THE SOLUBILITY PRODUCT OF THALLOUS IODIDE AT 25°.

By Cecil W. Davies and Robert A. Robinson.

Received 9th March, 1937.

During an investigation of the conductivities of some thallous salts we had occasion to make conductimetric titrations involving the precipitation of thallous iodide. The solubility of this salt proved to be so high that the titrations, employing very dilute solutions, were unsuitable for analytical purposes; but by calculating the contribution of the dissolved thallous iodide to the total conductivity we found it possible to determine the solubility product of thallous iodide by a

method which is superior in three respects to the usual method, in which the conductivity of a saturated solution is determined: (*a*) it does not involve the isolation of the insoluble salt freed from all adhering traces of soluble salts; (*b*) the subsequent solution of the purified salt in conductivity water, usually a tedious process, is avoided, and (*c*) each conductivity measurement leads to a separate determination of the solubility product, so that unsuspected impurities or other causes of error are unlikely to escape detection.

A 0·002859 *N*-solution of thallous acetate in water (288·54 g.) was titrated at 25° ± 0·005 with a 0·08769 *N*-solution of potassium iodide, the conductivity being measured at intervals both before and after the end-point. This occurred at 9·567 g. of iodide solution, the solution then being 0·002768 *N* with respect to potassium acetate. The second column of Table I. gives the specific conductivities at the titres recorded in the first column. Using the data of MacInnes and Shedlovsky,[1] the conductivity of the solution at the endpoint should be 304·78 × 10^{-6} r.o., and assuming that the conductivity falls linearly with the titre (the ionic strength of the solution being almost constant until the endpoint is reached) the calculated

TABLE I.—Titration of Thallous Acetate Solution with Potassium Iodide Solution.

g. KI soln. added.	$\varkappa \times 10^6$.	$\varkappa_{calc.} \times 10^6$.	$\Delta\varkappa \times 10^6$.	$S_0 \times 10^8$.
0	317·43	—	—	—
1·7774	319·63	315·08	4·55	6·43
3·8230	318·57	312·38	6·19	6·46
6·2560	319·31	309·16	10·15	6·32
7·9171	324·50	306·96	17·54	6·31
9·0079	334·61	305·52	29·09	6·28
9·9127	351·53	319·01	32·52	6·28
11·610	402·31	386·96	15·35	6·34
13·650	476·45	467·60	8·85	6·48
15·802	557·22	551·05	6·17	6·55
18·193	646·53	642·08	4·45	6·39
			Mean:	6·38

TABLE II.—Titration of Potassium Iodide Solution with Thallous Nitrate Solution.

g. $TlNO_3$ soln. added.	$\varkappa \times 10^6$.	$\varkappa_{calc.} \times 10^6$.	$\Delta\varkappa \times 10^6$.	$S_0 \times 10^8$.
0	314·70	—	—	—
0·4285	318·97	313·89	5·08	6·56
2·3938	316·20	310·19	6·01	6·69
5·7744	311·97	303·83	8·14	6·56
11·3200	311·68	293·38	18·30	6·60
13·8384	321·27	288·63	32·64	6·61
15·0731	331·03	295·42	35·61	6·60
18·5425	375·33	358·57	16·78	6·62
22·2437	434·21	424·15	10·06	6·67
25·6563	489·73	482·82	6·91	6·29
30·1657	563·06	557·95	5·11	6·32
			Mean:	6·55

conductivities given in the third column are obtained. Beyond the end-point we have used the data on potassium iodide by Bray and McKay;[2] equivalent conductivity figures corresponding to the total ionic strength have been employed. The difference between the observed and the calculated conductivities, given in the fourth column is attributed to dissolved thallous iodide, from which the concentration of thallous iodide may be deduced. Thence the solubility product, $S_0 = f_{Tl}f_I C_{Tl}C_I$, is found (column 5), $f_{Tl}f_I$ being calculated from the limiting Debye-Hückel equation.

In the second titration a 0·0021525 *N*-solution of potassium iodide (268·00 g.) was titrated with a 0·039969 *N*-solution of thallous nitrate, the calculated conductivity at the endpoint (14·625 g.) being 286·98. The solubility product was calculated as in the preceding case.

It will be seen that the concordance between the two titrations is satisfactory, the mean value of the solubility product being 6·47 × 10^{-8}. If the dissociation constant of thallous iodide is of the same order of magnitude as that of thallous chloride,[3] the amount of undissociated salt in the

[1] MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1429.
[2] Bray and McKay, *ibid.*, 1910, **32**, 914.
[3] Onsager, *Physik. Z.*, 1927, **28**, 277.

saturated solution is negligible, and the solubility of thallous iodide in water at 25° is $2{\cdot}54 \times 10^{-4}$ g.-moles per litre.

Summary.

The application of conductimetric titrations to the determination of a solubility product is described, and the solubility product of thallous iodide at 25° is found to be $6{\cdot}47 \times 10^{-8}$.

Battersea Polytechnic,
London, S.W. 11.