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The Diamagnetism of Ions

W. R. MYERS

Physical Laboratories, University College, Southampton, England

INTRODUCTION

MEASUREMENT of the diamagnetic susceptibilities of solids and liquids has now been possible for over fifty years, so it is to be expected that the susceptibilities of the individual components forming the substance could be derived. No simple method for the derivation of ionic diamagnetic susceptibilities, however, has yet been found. The immediate aim of this article, therefore, is to present a comprehensive account of the state of this subject at the moment, the discussion being limited to the simpler ions, alkali, alkaline-earth, and halogen, both because there are too few reliable measurements available for compounds containing more complex ions and also on account of the very large variation in the estimates made by different workers. Although there has been little experimental work on the subject during the past decade, there are a few results which would appear to possess considerably improved precision, and the conclusions to be drawn from these figures are most important, but further measurements claiming similar accuracies are yet necessary to verify their interpretation.

Except where otherwise stated, susceptibility values throughout are given in units of emu per g mole (ion) $\times -10^{-6}$.

I. METHODS FOR DERIVING IONIC DIAMAGNETIC SUSCEPTIBILITIES FROM MEASUREMENTS ON COMPOUNDS

The numerous methods which have been employed for the deduction of ionic diamagnetic susceptibilities from experimental measurements may be divided into three broad categories which will now be considered in turn.

A. Use of Halogen Acid Measurements

Since the hydrogen ion, H^+, has no orbital electrons, we must assume that in the perfectly free state it exhibits zero magnetic susceptibility. On this account, Reicheneder[1] thus attributed the entire susceptibility of the halogen acids in aqueous solution to the halogen ion, X^-, and thereby assumed hydrogen ions to behave as free particles in such solutions.

In the following year (1930), Weiss[2] pointed out that the hydrogen ion in solution should have a strong polarizing effect on the solvent molecules due to the intense electric fields surrounding this ion, hence changing their magnetic susceptibility; in this way, the calculation of the susceptibility of the acid, HX, in solution using the Wiedemann additivity relation,[3] must lead to an incorrect result unless allowance is made for this polarizing influence. Using the data of Fajans and Joos[4] for the amount by which the presence of small cations changes the refractivity of pure water (Table I), Weiss has calculated the corresponding changes in diamagnetic susceptibility. This analysis points to an effective paramagnetism for all small cations when present in a polar solvent. Thus, the halogen ion susceptibilities, as deduced from measurements on halogen acids, will all be greater than if the H^+ ion were assumed devoid of magnetic effect. (The diamagnetic corrections for hydrogen and other ions are shown in Table II.)

The refractive properties of ions at optical wavelengths are the result of the outermost electron shells, whereas every electron contributes to the diamagnetism, so Weiss is not completely justified in assuming an exact analogy between the two phenomena. Since, however, it seems fairly certain from theoretical work that at least 70 percent of the diamagnetism comes from electrons in the outermost shell for alkali, alkaline-earth, and halogen ions, the method will not be much at

TABLE I. Change of the molar refractivity of water caused by presence of dissolved ions.

Data of Fajans and Joos per g ion					
H^+	-0.62	Mg^{++}	-1.85	F^-	$+0.3$
Li^+	-0.53	Ca^{++}	-0.65	Cl^-	0
Na^+	-0.3	Sr^{++}	-0.54	Br^-	0
K^+	0	Ba^{++}	0	I^-	0

TABLE II. Change of the molar susceptibility of water due to presence of dissolved ions (paramagnetic effect).

From data of Fajans and Joos per g ion					
H^+	1.1	Mg^{++}	3.2	F^-	-0.5
Li^+	0.9	Ca^{++}	1.1	Cl^-	0
Na^+	0.5	Sr^{++}	0.9	Br^-	0
K^+	0	Ba^{++}	0	I^-	0

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[1] K. Reicheneder, Ann. Physik 3, 58 (1929).

[2] P. Weiss, J. phys. 1, 185 (1930); Compt. rend. 190, 95 (1930).

[3] The Wiedemann law: For a dissolved substance, the susceptibility of the solution, according to the Wiedemann law, is given by

$$p\cdot\chi_u+(100-p)\cdot\chi_v=100\chi_s,$$

where p is the concentration of the solution in g solute per 100 g solution, and χ_u, χ_v, χ_s, are the specific susceptibilities of solute, solvent, and solution, respectively.

The validity of the linear relation between solution susceptibility and concentration has frequently been in question, but for all alkali and alkaline-earth halides in aqueous solution, there seems to be no sensible departure. The law has been assumed to be perfectly valid throughout this paper for the calculation of solute susceptibilities from solution measurements, but some workers report irregular behavior for a few dissolved substances. This matter will be discussed under Sec. III.

[4] K. Fajans and G. Joos, Z. Physik 23, 1 (1924).

fault as regards numerical values, particularly as the corrections are fairly small for most ions. But it is not permissible to assume that the data of Fajans and Joos are absolute, for, as with ionic diamagnetism, the refractivities of ions in solution presents the problem of how to divide the refractivity of the solution into the contributions from the solute anion and cation and solvent molecule, and a certain amount of arbitrariness must enter into the calculations.

Kido,[5] like Reicheneder, has assumed that H^+ ions in solution exhibit no magnetic effect. The same objection thus applies to this method as to that of Reicheneder, but in this case, Kido has tried to verify his assumption experimentally by plotting the susceptibilities of a few alkali halides against the number of electrons in the cation, N. Extrapolating the best straight lines through sets of points representing compounds containing a particular halogen ion, he finds that for $N=0$, corresponding to the hydrogen halide, the values obtained are in very close agreement with his measurements for the halogen acids. The construction of these linear graphs is not justified, however, unless we know that each electron contributes an equal amount to the diamagnetism of an ion no matter which ion of a homologous series we consider. In the light of more recent experimental and theoretical work, such an assumption is quite without foundation.

If it were possible to obtain reliable values for halogen ion susceptibilities by either of the preceding methods, then it would be possible to find various cation susceptibilities by assuming the additivity of ionic susceptibilities in solution. Such calculations invariably yield divergent results for a given cation as deduced from different halides, and the best that can be done would appear to be to take mean values, thereby implying one of the following possibilities: (a) Method of derivation of halogen ion values is incorrect. (b) Experimental measurements are inaccurate. (c) Ionic susceptibilities in solution are not strictly additive.

TABLE III. Brindley's method for ionic susceptibilities (using Slater's data). Cesium iodide.

Electron groups	$(Z-s)$	Cesium $-\Delta\chi\cdot10^6$	% of total	$(Z-s)$	Iodine $-\Delta\chi\cdot10^6$	% of total
$1s$	54.7	0.0015	0.0041	52.7	0.0016	0.0029
$2s, p$	50.85	0.0693	0.1893	48.85	0.0751	0.1356
$3s, p$	43.75	0.3930	1.0735	41.75	0.4318	0.7796
$3d$	33.85	0.8208	2.2420	31.85	0.9271	1.6739
$4s, p$	27.25	2.1734	5.9365	25.25	2.5314	4.5705
$4d$	15.85	8.0300	21.9335	13.85	10.5167	18.9882
$5s, p$	9.25	25.1266	68.6320	7.25	40.9108	73.8493
		36.6	100.0		55.4	100.0

$-\Delta\chi\cdot10^6\equiv$Susceptibility contribution of shell.

Of these, (a) and more especially (b) seem to have been mainly responsible for the unsatisfactory state of affairs. That (c) is less culpable than has generally been thought will be shown in Sec. II.

B. The Theoretical Division of Measured Alkali Halide Susceptibilities According to Atomic Theory

Joos[6] was the first to show that, for hydrogen-like atoms and ions, the simplest consideration of the Rutherford-Bohr atomic model leads to the linear dimensions being inversely proportional to the atomic number, and hence the diamagnetic susceptibility, being dependent upon the square of the electronic radius, is then inversely proportional to the square of the atomic number. This relationship will, of course, only hold true for ions of the same electronic structure, thus for the alkali halide compounds, we have the following pairs of ions, each with an inert gas configuration:

$$(Na^+\ F^-)-Ne;\ (K^+\ Cl^-)-A;\ (Rb^+\ Br^-)-Kr;$$

and

$$(Cs^+\ I^-)-Xe.$$

Joos therefore suggests that the ionic susceptibilities for all these ions may be found simply by dividing the molecular susceptibilities as measured in solution according to this rule.

At the time of Joos' first paper on this topic (1923), the measured values for the inert gases were about ten times the values for ions having the same structure. For instance, the measurements for argon gave a molar susceptibility of about 200 while the deduction for K^+ and Cl^- ions from potassium chloride in aqueous solution by the Joos method gives about 15 and 19, respectively. Now, we would expect that the susceptibility of argon should lie between these two limits since its atomic number, 18, is between those of chlorine, 17, and potassium, 19, while possessing the same number of orbital electrons. In the following year, Wills and Hector[7] made the first accurate measurements for the inert gases, thereby finding the molar susceptibility of argon to be 16.8, in excellent agreement with Joos' predictions.

Several workers have used the Joos method for deriving ionic susceptibilities of the alkali and halogen ions. It is well known that the problem is not so simple as has so far been suggested, because the inner electrons of an atom or ion must screen the outer electrons from the nucleus so that we ought to consider each electron under the influence of smaller nuclear charges for the derivation of orbital dimension relationships.

Nevertheless, Veiel[8] has divided his measured molar susceptibility for cesium iodide in aqueous solution in this manner, on the assumption that for such large ions,

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[5] K. Kido, Tokyo Imp. Univ. Sci. Rept. **22**, 835 (1933).

[6] G. Joos, Z. Physik **19**, 347 (1923); **32**, 835 (1925).

[7] A. P. Wills and L. G. Hector, Phys. Rev. **23**, 209 (1924).

[8] U. Veiel, Ann. Physik **24**, 697 (1935).

TABLE IV. Mean measured molar susceptibilities in aqueous solution.[a]

		Halogen acids		
	HF 9.0		HBr 32.8	
	HCl 21.8		HI 50.4	
		Alkali halides		
		KF 24.3		
LiCl 25.2	NaCl 30.3	KCl 39.4	RbCl 46.5	CsCl 61.9
LiBr 35.8	NaBr 42.0	KBr 50.8	RbBr 56.7(?)	CsBr 73.7
LiI 53.7	NaI 59.9	KI 67.9	RbI 67.1(?)	CsI 92.0
		Alkaline-earth halides		
$MgCl_2$ 49.7	$CaCl_2$ 56.1		$SrCl_2$ 64.8	$BaCl_2$ 76.4
$MgBr_2$ 72.2(?)	$CaBr_2$ 77.9		$SrBr_2$ 87.9	$BaBr_2$ 100.5
MgI_2 111.4(?)	CaI_2 111.7		SrI_2 122.9	BaI_2 136.5

[a] All data which show very large deviations have been omitted in the calculation of these mean values. The bracketed interrogatives behind the values for RbBr, RbI, $MgBr_2$, and MgI_2 indicate that the measurements for these compounds in aqueous solution are very few and widely divergent in magnitude. Publications from which these mean values have been calculated are P. Pascal, Compt. rend. **158**, 37 and 1895 (1914); R. Hocart, see reference 23; K. Ikenmeyer, Ann. Physik **1**, 169 (1929); K. Reicheneder, Ann. Physik **3**, 58 (1929); L. Abonnenc, see reference 37; J. Farquharson, see reference 28; F. W. Gray and J. Dakers, Phil. Mag. **11**, 81 (1931); F. W. Gray and J. Farquharson, J. Sci. Instr. **9**, 1 (1932); K. Kido, Sci. Rept. Tokyo Imp. Univ. **21**, 149 and 869 (1932); A. F. Scott and C. M. Blair, J. Phys. Chem. **37**, 475 (1933); M. Flordal and O. E. Frivold, see reference 24; O. E. Frivold and H. Sogn, see reference 32; U. Veiel, Ann. Physik **24**, 697 (1935); F. E. Hoare and G. W. Brindley, Proc. Roy. Soc. (London) **A159**, 395 (1937); O. E. Frivold and N. G. Olsen, see reference 20; P. Ehrlich, Z. anorg. u. allgem. Chem. **249**, 219 (1942).

their susceptibilities in the dissolved state are not very different from those when perfectly free. Values for other ions he then calculates additively, and by a comparison of the halogen ion susceptibilities with measurements for the halide acids, Veiel finds a small difference, almost identical to that attributed by Weiss to polarization of solvent molecules by the H^+ ion. On account of this consistency, Veiel has assumed the Joos method of division to be adequate.

Both Veiel and Joos, however, were well aware of the screening effects of electron shells. The various theoretical approaches to diamagnetic susceptibility all try to account for this, but only Slater's[9] method gives a tolerable agreement of theoretical susceptibilities with those deduced from experiment.

For hydrogen-like atoms and ions, Zener[10] had shown that the radial part of the wave function may be written as

$$\psi_{(r)} = r^{(n^*-1)} \cdot e^{-(Z-s/n^* r)}.$$

Having developed rules for the values of the total effective quantum number, n^*, and the screening numbers, s, for different electron groups and sub-groups by comparisons with experimental data for ionization potentials, x-ray levels, etc., Slater then shows how to calculate diamagnetic susceptibilities for any atomic system. The mean square orbital radius, if one uses Zener's approximate wave functions, becomes

$$\langle r^2 \rangle_{Av} = \frac{n^{*2}(n^*+\frac{1}{2})(n^*+1)}{(Z-s)^2} \text{ atomic units,}$$

hence the susceptibility per g atom or ion is

$$\chi_M = -\frac{Ne^2}{6mc^2} a_0^2 \sum \frac{n^*(n^*+\frac{1}{2})(n^*+1)}{(Z-s)^2},$$

where a_0 represents the atomic unit of length equal to 0.528A.

Brindley[11] was the first to use this theoretical method for the derivation of ionic values from experimental measurements on compounds. For an alkali halide compound comprising two ions of the same electronic structure, the molar susceptibility may be divided according to Slater's method, providing there is no appreciable interaction between the ions; thus calculations from measurements made on solutions are most likely to comply with the requirements of this method.

This way of dividing a measured susceptibility, however, yields results quite different from those given by the simple Joos method. For instance, using the mean value for the measured molar susceptibility of cesium iodide in aqueous solution, 92.0, (see Table IV) the Joos method gives 44.3 for Cs^+ and 47.7 for I^- compared with 36.6 and 55.4, respectively, when Slater's data are used. The proportional contributions to diamagnetic susceptibility of each electron group for these two ions by the Slater method are shown in Table III, where it may be seen that the outer shell, $5s$, p contributes about 70 percent to the total, the lowest shells being under the influence of such large effective nuclear charges that their contributions are almost negligible.

Having divided the mean molar susceptibilities of the compounds KCl, RbBr, and CsI as measured in aqueous solution (see Table IV), the remaining alkali and halogen ion values may be calculated additively, a mean being taken where more than one value may be derived. This provides the data of Table V, column I. Now the compounds above mentioned have been chosen for the division because each component has identical electronic structure, but if we assume there is no interaction between ions in any of the dissolved alkali halides (nor interaction with the solvent molecules), then there is no reason why the method should not be applicable to any one of these compounds. The author has thus evaluated the susceptibilities of the alkali and halogen ions using all possible "starting points" and taking

TABLE V. Ionic susceptibilities by Brindley's method.

	Slater		Angus	
	I	II	III	IV
Li^+	0.6	1.6	0.7	1.9
Na^+	4.3	7.1	4.3	7.4
K^+	14.0	15.5	14.1	15.8
Rb^+	22.7	22.2	23.2	22.5
F^-	9.1	8.9	8.8	8.6
Cl^-	24.8	23.2	24.6	22.9
Br^-	36.4	34.6	36.3	34.3
I^-	54.0	52.2	54.1	51.9

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[9] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[10] C. Zener, Phys. Rev. **36**, 52 (1930).

[11] G. W. Brindley, Phil. Mag. **11**, 786 (1931).

TABLE VI. Ionic additivity test.

Alkali halides (as solid, Bridley and Hoare's measurements)

	Li	$\delta\chi$	Na	$\delta\chi$	K	$\delta\chi$	Rb	$\delta\chi$	Cs
F	10.1	5.5	15.6	8.0	23.6	8.3	31.9	12.6	44.5
$\delta\chi$	13.0		14.6		15.2		14.5		12.2
Cl	23.1	7.1	30.2	8.6	38.8	7.6	46.4	10.3	56.7
$\delta\chi$	10.9		10.9		10.4		10.0		10.5
Br	34.0	7.1	41.1	8.1	49.2	7.2	56.4	10.8	67.2
$\delta\chi$	16.0(?)		15.9		16.5		15.8		15.4
I	c.50	7(?)	57.0	8.7	65.7	6.5	72.2	10.4	82.6

Alkaline-earth halides (as solid, Brindley and Hoare's measurements)

	Mg	$\delta\chi$	Ca	$\delta\chi$	Sr	$\delta\chi$	Ba
F_2	22.7	5.3	28.0	6.7	34.7	11.9	46.6
$\delta\chi$	26.5		26.7		26.8		25.7
Cl_2	49.2	5.5	54.7	6.8	61.5	10.8	72.3
$\delta\chi$			16.7		17.4		16.3
Br_2	—		71.4	7.5	78.9	9.7	88.6
$\delta\chi$			27.6		31(?)		35.8
I_2	—		109.0	2(?)	c.110	14.4(?)	124.4

Alkali halides (in aqueous solution; mean values of Table IV)

	H	$\delta\chi$	Li	$\delta\chi$	Na	$\delta\chi$	K	$\delta\chi$	Rb	$\delta\chi$	Cs
Cl	21.8	3.4	25.2	5.1	30.3	9.1	39.4	6.9	46.3	15.4	61.9
$\delta\chi$	11.0		10.6		11.7		11.4		10.4		11.8
Br	32.8	3.0	35.8	6.2	42.0	8.8	50.8	5.9	56.7	17.0	73.7
$\delta\chi$	17.6		17.9		17.9		17.1		10.4(?)		18.3
I	50.4	3.3	53.7	6.2	59.9	8.0	67.9	−0.8(?)	67.1(?)	24.9(?)	92.0

Alkaline-earth halides (in aqueous solution; mean values of Table IV)

	Mg	$\delta\chi$	Ca	$\delta\chi$	Sr	$\delta\chi$	Ba
Cl_2	49.7	6.4	56.1	8.7	64.8	11.6	76.4
$\delta\chi$	22.5		21.8		23.1		24.1
Br	72.2(?)	5.7(?)	77.9	10.0	87.9	12.6	100.5
$\delta\chi$	39.2(?)		33.8		35.0		36.0
I	111.4(?)	0.3(?)	111.7	11.2	122.9	13.6	136.5

averages. The only advantage of such a procedure is that it makes more use of the experimental data, but it can be seen from Table V, column II that it does not make very large differences to the derived susceptibilities, except, of course, for the small ions, Li^+ and Na^+, which have very small susceptibilities anyway.

The whole procedure has been repeated using Angus' theoretical method,[12] which is merely a modification of the Slater method whereby every electron sub-group is considered to be under the influence of a different nuclear charge, *e.g.*, the $2s$ and $2p$ electron shells are taken separately in the calculations. It is obvious that the method does not make any great difference in comparison with the Slater values. (See Table V, columns III and IV, which corresponds to columns I and II, respectively.)

C. Employment of Homopolar Susceptibility Values

Three distinct attempts have been made to derive ionic values from atomic (homopolar) susceptibilities, for which data, reference has been made to Pascal's extensive works.[13]

Weiss[14] first tried to derive ionic values by this type of method. He adopted a strange procedure whereby, to Pascal's atomic values, three units of molar susceptibility were added or subtracted, according as the ion is negative or positive, respectively, in order to obtain ionic susceptibilities on the grounds that this accounted for the removal of constraint formerly present when in the homopolar condition due to chemical binding. For atoms giving rise to doubly charged ions, six units were used for the conversion. This arbitrarily assumed constant bond effect, invariant with ionic structure, is difficult to visualize, and although results show fair accord with other methods, it is altogether unconvincing and lacks theoretical support.

Föex[15] assumes that if an electron is added to or removed from the outermost shell of a halogen atom, it does not disturb the charge distribution of those electrons already present, so that the ionic susceptibility of halogen ions is given by multiplying the corresponding homopolar values by 8/7. The figures thus derived show quite good agreement with other results, but in addition to the assumption already mentioned, the method assumes that only electrons in the outer shell contribute to the diamagnetism, and further, that each electron contributes an equal amount.

The third and most recent of these methods is due to Miss Trew.[16] She employs Pascal's data in a proportionality rule, again applicable to halogen ions. If A represents the theoretical atomic susceptibility, B the experimental atomic susceptibility, C the theoretical ionic susceptibility, then D, the required experimental (true) susceptibility is given by $A/B=C/D$. Miss Trew employs the Slater theoretical method since it has appeared to be the most satisfactory, but she in no way justifies the use of the proportion rule.

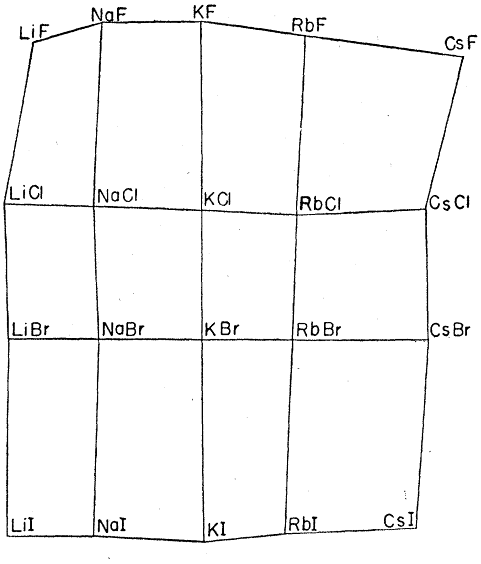

FIG. 1. Ionic additivity test. Alkali halides. Powdered crystal measurements of Brindley and Hoare.

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[12] W. R. Angus, Proc. Roy. Soc. (London) **A136**, 569 (1931).

[13] P. Pascal, Compt. rend. **152**, 862 and 1010 (1911); **158**, 37 and 1895 (1914); **173**, 144 (1921). (These represent only the more important of Pascal's papers with reference to the text.)

[14] See reference 2.

[15] G. Föex, Compt. rend. **190**, 481 (1930).

[16] Miss V. G. C. Trew, Trans. Faraday Soc. **37**, 476 (1941).

Briefly, these methods all depend upon theory and/or arbitrary assumptions, and rest on such sandy foundations as to serve no more useful purpose other than suggesting approximate ionic susceptibilities.

II. TESTS OF ADDITIVITY OF IONIC SUSCEPTIBILITIES

The simplest way of testing the validity of the additivity of ionic diamagnetic susceptibilities is to take differences between values for molar susceptibilities as shown in Table VI for the alkali and alkaline-earth compounds. The first half of the table uses the results of Brindley and Hoare[17] for solids (powdered crystals) as these are clearly the most reliable measurements; the second half of the table uses the mean values derived from aqueous solution measurements previously given in Table IV.

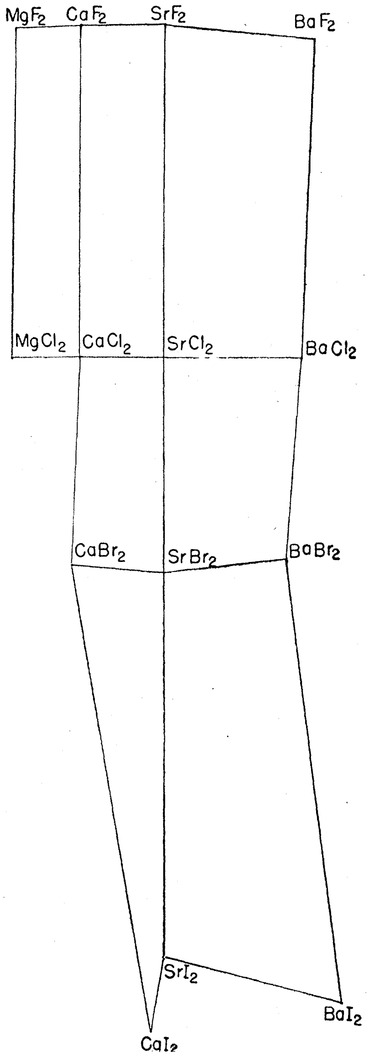

FIG. 2. Ionic additivity test. Alkaline-earth halides. Powdered crystal measurements of Brindley and Hoare.

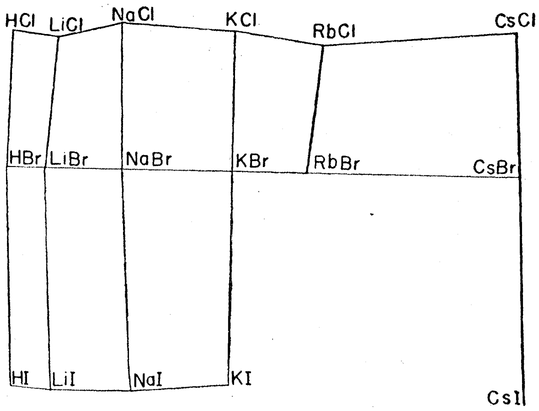

FIG. 3. Ionic additivity test. Alkali halides. Aqueous solution measurements (mean).

It can be seen that the differences, $\delta\chi$, in the columns and rows are nearly constant, thus indicating at least an approximation to additivity of ionic susceptibilities. However, even if these differences were exactly constant for each given row and column, it would not point unambiguously to additivity; should the effective susceptibility of ions vary from one compound to another, then we are no nearer verifying the additivity idea. But it may easily be shown that the variation in susceptibility of any particular ion with compound formation is not great, so this kind of test is, to a limited extent, a valid one.

A more illuminating graphical method of investigating ionic additivity is due to Veiel.[18] Considering the alkali halides, we may commence, say, with KBr as our reference point, alkali bromide susceptibilities being plotted along a horizontal line, potassium halide susceptibilities along a line at right angles through the KBr point; the remaining alkali halides may then be plotted by employing the relevant values of $\delta\chi$ from Table VI in Cartesian fashion.

Figures 1 to 6 are of this type; 1 and 2 use Brindley and Hoare's measurements for solids[19]; 3 and 4 use the mean values for compounds in aqueous solution (page 12); 5 and 6 use Frivold and Olsen's[20] measurements in aqueous solution.

If additivity were rigorously adhered to, all parts of all figures should appear as rectangles. From these graphs we see that the alkali halide results show closer agreement with additivity than do the alkaline-earth halides. Brindley and Hoare's measurements for solids are chosen as these undoubtedly form the most reliable set of results for solids; Frivold and Olsen's results from aqueous solution measurements are employed here because they too would appear to have a much higher accuracy than any other corresponding set of results.

Generally, the graphs indicate greater deviations from

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[17] F. E. Hoare, Proc. Roy. Soc. (London) **A147**, 88 (1934); G. W. Brindley and F. E. Hoare, Proc. Roy. Soc. (London) **A152**, 342 (1935); **159**, 395 (1937).

[18] See reference 8.

[19] See reference 17, G. W. Brindley and F. E. Hoare.

[20] O. E. Frivold and N. G. Olsen, Osloer Math. Naturwiss. Klasse, No. 2, 13 (1940).

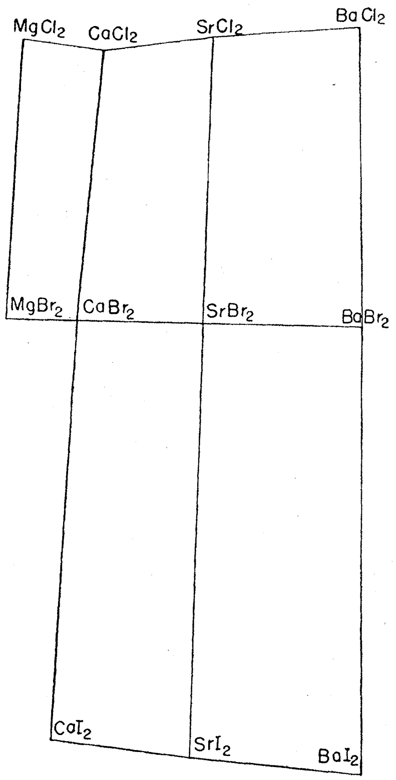

FIG. 4. Ionic additivity test. Alkaline-earth halides. Aqueous solution measurements (mean).

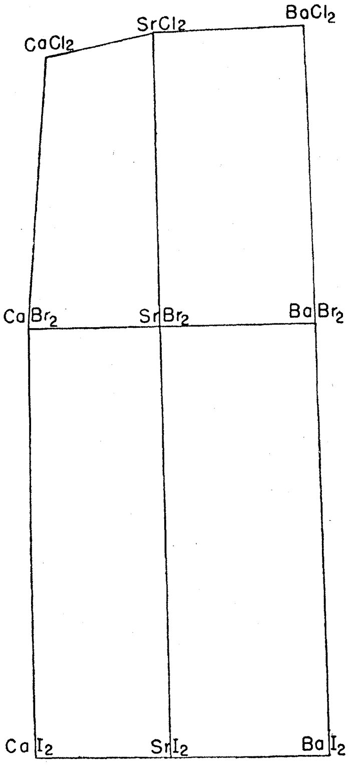

FIG. 6. Ionic additivity test. Alkaline-earth halides. Aqueous solution measurements of Frivold and Olsen.

additivity in those compounds containing small ions, but in view of the sensitivity of the test (in the case of Fig. 1 the susceptibility of CsI on the same scale would be about three times the over-all horizontal dimension), the approximation to additivity seems close.

The author has attempted yet another method of testing additivity. If the susceptibility of an ion be assumed constant irrespective of the ion in binary combination with it, then plotting the susceptibilities of the compound against the susceptibilities of the ions for a homologous series should result in a set of straight lines. For the ionic susceptibility values required by this test, Slater's[9] theoretical values have been employed, so that, in Fig. 7, the susceptibilities of the cesium halides, for instance, lie closely on a straight line when plotted against Slater's halogen ion susceptibilities.[21] Such a set of curves may be termed iso-alkali, and similarly, a set of iso-halogen curves has been plotted (Fig. 8). Figures 7 and 8 use Brindley and Hoare's measurements for solids; Figs. 9 and 10 represent the same procedure for mean measurements in aqueous solution.

An immediate criticism of such a method of test is that we are using theoretically derived susceptibilities, and it is undoubtedly a strong argument against its use. Nevertheless, the graphs are particularly interesting.

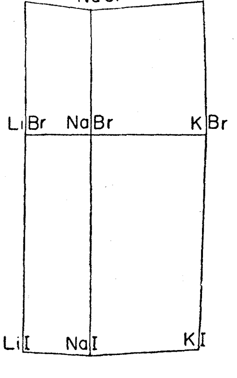

FIG. 5. Ionic additivity test. Alkali halides. Aqueous solution measurements of Frivold and Olsen.

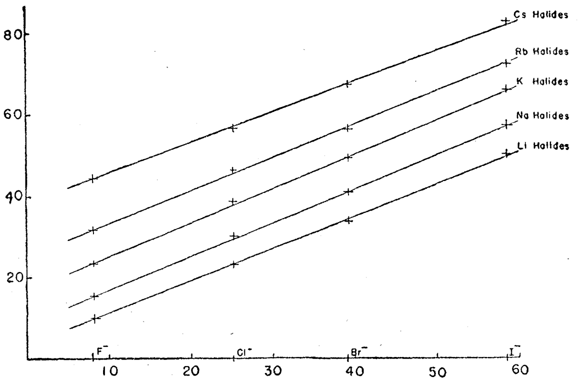

FIG. 7. Molar susceptibilities for solids plotted against Slater's theoretical values for halogen ion susceptibilities (per g ion $\times 10^6$).

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[21] The theoretical values employed differ slightly from those given by Slater himself because they have been recalculated with more recent data for Avogadro's number, electronic charge and rest mass, and velocity of light.

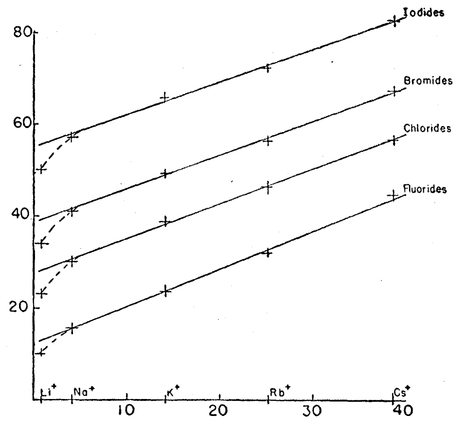

FIG. 8. Molar susceptibilities for solids plotted against Slater's theoretical values for alkali ion susceptibilities (per g ion $\times 10^6$).

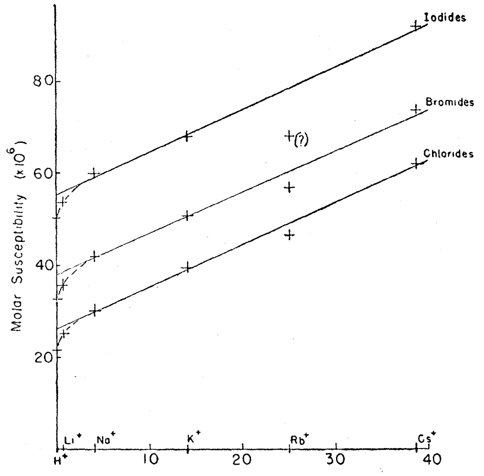

FIG. 10. Molar susceptibilities for aqueous solutions plotted against Slater's theoretical values for alkali ion susceptibilities (per g ion $\times 10^6$).

Figure 8 shows that Na, K, Rb, and Cs halides lie closely on straight lines, but that every lithium compound falls below its respective line. Now the susceptibility of Li^+ is obviously so small that, even were there a large error in Slater's theoretical method, here, it would make no appreciable difference to this effect. The curves for the mean measurements in aqueous solution and for Frivold and Olsen's measurements in aqueous solution (Fig. 11) both point to the same conclusion; results for halide acids have been included, and as would be expected, the effect of the H^+ ion is even more marked than that of Li^+. By taking the ordinate distance from the representative points to the relevant straight lines, the separations are approximately constant for a given ion, the averages being H^+ 4.7, Li^+ 2.2, (Fig. 10); H^+ 4.0, Li^+ 0.9 (Fig. 11). These numbers may then be taken to indicate the effective paramagnetism of these ions superimposed upon their inherent diamagnetism, if any, when present in aqueous solution. (They are rather dubious in Fig. 11, but some effect at least is evident.) Numerically, the figures are not in good agreement with the empirical estimates of Weiss,[2] but the indication of some paramagnetic effect appears more convincing by this method. Further, even if Pauling's high theoretical values[22] are used for the test, the effect still appears.

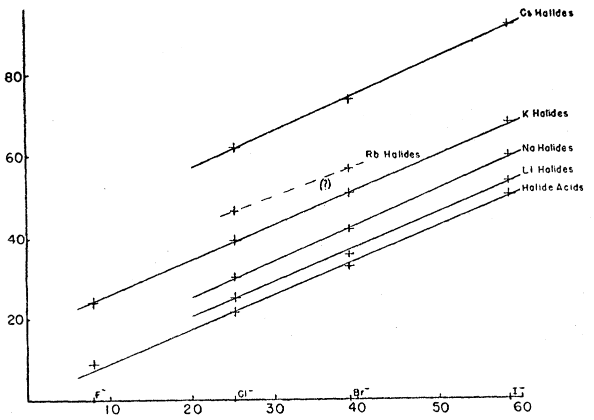

FIG. 9. Molar susceptibilities for aqueous solutions plotted against Slater's theoretical values for halogen ion susceptibilities (per g ion $\times 10^6$).

For the deviation of the representative points for the lithium compounds in Fig. 8, the interpretation of the paramagnetic effect (average value 4.4) must be somewhat different, for these results refer to measurements on solids. However, for both solid and solution, the effect must be caused by some kind of constraint upon the ion producing deformation, in solids, by a closer proximity of ions than in the higher compounds, and in solution, possibly by the intense electric fields surrounding these small ions and the consequent polarization of water molecules.

Unfortunately, the test cannot be repeated for the alkaline-earth halides because measurements for the magnesium halides are much too unreliable, and it is only from Mg^{++} ions that a measurable paramagnetic effect could be expected.

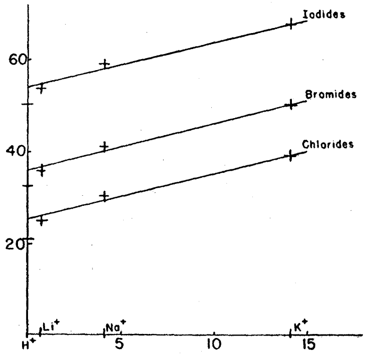

FIG. 11. Molar susceptibilities for aqueous solutions plotted against Slater's theoretical values for alkali ion susceptibilities (per g ion $\times 10^6$).

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[22] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

TABLE VII. Molar susceptibilities of alkali halides.

	LiCl	LiBr	LiI	CsCl	CsBr	CsI
(a) Solution				62.4	73.7	91.5
				3.0	4.1	5.8 $\delta\chi$
(b) Calculated using ionic values found from measurements on rock-salt type compounds	24.9	35.2	51.3	59.4	69.6	85.7
				2.7	2.4	3.1 $\delta\chi$
(c) Measured as solid	23.3	34.0	50.0	56.7	67.2	82.6

$\delta\chi\equiv$difference of molar susceptibilities

Allowing for experimental error, the general conclusion must be that susceptibilities may be regarded as additive for alkali and halogen ions, except for Li^+ (and H^+) where small size and intense fields cause discrepancies equivalent to an apparent paramagnetism of the ion; the magnitude of this effect can only be ascertained approximately by the method suggested.

III. IONIC SUSCEPTIBILITIES IN DIFFERENT STATES

For a discussion of the possible variations of ionic diamagnetic susceptibility with physical state, it must be borne in mind that first Hocart[23] and later, Flordal and Frivold,[24] produced evidence to show that the molar susceptibilities of compounds are invariably greater when calculated from measurements in aqueous solution than when measured as solid. Examination of all available data makes this conclusion certain. Thus, quite apart from other considerations, for neither the solid nor dissolved state can we be sure that the apparent derived ionic susceptibilities are those which would be found if measurements could be made on free ions. On this account, several attempts have been made to adjust the solid and dissolved ionic values to those relevant to free ions.

The method of Weiss[2] described in Sec. IA for the estimation of ionic values from solution measurements should give susceptibilities for free ions, as also should the methods described under Sec. IB.

A detailed investigation of these matters was essayed by Brindley and Hoare.[25] In order to determine ionic susceptibilities relevant to the crystal state, they have laid out a difference table (see Table VI) using their own measurements for crystalline alkali and alkaline-earth halides. By using only the molar susceptibilities of those rocksalt type crystals in which there is no close proximity of negative ions,[26] average differences were found and all the ionic susceptibilities were then expressed in terms of that of Li^+ by assuming simple additivity of ionic susceptibilities. Li^+ is chosen as it has the smallest susceptibility, and Brindley and Hoare therefore assume that the theoretical (free) value of 0.7 will not lead to sensible error in evaluation of the other values.

Turning now to the remaining alkali halides (principally, the chlorides, bromides, and iodides of lithium and cesium), simple additive calculation of their molar susceptibilities from the ionic values derived by the above procedure indicates clear divergence from the measured values in excess of experimental error (see Table VII). Brindley and Hoare thus conclude that departure from strict ionic additivity (or, what is the same thing, change of apparent individual ionic susceptibility) coincides with (a) close approach of negative ions (lithium compounds) and also (b) change of crystal structure (cesium halides, change from rocksalt to CsCl-type structure, *viz.*, simple cubic to body-centered cubic).

As the change from the rocksalt to the CsCl-type structure involves a change of coordination number from 6 to 8, Brindley and Hoare sought a connection between this fact and susceptibility changes. Together with their measurements for the cesium halides in aqueous solution, for which the degree of hydration is 4, there is a clear indication by the values of the differences, $\delta\chi$, of a change of molar susceptibility directly proportional to the change in coordination number if we take degree of hydration in solution to be equivalent to coordination number in crystals.

Investigation of their measurements for the alkaline-earth halides did not yield any definite conclusions, mainly on account of the numerous crystal types occurring in this class of compounds and the consequent difficulty of reliably attributing effect to cause.

Extending this work to the relation between ionic susceptibilities in the dissolved and crystal state, Brindley and Hoare present a table showing ionic packing radii, R, probable degree of hydration of ions in water, C, and the corresponding ionic susceptibilities for dissolved and crystal states. Taking $\Delta\chi=(\chi_{\mathrm{diss}}-\chi_{\mathrm{xtal}})$, the various values which this quantity takes for different ions is compared with the quantity, Cn/R^2 where n is the number of electronic charges which the ion carries, thereby attempting to discover some empirical relationship, but nothing of consequence appears. It may only be said that, very roughly, the diamagnetism, $\Delta\chi$, seems to increase with diminishing Cn/R^2, but no quantitative analysis is possible.

Brindley and Hoare's interpretation of their experimental measurements cannot, however, be criticized, because the uncertainty of these figures, although small compared with most other workers' results, is still too large to give data sufficiently reliable for this sort of semi-empirical work.

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[23] R. Hocart, Compt. rend. **188**, 1151 (1929).

[24] M. Flordal and O. E. Frivold, Ann. Physik **23**, 425 (1935).

[25] G. W. Brindley and F. E. Hoare, Trans. Faraday Soc. **33**, 270 (1937); Proc. Phys. Soc. **49**, 619 (1937); Proc. Roy. Soc. (London) **A159**, 395 (1937).

[26] Comparison of experimentally observed and calculated interatomic distances for the alkali halide crystals shows considerable differences between the two for LiCl, LiBr, NaBr, and NaI. In these cases, where small cations are present, the anions are brought very close, and as a result of the overlapping of the wave functions, a repulsive force of high inverse power is set up in addition to the Coulomb forces. Thus, it seems the "additivity of ionic susceptibilities" is not so likely for these substances.

After inspection of Brindley and Hoare's work, Lee[27] has noticed a simple relation between susceptibilities in the solid and dissolved states, *viz.*:

$$-\chi_{\mathrm{diss}} = -a\chi_{\mathrm{xtal}} - b,$$

where the constants a and b are 1.09 and 1.0 for the alkali and halide ions, 1.15 and 5.8 for the alkaline-earth ions. The explanation of such an equation in terms of the properties of ionic solutions and crystal structure would indeed be interesting, but if we are to assume any dependence of susceptibility on coordination number, then the constant in the equation will have to be different for cesium ions, for example, from those constants applicable to other alkali ions on account of their different coordination number in the crystal state.

Several researches have been carried out with a view to determining the effect of conditions upon ionic diamagnetism, and of these, the implications of deviations from Wiedemann additivity are particularly important.

Farquharson's measurements[28] show quite extraordinary behavior for hydrochloric acid solutions; on plotting a graph of solution susceptibility against concentration, the curve, while following a generally straight line direction, contains a series of smooth undulations. Computing the composition of the solutions, Farquharson finds that there are, corresponding to strengths HCl 3, 4, 5, 7, 8, 9, and 10, H_2O positions of minimum susceptibility along the curve. This effect we can reasonably ascribe to the constraint produced on an ion when surrounded with solvent molecules; that there is a maximum at $HCl\cdot6H_2O$ Farquharson explains as due to the Cl^- ion having a complete sub-group of six electrons in the L shell. However, no other worker has managed to repeat his results, nor is any explanation forthcoming for the existence of maxima and minima on the curve at concentrations below $HCl\cdot10H_2O$. Further, the maximum deviation from strict additivity is only about 1 percent, and this is dangerously close to the probable error of measurement.[29] (A Curie-Chéneveau balance was employed.)

Nevertheless, we cannot lightly dismiss this work, for the existence of apparent hydration effects on diamagnetic behavior has also been observed for H_2SO_4 and HNO_3.[30] Together with work on the temperature dependence of aqueous solutions,[8, 31] there has been considerable controversy about the explanation of these phenomena. Since water is a highly polymerized liquid, and it is well known that the presence of ions, particularly those of small size and high charge, causes a breakdown of the higher complexes, many of the observed irregularities in solution susceptibility behavior may be explained by either a hydration or a depolymerization hypothesis, or even both. Much could be cleared up by making measurements in completely non-polymerized solvents. Frivold and Sogn[32] have measured a few alkali halides dissolved in ethyl alcohol, a liquid similar in constitution to water which has been shown to be almost completely depolymerized at room temperatures.[33] Calculations of solute susceptibility from these measurements show close agreement with the corresponding measurements for solids, in sharp contrast to the distinct difference observed when water is used as a solvent. It seems, then, that depolymerization must be taken into account when water is used as a solvent, but since the difference between the completely depolymerized water susceptibility and that of "normal" water is only about 1 percent according to the measurements of Cabrera and Fahlenbrach,[33] this may not account entirely for the difference between solid and aqueous solution results. (Further reference to this matter will be made in Sec. VI.)

A large number of accurate results for simple compounds such as the alkali halides in various solvents would be necessary for an adequate interpretation of the relatively small amount of data available concerning the relation of ionic diamagnetism to polymerization and hydration. If we ignore these possible effects in solution, we must assume the truth of the Wiedemann relation for the calculation of ionic susceptibilities.

The most recent method for determining the susceptibilities of diamagnetic ions in different states is due to Klemm.[34]

Because no direct experimental method is possible for free ions, he utilizes the experimental results for the inert gases, and assumes a simple proportionality rule, which, in the case of the chlorine ion, Cl^-, may be written as

$$\chi_{\mathrm{Cl^-\,theor.}}/\chi_{\mathrm{A\,theor.}} = \chi_{\mathrm{Cl^-\,exp.}}/\chi_{\mathrm{A\,exp.}}.$$

By using all the theoretical estimates available, save those due to Pauling[35] and Stoner,[36] which deviate considerably from other experimental estimates, Klemm calculates a series of values for the experimental susceptibility of the Cl^- ion, ranging from 25.5 to 32.2, and takes a mean value.

Now the proportionality rule is only valid, assuming a high accuracy for the experimental diamagnetism of the inert gases, if the theoretical methods are reliable from the standpoint of susceptibility ratios; this is not proven for any method. Moreover, the arithmetic mean

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[27] F. H. Lee, Science **104**, 1931 (1946).

[28] J. Farquharson, Phil. Mag. **12**, 283 (1931).

[29] In a later paper, in collaboration with Gray [F. W. Gray and J. Farquharson, J. Sci. Instr. **9**, 1 (1932)] ±0.96 percent is given as the estimated accuracy for the molar susceptibility of hydrochloric acid using the same method of measurement.

[30] P. S. Varadachari, Proc. Indian Acad. Sci. **A2**, 161 (1935); S. R. Rao, Proc. Indian Acad. Sci. **A3**, 188 (1936); S. P. Ranganadham and M. Qureshi, Z. physik Chem. **B33**, 290 (1936).

[31] B. Cabrera and H. Fahlenbrach, Z. Physik, **89**, 166 (1934).

[32] O. E. Frivold and H. Sogn, Ann. Physik **23**, 415 (1935).

[33] B. Cabrera and H. Fahlenbrach, Z. Physik **85**, 568 (1933).

[34] W. Klemm, Z. anorg. u. allgem. Chem. **244**, 377 (1940); **246**, 347 (1941).

[35] See reference 22.

[36] E. C. Stoner, Proc. Leeds Lit. & Phil. Soc. **1**, 484 (1929).

of such a wide range of values can have little significance when we are seeking accurate results.

For dissolved ions, Klemm compares the experimental susceptibility for a compound in solution with the corresponding sum of his "free" ionic values. With cesium chloride, for example, his free ionic values add up to 62.0, whilst Abonnenc's measurement[37] gives 61.4. In the fashion of Weiss's hypothesis,[2] this difference in aqueous solution is attributed to the effect of the Cs^+ ions on the water, thus giving $Cs_{diss}{}^+=33.4$ and $Cl_{diss}{}^-=28.0$ (unchanged). The remaining alkali, alkaline-earth, and halogen ion susceptibilities Klemm then calculates by employing additivity and assuming all the halogen ion susceptibilities, except F^-, are unchanged. The reason for commencing with cesium chloride is simply that any change in the ionic diamagnetism of the cation is likely to be smaller here than for smaller cations.

For crystals, Klemm finds that Brindley and Hoare's experimental values are less in every case than the sum of the appropriate free ionic values. For the salts of a particular cation, this difference is found as a percentage for each and a mean value calculated, thus for lithium salts:

	F	Cl	Br	I	
Li	12.7	28.7	39.7	57.7	Sum of free values
	10.1	23.3	24.0	c.50.0	Brindley and Hoare's measurements.
	2.6	5.4	5.7	7.7	
	20	19	14	14	percent difference

Mean percentage difference = 17

Thus, for Li^+,

$$\chi_{Li^+xtal}=\chi_{Li^+free}-\frac{17}{100}\cdot\chi_{Li^+free}=(0.7-0.1)=0.6.$$

Such a procedure again requires that the halogen ion susceptibilities do not change with change of state; but at the same time, different susceptibilities have to be ascribed to halogen ions in combination with different cations!

The whole series of results for the three states rests on the validity of the proportion rule, and this has not been sufficiently substantiated. Klemm's work has previously suffered severe criticism, and this would seem to be completely justified.

In conclusion to this section, then, it appears that the "observed" susceptibilities of diamagnetic ions do vary with physical state, but that methods of investigating these changes are not yet satisfactory, largely owing to a lack of accurate experimental data.

V. COMPARISONS BETWEEN THEORY AND EXPERIMENT

The extent to which experiment is in accord with the theory which has been proposed for any branch of a particular science is frequently the most certain indicator of the completeness and consistency of that subject. This is especially true of diamagnetism.

Numerical agreement among experimental measurements has not been good, and it is still true to say that for the vast majority of inorganic diamagnetic compounds, the results are not sufficiently reliable to use even for the calculation of approximate values for ionic susceptibilities. For the simpler compounds, however, measurements are in better agreement and hence, we must assume, more reliable, but when the derived ionic values are compared with theoretical ionic values, again we find large discrepancies.

Of the various theoretical methods used for the estimation of ionic susceptibilities, those of Pauling[22] and Stoner[36] are without doubt the most rigorous, yet generally they give values considerably in excess of all deductions from experiment, and this is very likely due to the use of too large screening constants, that is, the amounts by which electrons deeper in the ion than the shell under consideration will diminish the field of the nuclear charge existing in the neighborhood of that shell.

Slater's[9] method has already been outlined under Sec. IB. Its principal advantages are that ionic susceptibilities are easily calculated, and moreover, we have a greater certainty of accuracy for our results since the theory has been made to fit experimental observations of other physical properties. Indeed, we find that the Slater method does give the best agreement with experimental susceptibilities. A modification, due to Angus,[12] in which every sub-group in the electronic configuration is considered separately, provides very similar results, sometimes showing improved, sometimes inferior accord with experiment.

In order to obtain numerical values, all theoretical methods must make recourse to experimental data, although sometimes these are remote from the topic of diamagnetic susceptibility. At the same time, it must be remembered that all experimental methods also require the use of theoretical interpretations of diamagnetism either directly, or indirectly by the use of analogies (e.g., refraction and diamagnetism) for the calculations.

In Table VIII, I have attempted to cover a wide field of experimental and theoretical methods for alkali, alkaline-earth, and halogen ion susceptibilities, in order to make a comparison of the various methods. For the experimental values, the mean measured susceptibilities in aqueous solution of Table IV are employed.

The use of average measurements has frequently been suggested, but when we compare estimates by different methods from the same set of experimental data, this does not seem justifiable (see columns 2, 3, and 4 in Table VIII); if accurate ionic susceptibilities do result from such averaging, it must be entirely fortuitous. One or two empirical methods of "improvement" of such average values have been employed (*e.g.*, Trew[16]), but it is all too simple to denounce such methods on the score of invalid assumptions.

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[37] L. Abonnenc, Compt. rend. **190**, 1395 (1930); **198**, 2237 (1934).

Criticism of the individual methods used in the calculations of the values in the table has already been made. As already mentioned, of the theoretical values, most reliance can be placed on the Slater results, and hence, for a comparison of experimental methods, there is some justification for using the Slater results as reference. By this procedure it immediately appears that the results of the Joos method are badly in error, which must indeed be true. The Angus method, which sums the diamagnetic contribution from every sub-group of electrons in the ion, may be regarded by many as being equally reliable to the Slater method, although it has been criticized by several authors. Even allowing this, however, it makes little or no difference to the present conclusions as regards comparison of experimental with theoretical value.

In column 2, the halogen ion values appear to be low in comparison with the Slater figures while the alkali ion values appear high. Now, the results of the additivity test employed in Sec. II (Figs. 7 to 11 inclusive) indicated an effective paramagnetism for the ions H^+ and Li^+ in aqueous solution and for Li^+ in solids. Also, Fig. 9 shows perhaps an extra diamagnetic effect for the F^- ion in solution; this is rather doubtful, as it rests on the accuracy of one measurement, but at least it agrees with the prediction of a similar effect for this ion in Weiss' work. However, taking both these para- and dia-magnetic effects into account, and employing the Weiss method of starting from halide acid measurements, the predictions of ionic values from solution measurements approximate not only to Slater's theoretical values, but also to Brindley and Hoare's results for the crystal state. They are: Li^+ 1.2; Na^+ 5.1; K^+ 13.1; Rb^+ 20.3; Cs^+ 36.9; F^- 11.0; Cl^- 25.8; Br^- 36.8; I^- 54.4. These figures, of course, would correspond to free state susceptibilities if the adjustment is reliable.

TABLE VIII. Ionic diamagnetic susceptibilities.

Experimental theoretical
free dissolved crystal

	1	2	3	4	5	6	7	8	9[a]
F^-	10.5	—	12.1	—	9.4	8.1	16.9	8.1	7.1
Cl^-	26.5	22.9	18.3	25.3	24.2	29	39.5	25.2	22.3
Br^-	35.4	33.9	30.0	37.1	34.5	54	—	39.2	35.9
I^-	53.6	51.5	47.7	55.4	50.6	80	—	58.5	54.1
Li^+	0.75	3.0	6.7	−0.1	0.7	0.6	0.7	0.7	0.7
Na^+	5.25	8.5	12.5	5.3	6.1	4.2	5.4	4.1	3.7
K^+	14.8	16.6	21.1	13.4	14.6	16.7	17.2	14.1	12.8
Rb^+	22.6	23.4	28.2	20.4	22.0	35	29.4	25.1	23.5
Cs^+	35.4	39.8	44.3	36.6	35.1	55	—	38.7	36.4
Mg^{++}	4.0	7.3	13.6	1.6	4.3	3.2	4.3	3.1	2.8
Ca^{++}	11.6	10.8	18.5	4.5	10.7	13.3	13.1	11.1	10.2
Sr^{++}	19.0	20.8	28.5	14.0	18.0	28	—	21.0	19.7
Ba^{++}	29.9	32.6	41.1	25.3	29.0	46	—	32.6	30.9

[a] Columns:
1. Klemm's method (Slater theory employed).
2. Weiss' method. Start from halide acids, making small cation correction, assume additivity, then take mean values.
3. Joos method. CsI value divided. Remaining ions calculated additively.
4. Brindley method. CsI value divided. Remaining ions calculated additively, Weiss small cation correction being applied.
5. Brindley and Hoare's method for solids.
6. Pauling method.
7. Stoner method.
8. Slater method (recalculated by author using more recent data for fundamental constants).
9. Angus method (recalculated by author using more recent data for fundamental constants).

But we must go no further. Were there a complete set of accurate measurements for the alkali halides, then analysis such as this would assist considerably in the research. Results for some of the compounds (principally rubidium halides and the fluorides) are so uncertain that conclusions are dangerous. That experimental results for the alkaline-earth halides are less accurate than those for alkali halides is well known, and this shows up clearly in a larger variation of apparent ionic susceptibility for the alkaline-earth ions (see Table VIII). A series of researches carried out by Prasad and his co-workers during the past few years shows this variation up even more clearly, and at the same time may help to throw some light on the apparent variation of susceptibility of these ions with conditions. For example, for the Ca^{++} and Sr^{++} ions, Prasad, Dharmatti, and Gokhale[38] measured the susceptibilities of a large number of solid organic and inorganic heteropolar compounds containing these ions; using all available anion estimates, direct subtraction of these numbers leads to the conclusion that the ionic susceptibilities of Ca^{++} and Sr^{++} are less in inorganic compounds than in organic. Average values are: from inorganics, Ca^{++} 10.65, Sr^{++} 22.61; from organics, Ca^{++} 12.33, Sr^{++} 26.36. For barium, even more widely varying values are obtained by this procedure, from which a mean value of 32.3, with deviations up to 20 percent in the separate values is given by Prasad, Dharmatti, and Kanekar.[39] Completing their survey of the alkaline-earth ions in association with Amin, Prasad, and Dharmatti[40] have investigated the case of Mg^{++} ions in a similar way. Again they come to the same conclusion: a large variation of cation susceptibility; from inorganics, 2.91 up to 14.79 (mean = 7.45), from organics, 0.38 up to 13.73 (mean = 7.04). A method is also suggested for deriving an average value for the magnesium ion's susceptibility, but this consists of plotting a linear graph, which, by the simplest considerations of diamagnetism, should not strictly be linear, and the necessary extrapolation employed is certainly not valid. The most severe criticism of this work is that use is made of all available estimates for anion susceptibilities without discrimination as regards reliability.

These considerations serve to underline the difficulty of making comparisons between experiment and theoretical ionic diamagnetic susceptibilities. Either some reliable way of correcting experimental results to "free" values must be found, or a theory derived which will

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[38] Prasad, Dharmatti, and Gokhale, Proc. Indian Acad. Sci. **A20**, 224 (1944).

[39] Prasad, Dharmatti, and Kanekar, Proc. Indian Acad. Sci. **A16**, 307 (1942).

[40] Prasad, Dharmatti, and Amin, Proc. Indian Acad. Sci. **A26**, 312 (1947).

give ionic susceptibilities as a function of conditions. The two requirements cannot really be separated; they express one and the same need.

VI. NOTE ON THE ACCURACY OF EXPERIMENTAL MEASUREMENTS

Very accurate measurements of susceptibility are required if reliable ionic values are to be derived. Until recently, these have not been forthcoming. The very numerous difficulties in the search for a technique of accurate measurement are not generally appreciated. First, regarding the substance itself, purity is of essential importance. The presence of minute quantities of ferro- or para-magnetic impurities can completely vitiate the results. In certain cases it is impossible to remove completely all traces of foreign elements from the compounds to be measured and here corrections must be made, but generally these are sufficiently small as to cause no great error even if our method of correction is slightly at fault. (In Brindley and Hoare's work, the largest correction which they had to employ was about 2 percent.) The effective susceptibilities of ferromagnetic elements in the various forms in which they may exist as impurities are not certain, but where these corrections are small (less than 1 percent) we can be reasonably sure that the calculations are sufficiently correct; if error is introduced, it will almost certainly be less than other errors involved in the measurement.

In the case of powdered crystalline solids (e.g., Brindley and Hoare), there is the uncertainty in density due to possible variations in the degree of packing, and this, coupled with errors in the magnetic measurements, seems to point to a limit of accuracy in the neighborhood of 0.5 percent. For solutions, measurements can be made more accurately since there is no packing error, and further, the Quincke method may be used (except where only small amounts are available) which, in the light of present data, undoubtedly provides an accuracy better than any other of the existing methods.

Since measurements with powdered solids are necessarily limited in accuracy, it may be we shall have to rely on solution measurements to obtain a sufficient accuracy of results for the compounds here under consideration. Up to the present, data seem to show that the Wiedemann law is obeyed quite rigorously by the alkali and alkaline-earth halides in aqueous solution, and with this assumption we can therefore estimate the probable error in the determination of the solute susceptibility. In the relation,

$$p\cdot\chi_u+(100-p)\cdot\chi_v=100\cdot\chi_s$$

(see reference 3) χ_v, the solvent susceptibility will be assumed accurate to a high degree. (Auer's determination[41] for water is probably the most accurate measurement yet carried out on a diamagnetic substance.) There are thus two sources of error apart from impurity effects: (a) Errors in the purely magnetic measurement of solution susceptibility, χ_s. (b) Errors in the value of the concentration, p.

The Wiedemann law shows that χ_u, the solute susceptibility, is a function of χ_v, χ_s, and p, hence the error in χ_u due to errors in χ_v, χ_s, and p may be written as

$$\delta\chi_u=(\partial\chi_u/\partial\chi_v)\cdot\delta\chi_v+(\partial\chi_u/\partial\chi_s)\cdot\delta\chi_s+(\partial\chi_u/\partial p)\cdot\delta p.$$

If the error in the measurement of solution susceptibility be considered alone, then this gives rise to an error in χ_u of

$$\delta\chi_u=(100/p)\cdot\delta\chi_s. \tag{1}$$

For an error in the concentration, the error in χ_u is

$$\delta\chi_u=[(\chi_v-\chi_u)/p]\cdot\delta p=100\cdot[(\chi_v-\chi_s)/p^2]\cdot\delta p. \tag{2}$$

It is clear from both Eqs. (1) and (2) that for maximum possible accuracy, p should be large. For the alkali and alkaline-earth halides, 30 percent seems to be about the highest concentration used by most workers, except for one or two isolated substances such as potassium iodide. This figure will therefore be used in order to derive a limiting accuracy for past measurements.

The error due to inexactitude in the concentration determination is likely to be very small. There is no difficulty in finding the ratio of the two weighings which are necessary to an accuracy of 0.1 percent, then putting $p=30$ percent, $\delta p=0.1$ percent, $\delta\chi_u=(\chi_v-\chi_s)/90$. For sodium iodide, for instance, $(\chi_v-\chi_s)$ is approximately 0.09×10^{-6} at 30 percent concentration, thus $\delta\chi_u\approx1\times10^{-9}$. χ_u itself is about 0.4×10^{-6}, so the error is about 0.25 percent. On the other hand, if only weak concentrations are employed, the accuracy soon deteriorates; in the case of sodium iodide, if concentrations of only 10 percent were used, then the error in χ_u resulting from $\delta p=0.1$ percent would rise to 0.8 percent.

To error in the solution susceptibility measurement, the result for χ_u is most sensitive. For an error of 0.1 percent in this measurement, the corresponding error in χ_u at 30 percent concentration is 0.33 percent.

It is clear, then, that taking an individual measurement for a dissolved substance, with an accuracy of 0.1 percent for both p and χ_s, no better accuracy than 0.6 percent can be relied upon for χ_u. However, a series of measurements is invariably made, so the position is not so unsatisfactory as would appear from this elementary analysis, but it is obvious that, even taking a large number of measurements, a very high accuracy is required for both p and, more especially, χ_s, particularly in those cases where the concentration which can be used is limited to low values. Very few of the methods so far employed for the measurement of diamagnetic susceptibility are capable of giving much better accuracy then 0.5 percent for χ_s, and this inevitably means inaccuracies of about 1.5 percent for the individual measurements of χ_u. This is quite large, and even taking many measurements for a given compound at a series of concentrations, we cannot be sure of the final ac-

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[41] H. Auer, Ann. Physik **18**, 593 (1933).

curacy obtained when the usual graphical process of averaging has been effected.

A pointer to such a figure of merit is perhaps obtained from the results of Frivold and Olsen.[20] If we "adjust" their measurements for the alkali halide susceptibilities so that ionic additivity is strictly adhered to, and simultaneously assume that ionic susceptibilities are independent of the compound, then the amount by which each molar susceptibility must be "corrected" is nowhere more than 0.5 percent.[42] It seems reasonable to assume that this is the order of accuracy of these results, for it has already been shown here that, apart from the lithium ion, the principle of ionic additivity in aqueous solutions is fairly firmly established.

Up to now in this paper, the susceptibility of water, as measured by Auer,[41] has been assumed accurate to a high degree, but, taking into account the work of Cabrera and Fahlenbrach[31] (see Sec. IV), it is doubtful whether such a measurement is still valid for water when ions are present.

If there is an error in the solvent susceptibility value of $\delta\chi_v$, then, by the Wiedemann law, the corresponding error in solute susceptibility is given by

$$\delta\chi_u = (\partial\chi_u/\partial\chi_v)\cdot\delta\chi_v = -[(100-p)/p]\cdot\delta\chi_v. \quad (3)$$

Cabrera and Fahlenbrach discovered an apparent variation in the susceptibility of water with concentration of a dissolved substance, and this they attributed to depolymerization of the water aggregates. For complete depolymerization, they find an increase in the susceptibility of water of about 1 percent. Now, by Eq. (3), it is obvious that such a change as this will effect a relatively large alteration in the calculated value of the solute susceptibility from solution measurements. It will, in fact, correspond to values of $\delta\chi_v$ up to -1 percent, and by Eq. (3), for a 30 percent concentration which produces complete depolymerization, there will be an error of $+2\frac{1}{3}$ percent in the value for χ_u. Cabrera and Fahlenbrach also found a hydration effect which occurred, for potassium iodide solutions, only at temperatures higher than the normal (room) temperature of measurement; ignoring any possible hydration effect at room temperatures then, it is interesting to see that the figure of $+2\frac{1}{3}$ percent calculated here already lessens the gap between results from solid and solution measurements. The mean difference, $(\chi_{\text{diss}}-\chi_{\text{solid}})$ is about 4 percent.

Cabrera and Fahlenbrach had investigated both concentration and temperature variation of aqueous solutions of potassium iodide only, and clearly, some repetition of the work using a number of different dissolved substances would be of great advantage. If the diamagnetic susceptibility of water corresponding to varying degrees of polymerization were known, and if numerical values for the variation of polymerization with concentration of any particular dissolved substance were available, then, and only then, could it be sure that the relevant susceptibility for water were being used for results calculated from measurements on dissolved compounds.

In this section it has been seen that most results suffer from inaccuracies in the measurement of solution susceptibilities and concentrations, and also from uncertainties in the solvent susceptibility values to be employed in the calculations. With the combination of three such difficulties, quite apart from the interpretation of results, it is hardly surprising that ionic diamagnetic susceptibility estimates of various authors are so different!

VII. CONCLUSION

In trying to derive the diamagnetic susceptibilities of the simpler ions, it transpires that a large number of new measurements is required with a high degree of accuracy (around ±0.2 percent). Only with such figures can several of the problems involved be satisfactorily solved. To date, very few measurements on compounds are even claimed to have accuracies of this order, and those few do not cover a wide enough range of compounds for a really worth-while analysis in terms of ionic diamagnetism.

One new method due to Broersma[43] is claimed to have an accuracy of ±0.1 percent for diamagnetic measurements, but this does not appear to be so from the figures published. The method does, however, show some advantages over previous arrangements in that the measurement is electrical and not mechanical. It may be that methods such as this will provide the necessary high accuracies; the author is at present engaged upon setting up a new method in which the diamagnetic effect is measured directly as an ac voltage.

Many of the suggested methods for the derivation of ionic susceptibility values have been shown to be unreliable, and an increased number of accurate measurements, including temperature variation investigations of solutions, would surely help to confound more effectively such doubtful procedures. Without such measurements one is led to read more into the data than is justifiable, and this is indeed both an easy and dangerous step. In the words of Van Vleck, "One could go on with no end of numerical discussion on the best way of juggling the results. . . ."[44]

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[42] A method of such "adjustment" of molar susceptibilities is given by Veiel (see reference 8).

[43] S. Broersma, Rev. Sci. Instr. **20**, 660 (1949).

[44] Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).