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THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES. II. TESTING OF THE THEORY WITH EXPERIMENTAL DATA

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The Ion-Activity Relations Predicted by the Theory

In the first article[1] of this series there was given a critical presentation of the theory of inter-ionic attraction recently developed by Milner,[2,3] by Debye and Hückel,[4] and by Debye.[5] According to this theory the anomalies of largely ionized substances are accounted for, not primarily by the assumption of incomplete ionization, but by the considerations that, owing to the electrical attraction between the positive and negative ions, there are on the average in the neighborhood of any ion more ions of unlike sign than of like sign, and that consequently when a solution is diluted the separation of the ions involves internal work and a corresponding increase in the energy content and free-energy content of the solution.

From this theory there results the following expression for the activity coefficient or activation[6] α of an ion of valence ν in a solution in which ions are present of such valence and at such concentrations as corresponds to the sum $\Sigma(c\nu^2)$.

$$ln\ \alpha = -\frac{A\nu^2\sqrt{\Sigma c\nu^2}}{R\ (\kappa T)^{1.5}} \text{ where } A = e^3\tilde{n}^2\sqrt{\frac{\pi}{R}} \qquad (41)$$

In this expression R is the gas constant and the factor A is the product of certain universal constants (e being the electronic charge, and $\tilde{n}$ the number of molecules per mole) which has in c.g.s. units the numerical value 7.77×10^{15}, when the concentrations are expressed in moles per cubic centimeter.

Since this activation expression is to be used throughout this article for numerical calculations referring to dilute aqueous solutions at 0° and 25°, for which the dielectric constant κ is found by plotting the data of Drude[7] and Coolidge[8] to have the values 87.8 (at 0°) and 78.8

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

[2] Milner, *Phil. Mag.*, **23**, 551 (1912).

[3] Milner, *ibid.*, **25**, 742 (1913).

[4] Debye and Hückel, *Phys. Z.*, **24**, 185 (1923).

[5] Debye, *ibid.*, **24**, 334 (1923); also in *Rec. trav. chim.*, **42**, 597 (1923).

[6] It was proposed in the preceding article that the term *activation* be adopted in place of the cumbrous expression activity coefficient; and for the quantity $\frac{1}{2}\ \Sigma(c\nu^2)$ Lewis and Randall have proposed the term *ionic strength*. These terms will be employed throughout this article.

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

[8] Coolidge, *ibid.*, **69**, 134 (1899).

(at 25°), this equation may be written with numerical coefficients for these cases. Using also the ordinary logarithm ($\log \alpha$) in place of the natural one ($ln\ \alpha$) and expressing the concentrations in moles of ion per liter instead of per cubic centimeter, Equation 40 becomes

$$\text{At } 0°, \log \alpha = -0.346\, \nu^2\sqrt{\Sigma c\nu^2}. \quad \text{At } 25°, \log \alpha = -0.357\, \nu^2\sqrt{\Sigma c\nu^2}. \quad (41a)$$

The corresponding expressions for the activation function for a substance with two ions A and B are

$$\frac{\log\ (\alpha_A)^{\frac{1}{\nu_A}}\ (\alpha_B)^{\frac{1}{\nu_B}}}{\nu_A + \nu_B} = 0.346\sqrt{\Sigma c\nu^2} \text{ at } 0°;$$
$$\text{or } = 0.357\sqrt{\Sigma c\nu^2} \text{ at } 25°. \quad (42)$$

This numerical factor is uncertain or inexact for three reasons of a theoretical character. First, the value of the factor A in Equation 41 was found by Debye and Hückel to have the value given above, while Milner's method of derivation led to a value of A varying somewhat with the concentration, but having at the significant concentrations a value about two-thirds as large. Second, the dielectric constant prevailing in the immediate neighborhood of the ions, which is the one theoretically involved, must be considerably greater than that of the water as a whole, which is that employed in evaluating the numerical factors of Equations 41a and 42. And third, as Debye and Hückel show, the here neglected size of the ions must have an effect lying in the same direction, which probably becomes appreciable at fairly small concentrations. In view of these considerations it is to be expected that the theoretical value of the numerical factor will be considerably less than that calculated by Equation 40, which corresponds to the result of Debye and Hückel; and it seems probable that a better expression of the theory may be afforded by adopting for the numerical factor a value say five-sixths as large as that of A in that equation, which incidentally would lie about midway between the values required by the derivations of Milner and of Debye and Hückel. Doing this, we may write for the solvent water at 0° and 25° the following values of the activation function of Equation 42.

$$0.288\sqrt{\Sigma c\nu^2} \text{ at } 0°; \text{ and } 0.298\sqrt{\Sigma c\nu^2} \text{ at } 25° \quad (43)$$

Previous Experimental Tests of the Theory. Purpose of this Article

Milner in his original article[9] presented graphs which showed that for uni-univalent salts up to 0.1 M there was at least a fair degree of agreement between the observed freezing-point lowerings and those predicted by the inter-ionic attraction theory under the assumption of complete ionization. Debye and Hückel[10] made a more extended study of existing freezing-

[9] Ref. 3, pp. 749–751.

[10] Ref. 4, p. 201.

point data, and showed graphically that for ionic strengths up to about 0.03 *M* uni-univalent, uni-bivalent, and bi-bivalent salts give freezing points differing from those for perfect solutes roughly by amounts predicted by the theory. They also showed that at higher concentrations good agreement could be secured by introducing one new empirically determined constant, corresponding theoretically to the average diameter of the two ions.

Nevertheless it seems desirable to test the theory further, using other data available, and evaluating quantitatively the magnitude of the deviations from it at different concentrations. The simplest method of attacking this problem, and one which at the same time is especially significant in that it utilizes weighted mean values derived by a critical consideration of the available freezing-point and electromotive-force data, is to compare the activation values recently published by Lewis and Randall with those predicted by the theory. To such a comparison the next section of this article is devoted.

Other extended series of experimental data that can well be utilized for testing the theory are afforded by the numerous researches that have been made on the effect of largely ionized substances on the solubility of one another in dilute solution. The more important of these available solubility data have been collected from the literature, interpreted from the viewpoint of their activity significance, and compared with the requirements of the theory, in a later section of this article.

For assistance in the computations and in preparing the experimental material and plots for publication I am greatly indebted to Dr. R. M. Bozorth and Mr. R. H. Dalton; and for financial aid in support of these researches to the Carnegie Institution of Washington.

Testing of the Theory with Activation Values Derived from Freezing-Point and Electromotive-Force Data

Lewis and Randall[11] have computed from available freezing-point and electromotive-force data values of the activation product $(\alpha_A)^{\frac{1}{\nu_A}}\ (\alpha_B)^{\frac{1}{\nu_B}}$ for various salts with two ions A and B of valences ν_A and ν_B at a series of concentrations (expressed in formula weights of salt per 1000 g. of water). These values, grouped in correspondence with the valence type, are reproduced in Table I. At the head of each group in the rows designated "theory (Eq. 42)" and "theory (Eq. 43)" are given the values of this activation product, as calculated by Equations 42 and 43, respectively.

In Fig. 1 have been plotted as ordinates the values of $-\log \dfrac{(\alpha_A)^{\frac{1}{\nu_A}}\ (\alpha_B)^{\frac{1}{\nu_B}}}{\nu_A + \nu_B}$

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[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., **1923**, p. 362.

corresponding to these experimentally derived activation products against the values of $\sqrt{\Sigma(cv^2)}$ as abscissas; thus, against the values of $\sqrt{2c'}$ for salts A^+B^-, of $\sqrt{6c'}$ for salts $A^+{}_2B^=$ or $A^{++}B^-{}_2$, of $\sqrt{8c'}$ for salts $A^{++}B^=$, etc., where c' is the formality of the salt. Along the lower side of the plot, here and in later figures, are given the corresponding values of the ionic strength $\frac{1}{2}\Sigma cv^2$. In all these figures the theoretical values of the activation function corresponding to the form of Equation 42 applicable at 25° are shown by the lower of two broken straight lines; and the values corresponding to a numerical factor two-thirds as large are shown by the upper broken straight line. The values required by Equation 43 would therefore lie midway between these two lines.

Table I

The Experimental and Theoretical Values of the Activation Product Compared

Valence type	Temp. °C.	Substance	Formula weights per 1000 g. of water				
			0.01	0.02	0.05	0.10	0.20
1 × 1	25	Theory (Eq. 42)	0.792	0.720	0.594	0.480	0.354
		Theory (Eq. 43)	.823	.761	.650	.542	.421
		HCl	.854	.801	.740	.662	.612
		LiCl	.852	.799	.711	.647	.600
		NaCl	.852	.799	.710	.639	.568
		KCl	.852	.799	.706	.630	.561
		KOH	.852	.799	.706	.629	..
1 × 1	0	Theory (Eq. 42)	.799	.728	.604	.491	.366
		Theory (Eq. 43)	.827	.768	.658	.552	.433
		KNO_3	.841	.770	.652	.537	..
		$AgNO_3$	.816	.735	.613	.523	.429
		KIO_3, $NaIO_3$	.780	.707	.586	.472	..
2 × 1	0	Theory (Eq. 42)	.557	.436	.271	.157	..
		Theory (Eq. 43)	.614	.501	.336	.214	..
		$BaCl_2$	.607	.530	.429	.355	..
		K_2SO_4	.571	.481	.359	.273	..
2 × 2	0	Theory (Eq. 42)	.406	.279	.133	.058	.018
		Theory (Eq. 43)	.472	.346	.187	.093	.035
		$MgSO_4$	.405	.322	.227	.166	.119
		$CuSO_4$	.405	.322	.216	.158	.110
		$CdSO_4$	.405	.324	.221	.160	..
3 × 1	0	Theory (Eq. 42)	.332	.210	.085	.031	.007
		Theory (Eq. 43)	.339	.272	.128	.055	.016
		$La(NO_3)_3$	.474	.388	.286	.224	.176

Owing to the uncertainty, referred to above, as to the exact theoretical value of the numerical factors occurring in Equation 42 a more satisfactory test of the theory in most of its aspects is afforded by a study of the graphs of Fig. 1 rather than by inspection of the data of Table I.

The theory, as expressed by Equation 42, evidently requires: (1) that these graphs be straight lines for all salts; (2) that they coincide for different substances of the same valence type; (3) that they coincide for substances of different valence types; and (4) that they have the slope corresponding to the factor 0.346 at 0° or 0.357 at 25°. Let us now consider the conformity of the results with each of these theoretical requirements.

The first requirement that the graphs be straight lines, which corresponds to the principle that the logarithm of the activation product for any definite substance is proportional to the square root of its concentration, is evidently well fulfilled for all the uni-univalent substances up to an ionic strength (which is equal in this case to the salt concentration) of 0.05 *F* (formal), and for all these substances except hydrogen chloride and lithium chloride up to an ionic strength of 0.1 *F*. This principle does not seem to be so closely conformed to by the uni-bivalent and bi-bivalent salts; but the graphs for these substances are based on only three points corresponding to the concentrations 0.01, 0.02 and 0.05 *F*, the first two of which are so small that the activation values derived from freezing-point data are very inexact, and the third of which is so large that it corresponds to an ionic strength of 0.15 or 0.2 *M*, where the principle for theoretical reasons has become only roughly approximate.

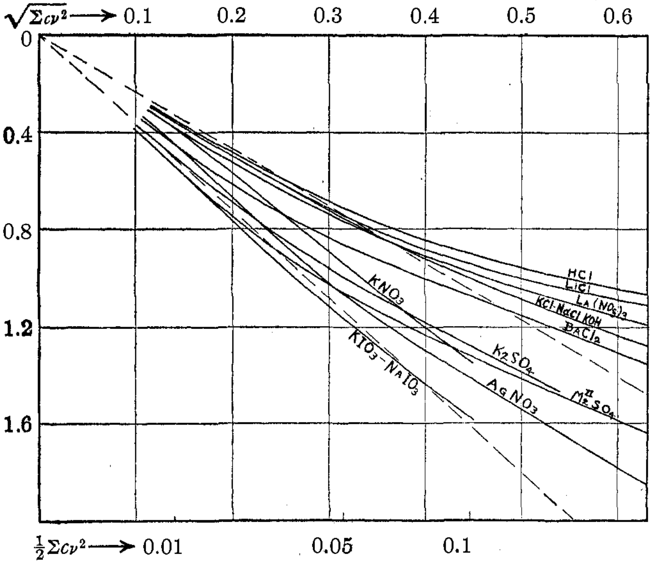

Fig. 1.—Activation values from freezing point and electromotive force.

The second requirement that salts of the same valence type have the same activation values is evidently only approximately fulfilled. Thus Table I shows that the nine uni-univalent substances have at 0.05 *F* values of the activation product varying between 0.74 and 0.59; also that the two uni-bivalent salts have even at 0.02 formal values of 0.53 and 0.48. On the other hand, the three bi-bivalent salts, which, however, are of similar chemical nature, have nearly identical activation values even up to 0.10 *F*. These results show that specific effects characteristic of the separate ions must be recognized, even at these rather small concentrations, in order to express activation values with greater accuracy than corresponds to the mentioned limits. These limits are, however, not very wide; thus at 0.05 *F* the activation product of any of the nine uni-univalent salts can be expressed within the limits of the observed variations (0.66 ± 0.08) by assigning to any ion an activation value of 0.81 ± 0.05 or, excluding hydrochloric acid and the iodates, one of 0.81 ± 0.03.

The third requirement that substances of different valence types have graphs of the same slope is seen from the figure to be fulfilled within the limits of variation of substances of the same valence type. Thus, the graphs for the two uni-bivalent salts, for the three bi-bivalent salts, and for the uni-tervalent salt lie between those for the various uni-univalent substances, namely between that for potassium chloride, sodium chloride and potassium hydroxide and that for potassium iodate and sodium iodate.

That the fourth requirement as to the slopes of the graphs representing the experimental data is roughly fulfilled is shown by the fact that up to an ionic strength of 0.05 *M* these graphs are almost wholly contained within a sheaf bounded on the two sides by the two broken straight lines representing the theoretical slope corresponding to the factor 0.357 of Equation 42 and representing the slope corresponding to a factor two-thirds as large. In order to determine to what numerical factors the actual slopes of the graphs correspond at the smaller concentrations, we may find these factors from the plot by reading off for each graph the value of the ordinate corresponding to the abscissa 0.25 and multiplying it by 4. The results so obtained for the various substances are $M^+IO_3^-$, 0.38; $M^{++}SO_4^=$, 0.36; $AgNO_3$, 0.34; K_2SO_4, 0.33; $BaCl_2$, 0.29; KNO_3, 0.29; $La(NO_3)$, 0.25; KCl, NaCl, LiCl, KOH, 0.24; HCl, 0.23. These values will be seen to lie about equally on the two sides of the factor 0.30 of Equation 43, and not to differ from it (except in two cases) by more than 20%.

In view of all these results, the conclusion is clearly warranted that at least the general magnitude of the observed effect is in striking accord with the requirements of the interionic attraction theory. This becomes even more evident when it is considered that the theory involves complicated kinetic considerations and molecular and electronic constants; that the derivation of Debye and Hückel and that of Milner lead, respectively, to approximately the two slopes bounding the sheaf of experimental values; that, adopting the result of the simpler derivation of the former authors, there is still a considerable theoretical correction in the direction of a smaller factor to be made for increase in the dielectric constant in the neighborhood of the ions and for the size of the ions at even fairly small concentrations; that incomplete ionization probably affects some of the experimental activation values; and that some of these, derived from the freezing points of very dilute solutions and involving an empirical method of extrapolation to zero concentration, may well be largely in error.

It must, however, be recognized that on the general effect predicted by the theory there are superposed secondary specific influences of the separate ions which may cause considerable variations in the activation values. By adopting, as in Equation 43, an intermediate value for the numerical factor, which is justified not only by the variation of the experimental results, but also by the theoretical uncertainty as to its exact value, activation products may, however, be calculated which do not deviate very largely from the experimentally determined ones. The magnitude of such deviations may be seen from Table I by comparing the values in the rows designated "Theory (Eq. 43)" with the experimentally derived values beneath them. These deviations for concentrations up to 0.05 equivalent per liter) seldom exceed 10% of the value of the activation product, corresponding to 5% of the activation value for each of the two ions.

The superposed specific effects will not receive detailed consideration here. It is, however, worthy of mention that for the four uni-univalent halides the decrease in activation at any given concentration increases with the molecular weight, and that the salts of the type $M^+XO_3^-$ have considerably smaller activation values, which also decrease with increasing molecular weight. This result may be of much significance in the further, more exact development of the theory, as it indicates that the size of the ion has an influence even at very small concentrations.

Testing of the Theory with Solubility-Effect Data

A further testing of the inter-ionic attraction theory can be made with the aid of existing data on the effect of salts on the solubility of one another. The test thereby afforded is also more varied in that it is possible to determine the effect on the activation of a given salt exerted not only by its own ions, but also by those of a variety of other added salts.

The simplest method to employ here is to interpret in the first place the solubility results in terms of the corresponding activation effects, and then to compare these with the requirements of the theory, as was done in the foregoing section of this article.

In any solution saturated with respect to a definite solid phase at a definite temperature the usual solubility-product equation when expressed in terms of the activities of the ions (instead of their concentrations) has in virtue of the definition of activity a constant value, even though the ions be not perfect solutes. This principle may be expressed for a salt with two ions A and B in two different saturated solutions by the following equations, in which the ion concentrations and activations with subscript zero refer to a saturated solution in which the salt saturating the solution is alone present.

$$\text{For a di-ionic salt: } c_{\mathrm{A}}\alpha_{\mathrm{A}}c_{\mathrm{B}}\alpha_{\mathrm{B}} = c_{\mathrm{A}_0}\alpha_{\mathrm{A}_0}c_{\mathrm{B}_0}\alpha_{\mathrm{B}_0};\ \text{or } \frac{\alpha_{\mathrm{A}}\,\alpha_{\mathrm{B}}}{\alpha_{\mathrm{A}_0}\,\alpha_{\mathrm{B}_0}} = \frac{c_{\mathrm{A}_0}c_{\mathrm{B}_0}}{c_{\mathrm{A}}\,c_{\mathrm{B}}} \qquad (44)$$

$$\text{For a tri-ionic salt: } c_{\mathrm{A}}^2\alpha_{\mathrm{A}}^2c_{\mathrm{B}}\alpha_{\mathrm{B}} = c_{\mathrm{A}_0}^2\alpha_{\mathrm{A}_0}^2c_{\mathrm{B}_0}\alpha_{\mathrm{B}_0};\ \text{or } \frac{\alpha_{\mathrm{A}}^2\,\alpha_{\mathrm{B}}}{\alpha_{\mathrm{A}_0}^2\,\alpha_{\mathrm{B}_0}} = \frac{c_{\mathrm{A}_0}^2c_{\mathrm{B}_0}}{c_{\mathrm{A}}^2\,c_{\mathrm{B}}} \qquad (45)$$

These equations evidently suffice to determine the relative values of the activation product in the saturated solutions of the salt alone in water and in the presence of other added salts.

On the basis of the inter-ionic attraction theory as expressed in Equation 42 the following expressions for the activation-product ratio in water at 25° are readily derived from that equation, provided complete ionization be assumed. In these expressions the subscript zero again indicates that the molal concentration or activation is that of the ions of the saturating salt when present alone in water. When one formula weight of the salt saturating the solution dissociates into one mole of ion A and one mole of ion B, each of valence ν, we have

$$-\frac{1}{2\nu^2}\log\frac{\alpha_{\mathrm{A}}\,\alpha_{\mathrm{B}}}{\alpha_{\mathrm{A}_0}\,\alpha_{\mathrm{B}_0}} = 0.357\left(\sqrt{\Sigma c\nu^2} - \sqrt{2c_0\nu^2}\right) \qquad (46)$$

When one formula weight of the salt saturating the solution dissociates into two moles of ion A of valence unity and one mole of ion B of valence two, we have

$$-\frac{1}{6}\log\frac{\alpha_{\mathrm{A}}^2\alpha_{\mathrm{B}}}{\alpha_{\mathrm{A}_0}^2\alpha_{\mathrm{B}_0}} = 0.357\left(\sqrt{\Sigma c\nu^2} - \sqrt{\Sigma c_0\nu^2}\right) \qquad (47)$$

Before proceeding to consider in detail the degree of conformity of solubility-effect data with these equations, it should be pointed out that Lewis and Randall[12] have already derived from an empirical study of such data a principle which, so far as it goes, is in full agreement with the requirements of the inter-ionic attraction theory. They showed, namely, that the activation of the ions of any given largely ionized substance is the same in all solutions in which there prevails the same value of $\Sigma c\nu^2$, summated for all the ions present; and in recognition of the general significance of this quantity, they proposed for it (or rather for one-half its value) the term "ionic strength." Their results may be mathematically expressed by $(\alpha_{\mathrm{A}})^{\frac{1}{\nu_{\mathrm{A}}}}\,(\alpha_{\mathrm{B}})^{\frac{1}{\nu_{\mathrm{B}}}} = f(\Sigma c\nu^2)$, where f denotes a function of undetermined form which may vary with the nature of the activated ions. It is evident that Equations 46 and 47 involve the validity of this ionic-strength principle. These equations, however, go much further, in that they show

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[12] This Journal, **43**, 1112 (1921); also Ref. 11, pp. 369–378.

definitely the form of the functional relation, and even the value of the numerical constant involved.

It should also be mentioned that Brönsted[13] has recently developed a general treatment of activity and solubility effects, based on thermodynamic considerations and empirical generalizations, which involves some of the principles predicted by the inter-ionic attraction theory; and he has shown that his treatment is in general in fair agreement with experimentally measured solubilities, of which he has determined for the purpose a large number of new values.[14]

In Table II the solubility data existing in the literature which seem most suitable for the purpose have been brought together, so far as they relate to added salt concentrations not greater than 0.2 N. To these should be added the data recently published by Dalton, Pomeroy and Weymouth,[15] giving the solubilities of silver bromate in solutions of potassium nitrate, potassium chlorate, potassium sulfate, sodium sulfate, magnesium nitrate, barium nitrate, magnesium sulfate, cadmium sulfate and cerous nitrate, and the corresponding activation-product ratios. Most of the headings are self-explanatory. The concentrations of the added salt and the solubilities of the salt present as solid phase are expressed in milliequivalents per 1000 cc. of solution. In the third column of figures of each series, headed "A P ratio," is given the ratio calculated by Equation 44 or 45 of the value of the activation product of the salt saturating the solution in the presence of the added salt to the value of that product when the saturating salt alone is present. The temperature was in all cases 25°.

The clearest way of showing to what extent the requirements of the theory are fulfilled is to plot as ordinates the values of the first member of Equation 46 or 47 calculated from the activation-product ratios (the "A P ratios") given in the tables against the square-root of the corresponding values of $\Sigma(cv^2)$ as abscissas. This has been done in Figs. 2–6 for silver bromate, for which the data were referred to but not reproduced above, and for the salts whose solubilities are given in Table II A–E. The nature of the added salt is shown by its symbol written close to the appropriate graph. The points corresponding to experimental values are indicated by short lines drawn perpendicularly across the graphs, or in cases where two or more graphs are nearly coincident by such lines on one graph and by crosses, circles, etc., on the others. The graph corresponding to the theoretical values given by Equation 46 or 47 is shown by the broken straight line nearer the bottom of the plots; that corresponding to a nu-

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[13] Brönsted, THIS JOURNAL, **42**, 761 (1920); **44**, 938 (1922).

[14] Since this article was submitted for publication, Brönsted and La Mer [*ibid.*, **46**, 555 (1924)] have published a paper in which they themselves show the general conformity of earlier data and of newly communicated solubility values with the requirements of the inter-ionic attraction theory at very small concentrations.

[15] Dalton, Pomeroy and Weymouth, *ibid.*, **46**, 63 (1924).

TABLE II

SOLUBILITIES OF VARIOUS SALTS

A. THALLOUS CHLORIDE

Added salt		Solubility	A P ratio
Nature	Concn.		
KCl NaCl NH_4Cl [16]	0.0	16.12	1.000
	25.0	8.72	0.878
	50.0	5.92	.780
	100.0	3.97	.626
	200.0	2.69	.474
HCl[16]	25.0	8.69	.882
	50.0	5.85	.790
	100.0	3.84	.648
	200.0	2.54	.486
$TlNO_3$[16]	25.0	8.83	.868
	50.0	6.26	.736
	100.0	4.23	.587
$TlClO_3$[16]	25.0	8.95	.817
KNO_3[17]	0.0	16.07	1.000
	20.0	17.16	0.882
	50.0	18.26	.779
	100.0	19.61	.676
	300.0	23.13	.486
	999.6	30.72	.275

Added salt		Solubility	A P ratio
Nature	Concn.		
$NaC_2H_3O_2$[18]	15.0	16.8	0.918
	30.0	17.2	.876
	78.7	18.5	.757
	157.4	19.6	.675
Tl_2SO_4[17]	20.0	10.34	.828
	50.0	6.77	.676
	100.0	4.68	.530
$MgCl_2$ $CaCl_2$ $BaCl_2$ $CuCl_2$ $ZnCl_2$ $MnCl_2$ [16]	0.0	16.12	1.000
	25.0	9.01	0.845
	50.0	6.20	.741
	100.0	4.17	.594
	200.0	2.83	.450
K_2SO_4[17]	20.0	17.79	.821
	50.0	19.42	.689
	100.0	21.37	.569
	300.0	26.00	.384
	1000.0	34.16	.223

B. CALCIUM SULFATE

NaCl[19]	0.0	30.0	1.000
	17.1	35.2	0.756
	85.2	44.6	.471
	179.0	52.4	.341
KNO_3[23]	0.00	30.64	1.000
	27.55	36.09	0.719
	52.67	40.17	.579
	123.6	48.20	.403
NH_4NO_3[21]	0.0	30.0	1.000
	124.9	46.7	0.429
$Ca(OH)_2$[20]	0.0	30.6	1.000
	2.21	29.8	0.982
	6.28	28.2	.963
	12.45	27.2	.868
	21.75	25.3	.787
	33.5	24.0	.679

$(NH_4)_2SO_4$[25]	0.0	30.60	1.000
	1.953	30.01	0.976
	3.906	29.32	.961
	15.62	26.54	.837
	31.26	24.36	.691
	62.50	22.62	.486
	125.00	21.15	.303
$MgSO_4$[24]	0.0	30.04	1.000
	53.2	23.79	0.493
	106.1	22.13	.318
	176.6	21.60	.211
$MgSO_4$[23]	0.0	30.64	1.000
	10.01	28.73	0.864
	20.22	27.15	.728
	30.49	26.12	.632
	54.92	24.11	.491
	104.55	22.82	.321
	204.95	21.96	.187

TABLE II (*Continued*)

Added salt		Solubility	A P ratio	Added salt		Solubility	A P ratio
Nature	Concn.			Nature	Concn.		
K_2SO_4[25]	0.0	30.04	1.000				
None	0.0	53.52	1.000	None	0.0	53.52	1.000
	58.4	22.96	0.483	$CuSO_4$[22]	0.0	30.0	1.000
	113.0	21.24	.316		14.3	30.4	0.689
Na_2SO_4[24]	0.0	30.04	1.000		44.7	29.2	.434
	33.7	23.68	0.664		75.8	28.6	.314
	134.2	21.40	.271		91.2	27.3	.289
	199.0	20.39	.202		185.6	25.9	.171
$CaCl_2$[26]	0.0	30.42	1.000	$CuSO_4$[23]	0.0	30.64	1.000
	136.0	18.42	0.325		25.01	27.11	0.661
					99.92	24.71	.304
					201.47	24.77	.167

C. BARIUM BROMATE[27]

None	0.0	40.18	1.000	None	0.0	40.18	1.000
$KBrO_3$	25.0	26.53	0.921	$Ba(NO_3)_2$	25.0	36.77	0.777
	50.0	17.37	.823		50.0	34.74	.634
	99.8	8.76	.628		99.9	32.63	.460
					199.5	30.95	.294
KNO_3	25.0	43.86	.769				
	50.0	47.03	.624	$Mg(NO_3)_2$	100.0	52.57	.447
	99.8	52.13	.458				

D. SILVER SULFATE[27]

$AgNO_3$	25.0	39.09	0.954	$Mg(NO_3)_2$	24.8	59.44	0.730
	49.8	28.45	.881		49.6	64.32	.576
	99.6	16.96	.665		99.4	72.70	.399
KNO_3	24.9	57.70	.798	$MgSO_4$	20.0	52.21	.779
	49.7	61.13	.671		50.1	50.93	.585
	99.8	67.93	.489		100.0	49.95	.410
					199.9	49.60	.250
K_2SO_4	25.0	50.66	.789				
	50.0	49.35	.634				
	100.0	48.04	.449				

E. LEAD CHLORIDE

None	0.0	77.7	1.000	$MgCl_2$ [28]	0.0	77.7	1.000
				$CaCl_2$	50.0	50.2	0.931
KCl[28]	50.0	48.2	1.009	$ZnCl_2$	100.0	35.1	.732
	100.0	34.1	0.765	$MnCl_2$	200.0	21.8	.437
	200.0	21.9	.435				
				$Pb(NO_3)_2$[29]	0.0	77.7	1.000
HCl[28]	50.0	47.9	1.023		20.0	76.8	0.811
	100.0	32.4	0.825		50.0	76.6	.632
	200.0	19.3	.506		99.5	78.0	.436

TABLE II (*Concluded*)

Added salt		Solubility	A P ratio	Added salt		Solubility	A P ratio
Nature	Concn.			Nature	Concn.		
F. BARIUM IODATE[30]							
None	0.00	1.579	1.000	None	0.00	1.579	1.000
KNO_3	2.00	1.624	0.919	$Ba(NO_3)_2$	1.000	1.362	0.898
	10.00	1.826	.647		2.000	1.212	.834
	50.00	2.640	.214		5.000	0.975	.693
	200.00	3.190	.121		20.000	.674	.419
					50.00	.613	.207
					100.00	.566	.122
G. LANTHANUM IODATE[31]							
None	0.00		1.000	None	0.00		1.000
$NaNO_3$	25.00	3.928	0.383	$La(NO_3)_3$	2.00	2.529	1.244
	50.00	4.476	.227		5.00	2.391	0.904
	100.00	5.244	.121		10.00	2.348	.570
	200.00	6.262	.059		50.00	2.496	.112
					100.00	2.809	.040
					200.50	3.359	.012

merical factor two-thirds as large as the factor in those equations is shown by the broken straight line nearer the top.

The conclusions that may be drawn from the various plots may now be considered in detail. In Fig. 2 are shown the results with silver bromate as solid phase (whose solubility in water is only 0.00806 *M*) in the presence of nine other salts of various valence types not having an ion in common with the silver bromate. Considering the graphs from the four viewpoints from which those of Fig. 1 have already been considered, we note:

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[16] Noyes, *Z. physik. Chem.*, **9**, 609, 614, 616, 617 (1892). Solubility values in the presence of $CdCl_2$ are also given; but these are here omitted on account of the abnormal ionization of this salt.

[17] Bray and Winninghoff, THIS JOURNAL, **33**, 1666 (1911).

[18] Noyes, *Z. physik. Chem.*, **6**, 264 (1890). Solubility values in the presence of $CdSO_4$ are also given; but these are here omitted on account of the abnormal ionization of the $CdCl_2$ that is produced by metathesis.

[19] Cameron, *J. Phys. Chem.*, **5**, 560 (1901).

[20] Cameron and Bell, THIS JOURNAL, **28**, 1220 (1906).

[21] Cameron and Brown, *J. Phys. Chem.*, **9**, 211 (1905).

[22] Bell and Taber, *ibid.*, **11**, 637 (1907).

[23] Harkins and Paine, THIS JOURNAL, **41**, 1162 (1919).

[24] Cameron and Bell, *J. Phys. Chem.*, **10**, 210 (1906).

[25] Sullivan, THIS JOURNAL, **27**, 532 (1905).

[26] Cameron and Seidell, *J. Phys. Chem.*, **5**, 643 (1901).

[27] Harkins, THIS JOURNAL, **33**, 1813–5 (1911).

[28] Ref. 16, pp. 623, 624.

[29] Ref. 27, p. 1816.

[30] Harkins and Winninghoff, THIS JOURNAL, **33**, 1829 (1911).

[31] Harkins and Pearce, *ibid.*, **38**, 2696–8 (1916).

(1) all the graphs (except that for cerous nitrate) are very nearly straight lines up to an ionic strength 0.1 *M*, confirming the required proportionality to the square root of the concentration; (2) there are considerable differences in the activating effects of the two uni-univalent salts, potassium nitrate and potassium chlorate; also in those of the four uni-bivalent salts, potassium or sodium sulfate, barium nitrate, and magnesium nitrate; (3) the differences between the effects of the salts of different valence types, including the bi-bivalent magnesium sulfate and cadmium sulfate and the uni-tervalent cerous nitrate, are, however, no greater than the variations shown by salts of the same valence type; (4) all the graphs up to an ionic strength 0.1 *M* lie within the sheaf bounded by the broken straight lines corresponding, respectively, to the numerical factor 0.357 of Equation 46 and to a factor two-thirds as great. A fairly satisfactory expression of all these solubility effects would evidently be given by adopting for this factor a value half-way between, as was done in Equation 43.

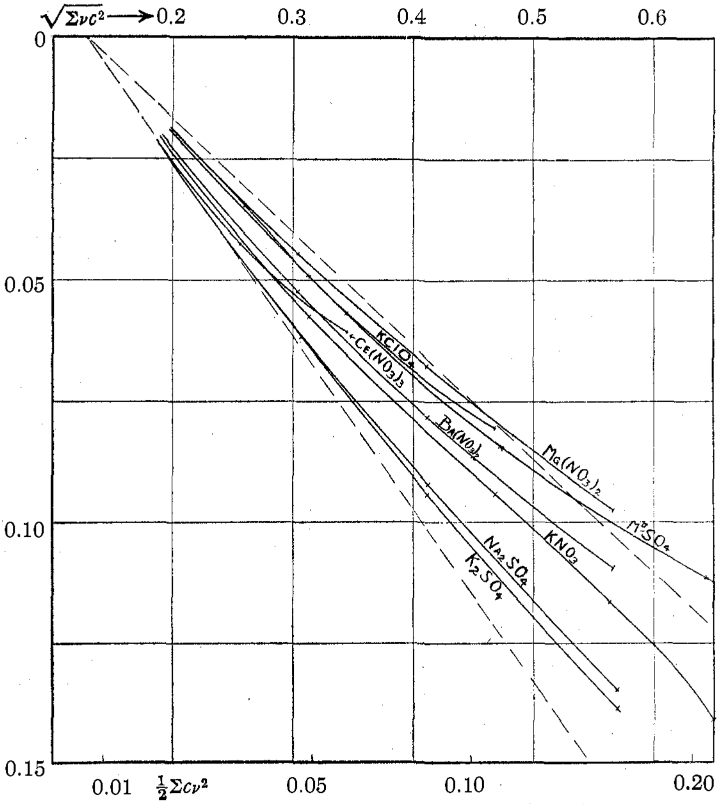

Fig. 2.—Activation values from solubilities of silver bromate.

In Fig. 3 are presented the results for thallous chloride as solid phase.

The data are more numerous than the graphs indicate. Thus the graph marked $M^{I}Cl$ represents the identical values for potassium, sodium and ammonium chlorides and approximately also those for hydrogen chloride and thallous nitrate, which will be seen by reference to Table II A to exert activation effects only a little smaller and a little greater, respectively, than the alkali-element chlorides. Similarly, the graph marked $M^{II}Cl_2$ represents the data for magnesium, calcium, barium, cupric, zinc and manganous chlorides, which in spite of the different chemical elements involved, have a scarcely distinguishable solubility effect. As to the significance of these results the same four specific statements may be made as were made about the figure representing the solubility effects in the case of silver bromate. Moreover, all the effects up to ionic strength 0.1 *M* would be fairly closely expressed either by Equation 46 with the numerical coefficient 0.357 or by one with a factor five-sixths as large. The confirmation of the theory is, however, here even more complete in

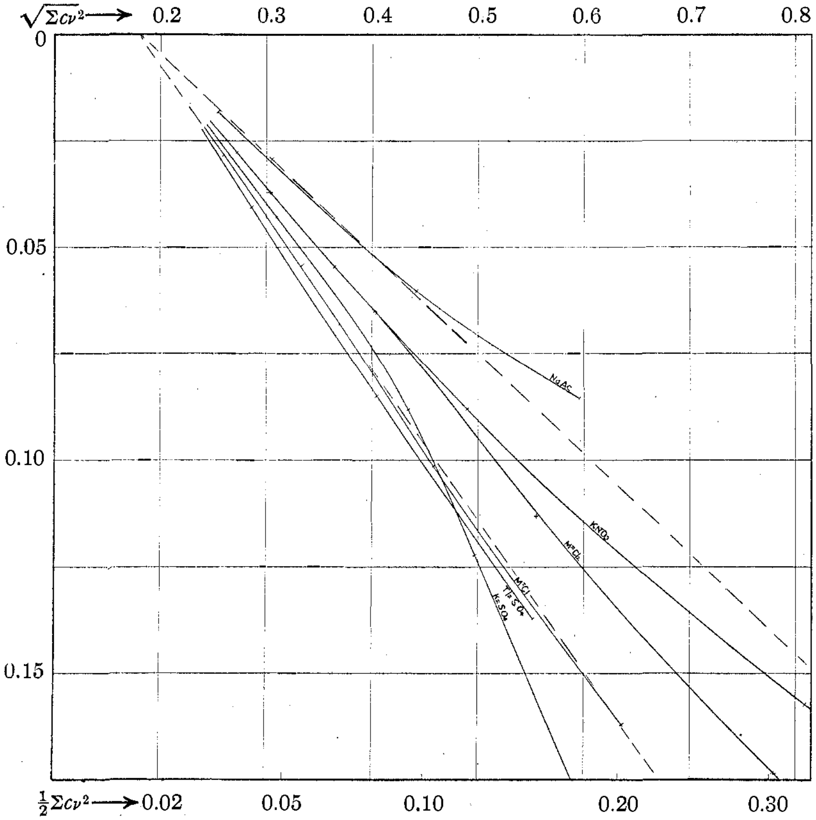

Fig. 3.—Activation values from solubilities of thallous chloride.

the respect that some of the added salts have an ion in common with the thallous chloride, and others do not, and yet there is no systematic difference between the calculated activation effects of these two classes of salts. According to the older hypothesis of incomplete ionization and normal activity, however, their solubility effects would be due to quite different causes; namely, in one case to the mass-action influence of the common ion, and in the other case to the partial formation by metathesis of two other un-ionized salts.

Fig. 4 shows the results with calcium sulfate as solid phase. Up to an ionic strength of 0.10 M the graphs for the two uni-univalent, five uni-bivalent, and two bi-bivalent substances form a narrow sheaf of nearly straight lines, thus in close accordance with the first three theoretical requirements considered in the previous cases. Here again it makes no difference whether or not the added substances have an ion in common with the substance saturating the solution; and this fact is in this case even more striking since the substances produced by metathesis under the hypothesis of complete ionization, being always of the uni-bivalent or bi-bivalent types, would be formed in fairly large proportion. The mean slope of this part of the sheaf is, to be sure, nearly coincident with

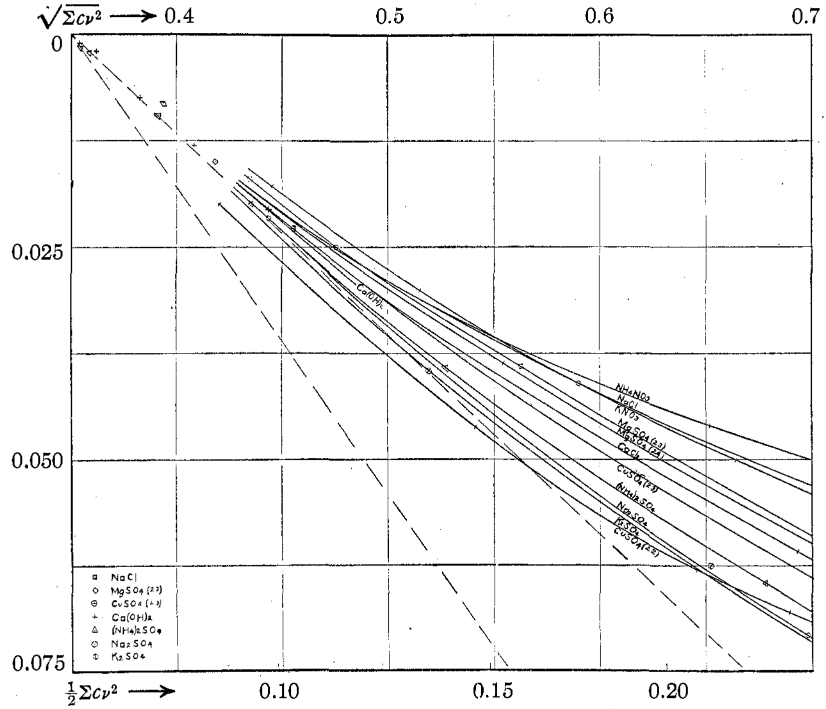

Fig. 4.—Activation values from solubilities of calcium sulfate.

the upper broken straight line corresponding to two-thirds of the theoretical factor 0.357, rather than with a slope midway between the two broken straight lines. At higher ionic strengths than 0.1 *M* all the substances cause fairly large deviations in this same direction.

Fig. 5 represents the few results available on the solubility of barium bromate. The two added salts, barium nitrate and potassium nitrate, though of different valence types and respectively with and without an ion common to the salt present as solid phase, have nearly the same activating effects up to an ionic strength of 0.15 *M*, and they have effects that lie close to the slope corresponding to the equation with a numerical factor two-thirds of the theoretical one. The added salt potassium bromate at the smallest concentration shows a somewhat abnormal result, perhaps owing to experimental error; but at higher concentrations its effect does not differ greatly from that of the other salts.

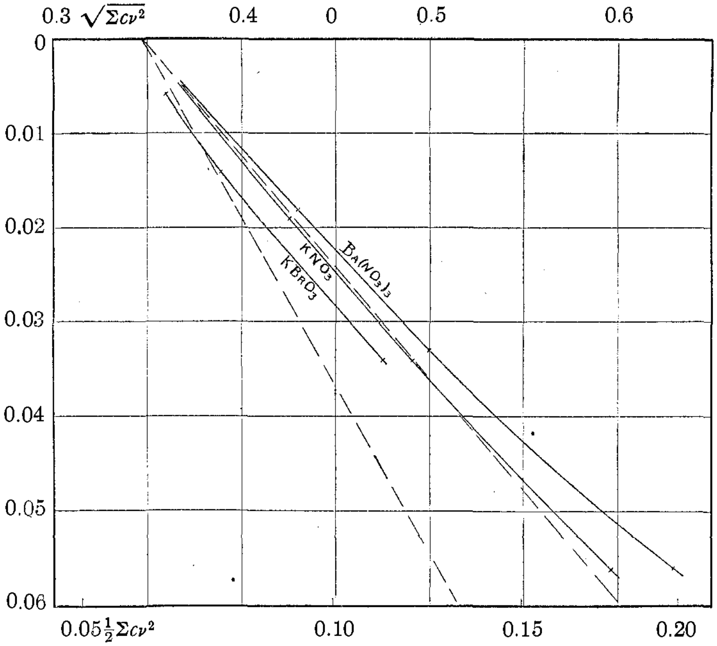

Fig. 5.—Activation values from solubilities of barium bromate.

The results with silver sulfate as solid phase shown in Fig. 6 are also in full conformity with the theory, so far as the first three requirements are concerned. Indeed, the five substances potassium nitrate, potassium sulfate, magnesium nitrate, calcium sulfate and magnesium sulfate produce so nearly the same activation that it was not possible to insert separate graphs for them, but only to draw a single nearly straight line, along which the effects corresponding to the experimental results for the separate salts are indicated by specially designated points. Here again, the slope of the best representative graph corresponds nearly to two-thirds of the theoretical factor. Only silver nitrate gives a graph deviating much from that for the other salts, and this deviates in the direction of the theoretical factor.

Fig. 6 also shows the results derived from the solubilities of lead chloride. In the case of this substance the effect of the added chlorides will be seen to deviate widely from the theory, perhaps owing to abnormal ionization of the lead chloride. The effect of the added lead nitrate, on the other hand, corresponds closely with the slope corresponding to the numerical factor two-thirds of that in Equation 47.

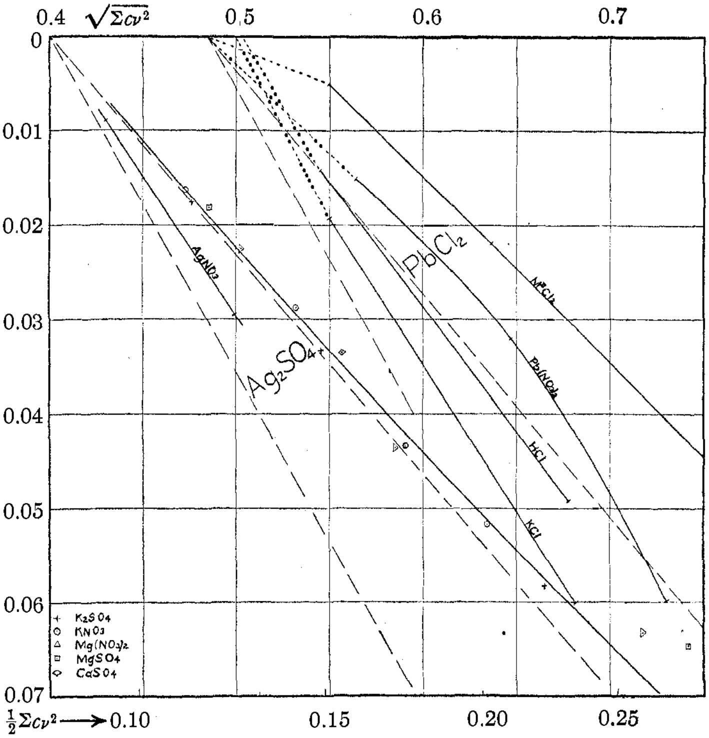

Fig. 6.—Activation values from solubilities of silver sulfate and lead chloride.

In Table II F–G are given the observed solubility effects and the calculated activation effects of potassium nitrate and barium nitrate on the slightly soluble barium iodate, and of sodium nitrate and lanthanum nitrate on the slightly soluble lanthanum iodate, the latter of which is of interest because of its high valence type. Without reproducing the plots here, it may be mentioned that these show that the effects of potassium nitrate and barium nitrate on the barium iodate agree closely with each other and with the requirements of Equation 47 up to an ionic-strength 0.05 *M;* also that the effect of sodium nitrate on the lanthanum iodate is represented by a line that is nearly straight and that closely coincides with the slope corresponding to a coefficient two-thirds as large as the theoretical one; and that lanthanum nitrate, though it has too small an effect on the iodate at the small concentrations, conforms closely to this slope at ionic strengths between 0.05 and 0.2 *M*.

In addition to the data already considered, there are available in the literature various other solubility results useful for testing the theory. Brönsted[32] alone and with La Mer has published several series of determinations of the solubilities of cobaltammine salts, and has already been employed for the purpose. Bozorth[33] has carried out an extensive series of measurements with potassium perchlorate as solid phase; but, owing to the large solubility of this salt and the necessarily high concentrations of the added salts, the solutions were so concentrated (0.2–0.5 *N*) that the specific effects characteristic of the separate ions obscured any general relation to valence or concentration.

Summary and Conclusions

In this article the inter-ionic attraction theory developed by Milner and by Debye and Hückel and critically re-presented in the preceding paper in THIS JOURNAL, has been tested, assuming complete ionization of the substances, first with the aid of the values of the activity coefficient (here called the activation) derived by Lewis and Randall from freezing-point and electromotive-force data, and second, with the help of activation values derived from most of the suitable series of solubility-effect measurements existing in the literature.

There has been derived from the theory and employed for the first of these purposes the activation function applicable to aqueous solutions at 0° or 25° (see Equation 42). For the second purpose corresponding equations (Equations 46 and 47) adapted to the solubility-effect conditions have been developed and employed.

Even at fairly small concentrations different salts of the same valence show considerable variations in their activation values, instead of giving identical values as required by the theory. Thus at 0.05 *F* the nine uni-univalent, but chemically very different, substances whose activation has been determined, have activation products varying from 0.59 to 0.74; and the two uni-bivalent salts barium chloride and potassium sulfate have the products 0.43 and 0.36 (see Table I). Nevertheless, the results considered as a whole with respect to the functional relations predicted, and even with respect to the average value of the numerical coefficient,

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[32] Ref. 13 and 14.

[32] Bozorth, THIS JOURNAL, **45**, 2653 (1923).

are strikingly in accord with the requirements of the theory, as shown by the following statements.

As required by the cited equation (42), for nearly all the single substances up to ionic strengths of 0.05, and often of 0.1 *M*, the logarithm of the activation product is found to be proportional to the square root of the concentration of the substance, and therefore when plotted against it to give a linear graph (see Fig. 1). Moreover, the effect of the valence of the ions is in general that predicted by the theory, as is shown by the fact that the uni-univalent, uni-bivalent, and bi-bivalent substances (also one uni-tervalent salt) all give graphs of the logarithmic activation function (forming the first member of the equation) against $\Sigma c\nu^2$, which lie within a narrow sheaf—one no wider than that including the various salts of the same valence type (see Fig. 1). Finally, the average slope of the experimental graphs for all the substances corresponds approximately to a numerical coefficient having a value about five-sixths of that in the equation, as is shown in Fig. 1 by the fact that up to ionic strength 0.05 *M* the graphs are irregularly distributed within a sheaf bounded by the broken lines corresponding to this coefficient and to one two-thirds as large. It is pointed out that in deriving the equations here considered two effects are neglected which might well lower the theoretical coefficient by this amount, namely, the increase of the dielectric constant of the water in the neighborhood of the ions and the size of the ions themselves.

The activation products derived from the solubility effects are shown to afford an even more extensive and varied testing of the theory. The confirmation is especially striking in the case of the effects upon the solubilities of the two uni-univalent salts, silver bromate and thallous chloride. Up to ionic strength 0.1 *M*, salts of the various valence types give activation graphs which are nearly straight lines, and which lie nearly within the narrow sheaf bounded by slopes corresponding to the theoretical coefficient and to one two-thirds as great (see Figs. 2 and 3).

The results derived from the solubilities of the uni-bivalent salts silver sulfate and barium bromate (Figs. 5 and 6) and of the bi-bivalent salt calcium sulfate (Fig. 4) again confirm the predicted functional relations between the activation and the concentration and valence. This is true whether the added salts have, or do not have, an ion in common with the salt saturating the solution; while according to the older hypothesis of incomplete ionization and normal activity, the solubility effects in these two cases are due to entirely distinct causes—the common-ion mass-action and the formation of un-ionized substances by metathesis, respectively. In the case of these three salts of fairly large solubility and of higher valence types the numerical coefficient corresponding to the slopes of the experimental graphs up to 0.1 *M* is about two-thirds of the theoretical one.

PASADENA, CALIFORNIA