Solubilities of Salts in Dioxane–Water Solvents[1]

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As a study in the problem of the relations between dielectric constant and solubility of electrolytes, we have made measurements of the solubilities of three insoluble compounds, barium iodate, silver acetate and silver sulfate in dioxane–water mixtures at 25° over the complete range of concentrations from 0 to 100% dioxane in intervals of 10% by weight. The measurements extended over a dielectric constant range from 2.10 to 78.55 (the widest variation so far reported in solubility work) and the results have been treated in the light of the interionic attraction theory and of Born's theory of solvent interaction.[2]

I. Materials and Methods

Barium Iodate.—A C. P. grade of barium iodate monohydrate was washed eight to ten times with distilled water, sedimented in tall cylinders to remove smaller sized particles, and dried at 100° before use. Iodometric titration gave 96.5% Ba(IO₃)₂ compared with 96.43% theoretical for the monohydrate. The several preparations gave a constant solubility in water.

Silver Acetate.—A C. P. product was used without further treatment. Volumetric analysis for silver gave 64.72% silver compared with a theoretical 64.64%.

Silver Sulfate.—A preparation from Merck was employed without further purification. On the basis of silver content, the salt was 99.9% Ag₂SO₄.

Other Inorganic Salts.—Standard C. P. grade chemicals were used after drying at 100°.

Dioxane.—This solvent came from several sources. The first step in the purification was usually either a refluxing with metallic sodium for several hours or treatment with sodium wire at room temperature for several days. This sodium treatment was then followed by distillation through a 24-inch (61-cm.) packed distilling column. In some cases the dioxane was first treated with alkaline permanganate, distilled, refluxed with lime and then redistilled before being treated with sodium.[3] The density, refractive index and dielectric constant of the preparations checked closely with values to be found in the literature. The freezing points ran between 11.5 and 11.73°, somewhat lower than those reported by several others[3,4] (about 11.8). Such differences have been neglected in the present work since the effect on the calculated dielectric constant of the mixed solvents would be very small. The rapid deterioration of the material is ascribed by Hess and

Frahm[4] to oxidation to give an aldehyde, peroxide and other subsequent products. Because of the unstable character of the liquid, it was prepared at frequent intervals during the course of the work.

Solubility Determinations.—The dioxane–water mixtures were made up by weight for each experiment, in glass-stoppered Pyrex solubility bottles of 250 ml. capacity. The liquid was rotated at 25 ± 0.02° with excess solid for one or more days.

Samples for analysis were withdrawn by suction through quantitative filters into calibrated 100-ml. pipets after allowing some time for the undissolved salt to settle. There was no evidence of colloidal character in any of the solutions. The silver-containing samples were titrated, after appropriate dilution in the case of high dioxane ratios, against standard 0.01 N potassium thiocyanate solution using weight burets. Some difficulty was encountered in fixing the end-point of this titration in the presence of varying quantities of dioxane; the precipitation of the silver thiocyanate is apparently slow near the equivalence point, and the color is also somewhat abnormal. Very vigorous and prolonged agitation is necessary to overcome the first difficulty, and comparison solutions were used as color standards to fix the final end-point in very high dioxane concentrations.

The iodate solutions were first evaporated to dryness to expel the dioxane which seriously interferes with the observation of the starch–iodine end-point, and which accelerates the liberation of iodine from an acidified potassium iodide solution. The titration of the iodate was performed with a carefully regulated procedure, using frequently standardized thiosulfate solutions delivered from weight burets, appropriate corrections being made for the blanks.

II. Solubilities in Presence of Dioxane

The solubility figures appearing in Tables II, III and IV are in every case the mean of one or more determinations from undersaturation and one or more from supersaturation.

In Table I we have collected the data on the properties of the solvents which are useful in interpreting our solubility figures. The dielectric constants are taken from the report of Åkerlöf and Short[3b]; the densities are interpolated from the measurements of Hovorka, Schaefer and Dreisbach.[5] The coefficients to be used in the Debye–Hückel equation at 25° are listed in the last two columns of the table. Column 5 of the table contains the differences between the reciprocal of the dielectric constants of the several media and the reciprocal of the dielectric constant of water.

(1) Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) M. Born, Z. Physik, **1**, 45 (1920).

(3) (a) C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933); C. A. Kraus and R. A. Vingee, ibid., **56**, 511 (1934). (b) G. Åkerlöf and O. A. Short, ibid., **58**, 1241 (1936).

(4) K. Hess and H. Frahm, Ber., **71B**, 2627 (1938).

(5) F. Hovorka, R. A. Schaefer and D. Dreisbach, THIS JOURNAL, **58**, 2264 (1936).

TABLE I

DATA AND CONSTANTS FOR SOLVENTS USED

Wt. % diox-ane	Den-sity	Mole % dioxane	Dielec. const. D	$\left(\frac{1}{D} - \frac{1}{D_0}\right)$	$\frac{352.6}{D^{3/2}}$	$\frac{2.914}{D^{1/2}}$
0	0.9970	0	78.55	0.000	0.505	0.3288
10	1.0030	2.223	69.71	.001614	.606	.3490
20	1.0097	4.667	60.81	.003714	.744	.374
30	1.0189	8.063	51.91	.006533	.943	.404
40	1.0263	12.004	43.00	.010525	1.250	.444
50	1.0311	16.987	34.28	.01644	1.757	.498
60	1.0345	23.485	25.86	.02594	2.681	.573
70	1.0372	32.32	17.70	.04377	4.627	.693
80	1.0349	45.01	10.72	.08055	10.04	.890
85	1.0320	53.68	8.16	.1098	15.12	1.020
90	1.0295	64.81	5.61	.1654	26.54	1.230
95	1.0280	79.52	3.69	.2583	49.73	1.517
100	1.0277	100.0	2.101	.4637	115.9	2.011

TABLE II

SOLUBILITY OF SILVER ACETATE IN DIOXANE-WATER MIXTURES AT 25°

Wt. % dioxane	Solubility, S moles/l. $\times 10^4$	$-\log S$	Solubility, X, mole fraction $\times 10^4$	$-\log X$	$\sqrt{\mu}$
0	666.3	1.1763	12.027	2.9198	0.2581
10	503.5	1.2980	9.819	3.0079	.2244
20	363.8	1.4391	7.714	3.1127	.1907
30	245.2	1.6105	5.693	3.2446	.1550
40	151.7	1.8190	3.905	3.4084	.1232
50	85.64	2.0673	2.485	3.6048	.09253
60	42.27	2.3740	1.409	3.8512	.06502
70	17.40	2.7595	0.6818	4.1663	.04171
80	6.11	3.2140	.2925	4.5339	.02472
85	2.85	3.5452	.1552	4.8090	.01688
90	1.54	3.8125	.0949	5.0228	.0124
95	0.21	4.676	.0151	5.8220	.0046
100	.000		.0000		

TABLE III

SOLUBILITY OF SILVER SULFATE IN DIOXANE-WATER MIXTURES AT 25°

Wt. % dioxane	S, moles/l. $\times 10^4$	$-\log S$	X, mole fraction $\times 10^4$	$-\log X$	$\sqrt{\mu}$
0	268.4	·1.5712	4.875	3.3121	0.2838
10	155.0	1.8097	3.026	3.5194	.2156
20	83.14	2.0802	1.764	3.7535	.1579
30	40.15	2.3963	0.9326	4.0302	.1098
40	17.03	2.7688	.4387	4.3580	.07157
50	6.02	3.2214	.1747	4.7577	.04245
60	1.80	3.7455	.0600	5.2220	.0232
70	0.63	4.201	.0247	5.6075	.0137
80	.23	4.646	.0110	5.9582	.0082
90	.063	5.201	.00388	6.4110	.0043
100	.0000		.00000		

The experimental figures on the solubilities of the three solutes investigated are presented in Tables II, III and IV both in moles per liter and in mole fractions, assuming normal molecular weights in the liquid. We have included the data in terms of both units because there is question as to which should be used in equilibrium studies. The general practice when dealing with

media of different molecular composition is to use mole fractions as the more fundamental units. Scatchard[6] has shown, for example, that the reaction of thiosulfate ion with bromoacetate ion in mixed solvents[7] is in better agreement with prediction when the volume concentrations are corrected to a mole fraction basis. Bell and Gatty,[8] however, have come to the conclusion on theoretical grounds that volume concentrations should be used in calculations of interaction energies in solution. If this is correct, then all the data should appear in volume concentrations. We accordingly have listed the solubilities, in Tables II–IV, in terms of molarities and of mole fractions both, and have in fact carried out most of the subsequent calculations for both sets of units. The same tables also list the figures for the square root of the ionic strength in the several solutions calculated on the basis of 100% dissociation throughout.

Since the barium iodate is a hydrated salt, its activity and solubility must depend on the fugacity of water in the solutions. In every experiment the solid phase at saturation was the monohydrate, as proved by actual analysis, even when the solvent was dioxane, the stability of the solid in the last case being a result of the very low solubility of the salt. In no experiment with barium iodate as saturating phase, or with silver acetate or silver sulfate, was any double compound with dioxane formed. The activity of barium iodate monohydrate in solution being proportional to the activity of the water, we would find the solubility of the hydrate to be greater in solutions of lower water activity, other factors being the same. Accordingly all the solubility figures have been multiplied by the ratio of the aqueous pressure from the solution to that from pure water, using for this purpose the data of Hovorka, Schaefer and Dreisbach.[9] The resulting figure, which is that actually plotted, is the hypothetical solubility of barium iodate monohydrate in pure water of dielectric less than 78.55.

The measurements given in Tables II–IV are plotted in Figs. 1 and 2. The full curves of Fig. 1 show $-\log S$ (molarity) for the three salts studied, as a function of D and of $\left(\frac{1}{D} - \frac{1}{D_0}\right)$,

(6) G. Scatchard, J. Chem. Phys., 7, 657 (1939).

(7) V. K. La Mer and M. E. Kamner, THIS JOURNAL, 57, 2669 (1935).

(8) R. P. Bell and O. Gatty, Phil. Mag., 19 [7], 66 (1935).

(9) F. Hovorka, R. A. Schaefer and D. Dreisbach, THIS JOURNAL, 59, 2753 (1937).

TABLE IV

SOLUBILITY OF $Ba(IO_3)_2 \cdot H_2O$ IN DIOXANE-WATER MIXTURES AT 25°

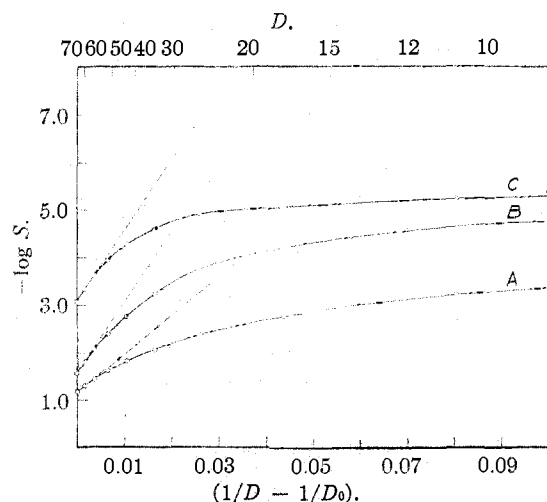| Wt. % dioxane	S, Moles/l. $\times 10^4$	$- \log S$	$S \dfrac{P_{H2O}}{P^\circ_{H2O}}$	$- \log S \dfrac{P_{H2O}}{P^\circ_{H2O}}$	X mole fraction $\times 10^6$	$X \dfrac{P_{H2O}}{P^\circ_{H2O}}$	$- \log X \dfrac{P_{H2O}}{P^\circ_{H2O}}$	$\sqrt{\mu}$
0	8.145	3.0891	8.145	3.0891	15.273	15.273	4.8161	0.04943
10	4.742	3.3240	4.687	3.3291	9.256	9.147	5.0386	.03772
20	2.526	3.5976	2.463	3.6086	5.361	5.226	5.2818	.02753
30	1.217	3.9147	1.167	3.9329	2.827	2.711	5.5669	.01911
40	0.553	4.2573	0.520	4.2842	1.424	1.3386	5.8733	.01288
50	.278	4.5560	.255	4.5934	0.8067	0.7401	6.1307	.00913
60	.140	4.8539	.124	4.9053	.4665	.4144	6.3826	.00648
70	.110	4.9586	.0933	5.0302	.431	.3655	6.4371	.00574
80	.074	5.1308	.0589	5.2302	.354	.282	6.5501	.00471
90	.0050	6.3010	.0035	6.4548	.0308	.0216	7.6651	.00122
100	.0000		.0000		.0000	.0000		

Fig. 1.—Molar solubilities of A (silver acetate), B (silver sulfate) and C (barium iodate hydrate) in water–dioxane mixtures.
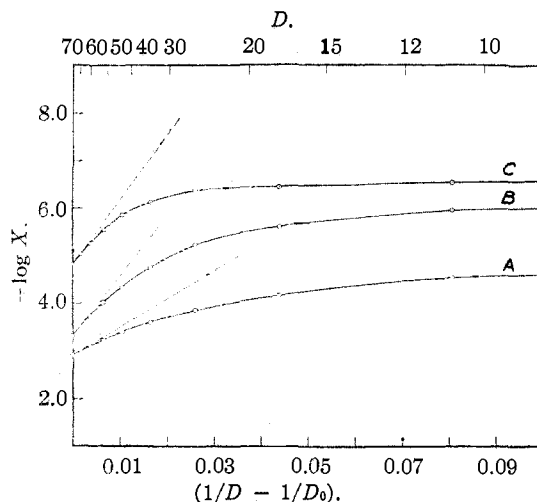

Fig. 2.—Solubilities in mole fractions of A (silver acetate), B (silver sulfate) and C (barium iodate hydrate) in water–dioxane mixtures.

values for which are given in Table I; Fig. 2 shows the corresponding variations of $- \log X$.

Values reported in the literature for the solubility of $Ba(IO_3)_2 \cdot H_2O$ at 25° are

Trautz and Anschütz[10]	5.7×10^{-4} M
Harkins and Winninghoff[11]	7.895×10^{-4} M
Macdougall and Davies[12]	8.10×10^{-4} M
Polessitskii[13]	8.33×10^{-4} M
Present investigation	8.145×10^{-4} M

The numerous determinations of the solubility of silver acetate were reviewed by MacDougall and Bartsch,[14] who themselves found a value of 0.06634 M, as compared with the value here reported of 0.06663 M.

(10) M. Trautz and A. Anschütz, Z. physik. Chem., **56**, 236 (1906)·

(11) W. D. Harkins and W. J. Winninghoff, THIS JOURNAL, **33**, 1827 (1911).

(12) G. Macdougall and C. W. Davies, J. Chem. Soc., 1416 (1935).

(13) A. Polessitskii, Compt. rend. acad. sci., U. R. S. S., **14**, 193 (1935).

(14) F. H. MacDougall and C. E. Bartsch, J. Phys. Chem., **40**, 649 (1936).

As for silver sulfate, the only previous determinations at 25° are of rather old date:

	M
Drucker[15] (1901)	0.0257
Rothmund[16] (1909)	.0267
Hill and Simmons[17] (1909)	.02677
Harkins[18] (1911)	.02676
Present investigation	.02684

III. Theory of Solubility

Born[2] has given the following equation for the free energy of charging spheres of radius r_i, in a uniform medium of dielectric constant D, in terms of the charge, $z_i e$, of the spheres, e being the charge of an electron

$$E = \frac{1}{D} \frac{z_i^2 e^2}{2r_i} \tag{1}$$

(15) K. Drucker, Z. anorg. Chem., **28**, 361 (1901).

(16) V. Rothmund, Z. physik. Chem., **69**, 523 (1909).

(17) A. E. Hill and J. P. Simmons, THIS JOURNAL, **31**, 821 (1909).

(18) W. D. Harkins, ibid., **33**, 1807 (1911).

For a very dilute solution of an electrolyte considered as completely dissociated into spherical ions of radii r_+ and r_-, the energy of interaction of the ions with the medium per mole will be the sum of the individual energies

$$E_+ + E_- = \frac{N\nu_+ z_+^2 e^2}{D \, 2r_+} + \frac{N\nu_- z_-^2 e^2}{D \, 2r_-}$$

$$= \frac{Ne^2}{D \, 2r} (\nu_+ z_+^2 + \nu_- z_-^2) \qquad (2)$$

independently of the concentrations as long as the solution is so dilute that interionic attractions can be neglected. In (2), r represents an averaged value of the two separate radii, and ν_+ and ν_- are the number of positive and negative ions, respectively, formed in the ionization of one molecule of the electrolyte. N is the Avogadro number.

Combining equation (2) with the ideal relation between free energies, activities and mole fractions, and rearranging the dielectric term, the solubilities in two different media will be related as follows

$$0 = RT \ln \frac{X''}{X'} + \frac{Ne^2}{2r}(\nu_+ z_+^2 + \nu_- z_-^2)\left(\frac{1}{D''} - \frac{1}{D'}\right) \quad (3)$$

$$0 = RT \ln \frac{(\nu_+ X'')^{\nu_+}(\nu_- X'')^{\nu_-}}{(\nu_+ X')^{\nu_+}(\nu_- X')^{\nu_-}} +$$
$$\frac{Ne^2}{2r}(\nu_+ z_+^2 + \nu_- z_-^2)\left(\frac{1}{D''} - \frac{1}{D'}\right) \quad (4)$$

the primes and double primes referring to the two different media and the z's both being taken as positive numbers. On dividing by $RT\,(\nu_+ + \nu_-)$, equation (4) becomes

$$\ln X' = \ln X'' + \frac{Ne^2}{RT 2r}z_+ z_-\left(\frac{1}{D''} - \frac{1}{D'}\right) \quad (5)$$

The solubility of a slightly soluble electrolyte, however, is also dependent on the concentration of ions in the solution, including those from its own dissociation. The effect of the ionic atmosphere is to decrease the activity coefficients of the ions and hence to increase the solubility; and Born's equation should be applied only to solubilities which have been corrected for this ion–ion interaction effect. The magnitude of the correction at 25° is given by the familiar Debye–Hückel expression for the logarithm of the mean activity coefficient of the electrolyte

$$\log f_\pm = -\frac{\dfrac{352.6}{D'^{1/2}}z_+ z_- \sqrt{\mu}}{1 + \dfrac{2.914}{D'^{1/2}}a\sqrt{\mu}} \qquad (6)$$

where μ represents the ionic strength and "a" the distance of closest approach of the ions (twice the average radius).

If the solubility of the electrolyte in a solution of ionic strength μ is S_μ, then in a solution of zero ionic strength the solubility S_0 will be given by an expression of the form

$$\log S_0 = \log S_\mu - \frac{B\sqrt{\mu}}{1 + Aa\sqrt{\mu}} \qquad (7)$$

Combining this equation with the Born equation, we find the solubilities in two different media related by the equation

$$\log S' - \frac{B'\sqrt{\mu'}}{1 + A'a\sqrt{\mu'}} = \log S'' - \frac{B''\sqrt{\mu''}}{1 + A''a\sqrt{\mu''}} + \frac{Ne^2 z_+ z_-}{RT\,2.303a}\left(\frac{1}{D''} - \frac{1}{D'}\right) \quad (8)$$

Actually the effect of the Debye–Hückel corrections is rather small, as the two terms, being about equal in magnitude, nearly cancel each other. It proves to be empirically true in many cases that the mean activity coefficient of an electrolyte in saturated solution is almost independent of the dielectric constant of the medium. While no especial mention has been made of this fact, several examples may be found in the literature, and data presented later in this report (Table VIII) illustrate approximately the same principle.[14,19,20,21] This regularity and its possible application will be discussed in a later report.

Equations similar to (8) (without the general valence factor) have been used by La Mer and Goldman[19] in connection with their study of thallous iodate in alcoholic solutions, and by Brönsted, Delbanco and Volqvartz.[22] An equivalent valence factor appears in the equation for equilibrium constants in ionic processes, used by MacDougall and Larson,[20] while Dunning and Shutt[23] use a similar equation for solubilities but with a different valence factor. The equation modified for the interionic attraction effects, as given by the Debye–Hückel limiting law only, has been used by Flatt and Jordan.[24]

Brönsted, Delbanco and Volqvartz compared the solubilities of a number of electrolytes in water and in pure organic solvents. The unmodified Born equation was found to be in qualitative agreement with the actual "distribution

(19) V. K. La Mer and F. H. Goldman, THIS JOURNAL, **53**, 473 (1931).

(20) F. H. MacDougall and W. D. Larson, J. Phys. Chem., **41**, 417 (1937).

(21) P. Walden, Z. physik. Chem., **55**, 683 (1906), reported tetraethylammonium iodide to be about 48% dissociated in saturated solution in many solvents.

(22) J. N. Brönsted, A. Delbanco and K. Volqvartz, Z. physik. Chem., **A162**, 128 (1932).

(23) W. J. Dunning and W. J. Shutt, Trans. Faraday Soc., **34**, 1192 (1938).

(24) R. Flatt and A. Jordan, Helv. Chim. Acta, **16**, 37 (1937).

ratio of the ions" or the ratio of the solubility in water to that in the organic solvent; but quantitative tests were not made, and intermediate strengths of the mixtures were not used. The data of Flatt and Jordan were extremely limited (the solubility of the perchlorates of potassium, rubidium and cesium in 0, 50 and 75% alcohol, by volume). With only three points for the solubility curve of a given electrolyte, it is no surprise that the theory was found to be in "splendid agreement" with observation. What we are attempting here is a test of the combined Born and Debye–Hückel equations on a whole series of media of varying dielectric constant, using different types of electrolytes, and with a sufficient number of dependable determinations to furnish a drastic test of the mathematical predictions.

IV.   Determination of "a" Values

With CARL G. SAUTER

In attempting to test the validity of equation (8), which we may call the "corrected" Born equation, the question immediately presents itself as to the correct values of a to be used in the several terms of the equation.

Ionic diameters for the three solutes examined in this investigation may be calculated from data on the solvent effects of strong electrolytes. Some of the data and computations are to be found in the literature. The values for silver acetate in water, alcohol–water and acetone–water solvents, in the presence of the various electrolytes shown in parentheses, given in Table IX below, are taken from the publications of MacDougall and co-workers.[14,20,25] That given for silver sulfate in the presence of potassium nitrate was calculated from some measurements of Harkins on the effect of potassium nitrate on the solubility of silver sulfate.[18] The value for barium iodate in the presence of potassium nitrate was calculated both from our own measurements and from the data given by MacDougall and Davies[12]; that for barium iodate in the presence of potassium chloride is taken from the measurements and calculations of Naidich.[26]

To supplement to some extent the data already found in the literature, we have made further similar determinations, studying the solubility of barium iodate monohydrate in water at 25°

(25) F. H. MacDougall and J. Rehner, THIS JOURNAL, **56**, 368 (1934).

(26) S. Naidich and J. E. Ricci, THIS JOURNAL, **61**, 3268 (1939).

in the presence of varying concentrations of potassium nitrate, barium nitrate, magnesium chloride and potassium bromate; and that of silver acetate in 10% dioxane in the presence of potassium nitrate, sodium nitrate and potassium chlorate, and in 20% dioxane in the presence of potassium chlorate. The results are presented in Tables V, VI and VII; in these tables, $m_\pm$ is the mean ionic concentration of the saturating salt, i. e., $^{(\nu_+ + \nu_-)}\sqrt{(\nu_+ S)^{\nu_+}(\nu_- S)^{\nu_-}}$, and μ is the ionic strength. S is the solubility in moles per liter of solution. The a values listed in these tables were calculated by the usual methods of applying equation (7).

TABLE V

SOLUBILITY OF BARIUM IODATE MONOHYDRATE IN AQUEOUS SOLUTIONS OF SOME ELECTROLYTES

Molarity of salt	Soly. $\times 10^4$	$-\log m_\pm$	$\sqrt{\mu}$	a calcd., Å.
0	8.145	2.8884	0.04943	
KNO₃				
0.002	8.513	2.8692	0.06748	1.79
.01	9.383	2.8270	.1132	1.64
.05	11.74	2.7296	.2314	1.82
.2	16.45	2.5831	.4527	2.01
Ba(NO₃)₂				
0.0005	6.955	2.8786	0.0599	3.89
.001	6.206	2.8676	.0697	2.07
.0025	4.963	2.8433	.0948	1.49
.01	3.426	2.7712	.1762	1.49
.025	2.854	2.6947	.2754	1.76
MgCl₂				
0.001023	8.596	2.8650	0.07515	3.53
.005069	9.591	2.8174	.1345	3.53
.02532	11.99	2.7205	.2820	3.53
.1014	16.11	2.5922	.5558	3.50
KBrO₃				
0.000997	8.3			
.002996	8.5			
.005045	9.0			

The figures in Tables VI and VII are summarized in Table VIII, which shows S, the observed solubility, S_0, the solubility calculated at zero ionic strength, and f, the mean activity coefficient $(= S_0/S)$. In agreement with the regularity pointed out above, the mean activity coefficient of silver acetate in its pure saturated solution seems to be roughly independent of the dielectric constant of the solvent.

The silver acetate solubilities in presence of salts, in various dioxane–water mixtures, are shown graphically in Fig. 3. The curve for silver acetate in water solvents is taken from the measurements of MacDougall and Rehner.[25] The

TABLE VI

SOLUBILITY OF SILVER ACETATE IN 10% DIOXANE, IN PRESENCE OF ELECTROLYTES

Molarity of salt	Soly., M	$-\log m_{\pm}$	$\sqrt{\mu}$	a calcd., Å.
0	0.05032	1.2980	0.2244	
KNO₃				
0.009978	0.05099	1.2925	0.2469	(5.47)
.04995	.05377	1.2695	.3221	4.64
.1002	.05619	1.2503	.3954	4.44
.2001	.05929	1.2270	.5093	4.50
.4992	.06476	1.1887	.7510	4.44
.9985	.06959	1.1575	1.033	4.41
NaNO₃				
0.005084	0.05081	1.2941	0.2392	
.009924	.05116	1.2910	.2472	4.01
.04979	.05413	1.2666	.3224	3.93
.09073	.05585	1.2530	.3829	4.21
.09996	.05649	1.2481	.3955	4.01
.1999	.05985	1.2229	.5096	4.07
.4927	.06583	1.1816	.7474	4.04
.9979	.07209	1.1429	1.034	3.90
1.999	.07781	1.1090	1.441	3.93
2.999	.08034	1.0951	1.752	4.01
3.172	.08067	1.0933	1.804	4.04
4.002	.08076	1.0928	2.021	4.21
KClO₃				
0.004987	0.05077	1.2944	0.2361	3.21
.01007	.05127	1.2901	.2477	3.24
.04995	.05429	1.2653	.3228	3.50
.05017	.05429	1.2653	.3232	3.53
.09987	.05695	1.2445	.3960	3.58
.2018	.06093	1.2152	.5126	3.30
.3045	.06453	1.1903	.6075	3.21
.4002.	.06637	1.1780	.6831	3.41

TABLE VII

SOLUBILITY OF SILVER ACETATE IN 20% DIOXANE, IN PRESENCE OF POTASSIUM CHLORATE

Molarity KClO₃	Soly., M	$-\log m_{\pm}$	$\sqrt{\mu}$	a calcd., Å.
0	0.03613	1.4421	0.1902	
0.009331	.03703	1.4315	.2153	(4.31)
.05005	.04023	1.3955	.3005	3.32
.09988	.04275	1.3691	.3777	3.67
.1506	.04487	1.3480	.4422	3.56
.2000	.04660	1.3313	.4966	3.51
.2996	.04913	1.3087	.5905	3.53

TABLE VIII

MEAN ACTIVITY COEFFICIENT OF SILVER ACETATE IN PURE SATURATED SOLUTION

Solvent	D	S_0	S	f
Water[14]	78.55	0.0531	0.0663	0.800
10% dioxane	69.71	.0396	.0503	.786
20% dioxane	60.81	.0279	.0361	.771

limiting slopes for the different dioxane solvents involved, namely, 0.505 for 0%, 0.606 for 10% and 0.744 for 20% dioxane are shown as dashed lines in the figure for comparison with the experimental curves. In the case of the barium iodate

solubilities, in which the measurements extend down to a much lower value of the ionic strength, the observed limiting slope, as has been shown also by Brönsted and La Mer[27] and by Macdougall and Davies,[12] is in actual agreement with the theoretical value of 1.01.
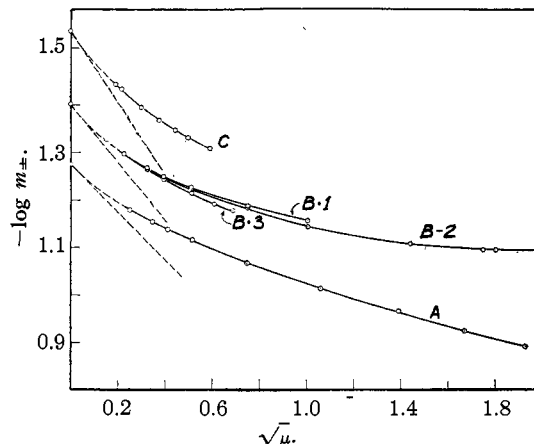

Fig. 3.—Solubility of silver acetate in dioxane–water mixtures in the presence of added salts: A, 0% dioxane, with NaNO₃; B, 10% dioxane, with (1) KNO₃, (2) NaNO₃, (3) KClO₃; C, 20% dioxane, with KClO₃.

The various Debye–Hückel values of the a parameter for silver acetate, silver sulfate and barium iodate are summarized in Table IX. Chloupek and Daneš[28] have reported another Debye–Hückel value of a for silver sulfate, determined, however, from studies on the e. m. f.'s of cells. Their values of 1 and 3 Å. for the diameters of the silver and sulfate ions, respectively, may be compared with the figure for this electrolyte given in the table.

TABLE IX

VALUES OF a FROM EFFECT OF SOLVENT SALTS ON SOLUBILITY

Solvent	AgC₂H₃O₂	Ag₂SO₄	Ba(IO₃)₂·H₂O
Water	4.35 (KNO₃)	2.43 (KNO₃)	1.80 (KNO₃)
	3.69 (NaNO₃)		3.20 (KCl)
			3.52 (MgCl₂)
			1.70 (Ba(NO₃)₂)
Alcohol (10–30%)	3.99 (KNO₃)		
	3.72 (NaNO₃)		
Acetone (10–30%)	3.99 (KNO₃)		
	3.87 (NaNO₃)		
Dioxane (10%)	4.48 (KNO₃)		
	4.03 (NaNO₃)		
	3.37 (KClO₃)		
Dioxane (20%)	3.52 (KClO₃)		

It is observed that the values are not and cannot be characteristic of the saturating salt itself

(27) J. N. Brönsted and V. K. La Mer, THIS JOURNAL, 46, 555 (1924).

(28) J. B. Chloupek and V. Z. Daneš, Coll. Czech. Chem. Comm., 4, 165 (1932); B.C.A., 572 (1932).

but are averages including the added solvent ions too. It is obvious that we cannot arbitrarily take an average of these parameters in applying Born's equation although we expect the a which should apply to be of the same order of magnitude. We have, therefore, thought it best to calculate a values by applying the "corrected" Born equation (Eq. 8) to solubilities experimentally observed in the several solvents. There may be some question whether the same a should be used in the Debye–Hückel terms as in the Born term, but inasmuch as the latter term far outweighs the others in numerical significance, appreciable variations in a have little effect on the Debye–Hückel

TABLE X

VALUES OF a FOR POSSIBLE USE IN TESTING EQUATION 8

Source	AgC$_2$H$_3$O$_2$	Ag$_2$SO$_4$	Ba(IO$_3$)$_2$·H$_2$O
Limiting slope of Fig. 1 (molarities)	3.1	3.1	3.1
Equation 8, 0–10% dioxane (using molarities)	3.05	3.41	3.30
Limiting slope of Fig. 2 (mole fractions)	4.2	3.6	3.2
Equation 8, 0–10% dioxane (using mole fractions)	4.14	3.93	3.57
Equation 8, 0–30% dioxane (using mole fractions)	4.59	4.59	4.28
Average of Debye–Hückel values, Table VIII	3.83	2.43	2.34

corrections, and it seems reasonable to use a single figure for the ion diameters.

We have calculated the a values for the several solutions, combining the solubility in water with the solubility in the several mixed media as indicated in equation 8. The resulting a's are listed in Tables XI, XII and XIII. In each case the values increase with increasing proportion of dioxane. As a result of the mathematical transformations involved in the change of units the a's calculated from molarities are smaller than those based on mole fractions. But whichever units are used, the a values are of about the same magnitude and of the same relative consistency over the entire range; furthermore, they are comparable with a parameters appearing in Table VIII, at least in the water-rich solutions. For the purpose of comparison the various a values for the three separate salts which might possibly be used in testing the Born equation (Eq. 8) are collected in Table X.

The a's so determined and their variations as D changes, test and disprove the validity of the fundamental assumption made in the simple application to solubilities of Born's equation corrected for interionic attraction, namely, that there is a value for a (an effective ionic diameter) which

TABLE XI

APPLICATION OF EQUATION 8 TO THE SOLUBILITY OF SILVER ACETATE IN DIOXANE–WATER MIXTURES

	Based on molarities				Based on mole fractions			
Wt. % dioxane	a calcd., Å.	Using a = 3.05 S calcd. × 10⁴	S calcd./S obsd. × 100	a calcd., Å.	Using a = 4.14 X calcd. × 10⁴	X calcd./X obsd. × 100	Using a = 4.60 X calcd. × 10⁴	X calcd./X obsd. × 100
10	3.05			4.14			10.04	102.2
20	3.26	349.4	96.0	4.36	7.48	96.9	7.99	102.4
30	3.49	206.9	84.3	4.59	5.18	90.9	5.69	99.9
40	3.80	98.6	65.0	4.91	3.03	77.5	3.54	90.6
50	4.29	32.2	37.6	5.48	1.34	53.9	1.71	69.0
60	5.01	5.30	12.5	6.36	0.355	25.2	0.522	37.1
70	6.37	0.186	1.07	7.99	.0293	4.30	.0494	7.24
80	8.98	2.1×10^{-4}	0.0035	11.2	1.9×10^{-4}	0.066	5.9×10^{-4}	0.197
90	14.1	2.5×10^{-10}	2.6×10^{-9}	17.3	2.1×10^{-9}	2.2×10^{-6}	1.9×10^{-8}	2.0×10^{-5}

TABLE XII

APPLICATION OF EQUATION 8 TO THE SOLUBILITY OF SILVER SULFATE IN DIOXANE–WATER MIXTURES

	Based on molarities				Based on mole fractions			
Wt. % dioxane	a calcd., Å.	Using a = 3.41 S calcd. × 10⁴	S calcd./S obsd. × 100	a calcd., Å.	Using a = 3.93 X calcd. × 10⁴	X calcd./X obsd. × 100	Using a = 4.60 X calcd. × 10⁴	X calcd./X obsd. × 100
10	3.41			3.93			3.297	109.0
20	3.68	74.36	89.4	4.24	1.601	90.8	1.948	110.4
30	4.00	27.29	67.9	4.59	0.671	72.0	0.940	100.8
40	4.42	6.639	38.9	5.07	.196	44.8	.329	75.1
50	5.00	0.858	14.3	5.72	.0326	18.7	.0703	40.3
60	5.96	.0353	1.96	6.78	.00202	3.38	.00588	9.81
70	8.19	1.01×10^{-4}	0.016	9.36	1.23×10^{-5}	0.050	6.3×10^{-5}	0.262
80	12.6	8.9×10^{-10}	3.9×10^{-7}	14.6	3.6×10^{-10}	3.3×10^{-6}	1.0×10^{-8}	9.3×10^{-5}
90	20.9	5.4×10^{-22}	8.6×10^{-19}	24.3	1.3×10^{-20}	3.3×10^{-16}	1.2×10^{-17}	3.2×10^{-13}

TABLE XIII

APPLICATION OF EQUATION 8 TO THE SOLUBILITY OF BARIUM IODATE MONOHYDRATE IN DIOXANE–WATER MIXTURES

| | Based on molarities
Using $a = 3.30$ | | | Based on mole fractions
Using $a = 3.57$ | | | Using $a = 4.30$ | |
Wt. % dioxane	a calcd., Å.	S calcd. $\times 10^4$	S obsd. $\times \dfrac{p_{H_2O}}{p^0_{H_2O}}$ $\times 100$	a calcd., Å.	X calcd. $\times 10^5$	X obsd. $\times \dfrac{p_{H_2O}}{p^0_{H_2O}}$ $\times 100$	X calcd. $\times 10^5$	X obsd. $\times \dfrac{p_{H_2O}}{p^0_{H_2O}}$ $\times 100$
10	3.30			3.57			10.01	109.4
20	3.51	2.274	92.3	3.93	4.684	89.6	5.75	109.8
30	3.80	0.862	73.9	4.28	1.908	70.4	2.735	100.9
40	4.32	.219	42.2	4.89	0.537	40.1	0.955	71.3
50	5.34	.0291	11.4	6.11	.0832	11.2	.201	27.2
60	6.95	.00115	0.93	8.07	.00420	1.01	.0168	4.06
70	11.1	2.8×10^{-6}	.0030	13.3	1.6×10^{-5}	0.0044	1.6×10^{-4}	0.044
80	17.9	1.1×10^{-11}	1.9×10^{-8}	21.9	1.6×10^{-10}	5.8×10^{-8}	1.2×10^{-8}	4.2×10^{-6}
90	23.6	4.5×10^{-24}	1.3×10^{-19}	27.8	5.1×10^{-22}	2.4×10^{-18}	3.2×10^{-18}	1.5×10^{-14}

should remain constant from one medium to another and should be related to the solubility and dielectric by the equations given above.

At this point it may be appropriate to note that deviations from theoretical curves similar to those noted in this communication have been observed and reported by Tomlinson in a study of reaction velocities.[29]

We could proceed, on the other hand, on the more practical basis that the effective a changes as D changes. Then, assuming in the original equation that there is a characteristic value of a ($= a_0$) for the electrolyte in water (this could be taken as the value approached by the composite a when the percentage of dioxane decreases), an appropriate a ($= a_1$) representing the behavior in each successive solvent can be calculated using the modified Born equation

$$\log S' = \log S_0 + z_+ z_- \left(\frac{B' \sqrt{\mu'}}{1 + A'a\sqrt{\mu'}} - \frac{B_0 \sqrt{\mu_0}}{1 + B_0 a\sqrt{\mu_0}} + \frac{242}{a_0 D_0} - \frac{242}{a_1 D_1} \right)$$

Since the a as already calculated (Tables XI–XIII) is in effect a composite of the diameters for each pair of media, although it is not an arithmetic average, the a values determined in the new way would be even larger than those already calculated. The principle, however, of an effective diameter varying with the medium would offer no possibility of testing the Born equation for the prediction of solubility, inasmuch as we have for the present no independent determination of the change of the diameter, a, for any given electrolyte with respect to change of dielectric. The a would in other words be an adjustable parameter only. We have consequently omitted

(29) H. M. Tomlinson, "Influence of Dielectric Constant upon the Kinetics of the Bromoacetate-Thiosulfate Reaction," Thesis, Columbia, 1939; cf. also V. K. La Mer, J. Franklin Inst., 225, 709 (1939).

such additional figures in the preparation of our tables.

V. Solubilities Calculated from Born's Equation

While the variations of the a's cited in the last three tables themselves indicate the failure of Eq. 8 to account for our experimentally determined solubilities, a clearer picture of the extent of this failure may be drawn from a comparison of predicted and determined solubilities. The calculations have been made in terms of mole fractions using first the a values for the 0 and 10% dioxane solutions and again with the a for the 0 and 30% solutions. The calculations have been repeated on a volume–molar basis using the a which fits the 0 and 10% observed solubilities. The calculations, as before, involve successive approximations; first the solubility is computed without correcting for the interionic attraction, then with this preliminary value the interionic attraction terms are added to the equation and a new solubility is computed. Two approximations are all that are needed except for silver sulfate. The calculated solubilities using the a values just noted together with the ratio of the calculated to the experimental figures are given in the three tables. The calculated and observed curves for log S are plotted together in the two sets of concentration units in Figs. 1 and 2. As can be seen from these figures, the calculated values for log S for both molarity and mole fraction units lie in every case on a very nearly straight line with a slight curvature in the first two or three points due to interionic effects where the ionic strength is appreciable, and with a nearly constant slope, given by

$$\text{slope} = 242 z_+ z_- / a$$

where a has the value used in the given series of calculations. All the predicted values are too small except at a few points where the 30% a is used for the computations since here the straight line of the calculated values cuts through the curve of the observed solubilities at the point for 30% dioxane.

While there is general agreement as to order of magnitude of the solubility down to 40–50% dioxane computed on the basis either of mole fractions or of molarities, even this degree of concordance disappears for solutions containing more than 50% dioxane. This disagreement is a little worse for the two higher valence type electrolytes than for silver acetate. The use of a larger a improves the agreement in the high-dioxane mixtures but makes the figures for the low-dioxane solvents higher than the experimental, as already pointed out.

VI. Discussion

The disagreement between the observed and the calculated solubilities is seen to be substantially the same for either the volume or the mole fraction units of concentration. The question then of the proper concentration units to use would seem to involve factors of minor importance as compared to the larger discrepancies noted between observed and theoretical solubilities.

In seeking some explanation for the wide deviations between prediction and experiment in these solubilities, we observe that three assumptions involved in Eq. 8 may have to be modified in such a way as to bring about better agreement. These assumptions are (1) a constant diameter for the several electrolytes independent of the medium, (2) a homogeneous structureless character for the dielectric medium and (3) the absence of molecular or ionic associations.

While it may seem reasonable to suppose that variable solvation will lead to a changing effective diameter in different media, it is likely that ions in solutions containing even small percentages of water will be fully hydrated or nearly so, so that for practically the whole range of dioxane–water mixtures, a should be nearly constant for a given electrolyte. Moreover, if the extent of solvation is actually smaller in dioxane-rich solutions, smaller diameters should be expected, whereas, as already seen, the observed solubilities require much larger values to bring about agreement with the Born equation. There seems to be no

independent method of estimating these ionic diameters in solution, so that our conclusions regarding them must remain speculative.

Scatchard[30] has shown that the e. m. f. of cells made up of hydrogen chloride in aqueous alcoholic solutions may be accounted for by taking a as equal to 4 Å. up to 50% alcohol and decreasing a to about 2 Å. in absolute alcohol. On the other hand, the values for sodium chloride and potassium chloride in aqueous alcohol are not much different from the a's for these salts in water.[27]

The observation also of rather constant values of a over a wide temperature range for cadmium sulfate and zinc sulfate in water[31] and the very small variation of a for hydrogen chloride in several dioxane–water solvent mixtures[32] may be noted as further evidence for the belief that for a given salt the values of a should be characteristic only of the electrolyte and independent of the medium. It would be pointless then to try to bring the Born equation into agreement with our experiments by artificial adjustments of the a's.

The assumption of continuous character of the solvent medium is apt to be a serious source of error in mixed solvents. The question is related to that of the effective diameter of solvated ions. It is to be expected that in a mixed solvent the more polarizable substance, water in the present case, will be preferentially oriented around the ions; with more soluble electrolytes such as sodium nitrate, this phenomenon may lead to the formation of two liquid layers. While this factor has often been mentioned (for example, by Scatchard[30] in 1925), few calculations of its consequences have been made. Using the Debye expression for the distribution of molecules in a dielectric mixture around a univalent ion,[33] in conjunction with Born's equation, Dunning and Shutt[28] report a calculation of the effective radius of silver chloride when dissolved in a one molar aqueous solution of urea, this radius agreeing more closely with crystallographic values than the radius determined from the Born equation alone. The calculation, however, is very tedious, and while the correction introduced will be in the right direction of increasing the solubilities calculated for a

(30) G. Scatchard, THIS JOURNAL, **47**, 2098 (1925).

(31) V. K. La Mer and W. G. Parks, ibid., **53**, 2040 (1931); I. A. Cowperthwaite and V. K. La Mer, ibid., **53**, 4333 (1931).

(32) H. S. Harned, J. O. Morrison, F. Walker, J. G. Donelson and C. Calmon, ibid., **61**, 49 (1939).

(33) P. Debye, Z. physik. Chem., Cohen Festband, 56 (1927).

given ion size, there is still doubt whether a constant a can be determined for the whole series of solvents, especially when ion association becomes important.

The effect of selective dipole concentration around the ions would not enter into solutions of salts in pure organic solvents of low dielectric; but in most of these liquids the solubility of electrolytes having slight solubility in water will be below the limit of quantitative estimation, and no tests can be applied. One may suggest that the small but detectable dissolving in 90% dioxane of such a difficultly soluble substance as barium iodate, while its solubility in a single solvent of the same dielectric capacity would probably be zero,[34] is evidence that the preferential adsorption of water around ions has a tremendous effect in determining solubility in solvents containing water.

Another effect particularly important in solvents of low dielectric constant is ion clustering in the Bjerrum sense.[35] Such clustering will result in an increased solubility over that calculated assuming complete dissociation. A formula for the formation of binary pairs for a uni-univalent electrolyte has been given by Fuoss and Kraus as a function of the diameter of the ions and the dielectric of the medium,[36] in the approximate and simplified form

$$\frac{1}{K} = \frac{4\pi N}{1000} a^4 \frac{DkT}{e^2} \exp\left(\frac{1}{a}\frac{e^2}{DkT}\right)$$

where K is the dissociation constant and the other letters have their usual significance. Application of this equation gives approximately 3.1×10^{-6} and 1.1×10^{-12} as the values of K for silver acetate in 80 and 90% dioxane, respectively, where our value of a, namely, 3.05, is taken to define the corresponding value of K. Such results would indicate negligible quantities of silver acetate in molecular form when the ion concentrations are of the magnitudes given in column 3 of Table XI. Smaller a values in the Fuoss and Kraus equation will give, it is true, a K sufficiently small to account for observed solubilities. If a is taken as one-half of 3.05 Å., roughly correct solubilities are predicted. The magnitude of K calculated according to this equation is extremely sensitive to small changes in a. Uncertain, therefore, as a itself is, any value of K derived in

the Fuoss and Kraus manner must be considerably in doubt. It is unlikely, furthermore, that the mean ionic diameter for silver acetate can be much smaller than 3.05 Å., for it usually has been found that the parameters fitted into the ordinary Debye–Hückel equation are smaller than expected in the sense that sometimes negative values are found, while a more extended treatment such as that of Gronwall, La Mer and Sandved[37] leads always to positive and hence physically plausible values of a. It is possible that the a's we have used, which are in general agreement with Debye–Hückel values, are too small also.

Several authors have declared that in media below about 60 in dielectric capacity, most of the divalent ions will be associated and that below a dielectric of about 30 univalent ions will be largely associated into neutral molecules. If this be the case in our experiments, the solutions should behave like non-electrolytes where the dioxane percentages exceed 50 approximately, and the solubilities should be nearly proportional to the mole fractions of water in the mixtures. This is not observed, as seen from the data in Tables II–IV, so that we may infer that the solutions of the un-ionized salts here studied are not ideal.

A complete prediction of solubilities in the light of modern theories would involve an estimation of the solubility by the corrected Born equation followed by a calculation of solvent segregation around the ions, a redetermination then of the ionic solubility and a determination of the Bjerrum ion association using the Kraus and Fuoss method of calculation. Such a series of calculations has not yet been made, but while laborious it would have some interest as a test of the combined theories.

Summary

The solubilities of silver acetate, silver sulfate and barium iodate have been determined at 25° in a series of dioxane–water solutions extending from 0 to 100% dioxane. The dielectric constants cover the range 2.1 to 78.55.

The solvent effect of potassium nitrate, barium nitrate, magnesium chloride and potassium bromate solutions on barium iodate in water has been examined experimentally. The solvent effects of potassium nitrate, sodium nitrate and potas-

(34) Thallous iodate has negligible solubility in alcohol, of much higher dielectric than 90% dioxane; cf. La Mer and Goldman, ref. 19.

(35) Cf. evidence from absorption curves reported by H. v. Halban and B. Szigeti, Helv. Chim. Acta, **20**, 746 (1937).

(36) R. M. Fuoss and C. A. Kraus, This Journal, **55**, 1019 (1933).

(37) T. H. Gronwall, V. K. La Mer and K. Sandved, Physik. Z., **29**, 358 (1928).

sium chlorate on silver acetate in 10% dioxane solutions, and of potassium chlorate on silver acetate in 20% dioxane, have also been investigated. The corresponding Debye–Hückel a parameters have been calculated.

The Born equation even when corrected for interionic effects fails to account for the course of the solubilities as the percentage of dioxane increases, predicting in each case lower solubilities than those observed. The differences increase in media of higher dioxane content, pre-

diction and observation disagreeing even as to order of magnitude in solvents containing more than 50% dioxane by weight. The disagreement is not diminished appreciably by substitution of mole fractions for volume concentrations, showing that this question is of minor importance as a factor in the application of the Born equation.

Modifications to be superimposed on the Born equation to bring it into line with the observations are discussed.

Kinetic Studies on Iodine Derivatives. I. The Thermal Decomposition of Acetyl Iodide[1]

BY J. LESLIE JONES

The thermal[2] and photochemical[3] decomposition of acetaldehyde into methane and carbon monoxide has been investigated by numerous authors. Since the deduction of a possible free radical mechanism for the thermal and photochemical decomposition of acetaldehyde by Rice and Herzfeld,[4] a great deal of controversy has arisen concerning its validity. The opposing theory[2c] assumes that the activation process, thermal or photochemical, is followed by a rearrangement of the acetaldehyde directly into the final products, methane and carbon monoxide.

On the basis of previous investigations[5] it seems probable that the thermal decomposition of alkyl iodides occurs by the breaking of the carbon–iodine bond (temperature range of 250–350°) as the primary process. This reaction is followed by the secondary reactions of the free radicals. By the substitution of an iodine atom for the hydrogen atom of the aldehyde group in acetaldehyde

it is possible to study the thermal decomposition of the product, acetyl iodide, in the same temperature range as the alkyl iodides. Such a study casts light upon the mechanism of the thermal decomposition of acetaldehyde, supporting the free radical mechanism. In addition information is gained concerning the secondary reactions of the free radicals involved.

Experimental Section

The rate of decomposition of the acetyl iodide was followed by the pressure change method, employing essentially the apparatus of Jones and Ogg.[5] The quartz spiral manometer prevented the iodine evolved in the reaction from reacting with the mercury in the absolute manometer. A hollow barrel stopcock was employed to close the reaction vessel, employing a plasticizer as lubricant. The compound, di-o-xenzyl-monophenyl phosphate,[6] has a vapor pressure of 5 mm. at 285° and a viscosity of 170 centipoises at 60°. The liquid was warmed in a high vacuum system for several hours in order to remove all solvents. All observations indicated that it was unaffected by the iodine generated in the system, as its structure suggested. It was necessary to heat the stopcock closing the reaction vessel to about 110° in order to prevent condensation of iodine.

The acetyl iodide was prepared by the treatment of Eastman Kodak Co. acetyl chloride with an excess of dry hydrogen iodide gas at 0°. The brown crude product (90% yield) was protected from the air and vacuum distilled in an all-glass fractionating system two times, large amounts of the first and third fractions being discarded. A third fractionation was carried out in high vacuum, the product being distilled directly into the reservoir of the system employed for the study of the reaction rates. In

(1) A preliminary report of this paper was presented at the Symposium on the Kinetics of Homogeneous Gas Reactions, University of Wisconsin, June 20–22, 1939.

(2) (a) Fletcher and Rollefson, THIS JOURNAL, **58**, 2135 (1936); (b) Letort, J. chim. phys., **34**, 265 (1937); (c) Staveley and Hinshelwood, J. Chem. Soc., 1568 (1937); (d) Brenschede and Schumacher, Ber., **70B**, 452 (1937); (e) Rollefson and Faull, THIS JOURNAL, **59**, 625 (1937).

(3) (a) See P. A. Leighton, J. Phys. Chem., **42**, 749 (1937), for a complete review to that date; (b) Blacet and Volman, THIS JOURNAL, **60**, 1234 (1938); (c) Gorin, J. Chem. Phys., **7**, 256 (1939); (d) Rollefson and Grahame, paper presented at the "Symposium on the Kinetics of Homogeneous Gas Reactions," University of Wisconsin, June 20–22, 1939.

(4) Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(5) See Jones, ibid., **60**, 1877 (1938), for complete references to earlier research.

(6) Furnished through the courtesy of the Dow Chemical Company, Midland, Mich.