that atoms may be loosened in a molecule by displacement of the electrons which hold them together, but not by direct displacement of the atoms.

Summary

1. Infra-red radiation did not cause the photochemical decomposition of nitrogen pentoxide.
2. The sensitivity of the tests and the possible decomposition, calculated from the energy input, have been critically discussed. At least 99.5% of the radiation, actually absorbed, was proved to be chemically inactive.
3. A *slightly* increased decomposition at room temperature was traced to thermal decomposition. The effect disappeared at 0°, at which temperature thermal decomposition is negligible.
4. Infra-red radiation was shown to be inactive also in the decomposition of carbon dioxide, the decomposition of hydrogen chloride gas and the oxidation of alcohol vapor.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 83]

THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES. V. TESTING OF THE THEORY BY SOLUBILITY EXPERIMENTS AT HIGHER TEMPERATURES

BY WARREN P. BAXTER[1]

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Introduction

The functional relation between the activation α_A of an ion of sort A, its valence z_A, and the ionic strength $\frac{1}{2}\Sigma(cz^2)$ prevailing in a solution of dielectric constant κ is given by the inter-ionic attraction theory[2,3] for sufficiently small concentrations by the following expressions, in which A is the product of certain universal constants,

$$-ln\ \alpha_A = \frac{A\ z^2{}_A\sqrt{\Sigma cz^2}}{(\kappa T)^{3/2}};\quad \text{or} -\log \alpha_A = 1.07 \times 10^{14}\,\frac{z^2{}_A\sqrt{\Sigma (cz)^2}}{(\kappa T)^{1.5}} \qquad (1)$$

when the concentrations are in moles per liter. Even at such fairly small concentrations as 0.02–0.10 M experimental observations[2,3] show considerable deviations from the requirements of this equation. The work of Brönsted and La Mer,[4] however, on the solubility of slightly soluble cobalt ammines in very dilute aqueous solutions of other salts seems to have veri-

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[1] Du Pont Fellow in Chemistry, 1925–1926.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). Debye, *ibid.*, **24**, 334 (1923); **25**, 97 (1924).

[3] Noyes, THIS JOURNAL, **46**, 1080, 1098 (1924).

[4] Brönsted and La Mer, *ibid.*, **46**, 555 (1924).

fied the equation as a limiting expression at very small concentrations. Nevertheless, a further testing of the theory at very small concentrations is desirable. Moreover, it seems important to test more fully the variation of the activation effect with the temperature and dielectric constant of the solution, or more specifically, to test the validity of the factor $(\kappa T)^{1.5}$ occurring in the denominator of Equation 1, especially as this factor is the direct expression of the electrical cause of the effect.

It has been shown by Scatchard[5] and by Noyes and Baxter[6] that the values of the activation of hydrochloric acid in water, in ethyl alcohol, and in an equimolal mixture of water and ethyl alcohol vary with the dielectric constant κ of the solvent, at any rate roughly, in the way required by the theory. A further test of the effect of the factor $(\kappa T)^{1.5}$ can be made in the case of aqueous solutions by measurements at higher temperatures. For this purpose the solubility of slightly soluble salts in the presence of other salts gives the greatest promise, since the determinations can be made simply and accurately, and since the solubilities give immediately values of the activation product for the two ions of the salt saturating the solution. Thus, since the activity of this salt remains constant, we may write for a di-ionic salt AB the following expression, in which the symbols with zero subscript refer to the ions of the salt when it is present at saturation in water alone, and the other symbols to the ions of the same salt when present at saturation in a solution containing another salt.

$$\frac{\alpha_{\mathrm{A}}\ \alpha_{\mathrm{B}}}{\alpha_{\mathrm{A}0}\ \alpha_{\mathrm{B}0}} = \frac{c_{\mathrm{A}0}\ c_{\mathrm{B}0}}{c_{\mathrm{A}}\ c_{\mathrm{B}}} \tag{2}$$

Accordingly, an investigation was undertaken on the solubility of silver iodate in solutions of other salts at various concentrations at a temperature of 75°. Because of the low solubility of this salt, 0.000840 *M*, and because the dielectric constant of water has been determined up to 75° by Drude,[7] these experiments afford an opportunity for further testing the theory.

Taking for κ the value 63.7 given by Drude's empirical equation at 348.1° A. and introducing the density of water (0.975) to take account of the fact that the experimental concentrations c' given below are expressed in moles per 1000 g. of water (instead of per liter of solution), Equation 1 takes the special form

$$-\log \sqrt{\alpha_{\mathrm{Ag}}\ \alpha_{\mathrm{IO_3}}} = 0.386\sqrt{\Sigma(c'z^2)} \tag{3}$$

This research was suggested by Professor A. A. Noyes and aided financially by a grant to him from the Carnegie Institution of Washington.

Preparation of Materials

Silver Iodate.—Several samples of silver iodate were used in this investigation. One sample was prepared by adding 0.4 *N* silver nitrate solution to a slight excess of

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[5] Scatchard, THIS JOURNAL, **47,** 2098 (1925).

[6] Noyes and Baxter, *ibid.*, **47,** 2122 (1925).

[7] Drude, *Ann. Phys.*, **59,** 61 (1896).

warm 0.15 *N* potassium iodate solution. The precipitate was divided into two portions; each was collected on hardened filters, washed first with cold water, then with 6 to 8 liters of hot water, sucked dry, and dried at 110° for a few hours. During the drying it darkened slightly on the surface. Its solubility, expressed in millimoles per 1000 g. of solution, was found to be 0.8415 (four experiments; maximum deviation from the mean, 0.17%) and 0.8414 (three experiments; maximum deviation, 0.12%). Another preparation was made by adding 0.3 *N* potassium iodate solution to a silver nitrate solution. One portion of the precipitate was washed and dried as before. This and subsequent samples remained pure white during the drying. Its solubility was found to be 0.8411 (four experiments; maximum deviation, 0.39%). Another portion was washed, dissolved in dil. ammonia solution, reprecipitated by the slow addition of nitric acid, washed and dried. Its solubility was 0.8395 (five experiments; maximum deviation, 0.43%). Some recovered silver iodate was dissolved in ammonia solution and similarly treated; its solubility was 0.8371 (five experiments; maximum deviation, 0.43%).

Potassium Nitrate, Perchlorate and Sulfate, and Barium Nitrate.—The C. P. salts were recrystallized one to three times until no test for chloride could be obtained. They were dried at 120° for five or more hours. The solutions were made up by direct weighing.

Magnesium Sulfate.—A very pure sample of the salt was recrystallized. The magnesium content of two 0.02 *M* solutions was determined by precipitating magnesium ammonium phosphate and weighing as the pyrophosphate, $Mg_2P_2O_7$.

Water.—The water used for the solubility measurements was ordinary distilled water, redistilled from a silver sulfate solution, and finally distilled again.

Experimental Procedure for Determining the Solubility

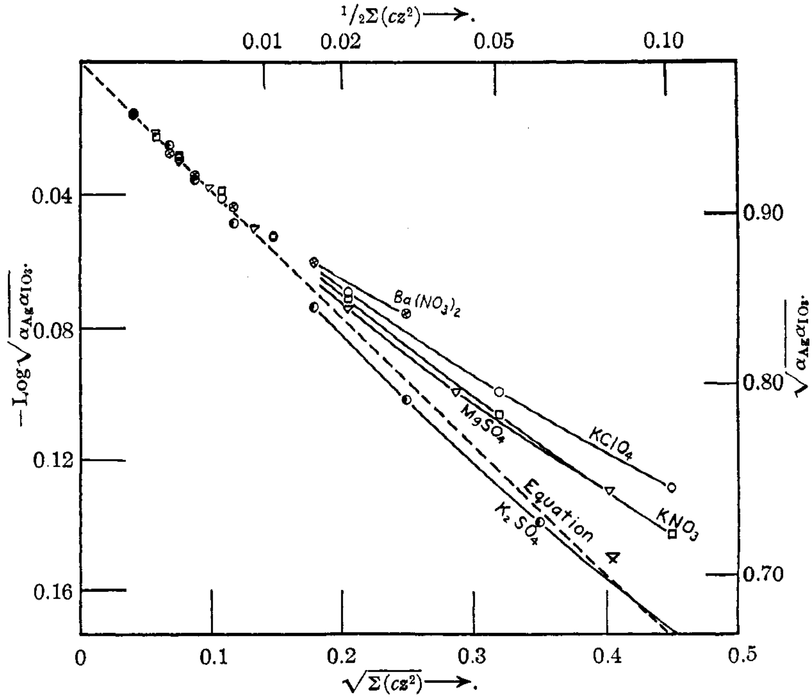
Saturation of the Mixtures.—A 1.5-g. sample of silver iodate was rotated with 350 cc. of the desired solution in bottles made of large Pyrex tubing and completely sealed for each determination. The thermostat, whose surface was covered with paraffin, was maintained at 75.00° ± 0.02°. The period of rotation was usually between 20 and 36 hours. No variation of the apparent solubility value in pure water was caused by varying the times of rotating from 20 to 100 hours. Each pair of determinations represents an equilibrium approached from both a low and a high temperature, the latter being obtained by removing a bottle that had been rotated for a short time and heating it above the thermostat temperature. More often than not the determinations from the hot side gave slightly lower values than those approached from the lower temperature, but the agreement generally was within at least 0.2%. The silver iodate remained pure white throughout each experiment.

Removal and Analysis of the Equilibrium Mixtures.—After a bottle had been rotated, it was placed in a rack in the thermostat, the tip of a side tube broken off, and a hole blown in the top of the neck through which a heated delivery tube was introduced. The delivery tube had a constriction which held in place a wad of asbestos fibers. A sample of 240–300 g. was blown by compressed air through the asbestos into a weighed glass-stoppered 500cc. flask containing 10 cc. of dil. hydrochloric acid.

After weighing, the contents of the flask were cooled to somewhat below room temperature, 2 g. of potassium iodide was added, and the resulting iodine titrated with 0.04 *N* sodium thiosulfate solution. The end-point was accurately obtained, without any difficulty arising from the presence of the precipitated silver chloride, by titrating the slight excess of thiosulfate used with 0.01 *N* iodine solution. For each analysis 30–40 cc. of the standard sodium thiosulfate was used. The thiosulfate solution was standardized by the method of Bray and Miller[8] against a standard solution of thrice recrystallized potassium dichromate. The strength of the thiosulfate solution was determined at least once a week. Its titer decreased 0.25% in six weeks.

The Solubility and Activation Data

The solubility data are presented in Table I. The first column gives the nature of the added salt; the second its concentration, and the third the



solubility of the silver iodate. The concentrations of added salt and the solubilities are expressed in millimoles per 1000 g. of water (weighed in air). The fourth column shows the number of determinations; and the fifth the percentage average deviation (A. D.) from the mean divided by the square root of the number of determinations. In the sixth column are given the

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[8] Bray and Miller, This Journal, **46**, 2204 (1924).

values of the solubility ratio s/s_0, obtained by dividing the solubility in a particular salt solution by the solubility in pure water of the silver iodate used in that determination. The last column gives the values of $\sqrt{\alpha_{Ag}\,\alpha_{IO}}$ obtained by dividing 0.964 by the smoothed values of s/s_0 obtained from large-scale curves similar to Fig. 1. The value 0.964 is the activation of silver iodate in its saturated solution in pure water, as given by Equation 3.

TABLE I

SOLUBILITY AND ION-ACTIVATION VALUES FOR SILVER IODATE AT 75°

Added salt Nature	Added salt Concn.	Solubility of $AgIO_3$	No. of expts.	Per cent. A. d.	Ratio s/s_0	$\sqrt{\alpha_{Ag}\,\alpha_{IO_3}}$
None	0	0.8403	9	0.07	1.0000	0.964
$KClO_4$	2	.8661	3	.09	1.0307	.936
	5	.8900	2	.03	1.0591	.911
	10	.9143	2	.06	1.0881	.886
	20	.9503	2	.08	1.1309	.852
	50	1.0183	2	.04	1.2118	.795
	100	1.0882	2	.04	1.2950	.744
None	0	0.8416	3	0.04	1.0000	0.964
KNO_3	1	.8547	2	.11	1.0156	.949
	2	.8660	2	.10	1.0290	.937
	5	.8875	2	.02	1.0545	.913
	10	.9158	2	.04	1.0882	.885
	20	.9570	1	..	1.1371	.848
	50	1.0365	2	.07	1.2316	.783
	100	1.1258	2	.11	1.3377	.721
None	0	0.8403	9	0.07	1.0000	0.964
K_2SO_4	5	.9603	2	.07	1.1428	.844
	10	1.0241	2	.04	1.2187	.791
	50	1.2932	2	.26	1.5389	.626
	0	0.8373	5	0.08	1.0000	0.964
	0.5	.8555	2	.08	1.0217	.938
	1	.8760	2	.04	1.0462	.921
	2	.9024	2	.12	1.0777	.894
	20	1.1110	2	.06	1.3269	.727
None	0	0.8417	4	0.06	1.0000	0.964
$Ba(NO_3)_2$	0.5	.8646	2	.02	1.0272	.940
	1	.8717	2	.05	1.0428	.924
	2	.8973	1	..	1.0661	.904
	5	.9322	1	..	1.1075	.871
	10	.9664	2	.15	1.1481	.840
None	0	.8417	4	0.06	1.0000	0.964
$MgSO_4$	0.2	.8522	2	.00	1.0125	.950
	.5	.8698	1	..	1.0334	.935
	1	.8855	2	.04	1.0520	.917
	2	.9111	2	.03	1.0825	.890
	5	.9629	1	..	1.1440	.843
	10	1.0201	2	.01	1.2120	.796
	20	1.0928	2	.35	1.2983	.742

It is, moreover, identical with that found by extrapolating the experimental results to zero concentration.

In Table I the theoretical value 0.964 given by Equation 3 was assumed for pure silver iodate at 0.000840 *M*. To check this assumption, each series of solubility measurements was plotted as described below, and extrapolation to zero concentration was made by two observers working independently. The values of $\sqrt{\alpha_{Ag}\ \alpha_{IO_3}}$ corresponding to 0.000840 *M* were then interpolated. They are recorded in Table II. The results show that the theoretical value 0.964 is substantially identical with that derived from the various series of solubility measurements.

TABLE II

MEAN ACTIVATION OF THE IONS OF SILVER IODATE AT 0.00084 MOLAL Derived from its Solubility in the Presence of Various Salts

$KClO_4$	KNO_3	K_2SO_4	$Ba(NO_3)_2$	$MgSO_4$	Mean
0.964	0.967	0.960	0.958	0.964	0.9626
.964	.968	.960	.956	.964	.9624

Conformity of the Results with the Limiting Equation Expressing the Theory at Very Small Concentrations

Equation 3 requires that a plot of log $\sqrt{\alpha_{Ag}\ \alpha_{IO_3}}$ against $\sqrt{\Sigma(cz^2)}$, which is the square root of twice the ionic strength, give a graph that is a straight line of slope —0.386. Accordingly, the values of log (s_0/s) + log 0.964, which are equal to those of log $\sqrt{\alpha_{Ag}\ \alpha_{IO_3}}$, were plotted against this square root in Fig. 1 for each of the five added salts. For convenience of reference, there is given along the top of the plot a scale of corresponding values of the ionic strength $\frac{1}{2}\Sigma(cz^2)$, and along the right-hand side a scale of corresponding values of the mean activation $\sqrt{\alpha_{Ag}\ \alpha_{IO_3}}$.

It is evident from the figure that for values of the ionic strength up to 0.01 *M* the agreement of the activation values with Equation 3, which is represented by the dotted straight line, is almost perfect. Since the results include added salts of the types 1 × 1, 2 × 1, 1 × 2 and 2 × 2, the effect of the valence is that predicted by the theory; or, in other words, the empirical ionic-strength principle of Lewis and Randall[9] is fully confirmed, up to an ionic strength of 0.01 *M*. The conformity of these results at 75° with the theory, considered together with the agreement with it of those of Brönsted and La Mer at 25° and of those from other sources at 25° and 0°, confirm also for very dilute solutions the validity of the equation with respect to the effect of the temperature and dielectric constant; that is, they show that, as required, log $\sqrt{\alpha_{Ag}\ \alpha_{IO_3}}$ is inversely proportional to $(\kappa T)^{1.5}$. With respect to this effect, it may be pointed out that between 0° and 75° this quantity varies by 11.6% (while $\kappa^{1.5}$ itself varies in the ratio 1.62:1), and that this corresponds to a decrease in the mean activation (at 75°) of only 1.8% at an ionic strength of 0.02 *M*.

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[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 373.

At ionic strengths above 0.01 *M* the results deviate from the limiting equation expressing the theory at very small concentrations in the direction of too large values of the activation, as has been found with almost all substances previously investigated. Moreover, the deviations differ considerably in the case of the different added salts. The magnitude of the variations of the mean activation ($\sqrt{\alpha_{Ag}\,\alpha_{IO_3}}$) at an ionic strength of 0.08 *M* ($\sqrt{\Sigma(cz^2)} = 0.4$) is as follows: potassium chlorate, 0.762; potassium nitrate, 0.744; potassium sulfate, 0.699; magnesium sulfate, 0.743; theory, 0.701.

Summary

The solubility of silver iodate has been determined at 75° in pure water (where it is 0.000840 *M*) and in the presence of potassium perchlorate, nitrate and sulfate, and of magnesium sulfate and barium nitrate, at concentrations ranging from 0.0002 to 0.1 *M*. The results conform, up to an ionic strength of 0.01 *M*, almost completely with the limiting equation of Debye and Hückel, and supplement the earlier work of Brönsted and La Mer in affording a particularly good verification of the ion-attraction theory at very small concentrations. Not only is the predicted functional relation between activation and concentration shown to be correct, but also the numerical coefficient of the equation is that required by the theory. At higher ionic strengths the observations show the usual deviations in the direction of too large mean activation values; thus, at an ionic strength of 0.08 *M* in the presence of potassium perchlorate, nitrate and sulfate, and of magnesium sulfate, these deviate from the value 0.701 given by the limiting expression for zero concentration by 8.7, 6.1, —0.3 and 6.0%, respectively.

Since these experiments were made at 75°, while the earlier ones were at room temperature, they afford specifically a confirmation of the theoretical effect of varying the temperature and of the concomitant variation of the dielectric constant in the case of the solvent water.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE NELA RESEARCH LABORATORY]

THE ELECTROSTATIC VIRIAL OF STRONG ELECTROLYTES

BY ELLIOT Q. ADAMS

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The thesis that "strong electrolytes" are almost completely dissociated in dilute aqueous solution, and that the failure of proportionality to concentration of osmotic pressure and of electrolytic conductivity is to be attributed to electrostatic forces between the ions has been defended by so many authors that even an enumeration is impracticable in a brief note.[1] From the standpoint of *a priori* plausibility, it may be pointed out that

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[1] Compare Milner, *Phil. Mag.*, **25**, 743 (1913).