Our value, obtained at 25°, we regard as undoubtedly accurate within a few tenths of a millivolt. Brislee's value was obtained in the neighborhood of 17° and the wide difference between the two values may be in part due to the difference in temperature, which would indicate, however, an exceptionally large temperature coefficient for the thallium electrode.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 48.]

THE IONIZATION OF SALTS IN MIXTURES WITH NO COMMON ION.

BY MILES S. SHERRILL.

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Contents.

1. Purpose of the Investigation.—The general purpose of this investigation was to determine what modification must be made of the empirical principles which have been found to express the ionization of salts in mixtures with a common ion, in order that they may be applicable also to mixtures with no common ion; in other words, to determine the *general* law governing the ionization relations of salts.

Although many researches have been carried out on the conductance of mixtures with a common ion, few data exist upon mixtures with no common ion suitable for the purpose just mentioned.[1] At the suggestion of Professor A. A. Noyes, this investigation was therefore undertaken, the plan being to measure the conductance of mixtures of two salts with no common ion, and to compare the results with the conductance calculated by the principle discussed in the following section. The salts chosen were potassium chloride and sodium sulphate, and sodium chloride and potassium sulphate. Thus mixtures of salts of two ionic types could be prepared, whereby a more satisfactory test of the theory would be afforded.

2. Principles Relating to the Ionization of Salts in Mixtures.—The principles already established may be first briefly reviewed.

The mass-action law requires that the ionization γ of any salt vary with the concentration C, in accordance with the equation:

$$\frac{(\gamma C)^n}{(1-\gamma)C} = K. \tag{1}$$

where K is the ionization constant for the salt, and n is the number of ions produced by the ionization of 1 molecule of the salt. The numerical

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[1] The only measurements that exist seem to be those of Barmwater (*Z. physik. Chem.*, **28**, 427 (1899)), on certain mixtures of uni-univalent salts.

value for n should therefore vary with the ionic type of salt, being 2 for uni-univalent salts, like potassium chloride, 3 for uni-bivalent salts like potassium sulphate, etc. As is well known, however, the mass-action law does not apply, even approximately, to the ionization of salts, strong acids, and bases when the conductance ratio Λ/Λ_0 is taken as a measure of the ionization.[1]

Kohlrausch,[2] Rudolphi,[3] and van't Hoff[4] first proposed various empirical functions containing only a single constant for the purpose of expressing the change of ionization with the dilution. Storch[5] then suggested that, in order to secure closer agreement with the observed values, a general expression of the form of equation (1) be employed, the exponent n being regarded as a second empirical constant to be derived for each particular salt from the conductance measurements. van't Hoff[6] had already shown that an approximate agreement between the formula and the existing data could be secured in the case of a large number of di-ionic salts by taking $n = 1.5$. Storch showed that a nearly complete agreement in the case of the eight di-ionic and four tri-ionic substances studied was attained up to 0.1 normal by assuming values of n varying only within the limits 1.42 and 1.52. Bancroft[7] showed that Storch's formula with values of n varying within about the same limits was applicable to certain other di-ionic salts. By the extended investigations made in this laboratory it has been shown that the same is true also for tri-ionic and tetra-ionic salts, and for the salts of all three types through a very wide range of temperature. Thus the values of n obtained, though varying somewhat with the nature of the salt and the temperature, all fall within the narrow limits of 1.40 to 1.55.[8]

Equation (1) may also be written in the following form, which expresses the ionization as a function of the ion concentration $(C\gamma)$:

$$\frac{\gamma}{1-\gamma} = K(C\gamma)^{1-n}. \qquad (2)$$

A study of the conductance of mixtures of two salts with a common ion has thrown further light on the ionization relations of salts. The results of such measurements can be satisfactorily expressed by the following principle derived from theory of isohydric solutions of Arrhenius,[9]

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[1] For general discussion of this subject see Noyes, *Z. physik. Chem.*, 52, 635 (1905); *Science*, 20, 584 (1904).

[2] *Wied. Ann.*, 26, 200 (1885); 50, 394 (1893).

[3] *Z. physik. Chem.*, 17, 385 (1895).

[4] *Ibid.*, 18, 300 (1895).

[5] *Ibid.*, 19, 13 (1896).

[6] *Loc. cit.*

[7] *Ibid.*, 31, 188 (1899).

[8] THIS JOURNAL, 30, 343 (1908); 31, 1000 (1909).

[9] *Z. physik. Chem.*, 2, 285 (1888); 31, 218 (1899).

and shown, most fully by the investigations of MacGregor, McIntosh, Archibald, and McKay,[1] to be valid not only for uni-univalent salts, but also for those of higher types, even in cases, as has been pointed out by Noyes,[2] where the mass-action law would require a very different effect. In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it has when alone present in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture.

This principle evidently shows that the ionization of any salt is the same function of the ion concentration, whether the salt is present alone or together with another salt with a common ion. Therefore, in correspondence with equation (2), it may be expressed as follows:

$$\frac{\gamma_1}{1-\gamma_1}=K_1(C_1\gamma_1+C_2\gamma_2)^{1-n_1}; \text{ and } \frac{\gamma_2}{1-\gamma_2}=K_2(C_1\gamma_1+C_2\gamma_2)^{1-n_2}; \quad (3)$$

the subscripts referring to the two salts, respectively. These equations may readily be transformed into the following ones:

$$\frac{C_1\gamma_1(C_1\gamma_1+C_2\gamma_2)}{C_1(1-\gamma_1)}=K_1(C_1\gamma_1+C_2\gamma_2)^{2-n_1}; \text{ and}$$

$$\frac{C_2\gamma_2(C_1\gamma_1+C_2\gamma_2)}{C_2(1-\gamma_2)}=K_2(C_1\gamma_1+C_2\gamma_2)^{2-n_2}. \quad (4)$$

That signifies that in a mixture of salts with a common ion the ratio of the product of the concentrations of the constituent ions of each salt to the concentration of its un-ionized part is proportional to the equivalent concentration of the common ion raised to the (2-n) power. In this case of a mixture of salts with a common ion, it is to be noted that the expression ($\gamma_1C_1 + \gamma_2C_2$) for the concentration of the common ion is also the expression for the sum of the equivalent concentrations (Σi) of all the positive or negative ions. If, as seems reasonable, it is this "total ion concentration" which in general determines the equilibrium, then for any salt of the general type A_xB_y present in any solution where the total equivalent ion concentration is (Σi), the following expression will hold true:

$$\frac{(A)(B)}{(A_xB_y)}=K(\Sigma \mathrm{i})^{2-n} \quad (5)$$

It is evident from this equation that for a given total ion concentration in the solution the ratio $(A)(B)/(A_xB_y)$ has a definite value which can be calculated from the values of K and n that may be derived by equation (1) from the ionization values of the salt when present in water alone. This makes it possible to calculate the concentrations of all the ions and the un-ionized substances present in a solution containing any definite mixture of salts, as will be shown later.

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[1] *Trans. N. S. Inst. Sci.*, Vols. 9 and 10 (1895–1899).

[2] *Loc. cit.*

3. The Experimental Method.—Exactly 0.2 normal solutions of the four separate salts[1] were made by weighing out the ignited substances, transferring them to a two-liter graduated flask, and adding sufficient conductivity water to bring the solution at 18° to the graduation mark. The more dilute salt solutions and the solutions of the mixed salts were prepared by mixing with the aid of carefully calibrated pipettes definite volumes of the stock solutions with water or with each other. The specific conductance of the water used did not exceed 0.9×10^{-6} reciprocal ohms.

The conductance measurements were made at 18°, observing the usual precautions, in a U-tube of one of the forms described by Kohlrausch and Holborn,[2] with platinized electrodes. The conductance capacity of this cell was calculated from the conductance values given by Kohlrausch and Maltby[3] for various solutions of potassium chloride. The thermometer, slide-wire, and resistance coils used had all been calibrated.

4. The Conductance Data.—The results of the measurements with the separate salts are given in Table I.

TABLE I.

	Specific conductance × 1000 at 18°.			
Equiv. conc.	NaCl.	KCl.	Na_2SO_4.	K_2SO_4.
0.2	17.546	21.592	13.99	17.57
0.1	9.202	11.203	7.707	9.491
0.05	4.785	5.787	4.182	5.098

The specific conductance values for potassium chloride, sodium chloride, and potassium sulphate agree within 0.1 per cent. with the latest measurements of Kohlrausch and Maltby and Kohlrausch and Grüneisen.[1] Compared with the earlier conductance values of Kohlrausch, marked deviations, amounting in the stronger solutions to 2 per cent., exist in the case of sodium sulphate.

In Table II are given the results obtained with the mixtures. The first column gives the number of the mixture. The next four columns show the equivalent concentrations of the solutions from which each mixture was prepared. The next four columns show the relative volumes of these solutions which were mixed. The last column gives the specific conductance (×1000) in reciprocal ohms of the mixture at 18°.

It may be pointed out that a check upon the purity of the salts and the preparation of the solutions is afforded by the complete agreement of the conductances of mixtures Nos. 3 and 7, of which the former was prepared from sodium chloride and potassium sulphate and the latter from potassium chloride and sodium sulphate.

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[1] These salts were kindly furnished to me by Mr. A. C. Melcher, who had prepared them in a pure state for other conductivity work.

[2] *Leitvermögen der Elektrolyte*, Fig. 10, p. 16 (1898).

[3] See *Landolt-Börnstein-Meyerhoffer Tabellen*, 3 *Auflage*, p. 744.

TABLE II.

Mixt. No.	Equivalent concentration.				Relative volumes mixed.				Specific cond. × 1000.
	$NaCl$.	K_2SO_4.	KCl.	Na_2SO_4.	$NaCl$.	K_2SO_4.	KCl.	Na_2SO_4.	
1	0.2	0.2	...	...	4	1	.	.	17.52
2	0.2	0.2	...	...	2	1	.	.	17.53
3	0.2	0.2	...	...	1	1	.	.	17.52
4	0.2	0.2	...	...	1	2	.	.	17.52
5	0.2	0.2	...	...	1	4	.	.	17.52
6	...	...	0.2	0.2	.	.	1	2	16.29
7	...	...	0.2	0.2	.	.	1	1	17.52
8	...	...	0.2	0.2	.	.	2	1	18.81
9	0.1	0.1	...	...	4	1	.	.	9.262
10	0.1	0.1	...	...	2	1	.	.	9.303
11	0.1	0.1	...	...	1	1	.	.	9.346
12	0.1	0.1	...	...	1	2	.	.	9.378
13	0.1	0.1	...	...	1	4	.	.	9.430
14	...	...	0.1	0.1	.	.	2	1	9.933
15	...	...	0.1	0.1	.	.	1	2	9.778

5. *Method of Calculation and Results.*—When two salts with no common ion (for example NaCl and K_2SO_4) are mixed there are formed by metathesis two other salts (KCl and K_2SO_4). In any definite mixture of this kind the composition shows the value of the total sodium (ΣNa), total potassium (ΣK), total sulphate (ΣSO_4), and total chloride (ΣCl). The various forms in which these constituents exist are expressed by the following equation, in which the symbols within parentheses represent the *equivalent* concentrations:

$$(\Sigma \mathrm{Na}) = (\mathrm{Na}^+) + (\mathrm{NaCl}) + (\mathrm{Na_2SO_4}). \qquad (6)$$

$$(\Sigma \mathrm{K}) = (\mathrm{K}^+) + (\mathrm{KCl}) + (\mathrm{K_2SO_4}). \qquad (7)$$

$$(\Sigma \mathrm{SO_4}) = (\mathrm{SO_4}^=) + (\mathrm{K_2SO_4}) + (\mathrm{Na_2SO_4}). \qquad (8)$$

$$(\Sigma \mathrm{Cl}) = (\mathrm{Cl}^-) + (\mathrm{NaCl}) + (\mathrm{KCl}). \qquad (9)$$

According to the principle stated in the second section, the ratio of the product of the concentrations of the ions of any one salt to that of its un-ionized part is proportional to the total equivalent ion concentration raised to the (2-n)-power. (This ratio will, in the following discussion, be designated the ion-product-ratio of the salt.)

This principle applied to each salt in the mixture furnishes the four additional equations that are needed in order to make it possible to solve for the concentration of each of the eight substances present. The equations are:

$$\frac{(\mathrm{Na}^+)(\mathrm{Cl}^-)}{(\mathrm{NaCl})} = K_1(\Sigma \mathrm{i})^{2-n_1}. \qquad (10)$$

$$\frac{(\mathrm{K}^+)(\mathrm{Cl}^-)}{(\mathrm{KCl})} = K_2(\Sigma \mathrm{i})^{2-n_2}. \qquad (11)$$

$$\frac{(\mathrm{Na}^+)(\mathrm{SO_4}^=)}{(\mathrm{Na_2SO_4})} = K_3(\Sigma \mathrm{i})^{2-n_3}, \qquad (12)$$

$$\frac{(K^+)(SO_4^=)}{(K_2SO_4)} = K_4(\Sigma i)^{2-n_4}. \qquad (13)$$

In these equations, $(\Sigma i) = (Na^+) + (K^+)$ or $(Cl^-) + (SO_4^=)$, and K_1, K_2, K_3, K_4, and n_1, n_2, n_3, n_4 are the coefficients and exponents for the respective salts which occur in the dilution formula, $(\gamma C)^n = KC(1-\gamma)$ expressing their ionization when present in water alone.

The above equations were easily solved by trial in the following way: The separate ion concentrations were estimated, and the numerical value of the ion-product-ratio for each salt corresponding to the sum of these ion concentrations was determined. This value for the salt in question was obtained from a curve plotted with its ion-product-ratios as abscissas and the corresponding ion concentrations as ordinates, the data given in Table I for the salts in water alone being employed. From these values of the ion-product-ratios and the values of the ion-concentrations estimated at the start, the concentrations of the un-ionized parts of the salts were calculated by equations (10) to (13). By substitution of the latter concentrations in equations (6) to (9) were obtained better values for the separate ion-concentrations. With these new values of the ion-concentrations the whole process was repeated until all eight equations were satisfied.

The specific conductance L of any given solution was then calculated from the equivalent concentrations, obtained as just described, and from the equivalent conductances (Λ_K, etc.), at zero concentrations of the separate ions by the equation

$$1000L = (Na^+)\Lambda_{Na} + (K^+)\Lambda_K + (SO_4^=)\Lambda_{SO_4} + (Cl^-)\Lambda_{Cl}. \qquad (14)$$

The values used for the equivalent conductances of the ions were those given by Kohlrausch,[1] namely, $\Lambda_{Na} = 43.6$, $\Lambda_K = 64.7$, $\Lambda_{SO_4} = 68.4$, and $\Lambda_{Cl} = 65.4$.

The results of the calculations are given in Table III. That the values given actually satisfy equations (6) to (9) can be readily proved by direct summation; and that they satisfy equations (10) to (13) can be shown by calculating the ion-product-ratios and comparing these with those plotted for the salts in water alone, as above described.

6. *Discussion of the Results.*—A consideration of the last column of percentage differences shows that in the case of the first eight mixtures, in which the total salt concentration was 0.2 normal, the calculated conductance is greater by an average amount of 0.48 per cent., and that the variations from this average in the case of the mixtures with different proportions of sulphate and chloride are insignificant. In the case of the last seven mixtures, in which the total salt concentration was 0.1 normal, the same is true except that the average value of the percentage

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[1] *Landolt-Börnstein-Meyerhoffer Tabellen*, p. 763.

difference is about one-half as large, namely 0.27 per cent., indicating that the deviation would probably be scarcely appreciable at 0.05 normal.

TABLE III.

Mixture No.	Concentrations in milli-equivalents per liter.								Spec. cond. × 1000.		
	NaCl.	KCl.	Na_2SO_4.	K_2SO_4.	Na^+.	K^+.	Cl^-.	$SO_4^=$.	Calc.	Obs.	% Diff.
1	24.55	5.35	12.85	2.75	122.60	31.90	130.00	24.40	17.59	17.52	0.40
2	16.86	7.40	17.75	7.65	98.69	51.62	109.10	41.27	17.60	17.53	0.45
3	9.33	8.24	19.77	17.23	70.90	74.53	82.43	63.00	17.61	17.52	0.51
4	4.07	7.24	17.43	30.59	45.17	95.50	55.36	85.31	17.61	17.52	0.51
5	1.44	5.17	12.38	43.71	26.18	111.10	33.39	103.90	17.62	17.52	0.57
6	8.16	3.64	34.54	15.15	90.60	47.88	54.87	83.61	16.36	16.29	0.43
7	9.32	8.25	19.77	17.23	70.91	74.52	82.43	63.00	17.61	17.52	0.51
8	8.45	14.80	9.01	15.50	49.21	103.00	110.10	42.16	18.89	18.81	0.48
9	9.82	2.20	5.29	1.18	64.89	16.62	67.98	13.53	9.276	9.262	0.15
10	6.75	3.02	7.31	3.26	52.61	27.05	56.90	22.76	9.321	9.303	0.19
11	3.75	3.37	8.13	7.31	38.12	39.32	42.88	34.56	9.374	9.346	0.30
12	1.64	2.97	7.16	12.92	24.53	50.78	28.72	46.59	9.420	9.378	0.45
13	0.58	2.11	5.08	18.50	14.34	59.39	17.31	56.42	9.460	9.430	0.32
14	3.37	6.04	3.68	6.57	26.28	54.06	57.26	23.08	9.964	9.933	0.31
15	3.29	1.49	14.27	6.45	49.11	25.39	28.55	45.95	8.795	8.778	0.19

Since the conductance is substantially determined by the sum of the concentrations of the ions (irrespective of their separate concentrations), these results show that *when the concentrations of the separate ions of the salts in the mixtures are calculated by the principle expressed by the equation* $(A)(B)/(A_xB_y) = K(\Sigma i)^{2-n}$ *the sum of the ion concentrations is obtained with an accuracy of about* $^1/_2$ *per cent. at 0.2 normal and of about* $^1/_4$ *per cent. at 0.1 normal.*

The possibility must, of course, be recognized that a compensation takes place owing to the un-ionized tri-ionic salts being present in a larger or smaller proportion and the un-ionized di-ionic salts being present in a correspondingly smaller or larger proportion than that calculated. This might be the case, for example, if the ionization relations of the di-ionic and tri-ionic salts were determined by a different principle, instead of by the same principle, as has been assumed. All that can be said is that there are at present no facts known that make necessary this more complicated assumption.

One possibility deserves, however, brief consideration because of its possible theoretical significance. It might be assumed, namely, that the law of the equilibrium for a tri-ionic salt like K_2SO_4 should be written, in closer correspondence with the mass-action law, in the form

$$\frac{(K^+)^2(SO_4^=)}{(K_2SO_4)} = K(\Sigma i)^{3-n}, \text{ instead of } \frac{(K^+)(SO_4^=)}{(K_2SO_4)} = K(\Sigma i)^{2-n}.$$

When the salt is present in water alone or in a mixture with another potassium salt, these two expressions are identical, since then $(\Sigma i) =$

(K^+); but this is not true in any case where other positive ions are present, for example in mixtures with another sulphate, or in mixtures with no common ion like those above considered. Making the assumption that equations of the first form hold for potassium and sodium sulphates (in place of equations (12) and (13)) and that the other equations (6) to (11) hold true as before, the composition and conductance of Mixture No. 3 was calculated with the following result:

Concentrations in milli-equivalents per liter.								Spec. cond. × 1000.		
NaCl.	KCl.	Na_2SO_4.	K_2SO_4.	Na^+.	K^+.	Cl^-.	SO_4^{--}.	Calc.	Obs.	% Diff.
9.70	8.40	12.40	10.91	77.9	80.7	81.9	76.7	19.22	17.52	9.6

It is seen that the conductance calculated under this assumption deviates very greatly (9.6 per cent. from the observed value).

BOSTON, April 10, 1910.

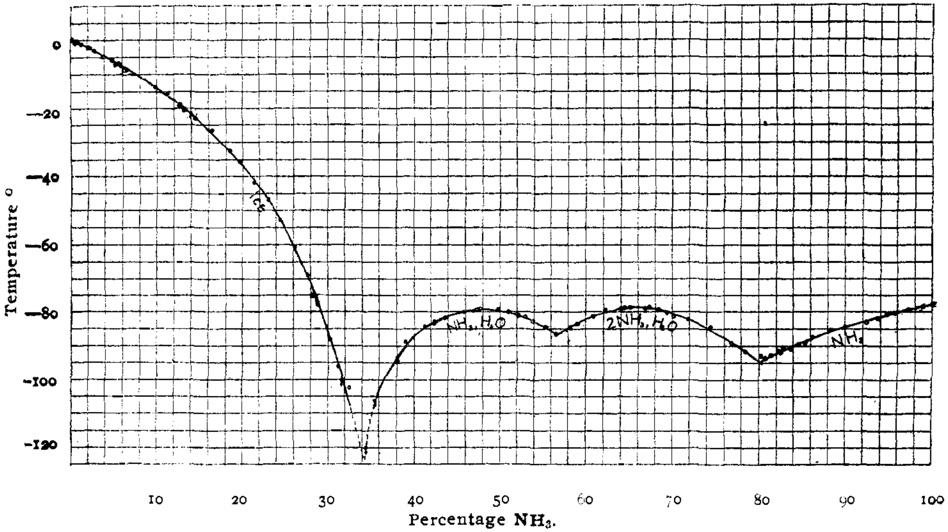
THE SOLID HYDRATES OF AMMONIA. II.

BY FRANK F. RUPERT.

Received April 11, 1910.

In a previous paper[1] the author gave the freezing-point curve for the system ammonia-water, showing the existence of two hydrates. Since then the work has been repeated, making a larger number of freezing-point determinations, and using better aids to accuracy.

The method used was substantially that described in the previous paper. Corrections were made for the weight of the ice inevitably collecting on the tube containing the solution, while being inserted in the vacuum tube. This amounted to 0.05 gram, with a possible error of 0.02 gram, in a total of 10 to 20 grams.



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[1] THIS JOURNAL, 31, 866 (1909).