shown in a contribution from this laboratory soon to be published by C. A. Kraus and W. C. Bray, this function has, in the case of uni-univalent salts, an extraordinary range of applicability. Thus it expresses satisfactorily the results from very small concentrations up to fairly high concentrations (0.5 normal and beyond) not only for solutions in water, but in a variety of non-aqueous solvents. It has, moreover, an obvious theoretical interpretation in the sense that the term $D(C\gamma)^m$ expresses the fact that the mass-action expression $(C\gamma)^2/C(1-\gamma)$ increases with the ion concentration $C\gamma$ in the solution. The function requires, moreover, that when $C\gamma$ becomes sufficiently small, the mass-action law hold true for any solute in any solvent. In the case of aqueous solutions of salts, strong acids, and bases, the value of K is so small in comparison with $D(C\gamma)^m$, except at small concentrations, that as has been seen above, an equation which contains only the latter term expresses the actual conductance fairly well within a limited concentration interval. This function appears to furnish by far the most general and satisfactory expression thus far discovered of the relation between the conductance and concentration of the uni-univalent salts. Further discussion of it in this article is, however, inappropriate, as it will be fully treated in the future paper just referred to.

In the case of salts of the uni-bivalent and higher types, the relation between concentration and ionization is probably further complicated by the presence of the intermediate ion. The most probable assumptions which can be employed for estimating its concentration in solutions of uni-bivalent salts have been discussed by W. D. Harkins in a recent contribution from this laboratory.[1]

BOSTON, FEBRUARY, 1912.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 81.]

THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. IV. COMPARISON OF THE IONIZATION VALUES DERIVED FROM THE FREEZING POINT LOWERING AND FROM THE CONDUCTANCE RATIO.

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CONTENTS.—18. Tabulation of the Ionization Values Derived from Freezing Point Lowering and from the Conductance Ratio. 19. Discussion of the Ionization Values Derived by the Two Methods.

18. Tabulation of the Ionization Values Derived from Freezing Point Lowering and from the Conductance Ratio.

In Table XVIII are brought together the values of the percentage ionization (100γ) corresponding to the mol-numbers derived from the

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[1] THIS JOURNAL, 33, 1863 (1911).

freezing point and presented in Table II, Part I,[1] and those corresponding to the conductance-viscosity ratio at 18° presented in Table XI, Part III,[2] of this series. It has already been shown in Section 15 of Part III that the conductance ratio for salts at 18° does not differ from that at 0° by more than the experimental errors commonly involved in the 0° values, so that an appreciable error is not introduced in employing the 18° values for the comparison.

The ionization values derived from the freezing point are preceded by the letters FP, those from the conductance-viscosity ratio by the letters CR. The figures at the head of the table express the concentration in milli-equivalents per liter.

TABLE XVIII.—IONIZATION VALUES DERIVED FROM FREEZING POINT LOWERING AND FROM THE CONDUCTANCE-VISCOSITY RATIO.

Substance.	Method.	5.	10.	20.	50.	100.	200.	500.
KCl	FP............	96.3	94.3	91.8	88.5	86.1	83.3	80.0
"	CR............	95.6	94.1	92.2	88.9	86.0	82.7	77.9
NH_4Cl	FP............	94.7	92.8	90.7	87.8	85.6	83.2	....
"	CR............	....	94.1	92.1	....	....	....	....
NaCl..	FP............	95.3	93.8	92.2	89.2	87.5	85.0	82.4
"	CR............	95.3	93.6	91.6	88.2	85.2	81.8	77.3
CsCl	FP............	....	....	93.0	89.2	86.3	82.9	77.8
"	CR............	95.4	93.7	....	....	84.7	....	....
LiCl	FP............	94.4	93.7	92.8	91.2	90.1	....	....
"	CR............	94.9	93.2	89.0	87.8	84.6	81.2	76.6
KBr	FP............	....	....	92.9	88.9	86.3	83.9	81.3
"	CR............	95.5	94.0	92.1	88.8	85.9	82.5	76.6
$NaNO_3$	FP............	....	90.3	88.5	85.5	83.0	79.8	...
"	CR............	95.0	93.2	91.0	87.1	83.2	78.8	71.9
KNO_3	FP............	....	90.1	88.0	83.6	78.1	71.1	....
"	CR............	95.3	93.5	91.1	86.7	82.4	77.2	68.8
$KClO_3$	FP............	....	91.4	89.1	84.9	79.8	....	....
"	CR............	95.2	93.3	91.0	86.6	82.7	78.0	70.3
$KBrO_3$	FP............	....	92.3	89.6	85.4	80.5	....	....
"	CR............	95.4	93.4	91.0	86.8	....	....	....
KIO_3	FP............	94.1	91.3	88.2	82.8	76.5	....	....
"	CR............	94.6	92.8	90.3	86.0	81.9	77.5	....
$NaIO_3$	FP............	93.9	91.6	89.0	84.2	77.3	....	....
"	CR............	93.9	91.7	89.0	84.2	80.1	75.2	....
$KMnO_4$	FP............	93.8	92.1	91.3	....	....	....	....
"	CR............	96.8	95.1	93.0	....	....	....	....
HCl	FP............	99.1	97.5	95.7	93.3	91.7	....	....
"	CR............	98.1	97.2	96.2	94.4	....	....	....
HNO_3	FP............	97.4	96.0	94.2	91.2	90.0	87.9	....
"	CR............	....	97.0	....	94.0	....	....	....

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[1] THIS JOURNAL, 32, 1026 (1910).

[2] See the preceding article.

TABLE XVIII (*continued*).

Substance.	Method.	5.	10.	20.	50.	100.	200.	500.
$BaCl_2$	FP	89.9	87.8	85.5	81.9	78.8	75.8	....
"	CR	....	88.3	85.0	79.8	75.9	72.0	67.2
$CaCl_2$	FP	....	....	87.6	83.7	81.5	80.4	....
"	CR	91.0	88.2	84.9	80.2	76.4	72.7	68.8
$MgCl_2$	FP	....	....	88.5	85.4	83.9	83.3	....
"	CR	91.0	88.3	85.1	80.3	76.5	72.8	68.7
$CdCl_2$	FP	....	79.1	76.8	69.0	60.5	53.9	....
"	CR	80.3	73.5	66.4	55.9	45.3	37.5	28.9
$CdBr_2$	FP	....	78.0	70.4	58.9	48.2	36.7	....
"	CR	74.9	66.1	57.3	....	....	....	....
CdI_2	FP	....	59.3	54.0	40.0	22.5	10.0	....
"	CR	67.5	57.3	46.9	....	....	....	....
$Cd(NO_3)_2$	FP	94.8	92.1	90.1	88.7	88.4	....	....
"	CR	91.7	87.1	84.8	79.2	73.1	68.4	62.8
$Ba(NO_3)_2$	FP	91.7	88.8	85.5	....	....	....	....
"	CR	89.8	86.1	81.8	74.4	67.9	60.9	50.4
$Pb(NO_3)_2$	FP	89.0	85.0	80.4	72.4	64.9	56.8	42.7
"	CR	88.6	84.5	79.3	70.8	63.5	55.9	45.4
K_2SO_4	FP	92.9	89.9	85.7	78.5	73.0	66.7	56.8
"	CR	90.5	87.2	83.2	77.1	72.2	67.3	61.8
Na_2SO_4	FP	....	....	86.7	79.5	73.6	67.2	56.7
"	CR	89.3	85.7	....	75.6	70.4	65.2	....
$MgSO_4$	FP	69.4	61.8	53.6	42.0	32.4	22.3	8.4
"	CR	74.0	66.9	59.6	50.6	44.9	40.3	....
$CuSO_4$	FP	61.6	54.5	45.5	31.8	....	....	....
"	CR	70.9	62.9	55.0	45.5	39.6	35.1	....
$ZnSO_4$	FP	66.5	58.2	48.9	....	....	....	....
"	CR	71.0	63.3	55.6	46.4	40.5	36.0	....
$CdSO_4$	FP	65.8	56.9	47.7	34.3	....	....	....
"	CR	69.4	61.4	53.4	43.7	37.7	33.2	29.0
$K_3Fe(CN)_6$	FP	89.4	86.8	77.8	....	....	....	....
"	CR	86.9	82.7	....	....	....	....	....
$K_4Fe(CN)_6$	FP	....	....	....	63.4	58.1	52.0	42.5
"	CR	....	....	....	59.1	53.8	49.8	....

19. Discussion of the Ionization Values Derived by the Two Methods.

A comparison of the two sets of ionization values at the concentrations between 20 and 100 millinormal inclusive shows the following deviations:

KCl, NH_4Cl, and KBr: less than 1% of the ionization value.

NaCl and CsCl: 1 to 2%.

LiCl: 4 to 6%.

$NaNO_3$ and KNO_3: 3 to 5%; but the probable accuracy of the freezing-point results is in these cases small.

$KClO_3$ and $KBrO_3$: 2 to 4%.

KIO_3: 2 to 7%, increasing with the concentration.

$NaIO_3$: practically zero up to 50, 3.5% at 100 millinormal.

HCl: 0.3 to 1.2%; yet the values are 5 to 10% greater than those for neutral salts.
$BaCl_2$: 1 to 4%, increasing with the concentration.
$CaCl_2$ and $MgCl_2$: 3 to 9%, increasing with the concentration.
$CdCl_2$, $CdBr_2$, CdI_2, and $Cd(NO_3)_2$: much larger deviations than with the other uni-bivalent salts.
$Pb(NO_3)_2$ and K_2SO_4: not more than 2%, even up to 200 millinormal.
Na_2SO_4: about 5%.
$MgSO_4$, $CuSO_4$, $ZnSO_4$, $CdSO_4$: very large deviations.
$K_4Fe(CN)_6$: 7 to 8%.

It will be seen from this summary that the two methods give ionization values which for most uni-univalent substances agree with each other within 2% up to 0.1 normal; and that the same is true of the uni-bivalent salts, potassium sulfate and lead nitrate, even up to 0.2 normal. The halides and sulfates of bivalent metals (and also lithium chloride and sodium sulfate) on the other hand show, as a rule, much larger deviations than this at 0.1 and 0.2 normal.

In considering the significance of the comparison of the ionization values, the principles involved in their derivation should be recalled. The calculation of ionization from freezing-point lowering is based on the principle that the molal effects of the ions and of the unionized substance are normal, like those of organic substances. The calculation of ionization from the conductance-viscosity ratio is based on the principle that the equivalent conductance or mobility of the ions does not vary with the concentration, except in so far as the fluidity of the solution varies. Both methods involve also the assumption that the only forms in which the substance exists in the solution are the unionized molecules and the ultimate simple ions into which they dissociate at extreme dilution.

As this last assumption is probably fulfilled in the case of most uni-univalent substances, the agreement of the two sets of ionization values for these substances might seem to substantiate the principles involved in the two methods. There is, however, the possibility that the agreement arises from a corresponding inaccuracy in both of the principles, or from a compensation of errors in the case of the freezing-point values arising from the unionized molecules having an abnormally large, and the ions an abnormally small, molal effect, or *vice versa*. That the agreement in reality arises from such a compensation is evident from the fact that the ionization values derived from the conductance ratio decrease with the concentration far more slowly than the mass-action law requires, showing, if these values are correct, that increase in concentration must cause an abnormally small increase in the activity of the ions or an abnormally large increase in the activity of the unionized molecules, or both. This conclusion is confirmed by other independent phenomena, especially the solubility effects,[1] which show that the activity of ions

[1] Cf. Bray, THIS JOURNAL, 33, 1684 (1911).

is somewhat decreased, and that of unionized molecules is very greatly increased, when the salt concentration or ion concentration in the solution is increased.

In the case of uni-bivalent salts the presence of the intermediate ion may introduce a further complication. It will be seen from equation (33) of Section 11 of the preceding paper that for the case that the conductance arises in part from the intermediate ion the mol-number i (which is then equal to $1 + 2\gamma_2 + \gamma_1$) must be somewhat larger (namely, by the amount $\gamma_1 \frac{\Lambda_{A^=} - \Lambda_{BA^-}}{\Lambda_{B^+} + \Lambda_{A^=}}$) than it is for the case that the conductance arises wholly from the simple ions (in which case $i = 1 + 2\gamma$). So long, however, as the proportion (γ_1) of the intermediate ion is not very large, the effect on the mol-number is not likely to be great,[1] and there may be a fairly close agreement between the two sets of ionization values, such as was observed with potassium sulfate and lead nitrate.

The effect of the formation of double molecules, such as $Mg_2(SO_4)_2$, and of complex ions, such as $Mg(SO_4)_2^=$, $BaCl_4^=$, or $BaCl_3^-$, on the other hand, can be shown (by formulating the appropriate expressions corresponding to equation (33) and the expressions for the mol-number) to decrease the mol-number and the ionization value derived from the freezing point. As was suggested by Arrhenius,[2] this may explain the much larger ionization values obtained from the conductance ratio in the case of the bivalent metal sulfates.

The most striking discordance between the two sets of ionization values is that presented by the bivalent metal halides, for which the values derived from the freezing point are always much larger than those derived from the conductance ratio. It has already been shown in Part II[3] of this series that the transference numbers of these substances are also abnormal, namely, in the respect that the cation transference decreases markedly with increasing concentration. There appears, however, to be no chemical explanation which would account for both of these anomalies; and it seems therefore probable that physical deviations must enter as a complicating factor.

BOSTON, February. 1912.

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[1] Thus the calculations of Bray cited by Harkins (THIS JOURNAL, 33, 1864 (1911)) show that the conductance of a 0.1 N K_2SO_4 solution could be accounted for either by assuming 72% $SO_4^=$ and 28% K_2SO_4, or by assuming 60% $SO_4^=$, 35% KSO_4^-, and 5% K_2SO_4. Under the former assumption, the mol-number i would be 2.44, and under the latter 2.55.

[2] *Z. physik. Chem.*, 1, 639 (1887).

[3] THIS JOURNAL, 33, 1454–9 (1911).