SPECIFIC INDUCTIVE CAPACITY AND ATOMIC CHARGES.

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IN a paper published in 1911¹ an attempt was made to find the explanation of the Volta effect in the different specific inductive capacities of the metals, though at that time it was quite generally held, especially by chemists, that the Volta effect is due to some kind of electrolytic charging of the opposed metallic surfaces by air or other gases. Since that time I have been able to show² that the Volta effect is independent of the character of the opposed surfaces, and that the potential difference between two metals when separated and in metallic contact with the earth must accordingly be due to some characteristic property of the metals themselves.

In several recent papers I have undertaken to show that the atoms of different elements have characteristic charges which are proportional to the products of the atomic mass into the mobility of the atomic ion in electrolysis, and that it is these charges which determine the position of the metal in the voltaic series. It is the purpose of this paper to call attention to the apparent relation of these atomic charges to the specific inductive capacities of their respective elements.

Unfortunately, these charges have been calculated for only three elements whose specific inductive capacities are known in the solid or liquid state. These elements are chlorine, bromine and iodine. For these elements, the specific inductive capacity in the liquid or solid state varies as the square root of the atomic charge of the respective atom. This is shown in Table I., where e' represents the atomic charge and k the specific inductive capacity as given in Landolt & Boernstein's Tables.

TABLE I.

Element.	e'	k	e'/k^2
Cl.....	35.2	2	8.8
Br.....	82.8	3.1	8.6
I.....	129	4	8.06

¹ A Physical Theory of Electrification, Leland Stanford, Jr., University Publications.² On the Nature of the Volta Effect, *PHYS. REV.*, XXXV., 484, December, 1912.

Since the atomic volumes of Cl, Br and I are nearly equal, their electrical densities will be proportional to their atomic charges, hence the relations shown in Table I. hold as well for the electrical densities of the atoms as for their atomic charges.

Since the specific inductive capacity of metals has not been measured, differences in its magnitude can only be inferred from other properties which are known to vary with specific inductive capacity in non-metallic substances. Fortunately, the metals have a number of such properties in common with dielectric substances. One of these properties is cohesion.

The relation of specific inductive capacity to cohesion is shown for a number of gases in Fig. 1, in which the specific inductive capacity of the gases is plotted as ordinates and the corresponding values of van der Waal's constant " a " are plotted as abscissas. The temperatures at which the specific inductive capacities were determined are not given in the tables (Kaye & Laby's) from which the data for Fig. 1 were taken. The constant " a " is calculated for the critical temperature. The data are given in Table II.

Fig. 1.

TABLE II.

Gas.	k	a
He.....	1.000074	.00006
H ₂	1.000264	.00042
N ₂	1.000581	.00259
Air.....	1.000586	.00257
CO.....	1.000695	.00275
CO ₂	1.000985	.00717
N ₂ O.....	1.000990	.00710

The relation of specific inductive capacity in the solid or liquid state to cohesion may be shown with the same three elements whose specific inductive capacities are given in Table I. In a paper in *Ann. d. Phys.*, XXXVII., 739, 1912, A. Heydweiller has calculated cohesion constants for a large number of elements. I have already shown¹ the relation of

Fig. 2.

Heydweiller's cohesion constants to the characteristic charges of the atoms. Heydweiller's values for the cohesion constants of chlorine, bromine and iodine are respectively 3.02, 6.68 and 10.27. In Fig. 2 these values are plotted as abscissas and the corresponding values of the specific inductive capacities as ordinates. It will be seen from this curve that Heydweiller's values may be calculated from the specific inductive capacities by multiplying them by a constant.

Another property of the elements which depends upon cohesion is the melting point. Both the melting point and the specific inductive capacity in the liquid or solid form are given for seven elements in Landolt and Boernstein's Tables. These are given in Table III., the melting point being given in absolute temperature.

TABLE III.

Element.	k	m.p.
Oxygen.....	1.465	38
Chlorine.....	2	171
Bromine.....	3+	266.7
Phosphorus.....	3.6	317
Iodine.....	4	387
Sulphur.....	4	387
Selenium.....	7.4	490

In Fig. 3 the specific inductive capacities of these elements are plotted as abscissas and their melting points as ordinates. It will be seen that with the exception of selenium the specific inductive capacities may be calculated by multiplying the melting points by a constant as closely as they may be measured by the usual methods.

The three curves already given seem to show that the cohesion between the molecules of elements vary as the specific inductive capacities of the elements. I have already shown in several papers that cohesion is an electrical force and that it varies proportionally with the characteristic

¹ On The Electrical Nature of Cohesion, *PHYS. REV.* I., 211, March, 1913.

charges of the molecules, hence the specific inductive capacity in the cases here considered must also vary proportionally with the molecular charges.

While the molecular charges can be calculated with a reasonable degree of probability for only a few compounds, we have in the halogen acids a group of three such compounds for which the specific inductive capacities have been determined. In a paper by Schaefer and Schlundt, *Jour. Phys. Chem.*, XII., 669, 1909, is given a determination of the specific inductive capacities of HCl, HBr and HI in the liquid state at temperatures of from 21.7 to 27.7 degrees and also at temperatures of from - 50 to - 90 degrees. In either set of determinations the specific inductive capacity decreases at a constant rate as the melting points and the

Fig. 3.

Fig. 4.

negative molecular charges (calculated as the algebraic sum of the charges of the positive and negative ion) increase. Both of these relations are shown in Fig. 4, the specific inductive capacities at the higher temperatures being used. The same relation is shown as well when the specific inductive capacities at the lower temperatures are used. In both curves given in Fig. 4 the specific inductive capacities are used as abscissas. In Curve I. the melting points and in Curve II. the molecular

charges are taken as ordinates. The data from which the curves are plotted are given in Table IV.

TABLE IV.

Molecule.	k	Mol. Chg.	Mltg. Pt. Abs.
HCl.....	4.6	-31.5	161
HBr.....	3.82	-79.9	186
HI.....	2.9	-127.5	223

The same relation between specific inductive capacity and melting point is shown in the compounds of the nitrogen group with hydrogen. In Jour. Phys. Chem., XVI., 253, 1912, Schlundt and Schaefer have given the specific inductive capacities of this group of compounds. Their values for specific inductive capacity at 15 degrees are given along with the melting points of the compounds in Table V.

TABLE V.

Compound.	k	Melting Point.
NH ₃	15.9	63
PH ₃	2.88	317
AsH ₃	2.05	631
SbH ₃	1.81	998

The data given in the preceding tables seem to show an unquestionable relation between specific inductive capacity and cohesion for groups of similar elements or compounds, and accordingly that in these cases a similar relation must exist between specific inductive capacity and atomic or molecular charges.

Another property which is generally understood to vary with specific inductive capacity is the refractive index or the refraction constant as calculated from the Gladstone or Lorentz formula. This refraction constant has been calculated by Gladstone for a large number of the elements, and was found to vary roughly with the square root of the atomic weight, a relation which also holds for the atomic charges. That it also, like specific inductive capacity, varies with cohesion is shown by the following considerations.

In Zeitsch. f. phys. Chem., VII., 140, 1891, J. W. Brühl gives a new determination of the atomic refraction for a considerable number of elements. For five of these elements van der Waal's constant " a " has been calculated and for six of them Kleeman¹ has calculated a con-

¹ Phil. Mag., XIX., 784, 1910.

stant " C_a " which determines the surface tension in the liquid state of the molecules to which the atoms belong. In Table VI. are given Brühl's atomic refractions, van der Waal's constant " a " and Kleeman's values of " C_a " for a number of elements.

TABLE VI.

Element.	At. Ref.	" a "	" C_a "
Hydrogen.....	1.103	.00042	1
Carbon.....	2.365	—	5.30
Nitrogen.....	2.76	.00165	—
Oxygen.....	2.328	.00273	5.94
Chlorine.....	6.014	.01063	8.40
Bromine.....	8.863	.01434	10.65
Iodine.....	13.808	—	15.49

The relations shown in the above table are represented graphically in Fig. 5. The refraction constants are plotted as abscissas. In Curve I. van der Waal's constant " a " and in curve II. Kleeman's constant " C_a " are plotted as ordinates.

Fig. 5.

The relation of refraction constant to cohesion may be shown even in the gases of the helium group, where cohesion is weakest. In Smiles's Chemical Constitution and Physical Properties, p. 245, is given a table from Cuthbertson in which are given values of $(n - 1)10^6$ for a considerable number of elements, among them the gases of the helium group. A. O. Rankine¹ has calculated Sutherland's cohesion factor " C " for these gases from experimental data on their viscosity. The data from Cuthbertson's and Rankine's tables are given in Table VII.

¹ Phil. Mag., XXI., 45, 1911.

TABLE VII.

Element.	$(n-1)10^6$	C
He.....	72	70
Ne.....	137	56
Ar.....	568	142
Kr.....	852	188
Xe.....	1380	252

These relations are shown graphically in Fig. 6.

It would be easy to multiply examples showing the relation of atomic refraction to cohesion. The sole purpose in introducing this relation here is to argue from it to the relation between atomic charges and specific

Fig. 6.

Fig. 7.

inductive capacity. I have elsewhere¹ called attention to the relation between atomic refraction and atomic charges in the alkali metals. It may not be superfluous to show here the same relation for the metals of the barium group.

Smiles has given, besides Gladstone's atomic refraction for the metals of this group a refraction equivalent for Mg, Sr and Ba determined by Pope from other considerations. Both these values as well as the atomic charges calculated from the actual velocity of the ions in electrolysis are given in Table VIII., and their relations are shown graphically in Fig. 7.

¹ Pressure-Shift of Spectral Lines, *Astrophysical Journal*, XXXV., 8, 1912.

Gladstone's atomic refractions are taken as abscissas in Curve I. and Pope's refraction equivalents in Curve II. The atomic charges are taken as ordinates in both cases.

TABLE VIII.

Element.	At. Ref. Pope.	At. Ref. Gladstone.	At. Chg.
Mg.....	8.81	6.99	13.2
Ca.....	—	10.1	34.8
Sr.....	13.95	13.3	77.5
Ba.....	18.94	16.1	123

The relation between atomic charges and refraction may also be shown after the atoms are combined into compound molecules. On page 272 of Ostwald's Solutions are given the refraction constants of a number of salts as calculated from the Gladstone formula $(n - 1)m/d$. These values and the sums of the atomic charges of the molecules are given in Table IX. It will be noticed that all but two of the salts are from monovalent acids, and that in the case of the two sulphates only one metallic ion has its charge counted. I do not know why this should be necessary to make the bivalent salts fall on the same curve as the monovalent salts, but I have observed that it is so.

TABLE IX.

Salt.	$\frac{n-1}{d}m$	Sum of Charges.
HCl.....	14.44	41.5
NaCl.....	15.11	52.3
KCl.....	18.44	76.1
HBr.....	20.63	90
NaBr.....	21.7	100.6
KBr.....	25.34	124.5
HI.....	31.17	137.5
NaI.....	31.59	148.2
KI.....	35.33	172
HNO ₃	17.2	70.1
NaNO ₃	18.7	81
KNO ₃	21.8	104.7
KSO ₄	30.5	143
HSO ₄	22.4	108.4

The above relations are shown graphically in Fig. 8.

Another property of transparent substances which H. Becquerel has shown to be related to their refraction¹ is their magnetic rotatory power

¹ Becquerel's law is $r/n^2(n^2 - 1) = \text{const.}$ where r is magnetic rotatory power and n is the refractive index.

Perhaps one further relation may be presented to show that elements from the extremes of the periodic series and with opposite characteristic charges show the same relation between their charges and cohesion, viz.,

that cohesion diminishes with increasing positive charges. Landolt and Boernstein give the atomic heats of fusion of four monovalent elements whose charges may be calculated from the mobility of their ions. These elements are potassium, sodium, bromine and iodine. Their atomic heats of fusion and their characteristic charges are given in Table XI., and the relation between the two sets of properties is shown graphically

Fig. 9.

Fig. 10.

in Fig. 10. The atomic heats of fusion are taken as abscissas and the atomic charges with their appropriate signs as ordinates.

TABLE XI.

Element.	Heat of Fusion.	Atomic Charge.
K.....	.6	+39.6
Na.....	.7	+15.75
Br.....	1.3	-84.9
I.....	1.5	-132.5

SUMMARY.

In this paper and in preceding papers¹ I have undertaken to show that

¹ The following papers dealing with this question have been published: A Physical Theory of Electrification, Leland Stanford Junior Publications, May 15, 1911; On Positive Atomic Charges, PHYSICAL REVIEW, XXXII., 512, May, 1911; Atomic Charges and Cohesion, PHYSICAL REVIEW, XXXII., 518, May, 1911; Pressure-Shift of Spectral Lines, Astrophysical Journal, XXXV., 1, Jan., 1912; On Characteristic Atomic Charges and Resultant Molecular Charges, PHYSICAL REVIEW, XXXV., 276, Oct., 1912; On Convergence Frequency in Spectral Series, Astrophysical Journal, XXXVI., 255, Oct., 1912; On the Electrical Nature of Cohesion, PHYSICAL REVIEW, 2d Series, I., 211, March, 1913.

if the mobilities of ions as calculated from electrolysis be multiplied by their respective ionic masses numbers are obtained which are closely related to many of the physical and chemical properties of the ions. On the assumption that the ions in electrolysis move only short distances as free ions, and that in a water solution of given concentration the ions of different solutes are free for the same average time between dissociation and recombination, these numbers become proportional to the electric charges of the ions, and I have accordingly spoken of them as the characteristic ionic charges. Relative ionic charges which agree among themselves in the same way as those calculated from electrolysis may be calculated from the ratio e/m determined from positive ions given off by hot bodies.

These ionic charges have been shown to be related to all the properties of bodies which depend upon cohesion or affinity. They have been, for considerable groups of elements, related by definite laws to cohesion constants however calculated, to melting points, boiling points, critical points, expansion coefficients, solubilities, specific gravity, hardness, compressibility, heats of formation and heats of fusion, both in elementary substances and compounds. They have also been shown to be closely related within a given group to the pressure-shift of spectral lines, and the convergence frequencies of spectral series have been calculated from them.

In the present paper their relation to specific inductive capacity, refractive power and magnetic rotatory power have been shown in some cases, while a number of other properties which have previously been related to them have been shown to be related also to specific inductive capacity and to refractive power.

There can be no doubt that these atomic charges are actual physical quantities which are widely related to the physical and chemical properties of the atoms. Their relation to specific inductive capacity in the non-metallic elements is such that a high positive charge is associated with a high specific inductive capacity and *vice versa*, and the indications are very strong that a similar law holds in the case of the metals. This would seem to indicate that the electric elasticity of the ether is greater around negative electrons than around or within positive sub-atoms of the elements, and that in metals as in non-metals it is greater around some kinds of positive atoms than around others.

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