 (1926).