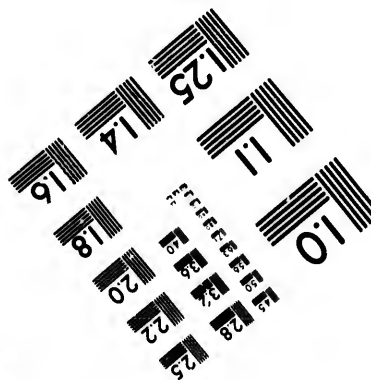
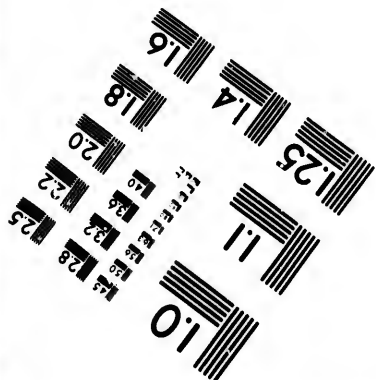
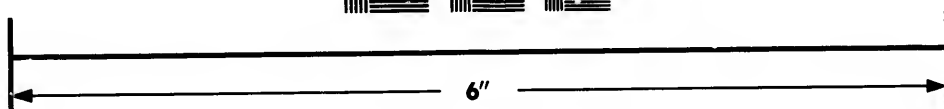
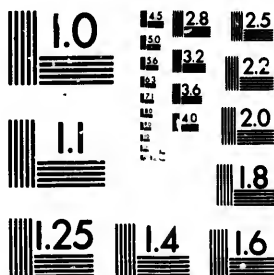


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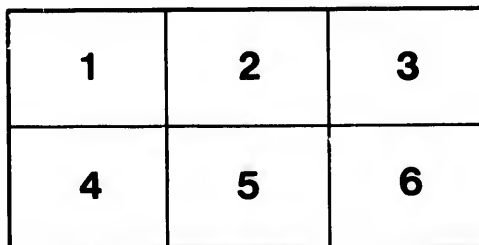
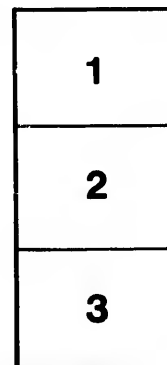
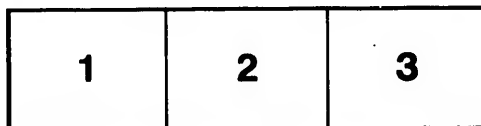
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WITH THE AUTHOR'S COMPLIMENTS.

On the Relation of the Physical Properties of Aqueous
Solutions to their State of Ionization.

BY PROFESSOR J. G. MACGREGOR,

Dalhousie College, Halifax, N. S.

*From the Transactions of the Nova Scotia Institute of Science,
Vol. IX, Session 1896-97.*

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I.—ON THE RELATION OF THE PHYSICAL PROPERTIES OF
AQUEOUS SOLUTIONS TO THEIR STATE OF IONIZATION.—
BY PROFESSOR J. G. MACGREGOR, *Dalhousie College,*
Halifax, N. S.

(Communicated 14th Decemler, 1896.)

It has often been pointed out that, according to the dissociation or ionization conception of the constitution of a solution of an electrolyte, the difference between the physical properties of one in which ionization is complete and those of the solvent must be compounded additively of the differences produced by the two ions. It would seem to be equally obvious that, in the case of solutions in which the ionization is not complete, the differences referred to must be similarly compounded of those produced by the undissociated molecules and by the free ions; and if so, it should be possible to express the numerical values of the various properties in terms of the state of ionization. Such an expression would take its simplest form in the case of solutions so dilute that the molecules, dissociated or undissociated, might be regarded as sufficiently far apart to render mutual action between them impossible, and in these circumstances the change produced in the properties of the solvent by the undissociated and the dissociated molecules respectively might be expected to be simply proportional to their respective numbers per unit of volume. It is the object of this paper to

test the applicability to sufficiently dilute solutions, of such an expression, viz.,

$$P = P_w + k(1 - \alpha)n + l\alpha n, \dots\dots\dots (1)$$

where P is the numerical value of any property (density, &c.), P_w that of the same property of water under the same physical conditions, n the molecular concentration of the solution, i. e., the number of gramme-equivalents of the dissolved substance per unit volume of the solution, α the ionization-coefficient and $(1 - \alpha)n$ consequently the numbers of dissociated and undissociated gramme-equivalents per unit of volume respectively, and k and l constants, which may be spoken of as ionization-constants, which will vary with the solvent, the substance dissolved, the property to which they apply, the temperature, and the pressure, but not with the concentration of the solution.

The formula can obviously apply only to properties for which P_w has a finite value. Thus it is inapplicable to electrical resistance, for which P_w would have a practically infinite value.

SIMPLE SOLUTIONS.

In order to test the applicability of the above expression I have determined the ionization-constants for the density, thermal expansion, viscosity, surface-tension, and refractive index of solutions of Sodium and Potassium Chlorides, by the aid of observations made by Bender*, Brückner†, and Rother‡. I selected these observations as a first instalment, not because of their precision (for in one or two cases more exact observations are available), but because these observers, in all cases but one, determined the values of the above properties for mixtures of solutions as well as for simple solutions. I selected the above chlorides partly because I thought it well to begin with salts of simple molecular structure, but largely also because, for the purpose of calculating the conductivity of mixtures of them (as described in my paper on this subject§), I had already obtained interpolation formulæ and curves which, judged by the results

* Wied. Ann. vol. xxii. (1884) p. 184, and vol. xxxix. (1890) p. 89.

† Ibid. vol. xlii. (1891) p. 293.

‡ Ibid. vol. xxi. (1884) p. 576.

§ Trans. N. S. Inst. Sci. ix. (1896) p. 101; and Phil. Mag. [5] xli. (1896) p. 276.

of that paper, gave with considerable accuracy the ionization-coefficients of the simple solutions of these salts in terms of their molecular concentration. To save space I may tabulate here the values of the ionization-coefficients used in the calculations for simple solutions. They are as follows :—

SODIUM CHLORIDE.		POTASSIUM CHLORIDE.	
Grm.-mols. per litre.	Ionization- coefficient at 18° C.	Grm.-mols. per litre.	Ionization- coefficient at 18° C.
·25	·792	·1875	·8267
·5	·736	·3402	·811
·8028	·6806	·375	·796
1·0	·676	·5	·788
1·5	·633	·6856	·769
1·8353	·601	·75	·768
2·0	·5806	1·0	·756
2·5	·5504	1·0167	·755
2·8373	·5255	1·4202	·731
3·0	·514	1·5	·731
3·9375	·4516	2·0	·712
		2·185	·7048
		2·5	·695
		2·986	·681
		3·0	·680

These coefficients were obtained from Kohlrausch and Grotrian's and Kohlrausch's observations of conductivity at 18° C.* In obtaining them I took the specific molecular conductivity (referred to mercury) at infinite dilution to be 1216×10^{-8} for KCl, and 1028×10^{-8} for NaCl, not being aware at the time that Kohlrausch had given 1220 and 1030 respectively as more exact values. Nevertheless, to save labor, I have used the above values of α in the calculations of this paper, having satisfied myself by a re-calculation in one case that no appreciable difference in the results would be produced by the employment of more exact values. It will be noticed that in one or two cases the above values of α are obviously a little out; but they would seem to be sufficiently accurate for my purpose. I did not foresee the extent of the calculations,

* Wied. Ann. vi. (1879) p. 37, and xxvi. (1885) p. 195.

or I should have determined all the values of α required at the outset, and checked them by comparison with one another.

I have determined the ionization-constants (k and l) in all cases in which more than two observations of a property on solutions of sufficient dilution were available, by the method of least squares. The constants thus determined and used in the calculations are tabulated below. In all cases the available observations had been made on solutions of such great concentration that the values of the constants obtained cannot be regarded as exact; but the calculations may serve as a test of the general applicability of the expression referred to above. The only available observations, as far as I know, on solutions of sufficient dilution for the determination of the ionization-constants and the limits of concentration within which the above expression is applicable, are those by Kohlrausch and Hallwachs* on the specific gravity of dilute solutions, from which two of my students have undertaken to determine the density-constants for the salts and acids examined.

With regard to the observations which I used in determining the various ionization-constants, the following statements should be made:—

Bender's determinations of density (*i. e.* specific gravity referred to water at 4° C.) were made at 15° C., but were readily reduced to 18° by the aid of his observations on the thermal expansion between 15° and 20° of the same solutions. According to his statement, the fourth place of decimals in his values may be in error by ± 2 or ± 3 . The density of water was taken to be 0.99863.

Bender's determinations of thermal expansion are for the interval between 15° and 20° C., and will therefore be sufficiently nearly proportional to the coefficients of expansion at 18° for my purpose. He considers that they may be in error by ± 2 in the sixth place of decimals. On plotting his observations, however, it becomes obvious that they do not all attain this degree

* Wied. Ann. liii. (1894) p. 14.

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of accuracy. The expansion of water was taken, according to his observations, to be 0.0878 for the same interval.

Brückner's observations of viscosity were made at 15° C.; but he gives an interpolation formula, applicable between 15° and 20°, by means of which at least approximate values for 18° were obtained. His values for water at 15° and 20° do not agree well with those given by Landolt and Börnstein. I have therefore taken 0.010613 as the viscosity at 18° of the water used by him, a value which has to his value at 15° the same ratio as Landolt and Börnstein's for the same temperatures. The actual concentrations of Brückner's solutions differed from those given in the tables below by about 0.1 per cent.; but so small a difference could produce no appreciable error in the result. He gives as his "mean probable error of observation," ± 2.4 in the fifth place of decimals for sodium-chloride solutions, and ± 1.8 for those of potassium chloride.

Rother's observations of surface-tension were made at 15° and are therefore not precisely comparable with calculated values based on the values of ionization-coefficients for 18°. From Kohlrausch's data,* however, it would appear that between 15° and 18° in the case of potassium-chloride solutions containing 0.5 and 3 gramme-molecules per litre, the ionization-coefficient changes only by about 0.13 and 1.3 per cent. respectively; and in the case of sodium-chloride solutions of the same concentrations only by about 0.4 and 0.6 per cent. respectively. For the more dilute solutions, therefore, my calculations will be practically comparable with Rother's observations. He seems to regard his determinations as possibly in error by ± 5 to 8 in the third place of decimals. The surface-tension of the water he used he found to be 7.357.

Bender's observations of refractive index were made at 15° C., but were reduced to 18° by means of data provided in his paper, based on observations made by Fouqué†. The refractive index of the water he used he found to be 1.33310

* Wied. Ann. xxvi. (1885) p. 223.

† Compt. Rend. lxi. (1867) p. 121.

224 RELATION OF PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS

SODIUM CHLORIDE SOLUTIONS.				POTASSIUM CHLORIDE SOLUTIONS.			
Grm.-mols. per litre.	Observed Value.	Calc. Value.	Difference.	Grm.-mols. per litre.	Observed Value.	Calc. Value.	Difference.
DENSITY (BENDER'S OBSERVATIONS).							
0.25	1.00808	1.00916	+0.0 ₈ 18	0.1875	1.00752	1.00731	-0.0 ₃ 21
0.5	1.01930	1.01929	- 01	0.375	1.01507	1.01586	+ 19
1.0	1.03925	1.03910	- 15	0.75	1.03317	1.03278	- 39
1.5	1.05834	1.05812	+ 08	1.0	1.04302	1.04401	+ 30
2.0	1.07772	1.07701	- 71	1.5	1.06630	1.06621	- 09
2.5	1.09633	1.09532	-0.0 ₂ 101	2.0	1.08707	1.08823	+ 56
				2.5	1.10755	1.11008	+0.0 ₂ 253
				3.0	1.13057	1.13177	+ 120
THERMAL EXPANSION (BENDER'S OBSERVATIONS).							
0.25	.001013	.001022	+0.0 ₅ 9	0.1875	.000963	.000968	+0.0 ₄ 03
0.5	.001111	.001111	± 0	0.375	.001037	.001040	+ 03
1.0	.001357	.001349	- 8	0.75	.001183	.001173	- 10
1.5	.001522	.001526	+ 4	1.0	.001249	.001255	+ 06
2.0	.001663	.001657	- 6	1.5	.001395	.001395	± 00
2.5	.001776	.001760	- 7	2.0	.001560	.001517	+ 17
3	.001876	.001848	-0.0 ₄ 28	2.5	.001580	.001621	+ 41
VISCOSITY (BRÜCKNER'S OBSERVATIONS).							
0.5	.010988	.010978	-0.0 ₄ 10	0.5	.010457	.010451	-0.0 ₄ 06
1.0	.011480	.011475	- 05	1.0	.010305	.010379	- 16
1.5	.012048	.012017	- 01	1.5	.010351	.010366	+ 15
2.0	.012707	.012730	+ 23	2.0	.010394	.010393	- 01
2.5	.013472	.013458	- 14	2.5	.010414	.010457	+ 13
3.0	.014373	.014267	-0.0 ₃ 106	3.0	.010566	.010555	- 11
SURFACE-TENSION (ROTHER'S OBSERVATIONS).							
0.8028	7.482	7.482	±0.000	0.3402	7.411	7.408	-0.003
1.8353	7.629	7.629	± 0	0.6856	7.460	7.432	+ 2
2.8373	7.780	7.798	+ 18	1.0167	7.518	7.519	+ 1
3.9375	7.954	7.907	+ 43	1.4202	7.584	7.583	- 1
				2.1851	7.705	7.709	+ 4
				2.9850	7.844	7.846	+ 2
REFRACTIVE INDEX, D LINE (BENDER'S OBSERVATIONS).							
0.5	1.33824	1.33824	±0.0 ₃ 00	0.5	1.33803	1.33806	+0.0 ₃ 03
1.0	1.34307	1.34306	- 01	1.0	1.34278	1.34274	- 04
1.5	1.34770	1.34770	± 00	1.5	1.34721	1.34722	+ 01
2.0	1.35213	1.35206	- 07	2.0	1.35179	1.35158	- 21
2.5	1.35673	1.35632	- 41	2.5	1.35623	1.35582	- 41

SOLUTIONS.

Difference.

31	- 0 0,21
30	+ 19
28	- 39
21	+ 39
21	- 00
23	+ 50
28	+ 0,253
7	+ 120

6	+ 0,0403
0	+ 03
3	- 10
5	+ 03
5	+ 00
7	+ 17
1	+ 41

- 0,0406
- 16
+ 15
- 01
+ 13
- 11

- 0,003
+ 2
+ 1
- 1
+ 4
+ 2

NS).

+ 0,0403
- 04
+ 01
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at 18° for the D line. He seems to regard his observations as possibly in error by ± 1 in the fourth decimal place.

The tables on page 224 contain the results of the calculations of the values of the physical properties mentioned, with both the observed values on which the determination of the constants was based, and a few additional observed values for stronger solutions.

The following comments may be made on these tables:

Density.—NaCl. The first four observations were used in determining the constants; and up to a concentration of 1.5 the differences are within the limits of experimental error, and show a satisfactory alternation of sign.—KCl. The first five observations were used. The differences are large, but the alternation of sign shows that the expression is applicable. On plotting Bender's values they are readily seen not to lie on a smooth curve.

Thermal Expansion.—NaCl. The first four observations were used. The differences up to a concentration of 2.5 are probably within the limits of experimental error, and their alternation of sign is satisfactory.—KCl. The first five observations were used. The differences are not so satisfactory as in the case of the sodium salt either as to magnitude or sign; but on plotting the observations the third is seen to be somewhat out; and it is obviously to this observation that the defective agreement is due.

Viscosity.—NaCl. The first five observations were used. The differences are within the limits of error, but the signs are not satisfactory. The fourth observation, however, appears to be defective. Mützel*, in applying a formula for viscosity in terms of density and concentration to these observations, found also that this observation was out. It is worth noting, also, that Mützel found his formula, which expressed the increase of viscosity due to the salt in solution on the assumption that the only action occurring was between salt and water, was applicable

* Wied. Ann. xliii. (1891) p. 35.

to only the first five of the above observations. To represent the viscosity of stronger solutions he had to introduce a term expressing the effect due to the mutual action of the molecules of salt.—KCl. All six observations were used. The agreement in this case is quite satisfactory.

Surface-Tension.—NaCl. Only two observations on sufficiently dilute solutions were available, and the applicability of the formula cannot therefore be tested. The constants were found, for use in the calculation of the surface-tension of mixtures.—KCl. The first four observations were used, and the agreement is quite satisfactory up to a concentration of 3 grm.-mols. per litre.

Refractive Index.—In the case of both salts the first three observations were used, and in both the agreement is quite satisfactory up to a concentration of about 2 grm.-mols. per litre.

The above tables seem to be at any rate quite consistent with the possibility of expressing the values of at least five of the physical properties of moderately dilute solutions in terms of their state of ionization. I hope to find leisure at an early date to extend the investigation to solutions of salts and acids of a more complex character and to other properties.

The following are the ionization-constants used in the above calculations:—

	SODIUM CHLORIDE		POTASSIUM CHLORIDE.	
	<i>k.</i>	<i>l.</i>	<i>k.</i>	<i>l.</i>
Density	+ '030841	+ '045679	+ '03543	+ '048591
Thermal Expansion.	- '0001445	+ '0007658	- '000614	+ '0006085
Viscosity	+ 002317	+ '0001504	+ '001904	- '0009217
Surface-Tension ...	+ '20574	+ '11001	+ '24249	+ '126806
Refractive Index...	+ '006318	+ '011713	+ '0027853	+ '011853

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These constants are obtained from solutions of too great concentration to be regarded as exact values. Nevertheless it may be admissible, tentatively, at least, and so far as these two salts are concerned, to draw the following conclusions:—Undissociated and dissociated molecules are nearly equally effective in increasing the density,—those dissociated, however, being somewhat the more effective of the two. (2) Undissociated molecules diminish the thermal expansion, those dissociated increasing it to a greater extent. (3) In the case of viscosity it is the undissociated molecules which have the preponderating influence, those dissociated having but a slight effect, which may be an increasing or a diminishing effect. Thus Arrhenius's expectation that all dissociated ions would be found to diminish viscosity seems to be only partially realized, though possibly from observations on more dilute solutions, both *l*'s might be found to be negative. (4) In the increase of surface-tension the undissociated molecules have about twice as great an influence as the dissociated. (5) In increasing the refractive index it is the dissociated molecules which have the preponderating influence; and their superiority is greater in increasing the refractive power than increasing the density.

MIXTURES OF SOLUTIONS.

For a solution containing several salts, 1, 2, etc., the value of a property, according to the conception under consideration, will be:—

$$F = P_w + k_1 (1 - a_1) n_1 + l_1 a_1 n_1 + k_2 (1 - a_2) n_2 + l_2 a_2 n_2 + \&c., \quad (2)$$

the *n*'s being numbers of gramme-equivalents per unit volume of the solution. If the solution have been formed by the mixture of the volumes *v*₁ and *v*₂ of two simple solutions of salts, having one ion in common, for which, before the mixing, the property had the values:—

$$\begin{aligned} P_1 &= P_w + k_1 (1 - a_1) n_1 + l_1 a_1 n_1, \\ P_2 &= P_w + k_2 (1 - a_2) n_2 + l_2 a_2 n_2, \end{aligned} \quad (3)$$

then, since on mixing, the state of ionization will, in general,

change, we shall have as the value of the property for the mixture, assuming no change of volume on mixing,

$$P = P_w + (k_1(1 - a_1')n_1 + l_1a_1'n_1) \frac{v_1}{v_1 + v_2} + (k_2(1 - a_2')n_2 + l_2a_2'n_2) \frac{v_2}{v_1 + v_2}, \quad (4)$$

the n 's being numbers of gramme-equivalents per unit volume of the original simple solutions, and a_1' and a_2' being the ionization-coefficients in the mixture. As the values of the k 's and l 's have been determined above for sodium and potassium chloride for a number of properties, and, as I have shown in my paper on the "Conductivity of Mixtures," cited above, how the ionization-coefficients after mixing may be determined, it should be possible to predict the values of these properties for mixtures of solutions of these salts.

The following tables show that this can be done. The ionization-coefficients were determined in the way described in the paper referred to. The constants k and l employed in the calculations were those determined above. The observations were made by the authors whose determinations for simple solutions were used above; in fact in most cases it was the solutions of the tables given above which were mixed. The limits of experimental error are thus of about the magnitudes mentioned above in each case. All remarks made above with regard to the reduction of observations to 18°C ., the values of the property for water, etc., apply also to the mixtures. In all cases, except that of surface-tension, the solutions mixed were mixed in equal volumes. Unfortunately, Bender made no observations on the refracting power of mixtures.

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Constituent Solutions (grm. mols. per litre.)		Ionization Coefficients in Mixture.		Observed Value.	Calculated Value.	Difference.
NaCl.	KCl.	NaCl.	KCl.			
DENSITY (BENDER'S OBSERVATIONS).						
1.0	0.1875	.7268	.7720	1.02358	1.02350	- 0.0 ₃ 08
"	0.375	.714	.7625	1.02785	1.02700	- .19
"	0.75	.688	.7620	1.03641	1.03600	- .41
"	1.0	.6728	.7632	1.04139	1.04158	+ .19
"	1.5	.6494	.7478	1.05203	1.05203	- 0.0 ₃ 30
"	3.0	.6143	.7283	1.08580	1.08505	+ .15
THERMAL EXPANSION (BENDER'S OBSERVATIONS).						
1.0	0.1875	.7268	.7720	.001174	.001174	± 0.0 ₄ 00
"	0.375	.714	.7625	.001208	.001203	- .05
"	0.75	.688	.7620	.001275	.001264	- .11
"	1.0	.6728	.7632	.001297	.001305	+ .08
"	1.5	.6494	.7478	.001376	.001376	\pm .00
"	3	.6143	.7283	.001513	.001506	+ .53
VISCOSITY (BRÜCKNER'S OBSERVATIONS).						
1.0	0.5	.7059	.7635	.010940	.010947	+ 0.0 ₄ 07
"	1.0	.6728	.7632	.010918	.010920	+ .02
"	1.5	.6494	.7478	.010876	.010915	+ .39
"	2.0	.6143	.7283	.010800	.010956	+ .66

SURFACE TENSION (ROTHER'S OBSERVATIONS).

CONSTITUENT SOLUTIONS.				Ionization Coefficients in Mixture.		Observed Value.	Calculated Value.	Difference.
Concentration (grm.-mols. per litre).		Volume (litres.)						
NaCl.	KCl.	NaCl.	KCl.	NaCl.	KCl.			
0.8802	0.0836	0.14487	0.14545	0.6006	0.7052	7.477	7.472	- 0.005
1.8109	1.411	0.13903	0.14096	0.6087	0.7279	7.607	7.602	- .5
0.8824	2.1822	0.14489	0.13659	0.6123	0.7311	7.600	7.591	- .9
2.8106	0.6802	0.13511	0.14544	0.6027	0.7208	7.622	7.616	- .6
1.8155	2.9887	0.13906	0.13241	0.5185	0.7125	7.734	7.810	+ .76

It will be noticed that in the case of the third mixture of the density and thermal expansion series (the same mixture) the differences are comparatively large; but it is obvious from the data of the fourth column in these series that the ionization-coefficients have not been accurately determined for mixtures of about the concentration of the one referred to. With these exceptions the agreement between observed and calculated values is satisfactory, the differences being either well within, or at worst on, the limit of observational error, up to mean concentrations of about 1.5. The determination of the ionization-coefficients was especially difficult in the case of the surface-tension observations, because Rother mixed equal weights of his simple solutions, not equal volumes. Nevertheless, in all except the strongest of these mixtures, the differences are probably not beyond the limits of experimental error. Obviously, alternation of sign is not to be expected in these calculations.

RELATIVE VALUES OF A PROPERTY FOR A MIXTURE AND FOR ITS CONSTITUENTS : "CORRESPONDING" SOLUTIONS.

As change of ionization in general occurs on mixing two solutions, it follows from (3) and (4) that the value of a property for a mixture of two solutions having one common ion will differ from the volume-mean, $(v_1 P_1 + v_2 P_2)/(v_1 + v_2)$, of its values for the constituents by the amount

$$(l_1 - k_1) \frac{n_1 v_1}{v_1 + v_2} (a_1' - a_1) + (l_2 - k_2) \frac{n_2 v_2}{v_1 + v_2} (a_2' - a_2) \dots \dots \dots (5)$$

The name of "corresponding" solutions has been given to solutions for which this quantity vanishes. In general it will obviously have a value, though that value may be small.

In most cases this conclusion is borne out by experience. But Rother has concluded from his observations that, in the case of surface-tension, throughout a wide range of concentration, solutions of all concentrations are "corresponding." Were this the case it would throw serious doubt on the possibility of expressing surface-tension in terms of state of ionization. If,

third mixture of the same mixture) is obvious from the ionization- for mixtures of to. With these and calculated er well within, or, up to mean of the ioniza- case of the mixed equal s. Neverthe- the differences imental error. cted in these

however, with the aid of the constants for surface-tension deter- mined above, we compute, in the case of Sodium and Potassium Chlorides, the difference between the value for a mixture and the volume-mean of the values for its constituents, we find it to be beyond the limit of Rother's power of observation. Thus, in the case of his first mixture calculated above, the difference amounts to only 0.0₃15. His conclusion should thus have been that the difference, if any, between the surface-tension of a mixture and the volume-mean of those of its constituents was within the limits of his experimental error. He might even have concluded, however, that there was probably such a differ- ence in the case of Sodium and Potassium Chlorides; for in all the mixtures of solutions of these salts which he examined, the volume-mean of the values for the constituent solutions were found to be less than the values for the mixtures.

The above expression (5) will vanish if the constituents of the mixture are isohydric, *i. e.*, have states of ionization which do not change in the mixing; and it will vanish in that case, whatever the values of the other quantities involved in the expression may be. When the constituents are not isohydric the condition of its vanishing will be

$$\frac{n_1}{n_2} = \frac{(l_2 - k_2)(a_2' - a_2)v_2}{(l_1 - k_1)(a_1 - a_1')v_1} \dots\dots\dots (6)$$

It is obviously improbable that in any case in which this con- dition may be fulfilled the numbers of gramme-equivalents per litre in the constituent solutions will have a simple relation, such as 1 : 2, 4 : 3, &c.

The conclusions drawn by Bender and Brückner from their observations on density, thermal expansion, electrical conduc- tivity, and viscosity, viz., that there is such a simple relation in the case of all "corresponding" solutions, so far as the proper- ties mentioned are concerned, is thus inconsistent with the possi- bility of expressing the values of these properties in terms of the state of ionization.

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Both Bender* and Brückner† obtained their results from numerous series of observations, in each of which a solution of given concentration of one salt was mixed in succession, in equal volumes, with a number of solutions of different concentrations of a second salt having one ion in common with the first. The values of the property under consideration were determined both for the simple solutions and for the mixtures, and the arithmetic means of the values for the constituents of the several mixtures were found. Curves were then plotted with molecular concentrations of the simple solutions of the second salt as abscissæ, and the observed values for the mixtures and the arithmetic means of the values for the constituents, respectively, as ordinates. The "corresponding" solutions were indicated by the points of intersection or contact of these curves. In all cases the two curves for each series are found to run very close together, so close that it is impossible to determine exactly at what points they touch or cross; and when the observational errors admitted by the authors are taken into account, they must be considered to be within touching or crossing distance at considerable distances on each side of the points at which Bender and Brückner assumed them to be contact or to intersect. I have plotted a number of these curves so as to indicate accurately all significant figures, and have found, on taking possible errors of observation into account, that in no case can a more definite conclusion be drawn than that "corresponding" solutions have pretty nearly the simple relations as to concentration claimed by the authors. It is not necessary to enter into details; but I may, by way of illustration, give the following:—

* Wied. *Ann.* xxii. (1884) p. 184, and xxxix. (1890) p. 89.

† *Ibid.* xlii. (1891) p. 293.

Molecular Concentrations of Corresponding and Isohydric Solutions.

NaCl.	KCl.		
	Values between which curves may be in contact.	Value assigned by Observer.	Isohydric Solution.
CONDUCTIVITY (BENDER'S OBSERVATIONS).			
0.5	0—1.0	0.375	0.47
1	0—1.1	0.75	0.80
2	1.2—1.5	1.5	1.00
3	1.8—2.55	2.25	2.20
4	2.6—3.15	3.0	2.57
VISCOSITY (BRÜCKNER'S OBSERVATIONS).			
1	0.5—1.0	1.0	1.2
2	1.25—2.5	2.0	2.6

The fourth column of the above table gives approximate values of the concentration of the solutions of KCl (obtained from Kohlrausch's data) which are isohydric with the solutions of NaCl in the first column; and it will be noticed that in most cases these values are within the limits within which Bender's and Brückner's curves must be regarded as being possibly in contact.

It would thus appear that both Bender and Brückner drew too definite conclusions from their observations, and that the observations themselves are not inconsistent with the applicability of expression (1) to the physical properties of solutions.

APPLICATIONS OF THE ASSUMED LAW OF IONIZATION-CONSTANTS.
RATIO AND DIFFERENCE OF THE VALUES OF A PROPERTY
FOR SOLUTION AND SOLVENT.

If the expression under consideration is applicable to solutions of moderate dilution it should give by deduction the laws which have been found to hold for particular properties of such

solutions, and might be expected to be of use in showing their relation to one another. I need not refer here to the more obvious of such deductions, as, for example, the properties of non-electrolytes, or of electrolytes at extreme dilution, but may restrict myself to cases in which both constants k and l play a part.

The ratio of P to P_w will be

$$\frac{P}{P_w} = 1 + \frac{k + (l - k)a}{P_w} n.$$

For dilute electrolytes throughout a certain range of concentration, and through a wider range in the case of non-electrolytes, a varies but slightly with n . Throughout such range the coefficient of n in the above expression will thus vary but slightly. Hence, n being small,

$$\frac{P}{P_w} = e^{\frac{k + (l - k)a}{P_w} n} = A^n,$$

approximately, where e is the base of Napier's logarithms and A a constant. Arrhenius,* Reyher† and Wagner‡ have found this result to hold in the case of the viscosity of both classes of solutions.

The difference between P and P_w will be

$$P - P_w = (k + (l - k)a)n.$$

and for the reason just given, will, throughout a certain range of low concentration, wider in the case of non-electrolytes than in that of electrolytes, be approximately proportional to n . This form of the expression obviously includes such laws as Raoult's for vapour tensions, and van 't Hoff's for the depression of the freezing point in non-electrolytes, as well as the approximate proportionality of the rotation of the plane of polarisation to concentration. It has recently been verified by Kohlrausch and Hallwachs's observations on density,§ they having found

* Ztschr. f. phys. Chemie, i, (1887) p. 285.

† Ibid. ii, (1888), p. 753.

‡ Ibid. v, (1890), p. 31.

§ Wied. Ann., liii, (1894), p. 36.

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that between concentrations of 0.005 and 1 gramme-equivalent per litre, $(P-P_w)/n$ varies in the case of certain salts and acids only by from 5 to 20 per cent, and in the case of sugar only by 1.5 per cent.

VARIATION OF TEMPERATURE AND OTHER COEFFICIENTS WITH CONCENTRATION.

The temperature-coefficient of any property of a solution of given concentration will be

$$\frac{1}{P} \frac{\delta P}{\delta t} = \frac{\frac{\delta P}{\delta t} + \frac{\delta k}{\delta t} n + \left(\frac{\delta l}{\delta t} - \frac{\delta k}{\delta t} \right) a n + (l-k) \frac{\delta a}{\delta t} n}{P_w + k n + (l-k) a n} \dots \dots \dots (7)$$

The pressure-coefficient will have the same form, p being written for t . The concentration-coefficient will be

$$\frac{1}{P} \frac{\delta P}{\delta n} = \frac{k + (l-k) \left(a + \frac{\delta a}{\delta n} n \right)}{P_w + k n + (l-k) a n} \dots \dots \dots (8)$$

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† have found
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In the case of a solution of a given salt of given concentration, temperature, and pressure, α , n , and α 's rates of change have definite values the same for all properties. For moderately dilute solutions, $\delta\alpha/\delta t$, $\delta\alpha/\delta p^*$, and $\delta\alpha/\delta n$ are all small, and $\delta\alpha/\delta t$ and $\delta\alpha/\delta n$ at least have the same sign. Also the k 's and l 's for the different properties all depend upon the mutual action between molecules and solvent, and may thus be expected to have more or less closely related values. We may therefore expect not only that the coefficients of one kind for the various properties of solutions of a given salt will vary with concentration in a somewhat similar manner, but also that the variation with concentration of all the coefficients, but especially the temperature and pressure-coefficients, will exhibit a certain family likeness. It is obviously not to be expected that the variation will be exactly similar in any case.

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This family likeness has been observed in the case of the temperature-coefficients for electrical conductivity and fluidity

* I have not seen Röntgen's paper, on which the statement that $\delta a/\delta p$ is small is based. The *Fortschritte der Physik* reports Tammann as quoting him to that effect.

by Grottrian*, who found that, in general, with increasing concentration both of these temperature-coefficients undergo changes in the same sense. Grossmann† claimed to have proved these coefficients to be equal; but afterwards withdrew the claim as based on an error‡. Kohlrausch and Hallwachs also have noticed for very dilute solutions a close similarity between the curves representing the density and the conductivity respectively of the same salt as functions of the concentration.

The following tables show that this family likeness extends, to a greater or less extent, to all the coefficients for at any rate a considerable number of the properties of solutions. The tables include some of Grottrian's coefficients with others calculated from the observations of Kohlrausch, Bender, Brückner, Rother, Röntgen and Schneider§, Fink ||, and Timberg ¶. The coefficients are in almost all cases mean values, the ranges of temperature, &c., to which they apply, though the smallest for which data are available, being not in all cases the same. As I wish to show only a general similarity, it is not necessary to specify the ranges. The temperatures, &c., of the lower limits of the ranges are also not in general exactly the same. The data of the tables are thus not exactly comparable; but they are sufficiently so for my purpose. The heading *n* stands for gramme-equivalents per litre.

* Wied. *Ann.* viii. (1879) p. 552.

† *Ibid.* xviii. (1883) p. 119.

‡ See Kohlrausch, Wied. *Ann.* xxvi. (1885) p. 224.

§ Wied. *Ann.* xxix. (1886) p. 194.

|| *Ibid.* xxvi. (1885) p. 505.

¶ *Ibid.* xxx. (1887) p. 545.

SODIUM CHLORIDE SOLUTIONS.

[illegible]

BARIUM CHLORIDE SOLUTIONS.

TEMPERATURE COEFFICIENTS FOR				CONCENTRATION COEFFTS. FOR	
Conductivity.		Fluidity.		Density.	
<i>n.</i>	Coeff.	<i>n.</i>	Coeff.	<i>n.</i>	Coeff.
.501	.0215	.781	.0240	1.	—0.258
1.051	.0207	1.704	.0226	1.5	—0.200
1.652	.0201	2.945	.0222	2.	—0.318
2.314	.0196			2.5	—0.341
2.895	.0193			3.	—0.361
				<i>n.</i>	Coefficient.
				.5	1.629
				1.0	.610

CALCIUM CHLORIDE SOLUTIONS.

TEMPERATURE COEFFICIENTS FOR SURFACE TENSION.	
n .	Coefficient.
About 6.4	-0.2134
" 10	-0.2179

A glance at these tables shows that if regard be had to sign, Grotian's conclusion as to the temperature-coefficients for conductivity and fluidity applies to all the coefficients for all the properties tested. A given change in the concentration produces a change in the coefficients in the same sense. Too much importance, however, must not be attached to this; for it is obvious that if we should tabulate, say, the coefficients for conductivity, surface tension, viscosity (instead of fluidity) and specific volume (instead of density), it would be found that the changes produced in the first two are in the opposite sense to those produced in the last two. It is interesting, however, to note that the expectation suggested by the above formulæ is distinctly realized.

At very great dilution of electrolytes, the temperature-coefficient becomes, approximately,

$$\frac{1}{P} \frac{\partial P}{\partial t} = \left(\frac{\partial P_w}{\partial t} + n \frac{\partial t}{\partial t} \right) / (P_w + nt), \dots\dots\dots (9)$$

the pressure-coefficient having the same form. The concentration-coefficient becomes

$$\frac{1}{P} \frac{\partial P}{\partial n} = t / (P_w + nt) \dots\dots\dots (10)$$

If we compare (9) and (10) with (7) and (8), it becomes obvious that the variation with concentration of the temperature and pressure coefficients will probably be more closely related at low than at high concentrations, but that the opposite will be true of the concentration coefficients. Accordingly, having plotted Grotian's coefficients and those of the above tables as functions of the concentration, I find that the temperature coefficient curves, for any one substance in solution, are in general more closely similar at low than at high concentrations; but that this is not the case for the concentration coefficient curves. In the case of the pressure coefficients the data are insufficient.

A corresponding similarity holds for the absorption spectra of solutions though it cannot be expressed in coefficients. In a former paper * I have shewn that for all solutions for which

* Trans. Roy. Soc. Can., ix (1891), sec. 3, p. 27.

data were available, the absorption spectra were similarly affected by elevation of temperature and increase of concentration.

THE OCCASIONAL CONSTANCY IN THE DIFFERENCE BETWEEN THE MOLECULAR VALUES OF PROPERTIES OF SOLUTIONS HAVING THE SAME MOLECULAR CONCENTRATION.

The difference between the values per grammic-equivalent of any property for two simple solutions, 1 and 2, of different electrolytes but of the same concentration, will be

$$(P_1 - P_2) / n = k_1 - k_2 + (l_1 - k_1) \alpha_1 - (l_2 - k_2) \alpha_2, \dots \dots (11)$$

Now α in all cases diminishes as n increases. Provided therefore, the values of the $(l-k)$'s have the same sign, and the rates of change of the α 's with concentration are inversely proportional, or approximately so, to the $(l-k)$'s of their respective solutions, we shall have $(P_1 - P_2)/n$ exactly or approximately constant. If we regard $(P_1 - P_2)/n$ as approximately constant when its absolute value changes with n only to a small extent, then the more nearly the $(l-k)$'s and the α 's are inversely proportional to one another the more nearly constant will $(P_1 - P_2)/n$ be. If, however, we regard this quantity as constant when its values for different values of n differ from one another by only a small percentage, then the magnitude of the $(l-k)$'s becomes of importance, and we may have $(P_1 - P_2)/n$ approximately constant, even though the $(l-k)$'s may be far from being inversely proportional to the α 's.

In the case of certain solutions of moderate strength, this approximate constancy of $(P_1 - P_2)/n$ has been observed by Valson and Bender* for the density and the refractive index, by Wagner† for viscosity constants, and by Jahn‡ for the electro-magnetic rotation of the plane of polarization; and a very close approximation to constancy in the case of the specific

* Wied. Ann., xxxix, (1890), p. 89.

† Ztschr. f. phys. Chemie, v. (1890), p. 31.

‡ Wied. Ann., xliii, (1891), p. 280.

gravities of very dilute solutions is clearly shewn in the results of Kohlrausch and Hallwachs's observations§.

So far as Sodium and Potassium Chlorides are concerned, Bender found that in respect to their density at 15° C.;

For $n =$	1.0	2.0	3.0
$(P_1 - P_2)/n =$.0243	.0249	.0251

The value of $l-k$ for NaCl is +0.01424 and for KCl +0.01316, while a glance at the first table (p. 221) shows that the ionisation coefficient of solutions of the former salt falls off with the concentration somewhat more rapidly than, indeed for some concentrations, about twice as rapidly as, in the case of the latter. There cannot, therefore, be a close approximation to constancy in the absolute values of $(P_1 - P_2)/n$, but as these values are comparatively large, the percentage difference between them is comparatively small.

For the thermal expansion of these salts we have from Bender's observations,

For $n =$	1	1.5	2	2.5
$(P_1 - P_2)/n =$.03108	.0385	.04815	.0478

The value of $l-k$ in this case for NaCl is +0.0391, and for KCl +0.0213. There is thus a closer approximation to equality in the values of $(l-k) \Delta\alpha/\Delta n$ for the two salts, for thermal expansion than for density. Accordingly the absolute differences in the values of $(P_1 - P_2)/n$ are smaller than in the case of density. But as the values themselves are much smaller, the differences between the values when expressed as percentages of any one of the values are greater. And thus the approximation to constancy, of $(P_1 - P_2)/n$, in the case of thermal expansion is not so great as in the case of density, when judged in this way.

For viscosity $l-k$ for NaCl is -0.0022 and for KCl -0.0028. The values of $(l-k) \Delta\alpha/\Delta n$ will thus be less nearly equal than in the case of the thermal expansion and the

§ Wied. Ann., liii. (1894), p. 14.

differences between the values of $(P_1 - P_2)/n$ will be somewhat greater. As the $(l - k)$'s in this case, however, are more than twice as great as in the case of thermal expansion, the differences in the values of $(P_1 - P_2)/n$, if expressed as percentages of one of them, will be smaller than in the case of thermal expansion. Accordingly we find from Brückner's observations,

For $n =$	0.5	1.0	1.5	2.0	2.5
$(P_1 - P_2)/n =$	0.116	0.122	0.126	0.128	0.135

For surface-tension $l - k$ for NaCl is -0.096 and for KCl -0.116 . The approximation to constancy (judged by the percentage criterion) will thus not be so close as in the last case. Rother's observations give, by graphical interpolation,

For $n =$	1.0	1.5	2.0
$(P_1 - P_2)/n =$	0.16	0.113	0.105

For refractive index $l - k$ for NaCl is $+0.0054$ and for KCl $+0.0091$. Thus the values of $(l - k)\Delta\alpha/\Delta n$ for the two salts are much more nearly equal than in the case of the other properties and consequently the differences in the values of $(P_1 - P_2)/n$ will be smaller than in the case of the other properties. Bender's observations give for the D line,

For $n =$	1.0	2.0	3.0
$(P_1 - P_2)/n =$	0.20	0.17	0.24

If the value for $n=2$ be omitted from consideration, as being probably in error, $(P_1 - P_2)/n$ is seen to be more nearly constant so far as absolute magnitude is concerned than in the other cases considered. As the values of $(P_1 - P_2)/n$ however, are small, their differences when expressed as percentages are comparatively large, and the approximation to constancy, viewed in this way is less than, *e. g.*, in the case of density.

The above account of this phenomenon may be further tested by the aid of Kohlrausch's observations of electrical conductivity; for in this case $l - k$ is the molecular conductivity at infinite dilution (usually written μ_∞). The

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following values of differences of molecular conductivity will be sufficient :

n	$(P_1 - P_2)/n$ FOR CONDUCTIVITY.			
	HCl and NaCl.	HCl and $\frac{1}{2}$ K_2CO_3	$\frac{1}{2}$ H_2SO_4 and $AgNO_3$	$AgNO_3$ and NaCl.
0.01	2454	2333	1838	+ 55
0.1	2379	2305	1198	+ 21
0.5	2260	2280	1171	- 29
1.0	2085	2120	1185	- 60

Compare with this the following table of values of μ_∞ and α :—

n	IONIZATION-COEFFICIENTS (α).				
	HCl $\mu_\infty = 3500$.	NaCl $\mu_\infty = 1030$.	$\frac{1}{2}$ K_2CO_3 $\mu_\infty = 1400$.	$\frac{1}{2}$ H_2SO_4 $\mu_\infty = 3700$.	$AgNO_3$ $\mu_\infty = 1060$.
0.01	.976	.934	.773	.772	.933
0.1	.927	.840	.628	.563	.791
0.5	.862	.735	.520	.513	.668
1.0	.794	.675	.471	.492	.582

The approximate constancy holds in the case of HCl and $\frac{1}{2}K_2CO_3$, because μ_∞ for HCl being more than twice as great as for $\frac{1}{2}K_2CO_3$, α for the latter falls off nearly twice as rapidly as for the former. In the case of $AgNO_3$ and NaCl there is no approximation to constancy, because the values of μ_∞ being nearly equal, the rates at which α varies with n are very unequal.

THE INDEPENDENCE OF THE CONTRIBUTIONS MADE TO THE VALUE OF A PROPERTY BY THE FREE IONS.

The constant l for a salt ap will, according to the dissociation conception, be composed additively of two parts, l_a and l_p , pertaining to the ions a and p respectively, and these constants

l_a and l_p will be characteristic of the ions and will not depend upon the salt from which they have been dissociated. A certain amount of evidence has been accumulated which may be said to point in this direction. In the case of several properties it has been shown that for solutions of considerable dilution, the difference between the values of the property for solutions of two salts (ap and bp) having a common ion and the same molecular concentration, is independent of what the common ion may be; and the value of the difference divided by the number of gramme-equivalents per litre of the salts in solution has been taken to be approximately the difference between the constant, l_a and l_b . Results of this kind have been obtained by Valsen and Bender for density and refracting power, by Kohlrausch for electrical conductivity, by Raoult for the depression of the freezing point, by Tiaube* for the change of volume on solution, by Röntgen and Schneider for compressibility, and by Jahn for the electromagnetic rotation of the plane of polarization.

Applying the above expression, we have for the difference in the values of a property per unit of molecular concentration, $(P_{ap} - P_{bp})/n = k_{ap}(1 - a_{ap}) - k_{bp}(1 - a_{bp}) + l_p(a_{ap} - a_{bp}) + l_a a_{ap} - l_b a_{bp}$, (12) and at infinite dilution

$$(P_{ap} - P_{bp})/n = l_a - l_b \dots \dots \dots (13)$$

Had the experiments referred to been all carried out at extreme dilution, as were those of Kohlrausch, afterwards extended by Loeb and Nernst†, the evidence would be quite satisfactory. But in general they have been made at only moderate dilution, and it is obvious from (12) that the approximate independence of the common ion on the part of $(P_{ap} - P_{bp})/n$, may be quite consistent with considerable variation in $l_a - l_b$. It is clear that the first three terms of (12) may readily mask any variation in the last two, and that, if the last two did not vary, $l_a - l_b$ could not in all cases be the same.

* *Ztschr. anorgan. Chemie*, iii. (1892), p. 1

† *Ztschr. für phys. Chemie*, ii. (1888) p. 918.

That no satisfactory conclusion can be drawn from experiments of this kind, unless conducted at extreme dilution, may be shown roughly in the case of density by the aid of the results obtained above. For we may assume that the ionization-constants for density obtained above will not be very different from those which would be derived from observations made at greater dilution*. We know from Kohlrausch and Hallwachs's observations that if a_p and b_p represent NaCl and $\frac{1}{2}\text{Na}_2\text{CO}_3$ respectively, $(P_{a_p} - P_{b_p})/n$ will have the value 0.0139 for solutions containing .005 gram-equivalents per litre, and that for NaCl and HCl it will have the value of 0.0235. We may assume that for NaCl and KCl it will be about .02. From the values of k for these salts we find the first two terms of (12) to be .0364. If we assume l_p to have half the mean value of l for NaCl and KCl, the third term will amount to $-.0498$. The first three terms thus amount to about .0354, or say 3 per cent. of the value of $(P_{a_p} - P_{b_p})/n$. Thus, observations of the kind referred to, for density, could give no satisfactory result, even if conducted at this very great dilution. At a dilution of .001 gram-molecules per litre, the first three terms of (12), calculated in the same way, amount to .031, or about 0.5 per cent of $(P_{a_p} - P_{b_p})/n$. A proved independence of p at this dilution would be more satisfactory.

Observations at such extreme dilutions, in the case of most properties of solutions, are probably impracticable. But they are fortunately unnecessary for the settling of the question under consideration. For if the values of the ionization-constants for any property have been obtained as above from observations over a range extending to great, though not necessarily extreme, dilution, the values so obtained may fairly be assumed to apply very approximately to much greater dilutions; and from the values of $l_a + l_p$, $l_b + l_p$, $l_a + l_q$, $l_b + l_q$, etc., thus obtained, it may readily be determined whether or not $l_a - l_b$ is independent of the ions p , q , etc. Unfortunately, Kohlrausch and Hallwachs's observations on specific gravity are not sufficiently numerous for this purpose.

* Mr. E. H. Archibald, one of my students, tells me that for magnesium sulphate, Kohlrausch and Hallwachs's data give $k = .05063$ and $l = .066887$.

THE DETERMINATION OF THE IONIZATION-CONSTANTS FOR THE
FREE IONS.

The values of the constants l_a, l_b, l_p , etc., may probably, in some cases at least, be determinable in the following way: The experiments just referred to would give $l_a + l_p, l_b + l_p$, etc., as well as k_{ap} and k_{bp} , etc. If now, guessing at the value of l_p , we find the first three terms of (12) to be negligible at dilutions at which P_{ab} and P_{bp} can be determined with sufficient accuracy, determination of these quantities will give the value of $l_a^{\alpha_{ap}} - l_b^{\alpha_{bp}}$; and if α_{ap} and α_{bp} be known with sufficient accuracy, l_a, l_b , and l_p may then be found. It would of course be necessary to check our guess at the value of l_p by substituting the value found in expression (12) and seeing whether or not with this value the first three terms would be negligible.

