TABLE III.—FREEZING-POINT DATA ON SODIUM CHLORIDE.

$\Delta t/N$.	Concentration.
3.650	0.005132
3.623	0.009544
3.616	0.009604
3.561	0.02012
3.560	0.02120
3.534	0.03516
3.498	0.06534
3.435	0.08360
3.448	0.1360

Summary.

This paper gives determinations of the freezing-point lowerings for solutions of sodium sulfate, potassium sulfate, and their equimolar mixture, for sodium chloride, and for a mixture of mannite and potassium chloride. The greatest temperature deviation to be found from the calculated value in the potassium-chloride-mannite mixture, was six one-hundred-thousandths of a degree.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

IONIZATION AND SOLUBILITY RELATIONS OF SALTS OF HIGHER TYPES.[1] IV.

INTERMEDIATE IONS IN SOLUTIONS OF UNI-BIVALENT SALTS, AND OF LANTHANUM IODATE, A TRI-UNIVALENT SALT.

BY WILLIAM D. HARKINS AND W. TUDOR PEARCE.[2]

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Introduction.

A survey of any general treatise on chemistry indicates that lower type salts, that is, those of the uni-univalent type, are few in number in comparison with salts of the higher types, yet the latter class of salts has received little attention from the standpoint of general ionization and solubility relations. So slight indeed is the attention paid

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[1] The part of this work which bears directly upon uni-bivalent salts was done by Harkins in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, and the importance of such an investigation was suggested by Dr. A. A. Noyes, who obtained financial support for the work from the Carnegie Institution of Washington. The first three papers on higher type salts (Papers V, VI and VII, The Effect of Salts upon the Solubility of Other Salts, THIS JOURNAL **33**, 1807–73 (1911)) were largely experimental and did not give an adequate discussion of the theoretical relations involved in the intermediate ion hypothesis.

[2] This paper, and one published later in this series, have been presented to the University of Chicago by W. Tudor Pearce as a dissertation in part fulfilment of the requirements for the degree of Doctor of Philosophy. In addition to the work here presented, a considerable time was spent upon the separation of the yttrium group elements.

to higher type salts, that although it was shown in 1911 by Harkins[1] that all salts of the uni-bivalent type ionize in two steps, and thus give solutions containing intermediate ions, almost none of the recent texts on general, inorganic, or physical chemistry[2] even mention the possibility of the existence of intermediate ions. This of itself might not be so bad if these texts did not persist in giving the altogether false percentage ionizations which are obtained by calculation when the presence of intermediate ions is neglected. Thus in two well-known college text books published recently the percentage ionization of potassium sulfate in a tenth normal solution is given as 72%, even although the work cited above shows that in all probability more nearly 95% of a salt of this uni-bivalent type is in the ionic form at this concentration. Even if the authors of these texts do not believe that intermediate ions exist in appreciable quantities in solutions of such salts, the better method would be to express their results in terms of the conductance ratio without the application of the hypothetical term "degree of ionization."

Previous to the publication of the first papers of this series it had been suggested by a number of workers that intermediate salt ions were present in certain specific cases, but these suggestions were made to cover only what seemed to be extraordinary cases. Thus Abegg and Spencer[3] assumed that when thallium oxalate ionizes it forms intermediate ions, but that potassium oxalate does not. Also Jellinek[4] concluded from freezing-point results that intermediate ions are formed by sodium sulfate, but not by potassium sulfate. The new feature of the intermediate ion hypothesis is that it assumes that intermediate ions are present in solutions of all salts of higher types, and that the percentage amount of the intermediate ion increases regularly with the concentration, somewhat as the concentration of the un-ionized part of a lower type salt increases.

The most striking fact found by Harkins was that, while the solubility of a uni-bivalent salt is depressed in a normal way by the addition of a salt with a univalent ion, and while on the whole the action of a salt with a non-common ion is also normal, that when the common bivalent ion is added the effect on the solubility is extremely abnormal for very soluble salts and in concentrated solutions, and is still quite abnormal in dilute solutions, but becomes almost normal in solutions of extreme dilution. The effect found is that the decrease in solubility produced by the addition of a salt with a bivalent common ion is very much less than would be expected in dilute solutions, and in concentrated solutions there is often

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[1] THIS JOURNAL, 33, 1807–73 (1911).

[2] Washburn's "Principles of Physical Chemistry" is an exception in this respect.

[3] *Z. anorg. Chem.*, 46, 406 (1905).

[4] *Z. physik. Chem.*, 76, 309 (1911).

even an *increase instead of a decrease* of solubility. Since salts which form complexes were avoided as much as possible in the experimental work, this behavior suggests what may be called a non-common ion effect. Now if strontium bromide and strontium nitrate in concentrated solutions were to ionize only to the extent of one step, the ions formed would be $SrBr^+$ and $SrNO_3^+$, Br^-, and NO_3^-. None of these is a common ion, and, therefore, from the standpoint of intermediate ions an increase of solubility is easily explainable.

There will now be considered the lowering of the solubility of a salt caused by the presence of (1) a common univalent ion, and of (2) a common bivalent ion. One calculation will be made assuming that intermediate ions are absent, and a second on the basis of the presence of such ions, and then a comparison of the results obtained in the two cases will be possible.

1. Solubility Effects when Intermediate Ions are Absent.—Let a salt A_2B ionize directly into $2A^+$ ions and one $B^=$ ion. Then, when formulated according to the mass law, and when S_o represents the solubility in water, S_1 when the common univalent ion is added, and S_2 when the common ion is bivalent, the following expressions are obtained:

$$(A_2B)_o = (A_2B)_1 = (A_2B)_2 \tag{1}$$

$$(A)^2(B)_o = (A)_1^2(B)_1 = (A)^2(B)_2 \tag{2}$$

$$S_o = (A_2B)_o + (B)_o \qquad S_1 = (A_2B)_1 + (B)_1 \tag{3}$$

$$2S_o = 2(A_2B)_o + A_o \quad (4) \qquad 2S_2 = 2(A_2B)_2 + (A)_2 \tag{5}$$

By combining these equations results may be obtained which represent the fractional decrease of solubility produced by increasing the concentration of the univalent ion from $(A)_o$ to $(A)_1$, and of the bivalent ion from $(B)_o$ to $(B)_2$:[1]

$$S_o - S_1 = \frac{(A)_1 - (A)_o}{(A)_o} \left[\frac{A_o B_o}{A_1} \left(1 + \frac{A_o}{A_1} \right) \right] \tag{6a}$$

$$S_o - S_2 = {}^1/_2 \, \frac{(B)_2^{1/2} (B)_o^{1/2}}{(B)_o^{1/2}} \left\{ (A)_o \left[\frac{(B)_o}{(B)_2} \right]^{1/2} \right\} \tag{7}$$

Equation 6*a* may be more simply expressed as follows:

$$S_o - S_1 = \frac{(A)_1 - (A)_o}{(A)_1} \left[(B)_o \left\{ 1 + \frac{(A)_o}{(A)_1} \right\} \right]$$

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[1] These calculations made on the basis of the law of mass action will be somewhat in error, since the principle that the concentration of the un-ionized part remains constant seems to be considerably in error if we judge from the behavior of uni-univalent salts, but the effect of the error on the result in case intermediate ions are present is exceedingly slight, since the concentration of the un-ionized part is very small in proportion to the total concentration. There is also some deviation from the solubility product principle, but this deviation is slight and the resultant error is in the opposite direction from the first one mentioned.

From these equations it would be expected that the addition of the common univalent ion would in all cases effect a considerable lowering in the solubility. The addition of the common bivalent ion would also produce a considerable effect of the same kind, though slightly smaller in magnitude.

2. Solubility Effects when Intermediate Ions Are Present.—When intermediate ions are present Equations 6 and 7 take the form

$$S_o - S_1 = \frac{(A)_1 - (A)_o}{(A)_1}\left[(B)_o\left(1 + \frac{(A)_o}{(A)_1}\right) + (AB)_o\right] \qquad (6b)$$

$$S_o - S_2 = {}^1/_2\frac{(B)_2^{1/2} - (B)_o^{1/2}}{(B)_o^{1/2}}\left[(A)_o\left(\frac{(B)_o}{(B)_2}\right)^{1/2} - (AB)_o\right] - (ADB)_2. \qquad (7b)$$

However, in Equations 6*b* and 7*b* the values of the concentrations are very different from what they are in Equations 6 and 7

The positive sign of the term $(AB)_o$ in Equation 6*b* shows that the effect of the presence of the intermediate ion is to make the *decrease* of *solubility* larger, and the effect of this term increases with the percentage of the intermediate ion. The experimental results show that curves of this type exhibit this effect, and especially with salts like lead chloride and calcium hydroxide, which contain in solution an exceptionally large percentage of the intermediate ions. The curves for these salts, and also for lead iodate fall below the theoretical limiting curve for this type in the more dilute solutions. (Fig. 1.) The theoretical limiting curve is calculated for a salt of 100% ionization, which means that the presence of intermediate ions is not considered.

The negative signs on the terms $(AB)_o$ and $(ADB)_2$ indicate that when intermediate ions are present the decrease in solubility would be much less than that calculated on the basis that they are not present, which is exactly in accord with the experimental results. However, with a slightly soluble salt to which the bivalent common ion is added, the effect of the presence of the intermediate ion will not be specially noticeable, so long as the concentration of the added bivalent ion $(B)_2$ is not greatly increased, since in this case the ratio of $(AB)_o$ to $A_oB^{1/2}/B_2^{1/2}$ is small.

The decrease in solubility with this type of curve will change over into an increase when with a moderately soluble salt the concentration of the added salt is moderately increased for in this case the ratio $(AB)_o/A$ is fairly large and the negative term $(AB)_o$ will soon compensate the steadily decreasing positive term containing $(A)_o$ to so great an extent that the whole latter term of Equation 7*b* becomes negative, and this occurs all the sooner since the negative term $(ADB)_2$ is constantly increasing.

When either the saturating salt is very soluble, or contains a specially large percentage of intermediate ion, even the first addition of a salt with a common bivalent ion may cause an increase in solubility, for where

$(AB)_0/(A)_0$ is sufficiently large the two negative terms may exceed the positive one, even when the factor of the latter $B_0^{1/2}/B_2^{1/2}$ is equal to unity. The general agreement of these equations, derived on the supposition that intermediate ions are present, with the experimental facts, is a strong argument in favor of the existence of intermediate ions.

3. Evidence against the Intermediate Ion Hypothesis.—The purpose of the present paper is to add experimental evidence which bears on the ionization of tri-univalent salts to that which has already been obtained in the case of salts of the uni-bivalent type. In studying such a problem it may be well to outline the evidence which has in the past seemed to indicate that intermediate ions do not exist in solutions of the latter type, and for this purpose there is cited a quotation from a paper by Noyes and Bray[1] as follows: "In the case of salts of the uni-bivalent type, there is furthermore the uncertainty as to whether intermediate ions (such as KSO_4^- or NO_3Ba^+) are present in considerable proportions. Certain remarkably simple principles have, however, been established, which have been thought to indicate that the complications which would arise from ionization in two successive stages do not exist, namely: 1. The conductance ratio of such salts changes with the concentration according to the same exponential law $(C\gamma)^n/C(1 - \gamma) = K$ that holds in the case of uni-univalent salts. 2. The conductance of mixtures of such salts can be approximately calculated from the conductance of the constituents by the same principle expressed by the equation $\left[\frac{C_{B^+} \times C_{A^-}}{C_{BA}} = K(C\gamma)^{2-n}\right]$ that holds for univalent salts. 3. The transference numbers of uni-bivalent salts (except those of the bivalent metal halides) change only slightly with increasing concentration. 4. Simple mixed salts (such as $BaClNO_3$) scarcely ever separate in the solid state when solutions of the constituent salts are evaporated." In order that this quotation may not be misunderstood it may be said that in spite of the above evidence, the paper from which it is taken seems to favor rather than oppose the idea that intermediate ions exist.

4. Conditions under Which the Objections Become Invalid.—The very fact that the same equation

$$C_B \times C_{A^-}/C_{BA} = K(C)^{2-n} = K(\Sigma i)^q \qquad (1)$$

which is found valid for the conductance ratios of single uni-univalent salts and which may also be used to calculate the conductance of mixtures of such salts, may be applied to salts of higher types without any essential change, should at once suggest that this equation, and other modified equations of this general type, are after all nothing more than they pretend to be, that is, entirely empirical equations which are valuable in

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[1] THIS JOURNAL, 33, 1645 (1911).

connection with calculations of conductance and of conductance ratios, but which, at least in the case of salts of higher types, are not directly related to the ionization. Thus, if the above equation is valid for the ionization of the simple type salts, for those of the uni-bivalent type the equation should be of the form

$$\frac{C_B^2 \times C_{A^=}}{C_{B_2A}} = K\ (\Sigma i)^q \qquad (2)$$

in case intermediates do not exist, and this latter equation would not change at all into the form of Equation 1 if intermediate ions are present.

Perhaps the most serious objection to the intermediate ion hypothesis is that given above under number (3), that the transference numbers of the uni-bivalent salts, except those of the bivalent metal halides, change only slightly with the concentration, even although the concentration of the intermediate ion if it is present, should increase rather rapidly with the concentration, at least in all cases where complex ions are not present. The fact is, from the experimental standpoint, that extensive researches on the transference numbers of potassium sulfate, barium nitrate,[1] and upon thallous sulfate and lead nitrate,[2] show that the change of the transference number with the concentration is very small, at least between 0.03 and 0.10 normal; in fact, there was no detectable change greater than might result from experimental errors. As a result of this work Falk comes to the following conclusion: "Some degree of probability therefore attaches to the hypothesis that such tri-ionic salts do not as a rule give rise to intermediate ions, at any rate in quantity exceeding a few per cent. at 0.1–0.2 normal; but that they dissociate directly into three ions. At any rate the statement can be made with positiveness that the transference relations of the tri-ionic salts afford no indication of the presence of intermediate ions, but whether this is due to the nonexistence of such ions or to the fact that they have a conductance of such magnitude as not to influence the transference, cannot be definitely stated."

In this connection it should be noticed that the transference method is by no means sufficiently accurate so that conclusions based upon transference results could be looked upon as at all conclusive, especially where the ions investigated have not very different speeds. In sulfuric acid, where the ions H^+, HSO_4^- and $SO_4^=$ have greatly different velocities, the intermediate ion has been detected by transference measurements.

5. Transference Number of Intermediate Ion.—The necessary relation between the migration values of the different ions in order that the existence of the intermediate ion may escape detection, may easily be calculated. Thus for potassium sulfate the existence of the intermediate

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[1] A. A. Noyes, This Journal, 23, 37 (1901).

[2] Falk, *Ibid.*, 32, 1555 (1910).

ion must not very greatly alter the transference number of the potassium ion as it is calculated on the supposition that no intermediate ion is present. In a general form the equations are given below, where T_o represents the transference number when no intermediate ion is present, and T_i gives its value if the intermediate ion is present, and when the ionization occurs only for the first step. Now for a salt A_2B

$$T_{oA^+} = \frac{\Lambda_{A^+}}{\Lambda_{A^+} + \Lambda_{B^=}} \tag{3}$$

$$T_{iA^+} = \frac{\Lambda_{A^+} - \Lambda_{AB^-}}{\Lambda_{A^+} + \Lambda_{AB^-}}. \tag{4}$$

Now if $T_{oA^+} = T_{iA^+}$

$$\frac{\Lambda_{A^+}}{\Lambda_{A^+} + \Lambda_{B^=}} = \frac{\Lambda_{A^+} - \Lambda_{AB^-}}{\Lambda_{A^+} + \Lambda_{AB^-}} \tag{5}$$

or

$$\Lambda_{AB^-} = \Lambda_{A^+} \times \Lambda_{B^=}/2\Lambda_{A^+} + \Lambda_{B^=}. \tag{6}$$

Equation 6 expresses the exact relationship which would absolutely prevent the detection of the intermediate ion, but since the transference method is not a very sensitive indicator in the case of salts, the conductance of the intermediate ion might vary considerably from this value without causing any very noticeable change in the transference number (T_A) with the concentration.

If it is assumed that when the ions A^+ and $B^=$ unite to form the intermediate ion AB^-, the resistance to the motion of the intermediate ion is equal to that of its constituent ions, or $R_{AB^-} = R_{A^+} + R_{B^=}$, then the equation for its conductance would be

$$\Lambda_{AB^-} = \frac{1}{R_{AB^-}} = \frac{1}{R_{A^+} + R_{B^=}} = \frac{1}{1/\Lambda_{A^+} + 2/\Lambda_{B^=}} = \Lambda_{A^+} \times \Lambda_{B^=}/2\Lambda_{A^+} + \Lambda_{B^=}, \tag{7}$$

which is the same as Equation 6. So the condition necessary in order that the intermediate ion may have no influence upon the transference number is that the resistance to motion of the intermediate ion shall be equal to the sum of the resistance of its component ions.

6. The Union of the Ions in Intermediate Ions and Probably in Molecules of Salts in Aqueous Solutions is a Loose One.—It has been pointed out by G. N. Lewis that in the case of intermediate salt ions this condition should be very nearly fulfilled, since the properties of salts in solution are additive properties of the constituent ions, and the heat of ionization is small, so that the union of the ions is a loose one. On the other hand, the heat of ionization of the dibasic acids is considerable, and therefore in the case of such intermediate ions as HSO_4^- the above relationship would not hold, and such ions should be detected by transference measurements, as is the case. Not only is this true but the great differences in the migration values of the constituent ions of such intermediate ions make the experimental detection of these ions by transference measurements much more feasible.

In spite of the failure of previous attempts to prove the presence of intermediate salt ions by transference measurements, it is not improbable that some evidence of their existence might be obtained by using salts of higher types in which one ion has a far greater migration value than the other, which might be done by loading up one of the ions with heavy organic radicals. However, the fact that such a method at the best would not prove a very sensitive one, makes it advisable to turn to other experimental methods.

A consideration of the migration values of some of the ions of salts of higher types will give some specific idea of the reasonableness of such an hypothesis in regard to the migration values of the ions. In the special case where these values are the same for both of the simple salt ions, Equations 5 and 6 give the result that the migration number of the intermediate should be one-third that of the constituent ions; or

$$\Lambda_{AB^-} = {}^1/_3\Lambda_{B^=} = {}^1/_3\Lambda_{A^+}. \qquad (19)$$

In the case of potassium sulfate at 25°,

$$\Lambda SO_4^=/2 = 80.0,\ \Lambda_{K^+} = 74.8 \text{ and } \Lambda_{KSO_4^-} = 26.$$

Since the $SO_4^=$ ion if it had one charge could be pulled only one-half as fast, the migration value would be 40. The potassium would still further load up the KSO_4^- ion, and thus increase its resistance. So that the decrease of the migration value from 40 to anywhere near 26 must be due to the resultant increase in size of the ion.

7. The Intermediate Ion Hypothesis.—The intermediate ion hypothesis, as proposed by Harkins in 1911, but not that time emphasized, may be stated as follows: (1) All salts, acids and bases which dissociate electrolytically into more than two ions, dissociate in steps, and thus form in solution intermediate ions. (2) These intermediate ions are present in dilute as well as in concentrated solutions, but the percentage of the salt present as intermediate ion decreases as the solution becomes more dilute.

When the intermediate salt ions, such as KSO_4^-, are compared with the corresponding intermediate acid ions, such as HSO_4^-, it is found that the intermediate salt ion has in general the higher ionization constant. It is well known that the intermediate ion of a strong acid (HSO_4^-) has a moderately high ionization constant, but that this constant is extremely small in the case of the weak acids (HCO_3^-). Undoubtedly the same relations are true for the intermediate ions of bases. The ionization of intermediate salt ions differs from that of the similar ions in acids and bases, somewhat as the ionization of uni-univalent salts differs from that of acids and bases;

that is, the ionization constants are in all cases relatively high in the case of salts (with of course such exceptions as occur in cadmium and mercury salts, which have a high tendency toward complex formation). However, the ionization constants of intermediate salt ions are not so high as to make these ions negligible in solutions of ordinary concentration.

8. Calculation of the Percentage of Intermediate Ions and Other Constituents in Solutions of Higher Type Salts.—The greatest difficulty which we encounter when an endeavor is made to calculate the percentage of intermediate ion present in the solution of a higher type salt, is that we do not as yet know how to calculate the percentage ionization of a salt of the simplest type. If we assume that the value of the conductance ratio, or of the conductance ratio modified by some function of the viscosity, gives the correct values for the ionization of simple type salts, then it is possible without the introduction of assumptions which are any more doubtful than those used in this simple case, to calculate the ionization of salts of the uni-bivalent type.

In order that comparisons may be made between the ordinary system of calculating the ionization of tri-ionic salts, and that which takes account of the existence of intermediate ions, and also so that the similar relations for uni-trivalent salts may be understood, the results of calculations of this kind will be given.

There are two assumptions which seem to afford the best basis for estimating the proportions of the constituents in solutions of uni-bivalent salts. The first of these is the assumption that the principle that different salts of the same valence type have approximately the same ionization values, or more properly the same ionization constants,[1] applies to the first stage of the ionization of uni-bivalent salts. Thus if a salt A_2B (such as Ag_2SO_4) ionizes at first into $A^+ + AB^-$, it ionizes as a uni-univalent salt, and should therefore be about 83% ionized in this way in 0.1 normal solution.

The second assumption is based on the fact that the transference numbers of uni-bivalent salts (excluding the halides of bivalent metals) vary scarcely at all with the concentration. As has been shown, it is a necessary consequence of this fact that the intermediate ion, if it be present in considerable quantity, has an equivalent conductance equal to $\Lambda_A\Lambda_B/(2\Lambda_A + \Lambda_B)$ where Λ_A and Λ_B are the equivalent conductances of the simple univalent and bivalent ions of a salt, A_2B. The method used was to calculate by a method of approximations the concentrations of the constituents which under the assumptions just stated cause the calculated specific conductance of the solution in each case to be the same as that experimentally determined. The results are given in Table I.

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[1] Noyes, THIS JOURNAL, 30, 351 (1908).

TABLE I.—CONCENTRATIONS OF THE INTERMEDIATE ION AND OF THE OTHER CONSTITUENTS IN SOLUTIONS OF UNI-BIVALENT SALTS WITH THE ORDINARY VALUES GIVEN IN PARENTHESIS.

Silver Sulfate.

Equiv. conc. of salt	0.01	....	0.05352	....	0.10	....
Conc. Ag = Σi	0.00878	(0.00836)	0.0403	(0.03035)	0.0702	(0.0617)
$AgSO_4$	0.00107	....	0.01004	....	0.02186	....
$SO_4^{=}$	0.00385	(0.00418)	0.01513	(0.01823)	0.02417	(0.03085)
Ag_2SO_4	0.000077	(0.00082)	0.001596	(0.00853)	0.00397	(0.0191)
$k_1 = \frac{[Ag^+][NO_3^-]}{[AgNO_3]}$	0.123	....	0.254	....	0.336	....
$k_2 = \frac{[Ag^+][SO_4^-]}{[AgSO_4^-]}$	0.0316	....	0.0608	....	0.0776	....
Per cent. sulfate as						
$AgSO_4^-$	21.4	....	37.50	....	43.7	....
$SO_4^{=}$	77.0	(83.6)	56.5	(68.1)	48.3	(61.7)
Ag_2SO_4	1.54	(16.4)	5.97	(31.9)	7.94	(38.3)
Total mols	0.01447	(0.01336)	0.06707	(0.06321)	0.1202	(0.1116)

Potassium Sulfate.

Equiv. conc. of salt	0.01	....	0.10	....	1.00	....
Conc. K = i	0.0090	(0.00869)	0.0774	(0.0710)	0.62	(0.592)
KSO_4	0.0009	....	0.0176	....	0.25	....
SO_4	0.00405	(0.004345)	0.0299	(0.0355)	0.185	(0.296)
K_2SO_4	0.00005	(0.000655)	0.0025	(0.0145)	0.165	(0.204)
$k_1 = \frac{[K^+][Cl^-]}{[KCl]}$	0.150	....	0.533	....	2.32	....
$k_2 = \frac{[K^+][SO_4^{=}]}{[KSO_4^-]}$	0.040	....	0.132	....	0.46	....
Per cent. sulfate as						
KSO_4^-	18.0	....	35.2	....	46.0	....
$SO_4^{=}$	81.0	(86.9)	59.8	(71.0)	42.0	(59.2)
K_2SO_4	1.0	(13.1)	5.0	(29.0)	12.0	(40.8)
Total mols	0.01400	(0.01369)	0.1274	(0.1210)	1.220	(1.092)

Sodium Sulfate.[1]

Equiv. conc. of salt	0.02	....	0.10	....	0.20	....
Conc. Na = Σi	0.01722	....	0.07640	....	0.1415	....
$NaSO_4^-$	0.00234	....	0.01732	....	0.03950	....
$SO_4^{=}$	0.00744	....	0.02954	....	0.051	....
Na_2SO_4	0.00022	....	0.00314	....	0.0095	....
$k_1 = \frac{[Na^+][SO_4^{=}]}{[Na_2SO_4]}$	0.18316	....	0.42142	....	0.58825	....
$k_2 = \frac{[Na^+][SO_4^{=}]}{[NaSO_4^-]}$	0.05475	....	0.13030	....	0.1827	....
Per cent. sulfate as						
$NaSO_4^-$	23.40	....	34.64	....	39.5	....
$SO_4^{=}$	74.4	....	59.08	....	51.0	....
Na_2SO_4	2.2	....	6.28	....	9.5	....

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[1] Calculated for us by Dr. S. D. Wilson.

It will be seen from this table that the proportion of intermediate ion increases rapidly with increasing concentration. The most striking result, however, is that K_2, the ionization function for the second stage of ionization, increases with increasing ion concentration, and is nearly proportional to K_1.

The assumption used in the calculation of the first step of the ionization of a tri-ionic salt was that usually adopted for salts of the simplest type, that is, that the conductivity ratio, or the conductivity ratio modified by a function of the viscosity, gives the ionization. When such an assumption is made, it is found empirically that the Storch[1] equation

$$\frac{\Lambda_0 - \Lambda}{\gamma\Lambda_0} = k\left(\frac{\Lambda}{\Lambda_0}\right)^x$$

or in its modified form as given by Bancroft[2]

$$C_2^n/C_3 = K$$

expresses the relations which are found, where $N = 2 - f(K)$, where $f(K)$ varies approximately between 0 and $^1/_2$. The latter equation is now often used in the following forms:

$$\frac{(C\gamma)^2}{C(1-\gamma)} = K_1(C\gamma)^{2-n},\ \frac{(C\gamma)^2}{C(1-\gamma)} = k_1(\Sigma i)^{2-n} \text{ or } \frac{C_{B^+} \times C_{A^-}}{C_{BA}} = k_1(\Sigma i)^{2-n}.$$

Since the value of $k(\Sigma i)$ becomes O at zero concentration, it has been proposed by Kraus,[3] and by Kraus and Bray that an additional constant be inserted, which gives the equation the following form when the viscosity correction is included:

$$(C\gamma\ \eta/\eta_0)^2/C(1-\gamma\ \eta/\eta_0) = k + k_1(C\gamma\ \eta/\eta_0)^h$$

which is perhaps better expressed:

$$\frac{(\Lambda\eta/\Lambda_0\eta_0)^2\,C}{(1-\Lambda\eta/\Lambda_0\eta_0)} = k + k_1\left(C\,\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)$$

However the simpler form of the equation gives sufficiently accurate results for highly ionized substances in aqueous solution at the concentrations given in Table I, so this simpler form has been used in the calculation, which would otherwise be extremely involved. The results of these calculations show that when it is assumed that the first step in the ionization follows the usual rule of the uni-univalent salts, the second step follows a similar rule, but with a much smaller value of $K(\Sigma i)^{2-n} = K_2$.

9. Values of the Exponent *n* for the Steps in the Ionization of the Tri-ionic Salt Silver Sulfate.—It is interesting in this connection to calculate the values of n in the equations which fit the different steps in the ionization.

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[1] Storch, *Z. physik. Chem.*, **19**, 13–19 (1894).

[2] *Ibid.*, **31**, 189 (1899).

[3] THIS JOURNAL, **35**, 1412 (1913).

Normal concn.	First step. $Ag_2SO_4 = Ag\ AgSO_4^{-}\ n_1$.	Second step. $AgSO_4 = Ag\ SO_4^{=}\ n_2$.
0.01 to 0.05	1.52	1.57
0.05 to 0.10	1.49	1.56

This shows that an equation of the Storch form also fits the second step in the ionization of salts of the tri-ionic type.

The equations for these two steps may be given as follows:

$$\frac{C_{B^+} \times C_{AB^-}}{C_{B_2A}} = K' (\Sigma i)^{2-n_1} \tag{1}$$

$$\frac{C_{B^+} \times C_{A^=}}{C_{BA^-}} = K'' (\Sigma i)^{2-n_2} \tag{2}$$

or combined in one equation:

$$\frac{C^2_{B^+} \times C_{A^=}}{C_{B_2A}} = K'K'' (\Sigma i)^{4-n_1-n_2} \qquad (3)^1$$

For silver sulfate:

$$\frac{C^2_{B^+} \times C_{A^=}}{C_{B_2A}} = K'K'' (\Sigma i)^{0.94} = K (\Sigma i)^{0.94}$$

So approximately $\dfrac{C_{B^+} \times C_{A^=}}{C_{B_2A}} = K_i$, for this salt, where K_i is a real constant.

The results given in Table I are compared with those obtained by Noyes and Eastman[2] in Table II.

TABLE II.—COMPARISON OF THE IONIZATIONS OF SULFURIC ACID AND OF POTASSIUM SULFATE, CALCULATED FROM THE STANDPOINT OF THE EXISTENCE OF INTERMEDIATE IONS.

	Salt.	Acid.	Salt.	Acid.
Equiv. concn.	0.01	0.01	0.1	0.1
Formal concn.	0.005	0.005	0.05	0.05
K^+ or $H^+ = \Sigma i$	0.0090	0.0081	0.0774	0.0625
KSO_4^- or HSO_4^-	0.0009	0.0017	0.0176	0.0315
$SO_4^=$	0.00405	0.0032	0.0299	0.0155
K_2SO_4 or H_2SO_4	0.00005	0.00010	0.0025	0.0030
$K_1 = A^+ \times AB^-/AB_2$	0.150	0.138	0.553	0.626
$K_2 = A^+ \times B^=/AB^-$	0.040	0.0152	0.132	0.0307

It will be seen that the first ionization constant obtained (K_1) is nearly the same for the salt or the acid at the same concentration, but that the ionization constant of the intermediate ion (K_2) is much smaller for the acid ion than for the salt ion, which is in accord with the idea presented earlier in this paper. In all cases the second ionization constant (K_2) is much smaller than the first (about $^1/_4$ as much in the case of the salts),

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[1] It must be remembered in applying this equation that the concentrations are not those usually used and are *not* equal to the conductance ratios, but are the concentrations given in Table I.

[2] Noyes and Eastman, THIS JOURNAL, 32, 1148 (1910).

as might be expected, since in the intermediate ion the univalent ion must separate from a doubly charged ion.

10. The Ionization of a Tri-univalent Salt.—The calculation of the concentration of the constituents in a solution of a tri-univalent salt, such as lanthanum nitrate or iodate has not been attempted, though it would be possible to make such a calculation. However, some additional assumptions would be introduced, and without making the calculations all of the general conclusions of value can be obtained by considering the results given in Table I. As compared with the uni-bivalent salt which on ionization forms only one intermediate ion, we would expect that in the uni-trivalent salt the percentage of univalent ion would be increased, the percentage of the ion of highest valence would be decreased, that of the molecules would be decreased, and the percentage of intermediate ion would be increased, since now there would be two intermediate ions instead of one. Thus lanthanum nitrate would ionize as follows:

$$La(NO_3)_3 = La(NO_3)_2^+ + NO_3^-$$
$$La(NO_3)_2^+ = La(NO_3)^{++} + NO_3^-$$
$$La(NO_3)^{++} = La^{+++} + NO_3^-$$

11. Discussion of the Valence-Product Rule.—From the standpoint of the above paragraph it may be said that for uni-univalent, uni-bivalent, and uni-trivalent salts, *the total percentage amount of salt in the ionic form increases with the valence product*, which is just the opposite of the rule which has been considered valid in the past.[1] Also when these salts are taken in the same order, the percentage of un-ionized salt decreases, which is again the opposite of the usual rule.

An inspection of Table I will show that the total number of particles (mols) present is not very greatly different when allowance is made for the presence of intermediate ions from that usually calculated when they are supposed to be absent. Thus in $N/10$ potassium sulfate the total number of mols is 0.1274 on the intermediate ion basis, and 0.1210 from the ordinary standpoint, so that the former method gives only a slightly larger number than the latter. When the number of ions is calculated for the same solution, the values are 0.1249 and 0.1065, respectively, so that many more ions are present from the intermediate ion standpoint. If 0.1 normal (0.05 molar) potassium sulfate were to completely dissociate it would give 0.15 mol of ions, so that with the intermediate ions present we have 83.3% of the possible number of ions instead of 71% as usually calculated. However, only 5% of the salt remains in the un-ionized form, so 95% is in the form of ions. There is no real contradiction in these values, but only an apparent one, due to the fact that the intermediate ions are intermediate in composition between the un-ionized molecules and the ions which result from complete ionization.

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[1] Noyes and Johnston, THIS JOURNAL, 31, 1002 (1909).

Since a salt of the uni-univalent type gives at tenth normal concentration only 85% of the total possible number of ions, and as seen above, a uni-bivalent salt gives about 83% of the possible number at the same normal concentration, there is not much difference between the ionization of the two types of salts when they are looked at from just this standpoint.

When the ionization of a higher type salt is calculated without reference to the presence of intermediate ions, the relations are found to be expressed by the valence-product rule, that the ionization decreases rapidly when the product of the valences of the constituent ions increases. This relation is shown in Table III.

TABLE III.—VALUES OF THE CONDUCTANCE RATIO (OR IONIZATION IF THE PRESENCE OF INTERMEDIATE IONS IS NOT TAKEN INTO ACCOUNT) IN RELATION TO VALENCE TYPE.

Salt.	Valence product.	Conductance ratio × 10^2 in 0.1 N soln. at 18°.
KCl	$1 \times 1 = 1$	86
KNO_3		83
NaCl		84
$AgNO_3$		81
$NaC_2H_3O_2$		83
K_2SO_4	$1 \times 2 = 2$	72
Na_2SO_4		70
$Ca(NO_3)_2$		73
$Ba(NO_3)_2$		68
$La(NO_3)_2$	$3 \times 1 = 3$	65
$K_3C_6H_5O_7$		65
$K_4Fe(CN)_6$	$1 \times 4 = 4$	53

Noyes and Johnston find that these results can be expressed in another form, in which they show that there is an approximate proportionality between the un-ionized *fraction* of a salt and the valence product, when no allowance is made for the existence of intermediate ions in the solution. It seems that the idea which led to the expression of the results in the latter form was undoubtedly that as the valence product increases the electrical forces tending to hold the ions together increase, and therefore, from a theoretical standpoint the un-ionized fraction should increase. From the intermediate ion standpoint, however, while the above rules still apply to the conductance ratio, they no longer apply to the ionization, since, as has been stated above, the ionized fraction seems to increase and the un-ionized fraction to decrease as the valence product increases if the salts are of the 1,1; 1,2; or 1,3 types. However, that the idea from which the valence-product rule was derived is itself correct is indicated by the ionization functions, often called ionization constants, for the two steps in the ionization of a uni-bivalent salt, as given by Table I. These show that the ionization is much greater for the first step where the two univalent ions separate according to the reaction $B_2A = B^+ + BA^-$, than when the univalent ion separates from the bivalent one, $BA^- = B^+ + A^=$, in fact the ionization function is only about one-fourth as large for the second reaction as it is for the first.

Experimental Part.

1. **Introduction.**—In the first three papers dealing with intermediate ions, the solubility and conductivity results on a large number of uni-bivalent salts were presented. Perhaps the most striking experimental result obtained was that while the salts of this type behave quite normally as to the variation of their solubility when either (1) a salt with a common univalent ion, or (2) a salt with *no common ion* is added to the solution, the same is not true when (3) a salt with a common bivalent ion is added. In the latter case the effect is on the whole a normal one, with one exception which will be pointed out later, when the saturating salt is of extremely slight solubility, as was the case with lead iodate, solubility 0.00011 equivalent per liter at 25°. However, as the solubility of the saturating salt increases, the effect becomes more and more abnormal, until for very soluble salts the solubility curve for the common bivalent ion takes on the form of a curve representing the addition of a salt with no common ion. The generality of the result at once suggests that the effect is not due to complex salt formation, which is more specific in its action.

The experimental work in this paper will deal with the solubility effects in the case of a tri-univalent salt. In solutions of salts of this type it would be expected that any abnormalities found in the relations of the uni-bivalent salts would become more pronounced, that is, when the two types of salts are compared at the same concentration. In the work on uni-bivalent salts all practical ranges of solubility have been studied from 0.0001 to 8.6 equivalents per 1000 grams of water, a range expressed by a factor nearly equal to 10,000. It was desired that the tri-univalent salt chosen should be as little inclined toward complex formation as possible, and in order that the principal part of the data might be obtained in very dilute solutions, a very slightly soluble salt was desired. There are as a matter of fact very few salts which meet these specifications, and of these lanthanum iodate seemed to be the best adapted for the purpose. Other suitable salts were certain cobaltammines, but lanthanum iodate has the advantage that it is a more stable salt, and that its solution can be analyzed with extreme accuracy.

2. **Preparation of Salts and Solutions. Lanthanum Iodate.**—Hot dilute solutions containing lanthanum nitrate and potassium iodate were brought together, the former being in excess. The solution was stirred, and then quickly cooled by pouring into a vessel surrounded with ice. The precipitated salt was filtered, washed and *recrystallized* (a very tedious process in the case of such a slightly soluble salt) from conductivity water, with a maximum specific conductance of 0.6×10^{-6}. The slightly soluble salt was recrystallized in large evaporating dishes heated on steam baths. The

white salt on analysis gave the value of La_2O_3 and iodine value as calculated from the formula $La(IO_3)_3$. Spectrographs made on a 6-in. Rowland concave grating showed the presence of no other rare earth.

Lanthanum Nitrate.—Crystals of the double nitrate of lanthanum and ammonium were obtained from the Welsbach Burner and Light Co., through the courtesy of Dr. H. S. Miner. These were recrystallized. A solution of the salt was made and the lanthanum precipitated as the oxalate, thoroughly washed and ignited in platinum dishes to the oxide. The lanthanum nitrate was then made by adding an excess of the oxide to nitric acid and crystallizing the salt from the clear solution. The salt was recrystallized from conductivity water.

All of the other salts used were chemically pure salts recrystallized from conductivity water. In making solutions and in diluting, conductivity water of the quality mentioned above was used.

The solubility was determined by the method formerly employed by Harkins in this kind of work.[1] At least four separate solubility determinations, two from undersaturation and two from supersaturation, were made for each.

3. **Methods of Analysis.** Iodate.—About fifty cc. of the saturated solution were quickly transferred from its container in the thermostat to a small weighed glass-stoppered Erlenmeyer flask. Two samples were taken from each bottle, making eight analyses for each determination of the solubility. The weighings were made at once, the solution transferred to a 700 cc. beaker and the flask rinsed until a volume of 400 cc. was obtained. Three cc. of concentrated hydrochloric acid were added, 5 grams of potassium iodide put in, and sodium thiosulfate was run in from a weight buret until the color of iodine had about disappeared. Then two cc. of a freshly made starch solution were added and the titration completed. The time for the titration was in each case three minutes.

The thiosulfate solution was made up with conductivity water and kept in a black bottle with a siphon attached. It was carefully standardized against resublimed iodine, pure recrystallized potassium iodate, and against a standard solution of potassium permanganate. For use as a reagent the stock solution, which was one-tenth normal, was transferred to another black bottle and diluted to ten times its volume.

Lanthanum.—(1) A weighed quantity of the solution was evaporated in a small weighed platinum dish or crucible in an air bath and ignited to the oxide. (2) The solution was diluted and the lanthanum precipitated as the oxalate. The oxalic acid was liberated and titrated in the usual way.

Table I gives the solubility of lanthanum iodate in water as 0.6842 gram per 1000 grams of water at 25°.

TABLE I.—SOLUBILITY OF LANTHANUM IODATE IN WATER AT 25°.
(Concentrations in milliequivalents per liter.)

No.	Conc. $La(IO_3)_3$.	Sp. cond. $\times 10^3$.	Equiv. cond.	Density 25°.
1	3.0900	0.3066	99.206	0.998250
2	3.0904	0.3066	99.206	0.998251
3	3.0905	....	....	0.998251
4	3.0908	0.3066	99.206	0.998251
5	3.0902	....	....	0.9982505
6	3.0902	0.3066	....	0.9982505

4. The Solubility of Lanthanum Iodate in Solutions of Lanthanum Nitrate, Potassium Iodate, Sodium Iodate, Sodium Nitrate and in Lanthanum Ammonium Nitrate.

—The results of these solubility determina-

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[1] THIS JOURNAL, 33, 1811 (1911).

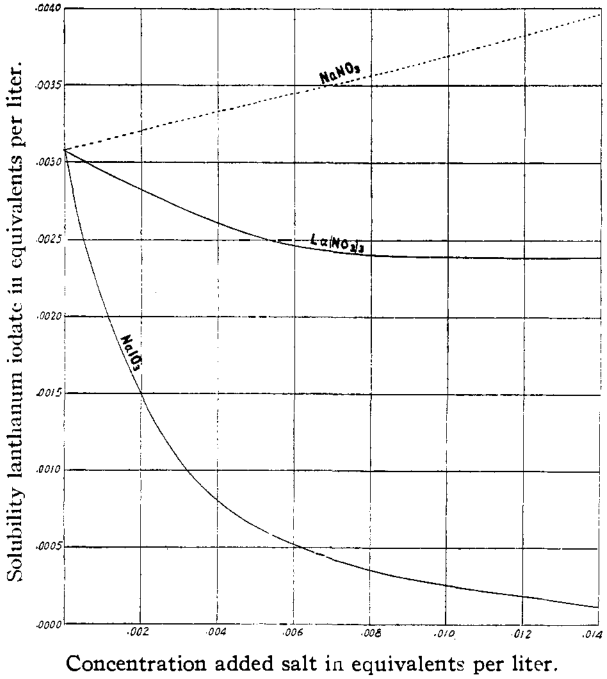

Fig. 1.—The solubility of the tri-univalent salt lanthanum iodate in very dilute solutions of other salts.

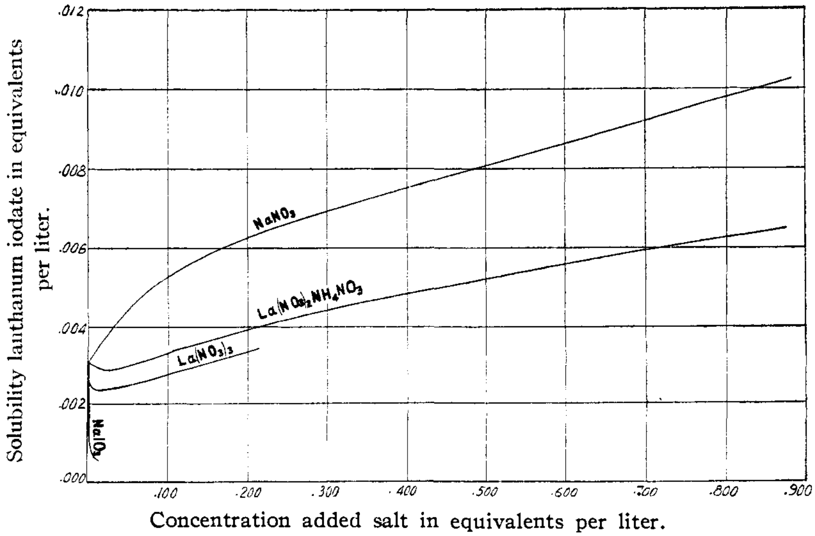

Fig. 2.—The solubility of lanthanum iodate in solutions of other salts. (For the dilute solutions see Fig. 1.)

tions are given in Table II. The mean values for the solubilities, with the solubility of the saturating salt expressed in millimols, are found in Table III together with the fractional concentrations of the added salt and the fractional solubility of lanthanum iodate. The "fractional conc. of added salt" is the ratio

$$\frac{\text{Equivalent conc. of added salt}}{\text{Equivalent solubility of the saturating salt}}$$

while the fractional solubility is the ratio

$$\frac{\text{Solubility of salt in salt solution}}{\text{Solubility of salt in water}}.$$

These ratios are used for plotting the curves in Fig. 5. The solubility data presented in Table II are given in a graphic form in Figs. 1 and 2, where the ordinates represent the equivalent solubility of lanthanum iodate and the abscissae, the equivalent concentration of the added salts.

TABLE II.—SOLUBILITY OF LANTHANUM IODATE IN SALT SOLUTIONS AT 25°.
(Concentrations in milliequivalents per liter.)

No.	Conc. added salt. None.	Solubility $La(IO_3)_3$.	Mean solubility.	Solubility in grams per liter.	Sp. cond. $\times 10^3$.	Density 25°/4°.
1	0.00000	......	3.0904	0.6841	......	0.998251
	$La(NO_3)_3$					
7	2.00	2.529	......	.....	......	......
8	....	2.529_5	......	.....	......	......
9	....	2.529	......	.....	......	......
10	....	2.529_5	2.529	0.5595	0.4763	0.997323
11	5.00	2.390	......	......	......	......
12	....	2.390_5	......	.....	......	......
13	....	2.390	......	.....	......	......
14	....	2.390_5	2.3905	0.5288	0.7991	0.998074
15	10.00	2.347	......	.....	......	......
16	....	2.347_5	......	.....	......	......
17	....	2.347	......	.....	......	......
18	....	2.347_5	2.3477	0.5194	1.3101	0.998590
19	50.00	2.496	......	.....	......	......
20	....	2.496_5	......	.....	......	......
21	....	2.496	......	.....	......	......
22	....	2.496_5	2.4960	0.5522	5.1076	1.002125
23	100.00	2.808_5	......	.....	......	......
24	....	2.808	......	.....	......	......
25	....	2.808	......	.....	......	......
26	....	2.808_5	2.8086	0.6214	9.286	1.006615
27	200.52	3.358	......	.....	......	......
28	....	3.358	3.3586	0.7431	16.752	1.015333
	KIO_3					
29	0.099	2.843_5	......	.....	......	......
30	....	2.843	......	.....	......	......
31	....	2.842	......	.....	......	......
32	....	2.842_5	2.8430	0.6290	......	1.00030

TABLE II (*continued*).

No.	Conc. added salt. None.	Solubility $La(IO_3)_3$.	Mean solubility.	Solubility in grams per liter.	Sp. cond. × 10^3.	Density 25°/4°.
33	0.4957	2.546*s*	......	.....	......	......
34	....	2.546	......	.....	......	......
35	....	2.546	......	.....	......	......
36	....	2.546*s*	2.5464	0.5634	......	1.000274
37	0.9914	2.246	......	.....	......	......
38	....	2.246*s*	......	.....	......	......
39	....	2.246	......	.....	......	......
40	....	2.246*s*	2.2465	0.4970	......	1.00030
41	1.9828	1.689*s*	......	.....	......	......
42	....	1.689	......	.....	......	......
43	....	1.68975*s*	......	.....	......	......
44	....	1.68974	1.68974	0.37388	......	1.000312
45	....	......	......	.....	......	......
46	....	......	......	.....	......	......
47	....	......	......	.....	......	......
48	....	......	......	.....	......	......
49	0.200	......	(2.730)	.....	0.28033	......
50	....	......	(2.540)	.....	0.30242	......
51	....	......	(2.240)	.....	0.32740	......
	$NaIO_3$					
52	0.0913	2.871	......	.....	......	......
53	....	2.872*s*	......	.....	......	......
54	....	2.871*s*	......	.....	......	......
55	....	2.871	2.8718	0.6353	......	1.00060
56	0.4560	2.552*s*	......	.....	......	......
57	....	2.552	......	.....	......	......
58	....	2.552*s*	......	.....	......	......
59	....	2.552	2.5521	0.5646	......	1.00059
60	0.9130	2.297*s*	......	.....	......	......
61	....	2.297	......	.....	......	......
62	....	2.297*s*	......	.....	......	......
63	....	2.297	2.2976	0.5083	......	1.00065
64	1.8260	1.804	......	.....	......	......
65	....	1.805*s*	......	.....	......	......
66	....	1.804	......	.....	......	......
67	....	1.805*s*	1.8050	0.3993	......	1.00065
68	3.6530	0.892*s*	......	.....	......	......
69	....	0.891	......	.....	......	......
70	....	0.891*s*	......	.....	......	......
71	....	0.892*s*	0.89200	0.1973	......	1.00069
72	4.5326	0.6048	......	.....	......	......
73	....	0.6057	0.60530	0.1339	......	1.00083
74	6.7989	0.4398	......	.....	......	......
75	....	0.4414*s*	0.44056	0.0973	......	......
	$NaNO_3$					
76	25.00	3.928*s*	......	.....	......	......
77	....	3.927	3.9277	0.8690	......	1.00250

TABLE II (*continued*).

No.	Conc. added salt. None.	Solubility $La(IO_3)_3$.	Mean solubility.	Solubility in grams per liter.	Sp. cond. $\times 10^3$.	Density 25°/4°.
78	50.00	4.477*s*	......	.....	......	......
79	....	4.475	4.4763	0.9904	......	1.00385
80	100.00	5.244	......	.....	......	......
81	....	5.244*s*	5.2443	1.160	......	1.00742
82	200.00	6.263	......	.....	......	......
83	....	6.260*s*	6.2619	1.385	......	1.01290
84	400.00	7.396	......	.....	......	......
85	....	7.397*s*	7.39717	1.636	......	1.02422
86	800.00	9.741*s*	......	.....	......	......
87	....	9.750	9.7462	2.156	......	1.046775
88	1600.00	12.934*s*	......	.....	......	......
89	....	12.934	12.9344	2.859	......	1.09005
90	3200.00	13.697	......	.....	......	......
91	....	13.696*s*	13.6972	3.030	......	1.17243
92	1.00	(3.129)	......	.....	0.41475	......
93	2.00	(3.169)	......	.....	0.52983	......
94	10.00	(3.450)	......	.....	1.41293	......
	$La(NO_3)_3.2NH_4NO_3$					
95	26.34	2.852	......	.....	......	......
96	....	2.854*s*	......	.....	......	......
97	....	2.853	......	.....	......	......
98	....	2.852*s*	2.853	......	......	1.001122
99	56.682	3.047*s*	......	.....	......	......
100	....	3.048	......	.....	......	......
101	....	3.046	......	.....	......	......
102	....	3.047*s*	3.047	......	......	1.003554
103	105.364	3.410	......	.....	......	......
104	....	3.410*s*	......	.....	......	......
105	....	3.410	......	.....	......	......
106	....	3.410*s*	3.4102	.....	......	1.009711
107	158.048	3.691*s*	......	.....	......	......
108	....	3.691	3.69105	.....	......	1.016089
109	196.8375	3.918*s*	......	.....	......	......
110	....	3.918	3.9184	.....	......	1.021833
111	393.673	4.804	......	.....	......	......
112	....	4.805*s*	4.8050	.....	......	1.043438
113	787.35	6.165*s*	......	.....	......	......
114	....	6.165	6.1554	.....	......	1.08286
115	1574.70	8.690	......	.....	......	......
116	....	8.690*s*	8.6904	.....	......	1.16652

( ) = calc. from curve

s = equilibrium approached from supersaturation

5. Theoretical Limiting Solubility Curves for Various Type Salts.—An examination of Figs. 1 and 2 shows that in the case of the tri-univalent salt, the addition of the common univalent ion gives the same form of curve as would be expected; that when a common trivalent ion is added the solubility decreases slightly, passes quickly through a minimum, and then rapidly increases to a solubility greater than in water, with increasing concentration of the added salt. The rise of the curve in the latter case is far greater than would be the rise of a salt of the bi-univalent type of the same order of solubility. Fig. 2 shows the striking change of the curve from the type of the common ion to the one of the non-common ion.

TABLE III.—MEAN VALUES FOR THE SOLUBILITY OF LANTHANUM IODATE IN SOLUTIONS OF SALTS.

Salts added.	Milli-normal conc. salt solution.	Solubility in millimols.	Fractional conc. added salt.	Fractional conc. solubility.	Solubility grams per l.	Density 25°/4°.
$La(NO_3)_3$	0.00	1.0301	0.0000	1.0000	0.6841	0.99825
	2.00	0.8430	0.6471	0.8183	0.5595	0.99732
	5.00	0.7968	1.6178	0.7733	0.5288	0.99807
	10.00	0.7825	3.2358	0.7596	0.5194	0.99859
	50.00	0.8320	16.1789	0.8076	0.5522	1.00212
	100.00	0.9362	32.3580	0.9088	0.6214	1.00661
	200.52	1.1195	64.8830	1.0868	0.7431	1.01533
KIO_3	0.0000	1.0301	0.000000	1.0000	0.6841	0.99825
	0.0990	0.9476	0.032035	0.8785	0.6290	1.00030
	0.4957	0.8488	0.160175	0.8239	0.5633	1.00027
	0.9914	0.7488	0.320350	0.7269	0.4970	1.00030
	1.9828	0.5632	0.640700	0.5467	0.3738	1.00031
$NaIO_3$	0.0000	1.0301	0.00000	1.0000	0.68410	0.99825
	0.0913	0.9572	0.02954	0.9292	0.63538	1.00060
	0.4560	0.8507	0.14771	0.8258	0.56466	1.00059
	0.9130	0.7658	0.29543	0.7434	0.50835	1.00065
	1.8260	0.6016	0.59086	0.5841	0.39938	1.00065
	3.6530	0.2973	1.18173	0.2886	0.19736	1.00069
	4.5326	0.2017	1.46670	0.1958	0.13393	1.00083
	6.7989	0.1468	2.20050	0.1425	0.09733	1.00130
$NaNO_3$	0.00	1.0301	0.000	1.0000	0.68410	0.99825
	25.00	1.3092	8.089	1.2709	0.86901	1.00250
	50.00	1.4921	16.179	1.4487	0.99040	1.00385
	100.00	1.7481	32.358	1.6970	1.1603	1.00742
	200.00	2.0873	64.717	2.0264	.....	1.01290
	400.00	2.4657	129.43	2.3937	.....	1.02422
	800.00	3.2487	258.8	3.1537	.....	1.046775
	1600.00	4.3114	517.7	4.1822	.....	1.09005
	3200.00	4.5657	1035.4	4.4322	.....	1.17243
$La(NO_3)_3.2NH_4NO_3$....	0.00	1.0301	0.000	1.0000	.....	0.99825
	26.34	0.9510	8.523	0.9231	.....	1.00112
	52.68	1.0156	17.046	0.9861	.....	1.00355
	105.36	1.1367	34.093	1.1034	.....	1.00971
	158.04	1.2303	57.14	1.1943	.....	1.01608
	196.83	1.3061	63.69	1.2679	.....	1.02183
	393.67	1.6016	127.38	1.5547	.....	1.04343
	787.35	2.0551	254.77	1.9950	.....	1.08286
	1574.70	2.8968	509.5	2.8120	.....	1.16652

We will now turn to a study of Fig. 5. The ordinates represent the fractional solubility of the dissolved salt, and the abscissas the fractional concentration of the added salt. The heavy lines both solid and dotted represent the "theoretical limiting" curves for several types of salts. The coördinates for these curves were calculated by the following equations:

For a 1,1 + 1 or a 2,2 + 2 univalent salt with a univalent common ion added, or a bi-bivalent salt with a bivalent common ion added:

$$S(S + C) = 1.$$

For a 1,2 + 1 uni-bivalent salt with a univalent common ion added:

$$S(S + C)^2 = 1.$$

For a 1,2 + 2 uni-bivalent salt with a bivalent common ion added:

$$S^2(S + C) = 1.$$

For a 1,3 + 1 tri-univalent salt with a univalent common ion added:

$$S(S + C)^3 = 1.$$

For a 1,3 + 3 tri-univalent salt with a trivalent common ion added:

$$S^3(S + C) = 1.$$

For a 1,4 + 1 uni-tetravalent salt with a univalent common ion:

$$S(S + C)^4 = 1.$$

For a 1,4 + 4 uni-tetravalent salt with a tetravalent common ion:

$$S^4(S + C) = 1.$$

For a 2,3 + 2 bi-trivalent salt with a bivalent common ion:

$$S^2(S + C)^3 = 1.$$

For a 2,3 + 3 bi-trivalent salt with a trivalent common ion:

$$S^3(S + C)^2 = 1.$$

It was noted by Harkins, in the paper last referred to, that the curves of the salts of the 1,1 + 1 and the 1,2 + 1 types lie very close to the theoretical limiting curves, while the curves of the salts of the 1,2 + 2 type deviate from it very widely. Two experimental curves of salts of the

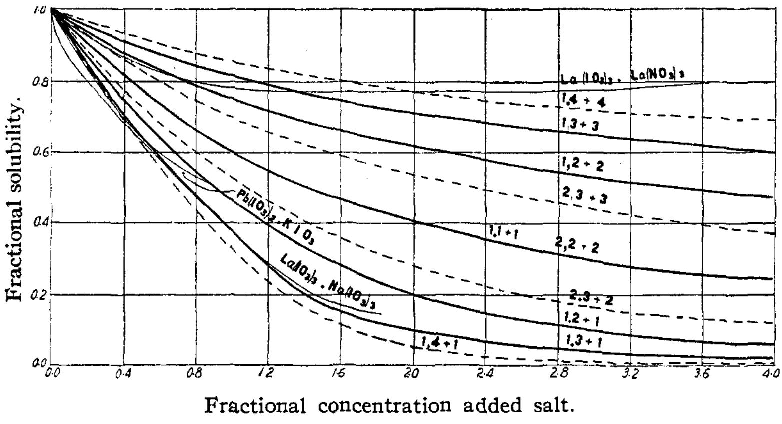

Fig. 3.—Theoretical limiting curves which express the fractional solubilities of various types of salts.

1,3 + 1, and the 1,3 + 3 types are interesting. In the first case the curve goes far below the theoretical limiting curve, then crosses and finally rises considerably above it, and in the second case we note a similar behavior, but the curve rises higher above the theoretical limiting curve. The latter part of this curve resembles the curves of the 1,2 + 3 type, and is similar to the curve showing the effect of the addition of a non-common ion. Harkins[1] found that several of the salts of the 2,1 + 1 type which he studied fell below the theoretical limiting curve. To see if a very insoluble salt of the 1,2 + 1 type would show this phenomenon to a greater degree, the curve for lead iodate in potassium iodate was plotted, and it may be seen that it falls about as far below as the curve for lanthanum iodate in potassium iodate and in general is similar in form. Of the two salts, lead iodate is much the more insoluble in water.

6. Calculation of the Specific Conductance of Mixtures of Salts of the Tri-univalent Type.—So far as is known to the writers no calculations have previously been made of the specific conductance of mixtures of salts of the tri-univalent type, at least not in cases where the salts in the mixture contain no common ion. For the calculations in this section the method employed is that previously used in the case of tri-ionic salts.[2] This method was first used to calculate the concentration of the constituents in mixtures of salts of the uni-univalent type, and has since been applied in a similar way for uni-bivalent salts. While from the standpoint of this paper, that is, that intermediate ions are present in solutions of salts of higher types, the calculated concentrations are only hypothetical, to those who still hold to the opposite theory they may appear to be real. In any event the results of such calculations will be of value for use in comparison of the uni-trivalent salts with those of lower types.

The values for the conductance and the conductance ratios of lanthanum nitrate and iodate, potassium and sodium iodates, and sodium nitrate, are given in Table IV, while Table V gives the apparent concentration of the constituents of mixtures in which lanthanum iodate is the saturating salt, and the added salts are lanthanum nitrate, potassium iodate and sodium nitrate. The logarithm of the apparent concentration of the un-ionized part of the saturating salt, lanthanum iodate (Table VI), is plotted against the logarithm of the apparent total ion concentration in Fig. 4, and Fig. 5 gives the similar values for the apparent solubility product, as calculated in Table VII. Tables VIII, IX and X give the similar values for a uni-bivalent salt, lead iodate.

When allowance is made for the fact that the concentration of a saturated lanthanum iodate solution is only about 0.001 molar, so that small errors in the conductance measurements produce a considerable per-

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[1] THIS JOURNAL, 33, 1855 (1911).

[2] Harkins, *Loc. cit.*

TABLE IV.—CONDUCTANCE RATIO FOR SEVERAL SALTS.

		Equivalent conductance			
Salt.	Conc. × 10^3.	measured Λ 25°.	from work of others.	100r.	$\Sigma i \times 10^3$.
$La(IO_3)_3$	3.09	99.206	....	88.92	2.7479
$La(NO_3)_3$	0.00	(142.6)	(142.6)[1]	100.00	0.0
	2.00	128.8	128.9	90.32	1.8065
	5.00	122.4	....	85.83	4.2917
	10.00	116.6	....	81.76	8.1768
	50.00	99.70	99.7	69.90	34.9533
	100.00	91.80	91.8	64.37	64.3780
	200.52	83.43	83.5	58.50	117.3135
KIO_3	0.00	(114.37)	....	100.00	0.0
	0.20	113.00	....	98.80	0.1976
	0.50	112.37	....	98.25	0.49125
	1.00	111.57	....	97.55	0.97550
	2.00	....	....	96.50	1.930
	5.00	....	....	94.60	4.730
	10.00	....	....	92.80	9.280
	20.00	....	....	90.30	18.060
	50.00	....	....	86.0	43.000
	100.00	....	....	81.9	81.900
	200.00	....	....	77.5	155.000
$NaIO_3$	0.00	....	....	100.00	0.0
	1.00	....	....	97.1	0.971
	2.00	....	....	96.0	1.920
	5.00	....	....	93.9	4.695
	10.00	....	....	91.7	9.170
	20.00	....	....	89.0	17.80
	50.00	....	....	84.2	42.10
	100.00	....	....	80.1	80.10
	200.00	....	....	75.2	150.40
$NaNO_3$	0.00	(121.80)	....	100.00	0.0
	1.00	120.47	....	98.90	0.9890
	2.00	119.19	....	97.79	1.955
	10.00	114.00	....	93.58	9.358
	20.00	....	....	91.0	18.200
	50.00	....	....	87.1	43.550
	100.00	....	....	83.2	83.200
	200.00	....	....	78.8	157.600

centage effect, it will be seen that the calculated specific conductances of the mixtures are very closely in accord with the determined values, when either the common univalent ion is added, or when the added salt is sodium nitrate, which has no common ion. It is remarkable that an empirical equation of the general form of the Storch equation, derived entirely from the behavior of uni-univalent or the simplest type salts, can be used to calculate with as good an accuracy as this, the conductance of mixtures of salts of such a high type as the uni-trivalent. However,

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[1] Cf. Noyes and Falk, THIS JOURNAL, **34**, 454–485 (1912).

Table V.—Apparent Concentration of the Constituents of Solutions Saturated with Lanthanum Iodate in Milliequivalents per Liter.

Salt added.	Conc. of salt.	Sol. La$(IO_3)_3$.	Conc. un-ion. La$(IO_3)_3$.	Conc. La^{+++}.	Conc. 10^{-3}.	Σi.	Conc. uni-on. $NaNO_3$.
La$(NO_3)_3$....	0.00	3.090	0.3424	2.748	2.748	2.748	.....
	2.00	2.529	0.336	3.918	2.193	3.918	.....
	5.00	2.391	0.379	6.197	2.011	6.197	.....
	10.00	2.348	0.455	9.911	1.890	9.911	.....
	50.00	2.496	0.761	36.498	1.739	36.498	.....
	100.00	2.809	1.003	65.981	1.805	65.981	.....
	200.52	3.359	1.391	119.217	1.967	119.215	.....
KIO_3.......	0.0000	3.0900	0.3424	2.748	2.748	2.748	.....
	0.0990	2.8431	0.3050	2.538	2.633	2.633	.....
	0.2000	2.7300	0.2950	2.535	2.627	2.627	.....
	0.4957	2.5463	0.2803	2.266	2.741	2.741	.....
	0.5000	2.5400	0.2800	2.260	2.739	2.739	.....
	0.9914	2.2466	0.2561	1.990	2.939	2.939	.....
	1.0000	2.2400	0.2550	1.985	2.938	2.938	.....
	1.9828	1.6897	0.2037	1.486	3.400	3.400	.....
	3.9656	0.7898	0.1078	0.682	4.440	4.440	.....
$NaNO_3$......	0.00	3.0900	0.3424	2.748	2.748	2.748	.....
	1.00	3.1299	0.3020	2.720	2.720	3.685	0.0087
	2.00	3.169	0.2642	2.720	2.720	4.620	0.0330
	10.00	3.450	0.1663	2.720	2.720	11.940	0.5561
	25.00	3.928	0.1209	2.853	2.853	25.253	2.2810
	50.00	4.476	0.0940	3.020	3.020	46.320	6.1840
	100.00	5.244	0.0754	3.220	3.220	86.070	16.34

	Conc. un-ion La$(NO_3)_3$.	Conc. un-ion. KIO_3 or $NaIO_3$.	Conc. Na$^+$ or K$^+$.	Conc. NO^{-3}.	L × 10^3 calc.	L × 10^3 detd.
La$(NO_3)_3$....	0.000	.....	.....	0.000	0.3066	0.3066
	0.275	.....	.....	1.725	0.4906	0.4763
	0.815	.....	.....	4.185	0.8212	0.7991
	1.980	.....	.....	8.020	1.3546	1.3101
	15.241	.....	.....	34.759	5.1505	5.1076
	35.820	.....	.....	64.180	9.3520	9.2858
	0.083270	.....	.....	117.250	16.9393	16.7520
KIO_3.......	.....	.....	.....	.....	0.3066	0.3066
	.....	0.00408	0.0949	.....	0.2940	.....
	.....	0.00820	0.1918	.....	0.2902	0.2803
	.....	0.0208	0.4749	.....	0.3071	.....
	.....	0.0210	0.4790	.....	0.3069	0.3024
	.....	0.0429	0.9485	.....	0.3306	.....
	.....	0.0430	0.9570	.....	.....	.....
	.....	0.0918	1.891	.....	0.3830	.....
	.....	0.2070	3.758	.....	0.5059	.....
$NaNO_3$......	.....	.....	.....	.....	0.3066	0.3066
	0.1093	0.0420	0.95	0.95	0.4192	0.4148
	0.1879	0.0747	1.90	1.90	0.5349	0.5298
	0.5700	0.2134	9.20	9.20	1.426	1.413
	0.9539	0.3715	22.40	22.40	3.0466	.....
	1.3607	0.5536	43.30	43.30	5.6108	.....
	1.9472	0.7963	82.85	82.85	10.4500	.....

TABLE VI.—CONCENTRATION OF THE UN-IONIZED PART OF LANTHANUM IODATE IN SOLUTIONS OF THE SALTS. (CONCENTRATIONS IN MILLIEQUIVALENTS PER LITER.)

Σi.	$La(NO_3)_3$.	KIO_3.	$NaNO_3$.
2.748	0.3424	0.3424	0.3424
2.633	....	0.3050	....
2.627	....	0.2950	....
2.739	....	0.2800	....
2.938	....	0.2550	....
3.400	....	0.2037	....
3.685	....	....	0.3020
3.918	0.3360	....	....
4.440	....	0.1078	....
4.620	....	....	0.2642
6.197	0.379	....	....
9.911	0.455	....	....
11.940	....	....	0.1663
25.253	....	....	0.1209
36.498	0.761	....	....
46.320	....	....	0.0940
65.981	1.003	....	....
86.070	....	....	0.0754
119.217	1.391	....	....

TABLE VII.—VALUES OF THE APPARENT SOLUBILITY PRODUCT FOR LANTHANUM IODATE IN THE PRESENCE OF OTHER SALTS.

(Σi in Milliequivalents, Solubility Product in Millimols.)

Σi.	$La(NO_3)_3$.	KIO_3.	$NaNO_3$.
2.748	19.0090	19.009	19.009
2.633	.....	15.442	....
2.627	.....	14.715	....
2.739	.....	15.472	....
2.938	.....	16.781	....
3.400	.....	19.467	....
3.685	.....	....	18.288
3.918	13.774	....	....
4.440	.....	19.895	....
4.620	.....	....	18.288
6.197	16.800	....	....
9.911	22.304	....	....
11.940	.....	....	18.288
25.253	.....	....	22.084
36.49	63.981	....	....
46.32	.....	....	27.729
65.98	129.345	....	....
86.07	.....	....	35.834
119.21	302.43	....	....

TABLE VIII.—CONCENTRATION OF THE CONSTITUENTS OF SOLUTIONS SATURATED WITH LEAD IODATE IN MILLIEQUIVALENTS PER LITER.

Salt added.	Conc. of salt.	Sol. $Pb(IO_3)_2$.	Conc. un-ion. $Pb(IO_3)_2$ $\times 10^3$.	Conc. Pb^{++}.	Conc. 10^{-3}.	Σi.	Conc. un-ion. KNO_3.
$Pb(NO_3)_2$.......	0.00	0.1102	1.762	0.10844	0.10844	0.10844	....
	0.10	0.0870	1.850	0.18303	0.08515	0.18303	....
	1.00	0.0411	2.240	0.98400	0.03886	0.98450	....
	10.00	0.0185	2.870	8.4626	0.01563	8.4626	....
	100.00	0.0160	5.840	63.57	0.01016	63.51	....
KIO_3..........	0.00000	0.1102	1.762	0.10844	0.10844	0.10844	....
	0.05304	0.0697	1.180	0.06852	0.12104	0.12104	....
	0.10610	0.0437	0.800	0.04290	0.14791	0.14791	....
KNO_3..........	0.00	0.1102	1.762	0.10844	0.10844	0.108	0.0000
	2.00	0.1141	0.463	0.10510	0.10510	2.044	0.0570
	10.00	0.1334	0.256	0.11150	0.11150	9.482	0.6114
	50.00	0.2037	0.208	0.14000	0.14000	43.490	6.6500

Salt added.	Conc. un-ion. $Pb(NO_3)_2$.	Conc. un-ion. KIO_3.	Conc. K^+.	Conc. NO^{-3}.
$Pb(NO_3)_2$........	0.00000	.....	.....	....
	0.00212	.....	.....	....
	0.0546	.....	.....	....
	1.553	.....	.....	....
	36.500	.....	.....	....
KIO_3...........	......	0.00000	0.00000	....
	......	0.00052	0.05252	....
	......	0.00105	0.10505	....
KNO_3...........	......	.....	0.000	0.000
	......	.....	1.939	1.939
	......	.....	9.370	9.370
	......	.....	43.350	43.350

TABLE IX.—VALUES FOR THE SOLUBILITY PRODUCT FOR LEAD IODATE IN THE PRESENCE OF OTHER SALTS. (Σi IN MILLIEQUIVALENTS, SOLUBILITY PRODUCT IN MILLIMOLS.)

Σi.	$Pb(NO_3)_2$.	KIO_3.	KNO_3.
0.10844	0.0006376	0.0006376	0.0006376
0.12104	......	0.0005087	.....
0.14791	......	0.0004693	.....
0.18303	0.00066351	.....	.....
0.98400	0.0007430	.....	.....
2.044	......	.....	0.0005810
8.4626	0.0010337	.....	.....
9.482	......	.....	0.0006931
43.490	......	.....	0.001372
63.500	0.0032783	.....	.....

TABLE X.—CONCENTRATION OF THE UN-IONIZED PART OF LEAD IODATE IN SOLUTIONS OF OTHER SALTS. (CONC. IN MILLIEQUIVALENTS PER LITER.)

Σi.	$Pb(NO_3)_2$.	KIO_3.	KNO_3.
0.10844	0.001762	0.001762	0.001762
0.12104	....	0.001180	....
0.14791	....	0.000800	....
0.18303	0.001850	....	....
0.98400	0.002240	....	....
2.044	....	....	0.000463
8.463	0.002870	....	....
9.482	....	....	0.000256
43.490	....	....	0.000208
63.510	0.005840	....	....

when the common ion is trivalent the agreement is not nearly so good, and the calculated values becomes several per cent. higher than that determined by experiment. This is in the direction of the change of conductivity which occurs when there is a small amount of complex formation.

Fig. 4 shows the variation in the apparent total ion concentration

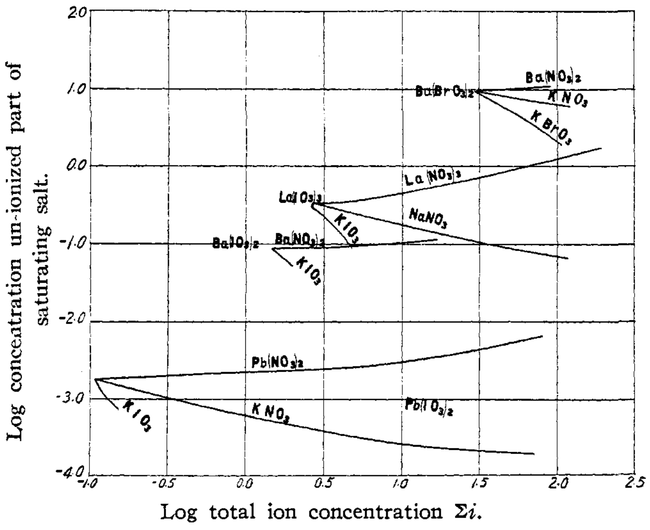

Fig. 4.—The solubility of the un-ionized part of the salts calculated on the assumption that intermediate ions are not present.

for three uni-bivalent salts, lead iodate, barium iodate and barium bromate, and for one uni-trivalent salt, lanthanum iodate. Raising and shifting the curve for barium iodate toward one side will show how closely parallel are the similar curves for barium bromate and iodate, even although the former salt is 25 times as soluble as the latter. Lead chloride is about seven hundred times as soluble as lead iodate, yet a comparison of the sets of curves for the two salts shows that the similar curves still remain very nearly parallel. It is remarkable that when a uni-univalent salt with a *non-common ion* is added, the curve for the apparent concentration of the un-ionized part of the saturating salt has practically the same slope whether the saturating salt is uni-, bi-, or tri-univalent.

In the case of the uni-univalent salt the apparent solubility of the un-ionized part always falls, at practically the same rate with the total ion concentration, no matter what the type of the added salt may be. However, in the case of the uni-bivalent salts the solubility of the apparent un-ionized part decreases much more rapidly when the common univalent ion is added, and what is much more remarkable, increases when the common ion is bivalent. We now find exactly the same result for the uni-trivalent salt, but in this case the apparent solubility of the un-ionized part increases much more rapidly at the same total ion concentration, than it does in the case of the uni-bivalent salts barium iodate and barium bromate, which are the most nearly similar in solubility. It may thus be said that these effects which are abnormal in the case of the uni-bivalent salts, become even more abnormal with this tri-univalent salt.

It is thus seen that when the concentration of the constituents of a mixture is calculated by the ordinary method, that in the case of higher type salts, the non-common ion salts have a seemingly normal effect upon the solubility of the non-ionized part of the salt, but that when a common univalent ion is added the effect is abnormal in giving an extraordinary depression in solubility, while with the common bivalent ion there is the much more abnormal and even absurd result that the solubility of the un-ionized part of the salt seems to rise rapidly. It has been shown by Harkins[1] that when calculations are made upon the basis of the non-existence of intermediate ions, just such abnormal results should be obtained in case intermediate ions are present, and that, if allowance is made for the presence of intermediate ions, according to the calculations presented in Table I of the present paper, these irregularities disappear, as well as the irregularities found in the behavior of the solubility product, as shown in Fig. 5. Thus assuming that Table I gives the proper percentage ionization of salts of the uni-bivalent type, it is found that upon calculation that the true solubility of the un-ionized part decreases at nearly the same rate, with the total ion concentration, no matter whether the salt added contains no common ion, a common univalent, or a common bivalent ion. That the somewhat greater abnormalities in the case of the tri-univalent salt could be as readily smoothed away seems certain

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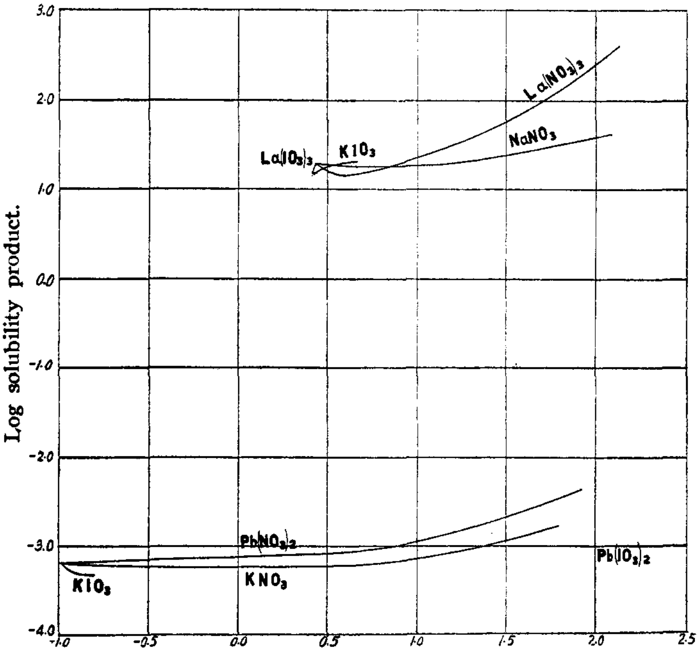
[1] *Loc. cit.*

when it is remembered that in the solution of such a salt there would be two intermediate ions instead of one.



Log total ion concentration Σi.

Fig. 5.—The solubility product calculated on the assumption that intermediate ions are not present.

7. Summary of Experimental Part.—1. Equations are given for the calculation of the constituents of mixtures of salt solutions both on the basis of the non-existence and existence of intermediate ions. A comparison of the degrees of ionization of several substances calculated on both assumptions is also made.

2. Pure lanthanum iodate was made and its solubility at 25° was determined in solutions of salts containing common univalent ions, common trivalent ions, and non-common ions. It was found that: (*a*) the solubility decreases rapidly as the concentration of the salt having a common univalent ion increases; (*b*) the solubility decreases slightly at first and then increases as a salt with a common trivalent ion is added, the curve approaching the curve for the non-common ion effect.

3. Conductance measurements were made on the dilute solutions.

4. Calculations of the constituents of the mixtures of the solutions were made and curves were drawn to show the changes in the solubility products and concentrations of the un-ionized part with changes in the total ion concentration. In these calculations, intermediate ions are

assumed to not exist. It was found that the apparent concentration of the *un-ionized part* is affected normally by the addition of non-common ion salts; is affected abnormally by the presence of salts having a common univalent ion in that it gives an extraordinary depression; is affected even more abnormally by the addition of salts having a common trivalent ion, giving a rapid rise in the apparent solubility. These abnormalities disappear if intermediate ions are assumed to be present.

5. The theoretical discussion has not been summarized, since it has been given in a condensed form in the body of the paper.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE EFFECT OF SALTS UPON THE SOLUBILITY OF OTHER SALTS. VIIIa. THE SOLUBILITY RELATIONS OF A VERY SOLUBLE BI-UNIVALENT SALT.

BY WILLIAM D. HARKINS AND HARRY M. PAINE.

Received August 14, 1916.

Introduction.

Since, as has been shown in previous papers of this series,[1] the moderately soluble uni-bivalent salts show such a wide variation from the solubility product principle, an investigation of the effect of the addition of salts to a bi-univalent salt of extremely high solubility was considered advisable. Strontium chloride with a solubility at 25° of 7.034 equivalents per 1000 grams of water, seemed to be the salt best suited for this purpose. Its solubility at 25° was determined in water and in various concentrations of strontium nitrate, sodium nitrate, nitric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, potassium iodide, potassium chloride, cupric chloride, and potassium nitrate. The densities of all solutions and mixtures were measured. In calculations the atomic weights for 1911 were used and all weighings reduced to vacuum.

Preparation of Salts.

Strontium Chloride.—A special grade of strontium chloride was recrystallized from conductivity water and the salt preserved in a moist condition in closely stoppered bottles.

Sodium Nitrate.—Sodium nitrate was recrystallized twice from conductivity water.

Hydrochloric and Nitric Acids.—"C. P." acids were used after careful testing.

Hydriodic Acid.—This acid was prepared by careful hydrolysis of phosphorus triiodide, with exclusion of air. The product obtained was carefully redistilled and showed no test for free iodine.

Hydrobromic Acid.—The acid was prepared in a manner analogous to that used for hydriodic acid.

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[1] THIS JOURNAL, 33, 1808 (1911).