ON THE ELECTRICAL NATURE OF COHESION.

By Fernando Sanford.

ONE of the most direct methods of measuring cohesion between a dissolved substance and its solvent is by means of volume changes in the solvent. This method has been used with great success by Heydweiller in a series of investigations, the results of which he has published in the Annalen der Physik.[1] In these papers Heydweiller has determined for a large number of the chemical elements a cohesion constant by means of which he is able to calculate the cohesion between water and compounds of these elements. This constant he calls the *Ionenmodulus*. It is calculated in various ways according to the assumptions made in regard to the relative change in the volume of the water and the dissolved substance. In the one here used, which he indicates by the symbol A_s, the modulus represents the percentage increase of the density of the water in which the ions are dissolved. The numbers are extrapolated for infinite dilution from curves plotted for various concentrations, so that complete dissociation may be assumed. It is also assumed that the ions, themselves, occupy the same volume which they occupied in the solid or liquid state before solution.

The values of A_s used in this paper are the final values adopted by Heydweiller, and are to be found in *Tabelle* 30[1], Ann. d. Phys., 37, p. 765, 1912.

I have already referred in several papers to an electrical constant which I have called the characteristic charge of the ion, and which is calculated by multiplying the mobility of the ion as determined in electrolysis by its ionic mass. I wish to show in the present paper that this electric constant of the ion is proportional to Heydweiller's *Ionenmodulus*.

If m = the mass of the ion and u = its mobility, Heydweiller's *Ionenmodulus* may be calculated from the equation $A_s = muk$, where k = .00112 for univalent ions and .00372 for divalent ions.

In the following table the mobility of the ions is taken from Kaye and Laby's Tables, p. 88. The velocities taken are those actually observed, *i. e.*, one half the numbers usually taken in the case of the divalent ions.

[1] A. Heydweiller, Ann. d. Phys., 30, p. 873, 1909; 33, p. 145, 1910; 37, p. 739, 1912.

If the usual numbers for the mobility of divalent ions be used, k becomes .00186 for these ions.

TABLE I.

Ion.	Mobility.	Ionic Mass.	*muk.*	A_s.
	k = .00112			
Li	34.6	7	.27	.35
Na	45.2	23	1.31	1.38
K	67	39.1	2.34	2.10
Rb	70.5	85.45	6.9	6.32
Cs	70.5	132.81	10.50	10.58
NH_4	66.3	18	1.33	.98
Cl	67.8	35.46	2.70	3.02
Br	70	79.92	6.28	6.68
I	68.8	126.92	9.80	10.27
OH	180	17	3.46	3.40
NO_3	64	62	4.68	4.54
$C_2H_3O_2$	42.1	59	2.78	3.04
	k = .00372			
H	330	1	1.22	1.05
F	48.3	19	3.42	3.16
Mg	23.8	24.32	2.17	2.66
Ca	26.8	40.09	4.00	4.04
Sr	26.8	87.62	8.74	8.76
Ba	28.7	137.37	14.66	13.08
Cd	24.6	112.40	10.30	10.86
Pb	31.7	207.1	24.4	20.68
Cu	24.5	63.57	5.79	7.26
Zn	24.2	65.37	5.88	7.22
Ag	56	107.88	22.46	10.02
SO_4	35.5	96	12.65	11.54

It will be seen that the values of A_s calculated in this way differ from the observed values by less than the probable error of determination except in a few cases. Hydrogen and fluorine are placed with the divalent ions, though they undoubtedly belong in the monovalent group, and silver, copper and zinc give too low values of A_s. Silver is placed with the divalent ions in the table, and it will be seen that with the divalent constant it gives A_s twice as high as it should be. On the other hand, it gives too small a value with the monovalent constant. For copper and zinc the values of *mu* should be multiplied by the sum of both constants to give Heydweiller's values of A_s.

Notwithstanding these discrepancies, which will probably be explained later, the evidence seems conclusive that the quantity *mu*, which I have called the characteristic charge of the ion, is a determining factor in cohesion.

The relations brought out in Table I. are shown graphically in Fig. 1, in which Heydweiller's values of A_s are plotted against the ionic charges, *mu*. Here the values of *u* for the divalent ions are those which are generally used, and are twice as great as those used in the table.

If the product *um* represents an electric charge, then in the case of the negative ions this charge must be negative, while in the case of the

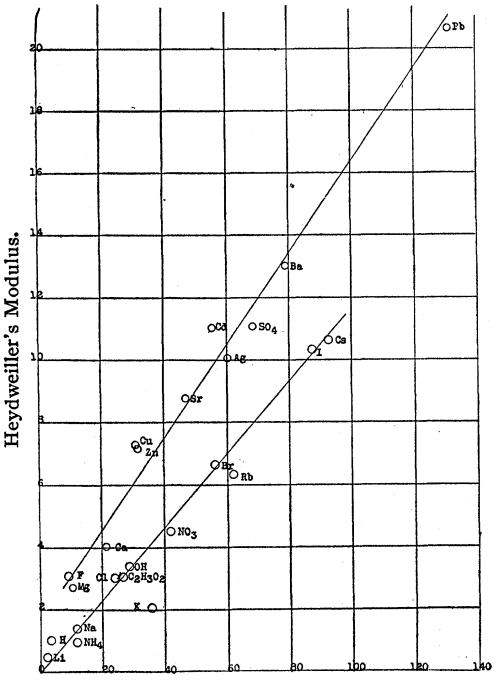

Fig. 1.

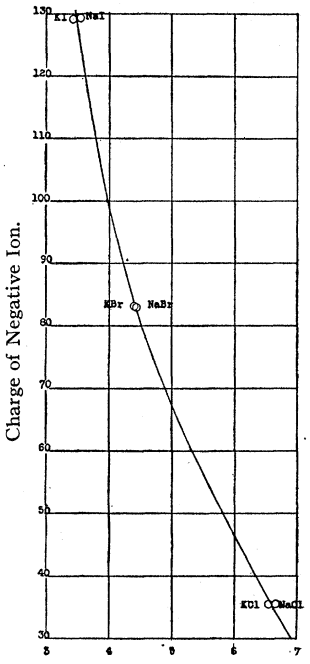

Fig. 2.

hydrogen and metallic ions it is positive. It will be seen from the above data that the attraction of the dissolved ions for water is practically independent of the character of the charge. In chemical combinations, however, the negative ion seems to play the principal part in determining cohesion. This is shown in Fig. 2, in which the specific cohesion of the sodium and potassium salts of chlorine, bromine and iodine are plotted against the charges of the negative ions as calculated from their mobility, assuming the hydrogen charge as + 4.84. The specific cohesion was determined by Motylewski by the drop method, using melted salts, and is quoted by Smiles (Chemical Constitution and Physical Properties, p. 40) from Zeit. Anorg. Chem., 38, 410, 1904.

It will be seen from the curve that the specific cohesion of the corre-

sponding sodium and potassium salts is nearly the same, the sodium salt regularly having the higher cohesion. If the mean cohesion of the corresponding sodium and potassium salts be taken, it may be calculated from the formula $C = 630/(e + 60)$, where C represents Motylewski's values for the specific cohesion and e = the charge of the negative ion. The values calculated in this way are compared with the observed values in the table below.

TABLE II.

Salt.	e	C Obs.	C Calc.
NaCl.....	35.2	6.63	6.59
KCl.....	35.2	6.55	
NaBr.....	82.8	4.44	4.43
KBr.....	82.8	4.41	
NaI.....	129	3.53	3.34
KI.....	129	3.44	

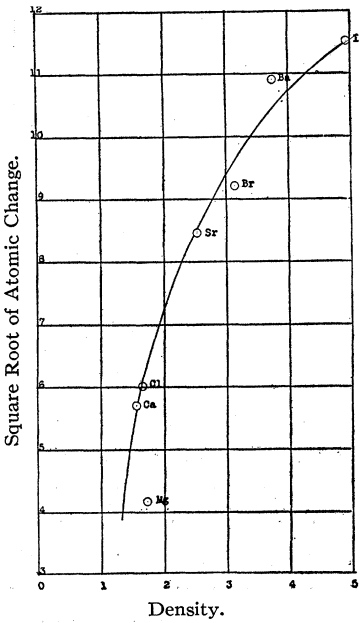

Fig. 3.

Another property which might reasonably be expected to vary with cohesion is density. When the density is compared with the atomic charge it is found that within a given group the density varies approximately as the square root of the atomic charge. If the usual numbers for the mobility of the ions of the barium group be used in calculating their atomic charges, the density of the elements of this group varies with the square root of the atomic charges at the same rate as does the density of the negative elements of the halogen group. This fact is shown graphically in the curve in Fig. 3, where the densities of the elements in the solid or liquid form are compared with the square roots of their atomic charges. Magnesium is the one element which is conspicuously out of place in this curve. Its density is proportionally greater in comparison with its other properties than that of any other element of its group.

The data from which this curve is drawn are given in Table III.

TABLE III.

Element.	Density.	$\sqrt{e}$.	Element.	Density.	$\sqrt{e}$.
F.....	——	3.8	Mg.....	1.74	4.16
Cl.....	1.66	6.04	Ca.....	1.58	5.7
Br.....	3.15	9.2	Sr.....	2.54	8.46
I.....	4.95	11.5	Ba.....	3.75	10.9

When two elements of the above groups combine to form salts, the specific gravities of the salts are approximately proportional to the products of the square roots of their atomic charges. Thus if e be the atomic charge of the positive ion and e' be the charge of a single atom in the negative ion, the specific gravity of these salts may be roughly calculated from the equation $d = k\sqrt{2ee'} + 1.5$, where $k = .022$. The observed values and the values calculated from this equation are given below.

TABLE IV.

Salt.	$\sqrt{2ee'}$.	d Calc.	d Obs.
$MgCl_2$.....	35.5	2.28	2.18
$CaCl_2$.....	48.7	2.57	2.26
$SrCl_2$.....	72.3	3.09	3.05
$BaCl_2$.....	93.2	3.55	3.85
$CaBr_2$.....	74	3.13	3.32
$SrBr_2$.....	109.7	3.90	3.96
$BaBr_2$.....	141.5	4.62	4.78
CaI_2[1].....	92.8	3.54	4.9
SrI_2.....	137.4	4.51	4.41
BaI_2.....	177	5.40	4.92

The fact that the above values are only rough approximations to the true values is explained by the curve in Fig. 4, where it is seen that the relation between the density and the products of the square roots of the atomic charges is not accurately represented by a straight line.

The fact that the specific gravities of these, and other, salts are related to the charges of their ions may be shown in another way. Thus, if the algebraic sum of the positive and negative ions of a molecule be taken, it should give a resultant molecular charge which may be either positive or negative. When these resultant molecular charges with their appropriate signs are plotted against the specific gravities, the salts are found to be

[1] The density of CaI_2 is clearly out of relation to the other salts in this table. It seems to have been determined but once, viz., by Ruff and Plato, Berliner Berichte, 35, and I will give further reasons in this paper for thinking that there is an error in the determination.

arranged in their appropriate groups with respect to both their positive and negative ions. In Fig. 5, the specific gravities of the chlorides,

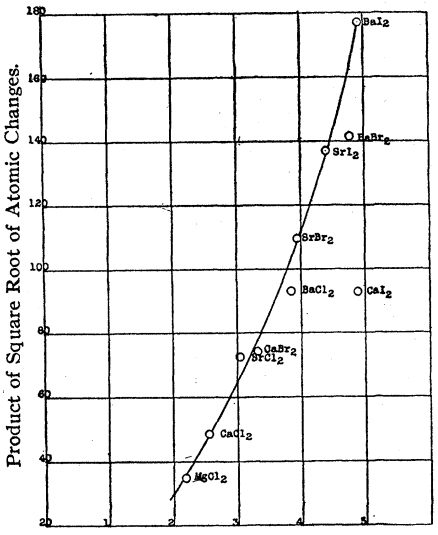

Fig. 4.

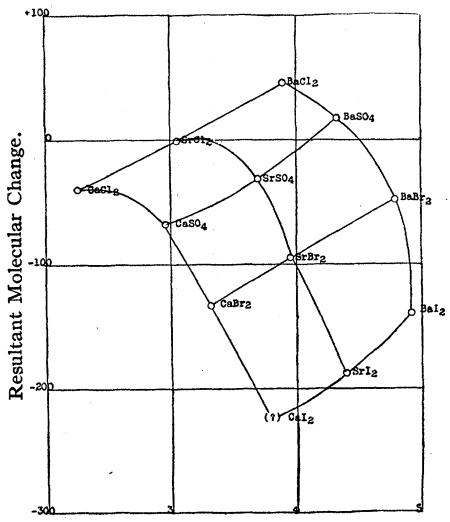

Fig. 5.

bromides, iodides and sulphates of calcium, strontium and barium are plotted as abscissas and their resultant molecular charges as ordinates.

It will be seen from this diagram that Ruff and Plato's value (4.9) for the specific gravity of CaI_2 is entirely out of relation to that of the other salts. I have accordingly ventured to give to this salt the provisional value 3.8, which it would seem to require from Fig. 4.

A closely analogous diagram to Fig. 5 is shown in Fig. 6. It seems to be a general law that those salts which produce the greatest volume contraction on solution in water give solutions which have the highest temperature expansion coefficients. The expansion coefficients used in Fig. 6 are given in the table below along with the specific gravities and the resultant molecular charges of the same salts. The expansion coefficient of the salt is determined by subtracting the expansion of water from that of the salt solution for the same temperature range. The increase in volume is for the interval between 19.5 degrees and 40 degrees, and is taken from Landolt and Boernstein's Tables. The molecular concentration is 20 gram equivalents of the salt in 10,000 grams of water. The increase in volume is given in hundred-thousandths of the volume taken at 19.5 degrees.

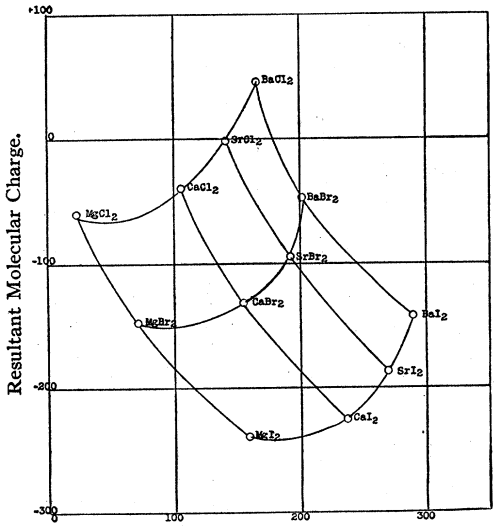

Fig. 6.

TABLE V.

Salt.	Resultant Charge.	Specific Gravity.	Expansion Coefficient.
$MgCl_2$	− 54.2		22
$CaCl_2$	− 39.6	2.26	105
$SrCl_2$	− 2	3.05	142
$BaCl_2$	+ 44.8	3.88	165
$MgBr_2$	−147.6		70
$CaBr_2$	−133	3.32	153
$SrBr_2$	− 95.4	3.96	182
$BaBr_2$	− 48.6	4.78	201
MgI_2	−240		158
CaI_2	−225	3.8(?)	236
SrI_2	−187.8	4.41	268
BaI_2	−141	4.92	288
$MgSO_4$	− 83		
$CaSO_4$	− 68.4	2.96	
$SrSO_4$	− 30.8	3.70	
$BaSO_4$	+ 16	4.33	

STANFORD UNIVERSITY,
November 9, 1912.