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List of Publications.

1. Physical properties of mixtures of Acetone and Bromoform.
Trans. Far. Soc. No. 133. Vol. 28 (1932). pp. 509-514.
2. Some physical properties of mixtures of certain organic liquids.
Trans. Far. Soc. No. 151. Vol. 29 (1933). pp. 1310-1318
3. Magnetic susceptibility and other properties of binary mixtures of organic liquids.
Trans. Far. Soc. No. 180. Vol. 32. (1936), pp. 701-708
4. Diamagnetic susceptibility of heavy water.
Letter to Nature. Vol. 137 (1936). p. 706
5. Diamagnetic susceptibility of heavy water.
Letter to Nature, Vol. 137 (1936). p. 998
6. Diamagnetism of mixtures of organic liquids.
Letter to Nature, Vol. 138 (1936) p. 974
7. Diamagnetic susceptibility of Thallium compounds.
Trans. Far. Soc. No. 188, Vol. 32 (1936) pp. 1658-1667
8. Ionic diamagnetic susceptibility and diamagnetic correcting constants.
Trans. Far. Soc. No. 245, Vol. 37 (1941) pp. 476-492
9. The diamagnetic susceptibility of some Alkyl and Aryl Halides.
Trans. Far. Soc. No. 282, Vol. 41 (1945) pp. 439-449
10. Diamagnetic susceptibility of Ammonium compounds.
Trans. Far. Soc. No. 315. Vol. 45 (1949), pp. 217-223
11. The Diamagnetic susceptibility of some Substituted Ethyl Malonates.
Trans. Far. Soc. No. 340. Vol. 47 (1951) pp. 365-370
12. The diamagnetic susceptibility of some Alkyl Benzenes and Higher Aliphatic Hydrocarbons.
Trans. Far. Soc. No. 366, Vol. 49 (1953) pp. 604-511

P.T.O.

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PHYSICAL PROPERTIES OF MIXTURES OF ACETONE AND BROMOFORM.

BY VIOLET CORONA GWYNNE TREW.

Received 16th February, 1932.

A reference to the literature dealing with physical properties of binary mixtures of organic liquids shows that while considerable work has been done on mixtures of acetone and chloroform, very few physical properties have been determined for mixtures of acetone and bromoform. Qualitative determination shows that a considerable heat change results on mixing acetone and bromoform.

The following investigation was carried out to determine if similar deviations from the mixture law occurred to those obtained by previous investigation for mixtures of acetone and chloroform. The following represent the results obtained for the properties; density (D_4^{25}), heat change on mixing, specific heat, viscosity and refractive index, for a series of mixtures of acetone and bromoform.

Experimental.

Preparation of Mixtures.—The purest specimens of acetone and bromoform obtainable were procured and were both submitted to further purification, by careful drying and fractional distillation until a constant boiling fraction was obtained. The density was then determined as a further test of purity, the following values being obtained.

Acetone	$D_4^{25} = 0.7847.$
Bromoform	$D_4^{25} = 2.8794.$

Throughout the experiments the bromoform was kept in the dark and as far as possible out of contact with the air in order to prevent decomposition.

A series of nine mixtures was then made up by starting with pure acetone at one end and adding increasing amounts of bromoform. A series was thus obtained having the approximate compositions of 10, 20, 30, moles per cent. of bromoform and ending with pure bromoform. The mixtures were made up by adding the approximate calculated volume of bromoform from a burette to a known volume of acetone to give the required composition, and the exact composition was then determined by weight, weighings being taken to the nearest 0.1 milligram. The liquids were weighed in a small flask, by difference, so that the small buoyancy correction involved could be neglected, as being almost the same for all weighings. The mixtures were then sealed in small glass flasks of the exact capacity of the contained liquid and kept in the dark until required for the experiments.

Table I. Column 2 gives the actual compositions in moles per cent. of bromoform in the mixtures used.

TABLE I.—ACETONE-BROMOFORM MIXTURES.

Mixture.	Composition in Moles. Per Cent. Bromoform.	Experimental Density D_4^{25} .	Density Percentage Deviation.	Viscosity (η^{25}) Experimental Value. ($\times 10^3$).	Viscosity Percentage Deviation.
Acetone	0	0.7847	0	3.05	0
I.	9.69	1.024	3.65	4.07	11.33
II.	20.14	1.270	4.98	5.29	15.36
III.	27.27	1.438	6.05	—	—
III.	33.20	—	—	6.96	16.35
IV.	42.80	1.784	6.13	8.47	14.02
V.	49.52	1.931	5.98	9.54	12.64
VI.	59.74	2.127	4.47	11.31	9.88
VII.	67.66	2.283	3.68	12.68	8.12
VIII.	79.97	2.507	1.95	15.03	4.63
IX.	91.66	2.720	0.59	17.30	1.76
Bromoform	100	2.879	0	18.94	0

Determination of Density.—The density of the pure liquids and of the mixtures was determined at 25° C. A small pycnometer of 2 c.c. capacity was used, and the density calculated from the mean of three determinations. The theoretical value of the density had the Mixture Law been obeyed was calculated, and hence the deviation in density was determined by difference.

Table I. shows in column 3 the observed density values, and in column 4 the calculated percentage deviation.

If a curve of deviation against composition is plotted, it will be seen that the maximum deviation occurs between the 30 and 50 moles per cent. composition, a deviation of as much as 6 per cent. being obtained here.

Viscosity.—The viscosity coefficient was determined for each of the pure substances and for the mixtures, using a form of the Poiseuille viscosimeter as modified by Ostwald. The viscosimeter was chosen of such dimensions that the minimum time of flow taken by any of the liquids used was not less than 60 seconds, so that from the dimensions of the viscosimeter used, Reynolds' criterion $v < 1000 \eta/\eta d$ for non-turbulent flow was well satisfied. All determinations were carried out at 25° C.

The viscosity of the pure liquids and the mixtures was calculated from the mean of three determinations differing by not more than $\frac{1}{4}$ second from each other, using the formula $\eta_1 = \frac{d_1 t_1}{dt} \times 8.91 \times 10^{-3}$ where η_1 = viscosity coefficient of the liquid, d_1 its density and t_1 the time of flow, and d and t represent the density and time of flow for water using the value 8.91×10^{-3} for the viscosity of water.

Table I. shows the experimental values in column 5. Column 6 represents percentage deviations from the theoretical values that should be obtained if the Mixture Law were obeyed, calculated from the viscosity of the pure constituents. On plotting the deviations a maximum deviation of about 16 per cent. is obtained at just over 30 moles per cent. composition.

Refractive Index.—The refractive index of the mixtures and the constituents was determined at 25° by means of a Pulfrich refractometer, using sodium light. The angle of refraction was taken in all cases from the mean of three determinations differing from each other by not more than one minute of arc.

Table II. shows the experimental refractive index in column 2, while column 3 gives the percentage deviation. Here a maximum deviation is given at the 50 moles per cent. composition, the deviation being about 0.8 per cent. at this point.

TABLE II.—ACETONE BROMOFORM.

Mixture.	Refractive Index Experimental.	Refractive Index Percentage Deviation.	Sp. Refractivity.	Mol. Refractivity.
Acetone	1.35657	0	.2794	16.21
I.	1.38342	0.275	.2280	17.54
II.	1.41143	0.491	.1994	19.40
III.	1.43046	0.619	.1798	19.99
IV.	1.46887	0.720	.1563	22.08
V.	1.48558	0.760	.1487	22.98
VI.	1.50838	0.647	.1401	24.43
VII.	1.52637	0.588	.1344	25.52
VIII.	1.55251	0.368	.1274	27.23
IX.	1.57705	0.146	.1219	28.82
Bromoform	1.59445	0	.1179	29.80

From the refractive index values the specific and molecular refractivities were calculated using the Lorentz and Lorenz formulæ

$$r = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{1}{d},$$

and

$$R = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{m}{d},$$

where r is the specific and R the molecular refractivity, μ the refractive index, d the density and m the molecular weight. In the case of the mixtures a mean molecular weight was calculated from the proportions of each constituent present.

Table II. columns 4 and 5 show the values obtained for these. On plotting the specific refractivity against the percentage composition in grams per cent. a straight line was obtained, and similarly on plotting the molecular refractivity against the composition in moles per cent. only a very slight positive deviation was obtained, the curve being very slightly above the straight line joining the two pure constituents.

The straight line obtained on plotting the specific and molecular refractivities against composition in grams and moles per cent. respectively does not indicate that the mixture is ideal for these properties. If the refractive index and density, calculated from the Mixture Law, for each mixture are substituted in the equation $r = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{1}{d}$ and the results obtained plotted against compositions in grams per cent, a curve is obtained lying slightly above the straight line joining the pure constituents. Hence the experimentally obtained straight line represents an actual deviation. That this deviation is not merely due to the density

deviation may be shown by using the theoretical refractive index and experimental density values in the above equation when again a curve results slightly below the straight line. Hence the experimental deviation is an actual, though small, deviation in refractive index.

Heat of Mixing.—The heat change, on mixing, was determined by the usual calorimetric method, using a silver-plated copper calorimeter. All readings were corrected for radiation. The usual precautions, *i.e.* use of double-walled thermal vessels, etc., were taken to prevent loss of heat by cooling during the experiments. The heat change on mixing was calculated from the equation

$$H = \frac{c(m_1 + m_2) \left(t_3 - \frac{t_1 + t_2}{2} \right) + w(t_3 - t_1)}{m_1 + m_2}$$

where H = heat change in calories, c specific heat of the mixture, m_1 and m_2 the weights of the two constituents, t_3 the final temperature at the time of mixing, t_1 and t_2 the two initial temperatures and w the water equivalent of the calorimeter and thermometer.

The specific heat for each mixture, required in this calculation, was determined by the method of mixtures, using a known weight of pure silver heated to 60° C.

Table III. shows in column 2 the specific heat of each of the first set of mixtures. Column 3 gives the compositions of the mixtures used for the heat change on mixing, while column 4 shows the values of the quantity of heat evolved in calories per gram for each mixture.

TABLE III.—ACETONE BROMOFORM.

Mixture.	Specific Heat.	Composition for Heat of Mixing Only. Per Cent. Bromoform in Moles.	Specific Heat for Heat of Mixing Calculation. (From Specific Heat Curve.)	Heat of Mixing in Calories Per Gram.
Acetone	.513	0	—	0
I.	.402	9.01	.406	1.06
II.	.323	20.68	.320	1.93
III.	.257	29.96	.271	2.27
IIIb.	—	37.15	.244	2.32
IV.	.225	—	—	—
V.	.216	49.52	.208	2.40
VI.	.182	59.48	.183	1.99
VII.	.169	67.45	.168	1.60
VIII.	.145	80.04	.150	1.09
IX.	.132	92.87	.131	0.55
Bromoform	.128	100	—	0

Theoretical.

From a consideration of the results obtained, it is evident that mixtures of acetone and bromoform show marked deviations from the Mixture Law. In the case of every property investigated a deviation was obtained. Even in the case of the refractive index a maximum deviation of nearly 0.8 per cent. was obtained.

This result is similar to those of Zawidski¹ and Hubbard² who found

¹ Zawidski, *Z. physik. Chem.*, **35**, 129, 1900.

² Hubbard, *Z. physik. Chem.*, **74**, 207, 1910.

for mixtures of acetone and chloroform a deviation of the refractive index values from the ideal values.

Quite a number of mixtures of organic liquids have been shown to give considerable deviations for some properties and yet exhibit none in the case of the refractive index. The deviation obtained in the case of this pair of liquids, as in the case of acetone and chloroform, indicates that some very marked change takes place on mixing the two liquids. It has been suggested that in the case of acetone and chloroform there are two types of change going on. (1) A formation of a compound between one molecule of acetone and one of chloroform, when these are

mixed in the solution giving a compound of the type $\begin{array}{c} \text{Me} \quad \text{OH} \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{Me} \quad \text{C} (\text{Cl}_3) \end{array}$,
or (2) A gradual deassociation of the originally associated acetone molecules as these are more and more diluted by the addition of chloroform.

The experimental results obtained in the investigation would indicate the same two tendencies at work in the case of mixtures of acetone and bromoform.

The deviations are in general somewhat larger than those for mixtures of acetone and chloroform, which would be expected from the greater divergence in density and molecular weight of the molecules of the two constituents. If the changes that take place on mixing were solely due to compound formation (one molecule + one molecule) the percentage deviation curves should be symmetrical about the 50 moles per cent. axis. That this is not the case can be seen on plotting the results, when, for all properties, a decided bias to the right of this line is obtained, mixtures containing less than 50 moles per cent. bromoform showing a higher deviation than corresponding mixtures on the other side of the 50 moles per cent. line. This bias might be explained as due to the formation of a co-ordination compound containing the acetone and bromoform in proportions, other than equimolecular. The fact that a well-defined maximum is not obtained at the same point for all properties makes this appear unlikely. This shift to the side of the 100 per cent. acetone concentration is explainable by considering that the acetone molecules which are known to be associated³ undergo de-association on adding the bromoform.

Thus the mixtures containing the least bromoform have actually a greater proportion of unassociated molecules. The deviation curves therefore show a bias to the acetone end. In addition, then, to the probable formation of a compound the deviations indicate that the properties of the mixture are influenced by at least one other factor, probably a gradual deassociation of the acetone.

The heat of mixing and density deviation curves show maxima at the same point, while the viscosity deviation curve gives one at a smaller, and the refractive index at a greater percentage of bromoform. The fact that the maximum deviation does not occur at the same point for every property appears to indicate that the factors causing deviation are considerably complex, some properties being more influenced than others. This would be expected as some properties are more truly molecular than others.

³ Beckmann, *Z. physikal. Chem.*, **2**, 715, 1888.

Summary.

1. The density, viscosity, refractive index, heat of mixing and specific heat of a series of mixtures containing varying proportions of acetone and bromoform have been determined.

2. In all cases deviations from the mixture law that should govern the behaviour of ideal mixtures are obtained.

3. Such deviations are similar to those obtained by other investigators for mixtures of acetone and chloroform.

4. It seems probable that, as in the case of mixtures of acetone and chloroform, the deviations are due to molecular-compound formation between the two constituents, modified by other factors such as deassociation of the one constituent in the presence of the other.

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SOME PHYSICAL PROPERTIES OF MIXTURES OF CERTAIN
ORGANIC LIQUIDS

SOME PHYSICAL PROPERTIES OF MIXTURES OF CERTAIN ORGANIC LIQUIDS.

BY VIOLET CORONA GWYNNE TREW AND GERTRUDE MARGARET CLARE WATKINS.

Received 12th October, 1933.

A number of physical properties of mixtures of certain aliphatic saturated alcohols have been investigated in order to compare the value of the various properties in studying deviations from the Mixture Rule and hence the conditions existing in liquid mixtures. The value of determinations of magnetic susceptibility in giving indications of such deviations was especially considered.

Four sets of mixtures were investigated each containing normal butyl alcohol as one constituent with normal propyl, isobutyl, isopropyl or γ -amyl alcohols as the other constituent. These liquids are members of a closely related aliphatic series so would be expected to show only small deviations. For purposes of comparison, a fifth mixture was considered, in which the two constituents were widely dissimilar and so would probably show marked deviations on mixing. Acetone and trichloroethylene, which contains both an unsaturated linkage and the strongly electro-negative chlorine atoms, were chosen as the pair of liquids for this mixture. Hence it was hoped that a good indication would be obtained of the relative suitabilities of magnetic susceptibility and other properties for investigating deviations in liquid mixtures, both in the case of related and widely differing substances. The properties measured include density, refractive index, magnetic susceptibility, and for some sets of mixtures viscosity, specific heat and heat of mixing.

Experimental.

A number of mixtures, in some cases seven and in other cases nine, of the two constituent liquids was made up accurately as described in a previous communication,¹ after rigorous purification of the constituents. Table I. gives the physical constants as determined for each of the pure liquids. Measurements of density, refractive index, viscosity, specific heat and heat of mixing were made as described previously.¹ Density determinations were made to the fifth place for mixtures showing slight deviations, to the fourth place for the acetone-trichloroethylene mixture which gave more marked deviations. Measurements of magnetic susceptibility were carried out by means of a modified Gouy method using an apparatus similar in principle to that described recently by Sugden.² A column of the liquid under investigation, of constant length, was suspended vertically so that the lower end was in a maximum homogeneous magnetic field, and the upper end in a region of no field. The force F exerted as a vertical pull on a material of permeability μ_1 suspended in a medium of permeability μ_2 is given by

$$F = \frac{\mu_1 - \mu_2}{8\pi} \cdot A(H_1^2 - H_2^2)$$

¹ Trew, *Trans. Faraday Soc.*, 28, 509, 1932.

² Sugden, *J.C.S.*, 161, 1932.

ACCOUNT
OF
MAGNETIC
BALANCE

TABLE I.—PHYSICAL CONSTANTS OF PURE LIQUIDS USED.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Liquid.	B.Pt.	Mean Density.	Refractive Index.	Viscosity.	Specific Heat.	Mass Suscept.	Molecular Suscept.	Molecular Suscept.
	Degrees Centigrade.	D ₂₅ ²⁵ .	n _D ²⁵ .	η ₂₅ .	Calories per Gram.	— 10 ⁶ χ _m .	(Calc.)	From Pascal's Values.
<i>N</i> -butyl alcohol .	117.25 ₇₆₀	0.80849	1.39748	0.025641	0.591	0.7908	58.58	58.3
<i>N</i> -propyl alcohol .	96.6 ₇₇₄	0.80236	1.38343	0.019666	—	0.7870	47.22	46.4
<i>Iso</i> -propyl alcohol .	81.6 ₇₄₅	0.78343	1.37538	0.020087	0.650	0.7930	47.63	46.4
<i>Iso</i> -butyl alcohol .	107.5 ₇₆₁	0.80041	1.39387	0.033556	—	0.8094	59.89	58.3
<i>Iso</i> -γ-methylbutyl (γ amyl alcohol) .	130.1 ₇₄₉	0.81286	1.40781	0.037563	—	0.8060	70.93	70.2
Acetone .	55.80 ₇₆₀	0.7847	1.35730	—	0.513	0.5772	33.52	33.9
Trichloroethylene	86.60 ₇₅₈	1.4550	1.47488	—	0.227	0.4961	65.15	67.9

where H_1 is the field at the lower, H_2 at the upper end and A is the area of cross-section of the material. If H_2 is zero and $\mu = 4\pi\chi \cdot d$ where χ is the magnetic mass-susceptibility and d the density then

$$\chi = \frac{2El}{w(H_1^2)} + \frac{(\chi \cdot d)_{air} \cdot lA}{w}$$

(where l = length of column, w the weight of liquid in the column, and substituting for $d = w/lA$). Of these quantities $(\chi \cdot d)_{air}$ is 0.03×10^{-6} v and w are directly measured, H_1 is constant for a given aperture of pole piece, l is constant for a given length of material whence

$$10^6\chi = \frac{\alpha F}{w} - \frac{V \cdot 0.03}{w}$$

where α is a constant for the apparatus using a constant length of material. If F is measured in milligrams, w in grams, v in cubic centimetres then

$$\alpha = \frac{2l \times 10^6 \times 981}{H_1^2 \times 1000}$$

For the present investigation with liquids, a balance of the Bunge type was used, sensitive to 0.01 of a milligram, modified so that the lever was worked from the right-hand side. The left-hand scale pan and support were replaced by a light aluminium support and a disc of the same dimensions as the right-hand pan, which carried on its lower side a hook. From the hook was suspended a fine platinum wire which passed through a hole in the floor of the balance-case and bench. To the lower end of this wire was attached a copper stirrup from which was suspended the tube containing the liquid under investigation. The length of platinum wire was adjusted so that the inside meniscus of the bottom of the tube was exactly level with a mark on the centre of the pole pieces of an electro-magnet arranged so that the gap between the pole pieces came vertically beneath the hole in the bench. The pole pieces of the electro-magnet

were detachable so that a variety of pole pieces could be used with the same magnet.

Since switching on the electro-magnet caused a considerable movement of the pole pieces towards each other, these were maintained at a constant distance by a brass distance piece kept in position on the top of the pole pieces by means of screws, and with a circular hole in the centre through which the tube containing the liquid passed freely. By having a number of distance pieces of varying sizes the distance between the pole pieces and hence strength of the field could be varied over a wide range.

Experiments were carried out to determine the best aperture and strength of field to use, and it was found that a current of 3 amperes and 220 volts passing through magnet coils of 20,000 turns produced a field of about 5000 gauss, when the aperture between the pole pieces was 1.2 cm. This aperture and field gave the largest pull for the liquids investigated. The aperture was maintained at 1.2 cm. throughout the experiments with organic liquids, although for other substances other apertures might be more convenient.

The amperage was controlled by means of a variable rheostat, in series, and was registered by an ammeter in the circuit. A two-pole switch was employed to switch the current, supplied by the mains, on and off.

The field vertically above the pole pieces was then explored, in a number of experiments in which the tube was filled with water and gradually raised using a shorter and shorter suspension. At a height of 5 cm. above the centre of the pole pieces, the pull was only 1 per cent. of its original value becoming zero at 6 cm. above the mark. Hence in all determinations a column of liquid between 6.5 and 7.5 cm. in length was used, a mark being etched on the tube and the volume determined to this point. In this way a constant length l and volume V were ensured and the upper level of the liquid under investigation was well within the region of zero field. The field was constant for 0.4 cm. either side of the centre mark ensuring that, even when weighing by oscillations, the bottom of the liquid was always well within the region of uniform maximum field.

The pull on a known volume of liquid was determined in the following way. The tube was weighed with the magnetic field off and then on, the liquid was measured out by means of a pipette constructed to deliver the volume of liquid to fill the tube exactly to the mark. The tube and liquid were then weighed in and out of the field. The value for the pull on the empty tube was redetermined during the course of the experiments and was found to be sensibly constant, hence an average value was taken and used throughout, being subtracted in each case from the total pull on the liquid and tube.

Weighings were made to 0.01 mg. the last place being determined by the oscillation method, using standardised weights and allowing only small amplitudes of swing to ensure that the tube did not swing out of the uniform field. The magnet and all apparatus below the bench was boarded in to prevent draughts. In addition, the suspension from the bench down to the top of the stirrup was surrounded by a copper tube to shield from draughts and sudden changes of temperature. The readings in and out of the magnetic field were made very rapidly so that they should be made at the same temperature as nearly as possible. A thermometer was placed between the pole pieces, and results were considered untrustworthy if the temperature rose more than 1° C. during the determination, as convection currents might be set up which would affect the readings. In order to avoid heating effects the current was kept on for as short a time as possible. The magnet coils were cooled between readings by an electric fan. Even with these precautions variations of 0.05 mgrms. were sometimes found, which were between 0.5-1.5 per cent. of the total pull. To minimise these, each reading was repeated several times and an average value taken.

TABLE II.

Mixture.	Gram Mol. Per Cent. <i>n</i> -Butyl Alcohol.	Density D_{25}^{25} .	Refractive Index at 25°.	Viscosity at 25°. $\times 10^3$.	Mass Susceptibility at 25°. $\times 10^6$.
<i>N</i>-Butyl Alcohol—<i>Iso</i>-Propyl Alcohol.					
<i>Iso</i> -propyl alcohol	0	0.78343	1.37538	2.0087	0.7939
I.	10.26	0.78662	1.37810	2.0571	0.7936
II.	20.12	0.78946	1.38086	2.1048	0.7952
III.	30.20	0.79242	1.38325	2.1452	0.7947
IV.	40.45	0.79533	1.38560	2.2074	0.7963
V.	50.86	0.79776	1.38767	2.2686	0.7974
VI.	60.02	0.79991	1.38967	2.3274	0.7962
VII.	73.40	0.80318	1.39233	2.4017	0.7975
VIII.	79.64	0.80462	1.39386	2.4371	0.7969
IX.	90.21	0.80675	1.39580	2.5059	0.7944
<i>n</i> -butyl alcohol	100	0.80888	1.39747	2.5628	0.7916
<i>N</i>-Butyl Alcohol—<i>n</i>-Propyl Alcohol.					
<i>N</i> -propyl alcohol	0	0.80236	1.38343	1.9666	.7870
I.	10.09	0.80331	1.38513	2.0241	.7874
II.	20.00	0.80402	1.38674	2.0816	.7878
III.	30.13	0.80460	1.38820	2.1355	.7899
IV.	40.26	0.80544	1.38987	2.1945	.7905
V.	50.09	0.80605	1.39128	2.2540	.7926
VI.	60.55	0.80653	1.39259	2.3189	.7941
VII.	62.79	0.80663	1.39293	2.3261	.7941
VIII.	79.83	0.80735	1.39504	2.4316	.7940
IX.	89.92	0.80792	1.39634	2.4941	.7933
<i>n</i> -butyl alcohol	100	0.80841	1.39749	2.5750	.7916
<i>N</i>-Butyl Alcohol—<i>Iso</i>-Butyl Alcohol.					
<i>Iso</i> -butyl alcohol.	0	0.80041	1.39387	3.5556	0.8094
I.	9.82	0.80117	1.39426	3.2385	0.8102
II.	20.07	0.80219	1.39474	3.1106	0.8111
III.	30.10	0.80292	1.39518	3.0157	0.8112
IV.	40.46	0.80378	1.39548	2.9354	0.8101
V.	50.26	0.80441	1.39584	2.8590	0.8080
VI.	62.61	0.80536	1.39638	2.7724	0.8069
VII.	70.24	0.80613	1.39658	2.7262	0.8025
VIII.	80.01	0.80671	1.39690	2.6719	0.7995
IX.	91.78	0.80780	1.39719	2.6076	0.7925
<i>n</i> -butyl alcohol	100	0.80839	1.39749	2.5569	0.7900
<i>N</i>-Butyl Alcohol—<i>Iso</i>-γ-Methyl-Butyl-Alcohol (γ-Amyl).					
γ -amyl alcohol	0	0.81286	1.40781	3.7563	0.8060
I.	10.33	0.81241	1.40706	3.6200	0.8056
II.	20.40	0.81191	1.40625	3.4722	0.8057
III.	29.77	0.81153	1.40538	3.3432	0.8031
IV.	40.26	0.81112	1.40449	3.2105	0.8001
V.	50.05	0.81067	1.40350	3.0928	0.7974
VI.	60.46	0.81033	1.40216	2.9719	0.7965
VII.	69.96	0.80988	1.40128	2.8507	0.7945
VIII.	80.15	0.80923	1.40010	2.7457	0.7868
IX.	91.72	0.80871	1.39871	2.6152	0.7833
<i>n</i> -butyl alcohol	100	0.80827	1.39749	2.5617	0.7776

The magnetic susceptibility was then calculated from the formula, the value of α having previously been obtained by a series of experiments with pure crystalline solids, and certain pure organic liquids, of well established susceptibility. Crystalline copper sulphate, nickel ammonium sulphate, ferrous sulphate and ferrous ammonium sulphate were used for the solids and acetone, benzene and chloroform for the liquids. The values obtained for α using the solids differed by as much as 5 per cent., while those obtained for the liquids differed among themselves by only 0.5 per cent. The mean of both sets of readings was, however, the same, *i.e.*, $\alpha = 0.660$. This value was therefore used throughout the subsequent experiments.

Results.

Table I. shows in columns II.-VII. the physical constants determined for each of the pure liquids, while column VIII. gives the molecular susceptibilities which are in good agreement with the theoretical values in column IX. calculated from Pascal's atomic susceptibility data. Tables II. and III. give the experimental values of the various physical properties measured for each of the mixtures, and Tables IV. and V. show the calculated percentage deviations of these from the theoretical figure required by the mixture law.

TABLE III.—ACETONE-TRICHLOROETHYLENE.

Mixture.	Gram. Mol. Per Cent. Trichlor.	Density D_{20}^{20} .	Mass Suscept. $\alpha - 10^6$.	Gram. Mol. Per Cent. Trichlor.	Refract. Index.	Gram. Mol. Per Cent. Trichlor.	Specific Heat in Calories per Gram.	Heat of Mixing in Calories per Gram
Acetone	0	0.7847	0.577	0	1.35730	0	0.513	—
I.	11.55	0.8782	0.564	12.32	1.37489	12.10	0.453	0.43
II.	27.04	0.9963	0.542	30.32	1.39876	29.64	0.390	1.05
III.	39.04	1.081	0.530	49.94	1.42393	46.76	0.337	1.20
IV.	48.07	1.143	0.523	63.93	1.43823	63.93	0.297	—
V.	59.32	1.217	0.520	71.76	1.44605	72.36	0.283	0.86
VI.	75.53	1.316	0.513	79.78	1.45488	79.78	0.285	—
VII.	88.74	1.392	0.503	89.38	1.46453	89.38	0.257	—
VIII.	—	—	—	—	—	89.86	—	0.34
Trichloroethylene	100	1.454	0.496	100	1.47488	100	0.227	—

Discussion of Results.

N-Butyl-Isopropyl Alcohols.—If the percentage deviation is plotted against composition it is found that all properties show marked deviations from the mixture rule. Density, refractive index and viscosity give curves with a slight but clearly marked displacement of the point of maximum deviation toward the *iso*-propyl alcohol end. The magnetic-susceptibility curve, however, shows a shift of maximum towards the *n*-butyl alcohol end.

These deviations may probably be explained as due to a certain degree of co-ordination between the molecules of the two alcohols concerned, and secondly to alterations in the degree of association of each pure constituent by addition of molecules of the other. The density, viscosity and refractive index deviations would indicate deassociation of the *iso*-propyl alcohol in presence of the normal butyl alcohol. The

TABLE IV.—PERCENTAGE DEVIATIONS.

No of Mixture.	Density.	Refract. Index.	Viscosity.	Mass Suscept.	Density.	Refract. Index.	Visc.	Mass Suscept.
<i>n</i> .-butyl— <i>iso</i> -propylalcohols. Per cent. gm. mol. deviation from calculated.				<i>n</i> .-butyl— γ -amyl alcohols. Per cent. gm. mol. deviation from calculated.				
I.	0.073	0.033	0.41	0.00	0.002	0.029	0.36	0.30
II.	0.115	0.075	0.74	0.23	0.001	0.039	1.12	0.67
III.	0.165	0.087	1.41	0.19	0.005	0.046	1.68	0.70
IV.	0.203	0.093	1.14	0.43	0.013	0.053	1.98	0.97
V.	0.174	0.077	0.95	0.59	0.013	0.061	2.06	0.71
VI.	0.150	0.073	0.59	0.47	0.031	0.044	2.04	0.97
VII.	0.133	0.053	0.56	0.68	0.028	0.048	2.39	1.06
VIII.	0.114	0.060	0.53	0.62	0.006	0.040	1.93	0.44
IX.	0.046	0.036	0.10	0.34	0.007	0.026	1.69	0.43
<i>n</i> .-butyl alcohol— <i>n</i> .-propyl alcohols. Per cent. gm. mol. deviation from calculated.				<i>n</i> .-butyl— <i>iso</i> -butyl alcohols. Per cent. gm. mol. deviation from calculated.				
I.	0.042	0.020	0.19	0.00	0.000	0.003	1.18	0.33
II.	0.056	0.036	0.32	0.00	0.002	0.010	2.67	0.69
III.	0.052	0.041	0.65	0.23	0.001	0.016	3.16	0.94
IV.	0.079	0.055	0.72	0.27	0.001	0.011	3.20	1.06
V.	0.076	0.057	0.76	0.48	—	0.011	3.22	1.04
VI.	0.063	0.046	0.70	0.61	0.001	0.017	2.91	1.10
VII.	0.058	0.048	0.90	0.60	0.001	0.012	2.44	0.91
VIII.	0.020	0.029	0.82	0.51	0.001	0.016	1.64	0.70
IX.	0.015	0.019	0.78	0.39	0.001	0.000	0.56	0.01

TABLE V.—ACETONE—TRICHLOROETHYLENE. PERCENTAGE DEVIATION FROM CALCULATED.

No. of Mixture.	Density.	Mass Susceptibility.	Refractive Index.	Specific Heat.
Acetone	0	0	0	0
I.	1.88	0.704	0.226	5.23
II.	3.18	2.34	0.417	8.88
III.	3.35	2.75	0.559	11.09
IV.	3.35	2.79	0.402	10.00
V.	3.05	1.70	0.303	7.52
VI.	2.02	0.570	0.260	5.61
VII.	0.48	0.370	0.152	3.51
Trichloroethylene	0	0	0	0

magnetic susceptibility curve would indicate deassociation of the normal butyl alcohol. The fact that all properties do not show a shift in maximum to the same side would suggest that at least two effects are taking place, some properties showing the one more markedly than others.

N-Butyl and *N*-Propyl Alcohols.—In the case of all the properties investigated, deviations on mixing these two alcohols were less than those using *iso*-propyl alcohol. Deviations were, however, obtained, showing some degree of co-ordination between these two alcohols, but probably less than for the previous two. As before, the curves are

not entirely symmetrical about the 50 moles. axis, density and refractive index curves showing a slight shift to the *n*-butyl alcohol end. This would again indicate that changes in the degree of association of each pure constituent are brought about on addition of the other.

***N*- and *Iso*-Butyl Alcohols.**—In the case of these two alcohols density and refractive index curves show very small deviations, but viscosity and mass susceptibility show even larger deviations than in the case of either of the two former mixtures. The magnetic susceptibility curve is very nearly symmetrical. The viscosity curve shows a definite shift in the direction of mixtures containing a higher proportion of *iso*-butyl alcohol, while the maximum of the refractive index curve is indefinite.

These results are difficult to correlate as the viscosity and magnetic susceptibility deviations would indicate a considerable amount of co-ordination, the density and refractive index curves indicating little or no co-ordination. This may be due to some fundamental difference in the extent to which the various deviations may be considered as due to the same causes. The evidence further indicates for this mixture that only slight changes in the degree of association of the original pure liquids result on mixing them.

***N*-Butyl and *Iso*- γ -Methyl-Butyl Alcohols (γ -Amyl Alcohol).**—For this mixture all properties show deviation, the density and refractive index deviations being small as in the previous case. The viscosity deviations are large, being slightly less in magnitude than those of the last mixture. The mass susceptibility deviations are also of about the same magnitude as those for the two butyl alcohols. The susceptibility and density curves are almost symmetrical, mixtures having a higher proportion of the *n*-butyl alcohol showing if anything a slightly greater deviation. This tendency is considerably more marked with the viscosity curve which would indicate deassociation of the *n*-butyl alcohol on addition of the *iso*-amyl alcohol. The refractive index deviation curve, like that of the susceptibility is practically symmetrical. Here again, then, we find different maxima given by the different property-deviation curves.

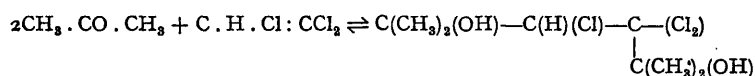
Acetone-Trichlorethylene.—As would be expected, in the case of this mixture considerably greater deviations were obtained for all properties, even refractive index deviations being about five times greater. All properties investigated showed considerable deviations. There was a marked evolution of heat on mixing the two liquids as shown by the heat of mixing curve, whereas in the case of the mixtures of alcohols, determination of heat of mixing had to be abandoned owing to the very slight changes obtained. The most marked deviations of all properties investigated occurred with the specific heat. Mass susceptibility deviations were quite considerably larger than in the case of mixtures of the alcohols. On plotting the percentage deviations against composition all properties showed a displacement of the maximum to the acetone end. The position of the maximum was the same for all properties, being between 40-50 moles per cent. of trichlorethylene. These results would clearly indicate definite co-ordination between these two liquids on mixing, and secondly, deassociation of the associated acetone molecules on addition of trichlorethylene. Such results are in agreement with these previously found for mixtures of acetone and bromoform.¹

General Conclusions.

The alcohols investigated may be represented by the general formula R_n-O-H and belong to the class of hydroxy-compounds in which the oxygen atom is capable of donating two electrons to an adjacent

hydrogen atom to give a co-ordination compound, *i.e.*, $H-O \begin{matrix} R_1 \\ | \\ \rightarrow \\ H-O \\ | \\ R_2 \end{matrix}$. Obviously the original pure alcohols will tend to be highly associated in this way, and a number of possibilities for co-ordination complexes arises on mixing two of the alcohols. The changes taking place are therefore somewhat complicated as is indicated by the experimental results given above. In the case of the mixture of acetone and trichlorethylene it would appear from the similarity of results given by the various physical properties that the changes are less complex, probably deassociation of the constituents and a definite co-ordination compound between the acetone and the trichlorethylene. The position of the maximum would indicate this as either due to one molecule of acetone co-ordinated with one of trichlorethylene and a shift due to deassociation of the acetone or to two molecules of acetone co-ordinated with one of trichlorethylene.

If the latter is the case, *i.e.*,



the maximum should be at 33 moles. per cent. trichlorethylene and the observed maximum at 40-45 moles. of trichlorethylene would indicate a shift due to deassociation of trichlorethylene. Deassociation of acetone may also have occurred but to a less extent than for the trichlorethylene. This latter would appear to be the most probable explanation.

A general consideration of the various properties investigated shows that density and refractive index give similar results and minimum deviations, and might be expected to be least suitable for investigating deviations from the mixture law. This, however, is somewhat offset by the ease with which accurate results to at least five decimal places can be obtained in both cases with simple apparatus. The variation in maxima shown by the different properties for the same mixture would appear to indicate that the properties do not necessarily depend on changes taking place in the mixtures in the same way. The results do not give any indication of a rule that may be applied to elucidate this.

Magnetic susceptibility and viscosity give similar high deviations, but in the case of viscosity measurements considerable care is required to ensure accurate results. In the case of magnetic susceptibility measurements, as described, the results can probably be considered as accurate to 0.5 per cent. As the maximum deviation for the mixtures of alcohols considered was only 1 per cent. it is perhaps not surprising that the curves show dissimilarities. That some of this may be due to experimental error is possible and would be supported by the agreement found in the case of mixtures having higher deviations. In general, however, the magnetic susceptibility gives clear indication of deviations from the mixture law and hence is a suitable property to consider with others in investigating such deviations.

Summary.

1. Every mixture investigated showed some departure from the additive mixture law, so that none of these pairs of liquids can be regarded as ideal.

2. The deviations obtained indicate co-ordination between the two constituents, together with deassociation of previously associated molecules of the pure constituent.

3. All properties investigated are not necessarily equally modified by changes occurring on mixing the two liquids as is indicated by the variation in the position of the maximum.

4. Density and Refractive Index give similar low deviations but are not very susceptible to unavoidable experimental error.

5. Viscosity and Mass Susceptibility give similar high deviations, but in the methods used the experimental error is higher than for the other two properties. Magnetic mass-susceptibility measurements are equally suitable for considering with other properties in measuring deviations from the mixture law.

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**MAGNETIC SUSCEPTIBILITY AND OTHER PRO-
PERTIES OF BINARY MIXTURES OF ORGANIC
LIQUIDS.**

BY V. C. G. TREW AND J. F. SPENCER.

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In a previous investigation,¹ it was shown that the physical properties of mixtures of liquids of a chemically dissimilar type, between which there is the possibility of combination, exhibit more marked deviations from

¹ "Some Physical Properties of Mixtures of Certain Organic Liquids," Trew and Watkins, *Trans. Faraday Soc.*, 1933.

the mixture law than mixtures of chemically similar liquids such as the members of an homologous series, but that even in the latter case considerable deviations do occur. In the present communication, some further binary mixtures are considered, in order to determine whether any general rule can be deduced connecting such deviations with differences in chemical constitution of the liquids mixed. It was thought that differences in molecular weight, and hence size of molecule, of the constituents might be a factor causing deviations from the mixture law. In addition, the presence of positive and negative groups might also contribute to such deviations.

Two groups of mixtures were investigated, the first consisting of mixtures of the aromatic hydrocarbons, benzene and toluene with *meta*-cresol and, for purposes of comparison, a set of mixtures of benzene and toluene. In the second group, mixtures of aniline with *meta*-cresol, nitrobenzene with *meta*-cresol and aniline with nitro benzene were investigated. Measurements of density, specific heat, heat of mixing, refractive index and magnetic mass susceptibility were made.

Experimental.

A.R. materials were employed throughout, and these were then carefully dried and fractionated until a constant boiling fraction was obtained.

TABLE I.—BOILING-POINTS AND DENSITIES OF PURE LIQUIDS.

Liquid.	Pressure.	Boiling-Pt.	Density D_4^{25} .
Benzene . . .	758 mm.	80.5° C.	0.8708
Toluene . . .	753 "	111.0° C.	0.8565
Aniline . . .	760 "	184.0° C.	1.0148
Nitrobenzene . .	762 "	210.6° C.	1.1937
<i>Meta</i> -cresol . .	760 "	202.4° C.	1.0292

The density of the pure liquids was determined, using a standard pycnometer, and was used as a criterion of purity, the values being compared with those given in the *International Critical Tables*. Table I. shows the physical constants obtained for each of

the constituent liquids.

A series of mixtures was then made up, as previously described,^{1,2} containing varying weights of the two components, the proportion of each being expressed as moles per cent. of the total composition. The methods employed for the determination of the density, refractive index, and thermal properties were as described previously. The molecular refractivity was calculated from the refractive index, using the Lorentz and Lorenz formula

$$R = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{m}{d}$$

when pure, or in the case of a mixture, the mean molecular weight. The molar magnetic mass susceptibility was calculated from the magnetic mass susceptibility measured by the method previously described.¹ The results are summarised in the following tables. Tables II. to IV. give the values obtained for the various properties, while in Table V. the maximum percentage deviation has been recorded for each property investigated, with the exception of the specific heat which was not measured to a sufficient degree of accuracy to give comparative values.

² "Physical Properties of Mixtures of Acetone and Bromoform," Trew, *Trans. Faraday Soc.*, 1932.

TABLE II.—DENSITY, D_4^{20} , REFRACTIVE INDEX AND MOLECULAR REFRACTIVITY.

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Density D_4^{20} .	Refractive Index n_D^{20} .	Mol. Refractivity.
Benzene—Toluene.				
Benzene	0	0.8702	1.49591	26.16
I.	8.5	0.8676	1.49519	26.63
II.	18.2	0.8670	1.49422	27.05
III.	26.4	0.8656	1.49384	27.48
IV.	35.7	0.8636	1.49327	27.95
V.	45.5	0.8606	1.49277	28.49
VI.	55.8	0.8592	1.49213	28.98
VII.	65.9	0.8586	1.49161	29.46
VIII.	76.8	0.8582	1.49098	29.98
IX.	88.1	0.8570	1.49074	30.53
Toluene	100.0	0.8563	1.49030	31.07
Benzene—<i>m</i>-Cresol.				
Benzene	0	0.8702	1.49591	26.16
I.	8.8	0.8878	1.50044	26.75
II.	17.6	0.9026	1.50525	27.38
III.	26.3	0.9177	1.50934	27.97
IV.	35.6	0.9350	1.51419	28.57
V.	45.1	0.9497	1.51869	29.22
VI.	56.0	0.9672	1.52319	29.95
VII.	66.1	0.9806	1.52629	30.63
VIII.	76.8	0.9977	1.53150	31.34
IX.	88.0	1.0142	1.53491	32.05
Cresol	100.0	1.0293	1.53812	32.84
Toluene—<i>m</i>-Cresol.				
Toluene	0	0.8562	1.49030	31.07
I.	12.5	0.8786	1.49663	31.29
II.	16.1	0.8847	1.49937	31.38
III.	31.0	0.9111	1.50620	31.61
IV.	41.5	0.9307	1.51133	31.77
V.	47.4	0.9401	1.51430	31.91
VI.	57.6	0.9570	1.51920	32.10
VII.	68.6	0.9754	1.52441	32.32
VIII.	77.6	0.9906	1.52787	32.45
IX.	89.1	1.0082	1.53329	32.74
Cresol	100.0	1.0292	1.53812	32.84
Aniline—Nitrobenzene.				
Aniline	0	1.015	1.58170	30.57
I.	8.7	1.031	1.57832	30.79
II.	18.2	1.048	1.57458	31.03
III.	27.7	1.068	1.57117	31.16
IV.	37.6	1.086	1.56778	31.42
V.	47.0	1.104	1.56478	31.61
VI.	58.6	1.123	1.56102	31.88
VII.	66.1	1.136	1.55875	32.04
VIII.	78.1	1.157	1.55518	32.32
IX.	89.1	1.176	1.55365	32.61
Nitro- Benzene	100.0	1.194	1.54928	32.73

TABLE II. (continued).

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Density D_4^{20} .	Refractive Index n_D^{20} .	Mol. Refractivity.
Aniline—<i>m</i>-Cresol.				
Aniline	0	1.0147	1.58170	30.57
I.	12.2	1.0187	1.57577	30.80
II.	13.7	1.0192	1.57502	30.85
III.	22.0	1.0212	1.57117	30.99
IV.	37.1	1.0232	1.56431	31.33
V.	45.4	1.0273	1.56075	31.45
VI.	57.3	1.0278	1.55579	31.77
VII.	66.2	1.0281	1.55187	31.96
VIII.	77.6	1.0287	1.54692	32.27
IX.	88.6	1.0290	1.54228	32.52
<i>m</i> -Cresol	100.0	1.0293	1.53812	32.84
Nitrobenzene—<i>m</i>-Cresol.				
Nitrobenzene	0	1.194	1.54928	32.73
I.	10.1	1.177	1.54794	32.78
II.	19.3	1.162	1.54685	32.76
III.	29.3	1.144	1.54560	32.82
IV.	39.2	1.128	1.54503	32.83
V.	51.5	1.108	1.54387	32.85
VI.	59.1	1.097	1.54282	32.80
VII.	69.2	1.081	1.54166	32.76
VIII.	78.8	1.063	1.54029	32.85
IX.	89.9	1.045	1.53860	32.81
Cresol	100.0	1.029	1.53812	32.84

TABLE III.—THERMAL DATA (SPECIFIC HEAT, HEAT OF MIXING, MOLECULAR HEAT).

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Specific Heat.	Heat of Mixing (Absorbed). Calories per Gram.	Molecular Heat.
Benzene—Toluene.				
Benzene	0	0.474	—	37.1
I.	19.6	0.449	0.119	36.3
II.	37.6	0.426	0.228	35.5
III.	52.9	0.415	0.279	35.5
IV.	69.3	0.413	0.228	36.2
V.	85.0	0.410	0.145	36.9
Toluene	100.0	0.383	—	35.3
Benzene—<i>m</i>-Cresol.				
Benzene	0	0.474	—	37.0
I.	24.3	0.455	2.05	38.8
II.	40.4	0.452	2.53	40.7
III.	69.8	0.479	2.39	47.4
IV.	76.7	0.487	2.28	49.2
V.	88.9	0.464	1.60	48.7
Cresol	100.0	0.515	0.00	55.6

TABLE III. (continued).

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Specific Heat.	Heat of Mixing (Absorbed). Calories per Gram.	Molecular Heat.
Toluene—<i>m</i>-Cresol.				
Toluene	0	0.383	—	35.3
I.	21.3	0.408	1.68	39.0
II.	38.6	0.425	2.02	41.8
III.	56.9	0.436	2.05	44.1
IV.	72.7	0.441	1.45	45.7
V.	87.1	0.456	0.80	48.3
Cresol	100.0	0.515	—	55.6
Aniline—Nitrobenzene.				
Aniline	0	0.448	—	41.71
I.	23.5	0.443	0.85	44.36
II.	43.9	0.426	1.24	45.28
III.	61.4	0.394	1.22	43.92
IV.	75.8	0.383	1.11	44.35
V.	90.0	0.367	0.55	44.08
Nitrobenzene	100.0	0.355	—	43.69
Aniline—<i>m</i>-Cresol.				
Aniline	0	0.448	—	41.7
I.	17.1	0.462	1.97 *	44.2
II.	39.9	0.473	3.88 *	46.5
III.	52.9	0.463	4.85 *	46.8
IV.	68.7	0.463	4.66 *	47.9
V.	84.8	0.463	3.06 *	48.9
Cresol	100.0	0.515	—	55.6
Nitrobenzene—<i>m</i>-Cresol.				
Nitrobenzene	0	0.355	—	43.7
I.	13.8	0.381	1.00	46.0
II.	26.3	0.395	1.27	47.0
III.	42.5	0.416	1.30	48.5
IV.	60.4	0.449	1.03	51.2
V.	79.0	0.490	0.57	54.5
Cresol	100.0	0.515	—	55.6

* Heat evolved.

TABLE IV.—DENSITY D_4^{25} , MAGNETIC SUSCEPTIBILITY, MOLECULAR SUSCEPTIBILITY.

Mixture.	Composition. Mols. Per Cent. of Second Constituent.	Density D_4^{25} .	Magnetic Susceptibility — $10^6 X$.	Molecular Susceptibility — $10^6 XM$.
Benzene—Toluene.				
Benzene	0	0.8722	0.710	55.4
I.	6.40	0.8710	0.711	56.2
II.	15.35	0.8692	0.714	57.3
III.	34.17	0.8668	0.719	59.6
IV.	45.44	0.8640	0.720	60.6
V.	52.58	0.8630	0.721	61.6
VI.	59.80	0.8626	0.723	62.5
VII.	67.77	0.8616	0.724	63.4
Toluene	100.00	0.8586	0.728	67.0

TABLE IV. (continued).

Mixture.	Composition, Mols. Per Cent. of Second Constituent.	Density D_4^{25} .	Magnetic Susceptibility $-10^6 X$.	Molecular Susceptibility $-10^6 XM$.
Benzene—<i>m</i>-Cresol.				
Benzene	0	0.8722	0.710	55.4
I.	10.65	0.8916	0.705	57.3
II.	26.04	0.9182	0.696	59.8
III.	40.73	0.9422	0.692	62.5
IV.	46.78	0.9510	0.689	63.5
V.	58.06	0.9670	0.685	65.4
VI.	73.64	0.9892	0.677	67.8
VII.	88.67	1.0051	0.671	70.2
Cresol	100.00	1.0302	0.672	72.6
Toluene—<i>m</i>-Cresol.				
Toluene	0	0.8586	0.728	67.0
I.	11.32	0.8788	0.718	67.4
II.	22.24	0.8978	0.710	67.9
III.	33.94	0.9186	0.705	68.7
IV.	45.06	0.9386	0.699	69.4
V.	54.66	0.9556	0.694	69.9
VI.	76.12	0.9922	0.683	71.2
VII.	87.74	1.0120	0.675	71.6
Cresol	100.00	1.0302	0.672	72.5
Aniline Nitrobenzene.				
Aniline	0	1.018	0.662	61.6
I.	12.18	1.040	0.641	62.0
II.	26.55	1.066	0.614	62.0
III.	39.85	1.092	0.588	61.8
IV.	50.37	1.111	0.571	61.8
V.	59.00	1.127	0.561	62.1
VI.	72.83	1.150	0.537	61.7
VII.	87.83	1.177	0.520	62.0
Nitro- benzene.	100.00	1.198	0.502	61.8
Aniline—<i>m</i>-Cresol.				
Aniline	0	1.0182	0.662	61.6
I.	12.05	1.0214	0.663	62.9
II.	26.79	1.0250	0.665	64.5
III.	42.75	1.0273	0.668	66.4
IV.	47.88	1.0282	0.669	66.9
V.	57.46	1.0309	0.670	68.1
VI.	75.13	1.0315	0.671	70.0
VII.	87.62	1.0303	0.671	71.3
Cresol	100.00	1.0302	0.672	72.6
Nitrobenzene—<i>m</i>-Cresol.				
Nitro- benzene	0	1.198	0.502	61.8
I.	12.98	1.176	0.522	63.2
II.	27.20	1.152	0.543	64.6
III.	41.48	1.128	0.566	66.1
IV.	47.90	1.117	0.578	67.0
V.	57.78	1.103	0.593	67.8
VI.	73.20	1.075	0.620	69.5
VII.	87.86	1.051	0.650	71.3
Cresol	100.00	1.030	0.672	72.6

TABLE V.—MAXIMUM PERCENTAGE DEVIATION.

Mixture.	Density D_4^{25} .	Density D_4^{28} .	Refractive Index.	Magnetic Mass Susceptibility.	Molar Refractivity.	Molar Susceptibility.	Heat Evolved.
Benzene—Toluene	-0.2	-0.3	-0.06	-0.2	+0.26	<0.1	-0.36
Benzene— <i>Meta</i> -cresol	+0.5	+0.9	+0.25	+0.5	+0.26	<0.1	-2.80
Toluene— <i>Meta</i> -cresol	+0.3	+0.3	+0.13	+0.4	±0	+0.1	-2.08
Aniline—Nitrobenzene	+0.2	+0.4	-0.15	+1.8	+0.13	-0.1(5)	-1.25
Aniline— <i>Meta</i> -cresol	+0.4	+0.5	-0.10	-0.1	-0.39	<0.1	+4.80
Nitrobenzene— <i>Meta</i> -cresol	±0	±0	+0.05	+1.1	±0	<0.1	-1.30

Discussion of Results.

1. Binary Mixtures from Benzene, Toluene and *m*-Cresol.

Examination of Table V. shows that, for all properties, slight deviations from the mixture rule are obtained, even for such chemically similar pairs of liquids as benzene and toluene. Density deviations at 28° C., were for all mixtures greater than for the lower temperature, 25° C. The results for these three mixtures show a close similarity in the direction of the deviation obtained in the case of most of these properties. The deviations in density, refractive index and magnetic mass susceptibility for the mixtures of the hydrocarbons with *m*-cresol are all of the same sign, indicating that the causes of deviation are probably similar for these properties, in both mixtures. Benzene and *m*-cresol mixtures show greater deviations in all properties than do toluene and *m*-cresol. This suggests that when other factors, such as chemical dissimilarity, are absent, the deviations are smaller the closer the molecular weights of the components are to one another. It seems also likely that the smaller deviation on mixing toluene and *meta*-cresol can be accounted for by the greater similarity of their molecular structure, that is, the presence of the methyl group in both. The shape of the toluene molecule would thus be more like that of the cresol, than would that of benzene.

2. Binary Mixtures from Aniline, Nitrobenzene and *m*-Cresol.

A marked change of colour was observed on mixing aniline and nitrobenzene, even in the absence of light, suggesting that some considerable change had taken place on mixing these liquids. The deviations obtained, however, were no greater than for other mixtures, indicating that any change is due to association, rather than to a definite chemical combination. The nitrobenzene—*m*-cresol mixture appears to be nearly ideal, a somewhat unexpected result in view of the nature of the constituent molecules. Unlike the first group of mixtures, there seems in these three sets of mixtures to be no simple common factor causing deviations since Table V. shows no relationship between the direction of the deviations for the properties investigated. It must therefore be concluded that deviations here are due to more than one determining factor.

General.

The most important general result brought out by a consideration of columns 4 and 6 of Table V. is that for the six sets of mixtures the molar magnetic susceptibility is more nearly an ideal property than the mass susceptibility from which it is calculated. This is fully in keeping with the theoretical view that diamagnetic susceptibility is a fundamental atomic property.

Summary.

(1) The density, refractive index, heat of mixing, specific heat and magnetic mass susceptibility of a series of mixtures of the liquids benzene, toluene, *m*-cresol, aniline and nitrobenzene have been measured.

(2) None of the pairs of liquid mixtures can be considered as ideal with the possible exception of the nitrobenzene—*m*-cresol mixture which showed least deviation from the mixture law.

(3) Similar deviations were obtained for different properties for mixtures of benzene and toluene, respectively, with *m*-cresol, the wider apart the molecular weights of the constituents the more marked the deviation.

(4) For mixtures of nitrobenzene and aniline, respectively, with *meta*-cresol, no general rule governing the deviation of the properties investigated could be discovered.

(5) The molar magnetic mass susceptibility proved to be a more nearly additive property than any other property investigated.

The authors desire to express their thanks to Miss J. Cattermole, for carrying out the measurements of refractive index, density at 28°, specific heat and heat of mixing recorded in this paper.

One of us (V. C. G. T.), desires to express thanks to the Council of the Chemical Society for a grant which partially defrayed the cost of materials.

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Diamagnetic Susceptibility of Heavy Water

MR. F. E. HOARE has directed attention¹ to the divergence in the mass susceptibility values for heavy water found by himself, Cabrera and Fahlenbrach, and Selwood and Frost. The mass susceptibility of deuterium oxide having been determined in this laboratory in connexion with other work, it may be of interest, in view of Hoare's remarks, to record our value for comparison with the values already published.

We find, using a modified Gouy balance² which has been calibrated with a number of highly purified organic liquids (benzene, acetone, chloroform) and inorganic salts (sodium chloride, copper sulphate, nickel sulphate and nickel ammonium sulphate) and with pure distilled water, that the mass susceptibility of heavy water is 0.637 ± 0.001 at 20°. Two specimens of heavy water of density 1.1049 and containing 99.2 per cent deuterium oxide were used. It was measured in two different containers, one of which held 4.0810 ± 0.0014 gm. and the other 3.7760 ± 0.0025 gm.; the mean mass susceptibility in the two tubes being respectively 0.639 ± 0.001 and 0.638 ± 0.001 units of 10^{-6} .

These values when corrected for 0.8 per cent of ordinary water, which is taken as having a mass susceptibility of 0.720 units of 10^{-6} , give a value for deuterium oxide of 0.637 ± 0.001 and a molecular susceptibility of 12.76 units of 10^{-6} on the assumption that D₂O has a molecular weight 20.027. This value is in complete agreement with that of Cabrera and Fahlenbrach.

Bedford College,
London.
March 25.

V. C. G. TREW.
JAMES F. SPENCER.

¹ NATURE, 137, 497 (1936).

² Trans. Faraday Soc., Dec. 1933.

D.S.

1955

(Reprinted from NATURE, Vol. 137, page 998, June 13, 1936.)

Diamagnetic Susceptibility of Heavy Water

SINCE our communication in NATURE of April 25 (p. 706), we have repeated the determination of the mass susceptibility of deuterium oxide using two specimens of purity 99.95 per cent. Our mean result now obtained is 0.638×10^{-6} , which agrees excellently with our previous value, obtained with a slightly less pure specimen, and also with the value obtained by Cabrera. This therefore may be taken to establish the value of the mass susceptibility of deuterium oxide at ordinary temperature at the figure named.

Bedford College,
London.
May 22.

V. C. G. TREW.
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Diamagnetism of Mixtures of Organic Liquids

CERTAIN measurements of the magnetic susceptibility of binary mixtures of organic liquids made by us¹, which are at variance with the determinations of several investigators and which we have agreed are in error for reasons stated², are still being quoted in text-books and the literature.

We have now completed the remeasurement of the susceptibility of the binary mixtures under discussion, namely, acetone-chloroform, acetone-trichloroethylene, chloroform-ether, by the Gouy method³ and find that the deviations of these mixtures from the mixture law do not exceed 2-3 per cent except in the case of acetone-chloroform, where a maximum deviation of about 4 per cent is obtained: results which are substantially in agreement with those of our critics.

Since our new apparatus came into use, full details have been published for the mixtures of acetone and trichloroethylene⁴. Details of other binary mixtures of organic liquids are to be found in the same paper and in a further paper⁵. The general conclusions to be drawn from the values obtained for about fifteen series of binary organic mixtures of substances of varying chemical type are that, in common with other physical properties, (i) the magnetic susceptibility exhibits slight deviations from the mixture law for most binary mixtures of organic substances; (ii) where the constitution and molecular weight of the constituents of the mixtures are similar the deviations are very small, rarely exceeding 0.5 per cent; and (iii) where there is considerable difference in chemical constitution or mass the deviations are slightly larger, about 1-4 per cent. When, however, molecular susceptibilities are compared, the deviations are much smaller, rarely exceeding 0.1 per cent, and thus come into line with the deviations of other physical properties from the mixture law.

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¹ *Proc. Roy. Soc., A*, **131**, 209 (1931).

² *NATURE*, (Jan. 16, 1932).

³ Trew and Watkins, *Trans. Far. Soc.*, **30**, 1310 (1933).

⁴ Trew and Watkins, *loc. cit.*

⁵ Trew and Spencer, *Trans. Far. Soc.*, **32**, 701 (1936).

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DIAMAGNETIC SUSCEPTIBILITY OF THALLIUM COMPOUNDS

DIAMAGNETIC SUSCEPTIBILITY OF THALLIUM COMPOUNDS.

BY VIOLET CORONA GWYNNE TREW.

Received 20th July, 1936.

Part I. Thallous Compounds

A study of the literature dealing with the magnetic properties of the chemical elements reveals that very little systematic study has been made of a wide range of compounds of one chemical element. The work of Ikenmeyer¹ on the magnetic susceptibilities of the alkali metal halides only covers one type of compound. Sugden,² in 1934, investigated a range of silver and copper compounds, and Spencer and Hollens³ the compounds of cadmium, but these represent practically the only systematic investigations in this field.

In the present paper the diamagnetic susceptibilities of some thirty thallous salts have been measured, covering a wide range of compounds. From the molar susceptibilities of the salts, the gram ionic susceptibility of the thallous ion has been calculated, and the value compared with the theoretical one obtained from Slater's approximate wave functions. Values of the average mean square radius, and the radius of the outer orbit of the thallous ion have been deduced from the experimental data and are compared with the corresponding values from theory.

Experimental.

Preparation of Compounds.

A good commercial specimen of thallous carbonate (99.95 per cent. pure) was used as starting material and was tested for ferromagnetic impurities, *e.g.*, iron, nickel, and cobalt, by B.D.H. spot tests and gave negative or negligible results. Lead was also tested for and found absent. The compounds measured were prepared and purified by the usual methods from A.R. materials. All acids used were tested and shown to be free from iron. In a few cases special methods were necessary to obtain a pure specimen. Thallous bromate prepared by addition of bromic acid to thallous carbonate resulted in an impure product, which even after recrystallisation contained an appreciable amount of thallic bromate as impurity. A pure specimen was obtained by addition of A.R. potassium bromate to pure recrystallised thallous nitrate, thallous bromate being precipitated. A pure specimen of the sulphite could not be prepared by double decomposition of thallous sulphate and sodium sulphite, but was obtained from a solution of the hydroxide, which was first saturated with sulphur dioxide to form the bisulphite. By addition of an equivalent amount of thallous hydroxide solution to this, crystals of the normal sulphite were obtained, on careful evaporation. Attempts to prepare

¹ Ikenmeyer, *Ann. Physik*, 1929, 169.

² Sugden, *J.C.S.*, 1932, 161.

³ Spencer and Hollens, *J.C.S.*, 1935, 495.

the permanganate by Meyer's method⁴ proved unsuccessful, oxidation of the thalious compound to thallic oxide resulting in every case, even at low temperatures.

Analysis.

The purity of the compounds prepared was determined by the tests for ferromagnetic impurities, and by estimation of the thallium content of the compound. Thallium was estimated as chromate, the method being previously tested with a pure recrystallised specimen of thalious sulphate and was found to give consistent results with an error of less than 0.1 per cent. under the following conditions: To 0.3-0.4 gm. of the thallium salt, dissolved in 200 c.c. of water, and made alkaline with a few drops of ammonia, 2 gms. of solid A.R. potassium chromate were added at the boiling-point. The precipitate was stirred until complete coagulation resulted, cooled, allowed to stand for 12 hours, and filtered cold through a sintered glass crucible. The precipitate was washed with 50 c.c. of 1 per cent. potassium chromate solution, and 100-150 c.c. of 50 per cent. alcohol, which was found to be the amount necessary in most cases to wash free from other ions. The precipitate was then dried at 120° and weighed.

It was found necessary to keep strictly to the above conditions as variable results were obtained with more dilute or concentrated solutions, or on washing with water alone. Any compound giving a thallium content differing by more than 0.2 per cent. from the theoretical value was recrystallised.

Measurement of Susceptibility.

The mass susceptibility was measured by a modified Gouy method as previously described,⁵ at atmospheric temperature. Six closely agreeing measurements, each the mean of three readings, were made on the solid salt with fresh packings of substance in each case. The maximum deviation from the mean value was never greater than 2 per cent. and in most cases of the order 1 per cent.

Results.

In Table I. results are tabulated in three groups, in order of increasing number of electrons N , the first consisting of salts of thallium with univalent negative ions, the second with divalent and trivalent ions, and the third of organic salts. The mean experimental magnetic mass susceptibility χ is recorded in column 3, for each compound, and the molar susceptibility, $\chi_M = \chi \times M$ in column 4. Column 5 gives values of δ representing the ionic susceptibility of the negative ion which must be subtracted from the molar susceptibility to give the ionic susceptibility of the thalious ion. This method of determining the ionic susceptibility assumes that the salts are polar, and that the molar susceptibility is made up of the sum of the ionic susceptibilities. The values of δ in the first two groups are taken from the International Critical Tables VI., p. 349, except those marked (a) which are due to Sugden,² and (b) which were specially determined, as described below, no values being given in the literature. In these latter cases the susceptibility of the corresponding potassium salt was measured and the value for the negative ion calculated from the known value for the potassium ion. The experimental results so obtained are shown in Table II. The values of δ for the organic salts were obtained from Pascal's values for atoms and linkages. In addition, the value for the nitrite ion was obtained by calculation from the

⁴ Meyer and Best, *Z. anorg. chem.*, 1899, 169.

⁵ Trew and Watkins, *Trans. Faraday Soc.*, 1933, 1310.

TABLE I.

	Substance.	N.	-10 ⁶ χ.	-10 ⁶ χ _M .	δ (Negative).	-10 ⁶ χ _A Thallium Ion.
GROUP I.; Univalent Anions.	TIF	90	0.201	44.4	6.3	38.1
	TICN	94	0.212	49.0	10.8	38.2
	TICI	98	0.241	57.8	20.1	37.8
	TICNO	102	0.225	55.5	16.2	39.3
	TINO ₂	104	0.203	50.8	13.4	37.3
	TICNS	110	0.254	66.7	30.0 ^a	36.7
	TINO ₃	112	0.212	56.5	18.0	38.5
	TIBr	116	0.225	63.9	30.6	33.3
	TIClO ₃	122	0.228	65.5	26.0 ^{a,b}	39.5
	TIClO ₄	130	0.238	72.5	29.6 ^b	42.9
	TI	134	0.248	82.2	44.6	37.5
	TIBrO ₃	140	0.229	75.9	35.6 ^b	40.3
	TIIO ₃	158	0.229	86.8	47.4 ^b	39.4
					Mean value	38.4
	GROUP II.: Divalent and Tervalent Anions.	Tl ₂ S	178	0.202	88.8	15.0
Tl ₂ CO ₃		192	0.217	101.7	28.0	36.9
Tl ₂ SO ₃		202	0.203	99.3	22.3	38.5
Tl ₂ SO ₄		210	0.223	112.6	37.0 ^a	37.8
Tl ₂ CrO ₄		218	0.075	39.3	+35.2 +33.0 ^b	36.7
Tl ₃ PO ₄		290	0.205	145.2	35.4	36.6
Thalious alum		620	0.416	532.1	456.5 ^b	38.3
				Mean Value	37.4	
GROUP III.: Organic Anions.	Formate	104	0.220	55.0	16.9	38.1
	Acetate	112	0.262	69.0	30.0 ^a	39.0
	Benzoate	144	0.349	113.5	66.1	47.4
	Tartrate	158	0.304	107.4	63.8	43.6
	Oxalate	206	0.220	109.4	27.9	40.7
	Malonate	214	0.240	122.6	39.8	41.4
	Citrate					
	(+1 H ₂ O)	330	0.274	224.8	92.1	44.2
				Mean Value	42.1	

nitrate ion, the chromate similarly from the dichromate, and the carbonate by the same method as the organic salts. Column 6, Table I., shows χ_A the resulting atomic susceptibility of the thalious ion.

Discussion of Results.

The molar diamagnetic susceptibility of a polar salt in the solid state may, in general, be regarded as the sum of the susceptibilities of the positive and negative ions. For a mononuclear spherically symmetrical atom or ion this is given by Langevin's equation:—

$$\chi_A = -\frac{e^2 L}{6mc^2} \Sigma \bar{r}^2 = -2.83 \times 10^{10} \Sigma \bar{r}^2$$

where $\Sigma \bar{r}^2$ on the classical theory is the mean square radius summed for all the electrons in the atom or ion, or on the newer quantum mechanical view is the square of the average effective electron density distribution.

In solid crystals the interionic distances depend on the ionic radii and hence the factors which determine such distances in a crystal must to a large extent influence the susceptibility. The ionic radius, or outer electron density distribution of an ion is limited in a crystal by adjacent ions, so that the radii of such ions, together with the diamagnetic susceptibility (to which the outer shell of electrons contributes by far the largest amount), should be less than that of the free ion, or the ion in solution.

TABLE II.—POTASSIUM SALTS.

 δ K-ion = -18.5×10^{-6} (I.C.T.).

Substance.	$-10^6 \chi$.	$-10^6 \chi_M$.	$-10^6 \chi_A$ Negative ion.
KClO ₃	0.361	44.3	25.8
KClO ₄	0.347	48.1	29.6
KBrO ₃	0.324	54.1	35.6
KIO ₃	0.308	65.9	47.4
K ₂ CrO ₄	0.020	4.0	+33.0
Potash alum *	0.520	493.5	456.5

* This value is taken from unpublished work by G. T. Oddie (Sister Mary Cecilia) working in this Laboratory.

Furthermore, Goldschmidt⁶ has shown that the ionic radius is modified by the co-ordination number of the ion (*i.e.*, the number of ions of opposite sign surrounding the ion in question) as also by the nature and size of such ions. The interionic distance has been shown to decrease with a diminution of the co-ordination number by an amount of the order 3.8 per cent. Similar variations in atomic diamagnetic susceptibility would be expected to follow. In particular, since the number of ions of opposite sign (and hence the co-ordination number), surrounding a given ion is less in its salts with divalent ions than with univalent ions, the diamagnetic susceptibility might be expected to be lower in the former case. The results in Table I. show that for the thallos ion the mean ionic susceptibility as determined from the salts with divalent and trivalent anions is -37.4×10^{-6} , while the value from the salts with univalent anions is -38.4×10^{-6} , in exact accord with Goldschmidt's observations on change of ionic radius with co-ordination number. Allowing for the fact that the salts investigated are not all of the same type, it is striking that this decrease is of the same order (about 3 per cent.) as that found by Goldschmidt.

In the case of the organic salts, it will be noted that while the simple salts give a value for the atomic susceptibility of the thallos ion in agreement with that derived from the salts with univalent anions, the salts with larger organic molecules give a very much higher value. This becomes very evident if these salts are rearranged in order of increasing number of carbon atoms in the molecule, when it will be seen that, roughly, the value of the ionic susceptibility increases with the number of carbon atoms. It should be noted that this increase is not due to any bond effects within the anion, as these have been included in calculating δ for the organic anion by Pascal's method. It appears, therefore, that the increase in size of the negative ions surrounding the thallos ion results in an increase in the effective ionic radius and hence of the susceptibility of that ion. The organic anion thus appears to have a "diluting" effect on the charge surrounding the thallos ion, and so raises its ionic susceptibility to a value nearer to that of a free ion.

⁶ Goldschmidt, *Trans. Faraday Soc.*, 1929, 253.

The results in Table I. have been arranged in order of increasing number of electrons within the molecule and it will be seen that there is, on the whole, a linear increase of molar susceptibility with increasing number of electrons, although certain very marked deviations do occur. In particular, the values for the chloride, thiocyanate and iodide are considerably higher than the average. Salts with anions of similar constitution, *e.g.*, nitrate, chlorate, bromate, and iodate, form a definite linear sequence. Ikenmeyer,¹ has shown that an approximately linear relationship holds for the gram molar susceptibilities of the alkali halides, determined from measurements in solution, when the susceptibilities are plotted against number of electrons in the molecule. The susceptibility can be expressed in the form $\chi_M = c_1 N_m + c_2$ where N_m is the sum of the atomic numbers of the atoms in the molecule, or total number of electrons, c_1 is a general constant $= 0.803 \times 10^{-6}$ and c_2 a constant specific for a given series of salts. The molar susceptibilities of the thallos compounds in general agree with the same relationship, allowing for the much wider difference in types of compounds considered. For thallos salts, c_1 , the average increase in diamagnetism per electron is approximately 0.7×10^{-6} (agreeing reasonably well with Ikenmeyer's value) while c_2 has an average value of -17×10^{-6} becoming lower by about five units for the chloride, acetate, thiocyanate and iodide, and similarly higher for the nitrate series of ions. The relation holds for the divalent and univalent anions if one-half and one-third of N and χ_M are used respectively. The citrate, benzoate and tartrate are again exceptional. These and the other deviations from linearity are probably due to the cause already discussed, namely, specific effects due to the crystalline form of the compounds investigated.

Comparison of Theoretical and Experimental Susceptibilities.

The values of $\Sigma \bar{r}^2$ in the Langevin formula have been evaluated for the different electron groups in atoms and ions, by Pauling⁷ from quantum mechanics, by Hartree⁸ using a self-consistent field method of determining the radial charge distribution, and by Slater⁹ from wave mechanics using an approximate solution of the wave equation of an electron. Brindley¹⁰ has shown that the Slater method gives results in best agreement with experimental susceptibilities for most atoms and ions, and in particular, for those with the larger values of r to which class the thallos ion belongs. Slater's rules for determining the screening constants for the various electrons in an atom or ion have been applied to obtain a theoretical value for the susceptibility of the thallos ion. Using this method, for any electron

$$\bar{r}^2 = \frac{(n')^2(n' + \frac{1}{2})(n' + 1)}{(Z - s)^2}$$

where n' is the effective principal quantum number and $Z - s$ the effective nuclear charge for each electron considered, Z being the atomic number and s the appropriate screening constant derived for any electron by considering the screening effects on it of other electrons in the atom, using Slater's rules. The susceptibility is obtained by

⁷ Pauling, *Proc. Roy. Soc.*, 1927, 181.

⁸ Hartree, *Proc. Camb. Phil. Soc.*, 1928, 111; *Proc. Roy. Soc.*, 1933, 141.

⁹ Slater, *Physic. Rev.*, 1930, 57.

¹⁰ Brindley, *Phil. Mag.*, 1931, 786.

summing over all the electrons in the ion. When \bar{r}^2 is expressed in atomic units (multiples of a_0 , the radius of the Bohr orbit in normal hydrogen = 0.528×10^{-8} cm.) then

$$\begin{aligned}\chi_A \times 10^6 &= -2.83 \times 10^{10} (0.528 \times 10^{-8})^2 \cdot \sum \frac{(n')^2(n' + \frac{1}{2})(n' + 1)}{(Z - s)^2} \\ &= -0.790 \sum \frac{(n')^2(n' + \frac{1}{2})(n' + 1)}{(Z - s)^2}.\end{aligned}$$

The appropriate values for the thallos ion are shown in Table III. whence $-10^6 \chi_A = 79.99 \times 0.790 = 63.19$, the theoretical atomic susceptibility of the thallos ion.

It will be seen that the theoretical and experimental susceptibility values are of the same order of magnitude, but the experimental value is rather less than two-thirds of the theoretical value. The calculated value is that for the free ion, whereas the experimental value is derived from measurements on the crystalline solid, and therefore, as considered previously, may to some extent be lower due to interionic forces, but these effects should only cause a difference of some 3.8 per cent. A real discrepancy between experiment and theory is therefore indicated by the above results. This is supported by Brindley's results¹⁰ for a number of other atoms and ions. He has shown that there is an increasing divergence between theoretical and experimental susceptibilities with increasing atomic weight of the element concerned. This point will be further considered later.

Ionic Radius.

From the experimental atomic susceptibility the value of $\Sigma \bar{r}^2$ can be evaluated by means of the Langevin equation, giving for the thallos ion $\Sigma \bar{r}^2 = 48.49$ in atomic units, or 13.44×10^{-16} in absolute units. The value $\Sigma \bar{r}^2 = 48.49$ is to be compared with the value of 79.99 deduced from theory. This average mean square radius or effective electron density distribution is, of course, not the square of the outer radius, but a composite factor depending on all the extra-nuclear electrons in the ion. A value for the actual outer radius cannot be obtained directly from this since there is no direct means of determining the contributions of the various shells to this factor. Although the outer (6s) shell will contribute a large proportion of the susceptibility, Table III. shows that

TABLE III.—SCREENING CONSTANTS AND $\Sigma \bar{r}^2$ FOR THE THALLOS ION.

$Z = 81$. Number of Electrons = 80.

Electron Groups.	s.	Z - s.	n'.	$\Sigma \bar{r}^2$.
1. s^2	0.30	80.70	1	0.00
2. s^2, p^6	4.15	76.85	2	0.04
3. s^2, p^6	11.25	69.75	3	0.21
3. d^{10}	21.15	59.85	3	0.35
4. s^2, p^6	27.75	53.25	3.7	0.76
4. d^{10}	39.15	41.85	3.7	1.54
4. f^{14}	52.30	28.70	3.7	4.59
5. s^2, p^6	57.65	23.35	4.0	5.28
5. d^{10}	71.15	9.85	4.0	37.12
6. s^2	75.65	5.35	4.2	30.10
			Total $\Sigma_n \bar{r}^2$	79.99

the $5d$ shell in the case of the thalious ion also contributes a large amount. By making use of the theoretical values in Table III. the radius of the outer shell can be estimated from the experimental susceptibility. Slater,⁹ has shown that the effective radial electron density (and hence 'a measure of the radius), of any shell is given by the formula $\bar{r}' = \frac{(n')^2}{(Z-s)}$.

Applying this to the $6s$ shell, with the appropriate value of $(Z-s)$, gives for the thalious ion the value \bar{r}' (theoretical) = 1.78 Å.U. It has already been pointed out that the theoretical susceptibility is too high, therefore this value of the radius of the outer shell will be correspondingly too large. A value of \bar{r}' from experimental data may be estimated from the value of $\Sigma\bar{r}^2$ derived from the experimental susceptibility as follows:—

Since $\sqrt{\Sigma\bar{r}_e'^2} : \sqrt{\Sigma\bar{r}_t'^2} :: \bar{r}_e' : \bar{r}_t'$ (where \bar{r}_e' and \bar{r}_t' are the radii of the outer shell, or orbit, given by experimental and theoretical data respectively, and $\Sigma\bar{r}_e'^2$ and $\Sigma\bar{r}_t'^2$ are the corresponding average mean square radii),

$$\text{then } \bar{r}_e' = \frac{\sqrt{48.49}}{\sqrt{79.99}} \times 1.78 = 1.38 \text{ Å.U.}$$

Goldschmidt's value for the ionic radius of the thalious ion from X-ray data is 1.49, slightly higher than the value from the susceptibility data. Bearing in mind the uncertainty of the theory involved in estimating the value 1.38 from the experimental susceptibility, this may be taken to be in good agreement with Goldschmidt's value.

Slater Wave Functions and Ionic Susceptibilities.

Brindley¹⁰ has shown that Slater's wave functions can also be applied to estimate the proportion of the molar susceptibility of a compound that is contributed by the constituent ions when these are simple mono-nuclear systems. It is thus possible from the experimental molar susceptibilities of those thalious compounds with single anions to deduce a value for the ionic susceptibilities based on the theoretical deduction that these are proportional to the average mean square radii of the ions concerned, as follows:—

$$\chi_A(\text{TI}') : \chi_M :: \Sigma\bar{r}^2(\text{TI}') : \Sigma\bar{r}^2(\text{TI}') + \Sigma\bar{r}^2_{\text{anion}}$$

$$\therefore \chi_A(\text{TI}') = \frac{79.99 \times \chi_M}{79.99 + \Sigma\bar{r}^2(\text{anion})}$$

TABLE IV.—IONIC SUSCEPTIBILITIES.

Calculated by Brindley's Method from Experimental Data.

Compound.	$-10^6 \chi_M$ Measured.	$\Sigma\bar{r}^2_{\text{anion}}$ Calculated.	$-10^6 \chi_A$ Thalious Ion.	$-10^6 \chi_A$ Anion.
TlF	44.4	10.27	39.34	5.06
TlCl	57.8	31.95	41.30	16.5
TlBr	63.9	49.73	39.41	24.5
TlI	82.2	74.19	42.64	39.6
Tl ₂ S	88.8	27.17	37.99	12.8
		Mean Value .	. 40.14	

$\Sigma\bar{r}^2$ for Thalious ion calculated by Slater method = 79.99 in Atomic Units.

Table IV. shows the results obtained in this way for the six compounds of this type that were investigated. The values of $\Sigma \bar{f}^2(\text{anion})$ in column 3 are taken from Brindley's values in the case of the chloride, bromide and iodide ions, and have been calculated similarly for the fluoride and sulphide ions. The values in column 5 are given by:

$$\chi(\text{anion}) = \chi_M - \chi(\text{TI})$$

It will be noted that the average value $-10^6 \chi_A = 40.14$ for the ionic susceptibility of the thallos ion, deduced in this way is somewhat higher than that from purely experimental data. Table V. shows

TABLE V.—COMPARATIVE VALUES.

Compound.	Thallos Ion — $10^6 \chi_A$.		Anion — $10^6 \chi_A$.				
	I	II	I	II	III	IV	V
Fluoride . . .	39.34	38.1	5.06	6.3	8.2	—	—
Chloride . . .	41.30	37.8	16.5	20.1	25.3	24.0	23.7
Bromide . . .	39.41	33.3	24.5	30.6	39.3	37.5	34.1
Iodide . . .	42.64	37.5	39.6	44.6	58.6	55.7	50.2
Sulphide . . .	37.99	36.9	12.8	15.0	—	—	—

Column I in each case shows values calculated in Table IV.

Column II in each case shows experimental values, from Table I.

Column III. (Purely theoretical values calculated from Slater's screening constants taken from Stoner, *Magnetism and Matter*, p. 271.)

Column IV. Experimental values representing average results for measurements on solid salts due to Brindley.¹⁰

Column V. Experimental values taken from experiments on solutions by Weiss.¹⁰

values for the atomic susceptibilities of the positive and negative ions collected together from various sources for comparative purposes. This table shows that application of the Slater rules to assess the relative contributions of the positive and negative ions to the molar susceptibility in thallos compounds gives higher values for the positive ion and lower values for the negative ions than any other method. This agrees with the previous evidence that the theoretical value of $\Sigma \bar{f}^2$ and hence of the diamagnetic susceptibility of the thallos ion is too high, again suggesting a need for a modification of the theory.

TABLE VI.—VALUES OF $\Sigma \bar{f}^2$ FOR THE VARIOUS SHELLS.

	6s ² .	5d ¹⁰ .	5s ² , p ⁶ .	4f ¹⁴ .	4d → 1s, p Inclusive.	Total $\Sigma_n \bar{f}^2$.
Mercury . . .	45.55	45.97	5.76	4.93	3.05	105.3
Thallium . . .	30.10	37.12	5.28	4.59	2.90	80.0
Lead ⁺⁺ . . .	21.37	30.59	4.87	4.29	2.57	63.7

Further light as to where this modification must be applied is given by a consideration of the adjacent elements in the periodic table, namely, mercury and lead. Thus, unionised mercury and the thallos and plumbous ions are electronic isomers, containing identical electronic shells and differing only in atomic number. The theoretical values of

$\Sigma\bar{\chi}^2$ for mercury and the plumbous ion, calculated by Slater's method, are shown in Table VI. giving 83.18 and 50.31 respectively, for the atomic susceptibilities, expressed in the usual units (*i.e.* all values are multiplied by -10^6). The corresponding experimental values are 38.75 for mercury, calculated from Honda's value of 0.193 for the mass susceptibility of liquid mercury at room temperature, and 44.3 for the plumbous ion. This latter value has been calculated from the mass susceptibilities for plumbous compounds quoted in the International Critical Tables, VI., p. 357, applying the appropriate corrections for the negative ions as in Table I. Comparing these theoretical and experimental values with those for the thalious ion, namely 63.2 (theoretical) and 38.3 (experimental), it will be seen that the discrepancy between theory and experiment is greatest for the element of lowest atomic number, *i.e.*, mercury. Examination of the values of $\Sigma\bar{\chi}^2$ for these three elements (Tables III. and VI.), shows that the susceptibility is in all three cases predominantly due to the ten $5d$ and the two $6s$ electrons. It is apparent, therefore, that the Slater rules give too high a value for the contribution of these shells to the diamagnetic susceptibility. The experimental atomic susceptibility of the plumbous ion is probably slightly high due to the tendency to covalency in its compounds. If the compounds were strictly polar the value would probably be about 38.0, by comparison with the corresponding values for mercury and lead, since there should be a slight decrease in the ionic susceptibility caused by the increase of the atomic charge Z . Allowing for this, the difference between the values of the theoretical and experimental susceptibilities is of the order 45 units for mercury, 25 units for thallium and say 12 units, or thereabouts, for lead. These differences represent a series of the type $(a+b)^2$, $(a)^2$, $(a-b)^2$. In Slater's formula for the susceptibility the only squared factor is $(Z-s)$, which will vary in the above way on passing from mercury to lead. It may then be inferred that the discrepancy between experiment and theory lies in the value of s the screening constant in Slater's formula. Thus, for either or both of the $5d$ and $6s$ shells the screening constant is too high, and hence the effective atomic number $(Z-s)$ is too low. Owing to this factor being squared in the formula, the deviation between theory and experiment will appear most marked for the element of least atomic number, namely, mercury. Angus¹¹ has suggested a modification in the method of grouping the s and p electrons, giving a slightly different value of the screening constant for these electron groups. In the case of the thalious ion this was found to make a difference of only one or two units to the theoretical susceptibility since it does not affect the values of $\Sigma\bar{\chi}^2$ for the $5d$ and $6s$ shells. This, therefore, does not explain the discrepancy, and the results given for the experimental susceptibility of the thalious ion support Brindley's view, based on theoretical considerations, that Angus' method is not justifiable. Some other modification which will explain all the above points seems to be needed in the theory.

Summary.

1. The magnetic mass susceptibility of 27 thalious compounds has been determined and a mean value of -38.4×10^{-6} obtained, from the salts with univalent anions, for the ionic susceptibility of the thalious ion.

¹¹ Angus, *Proc. Roy. Soc.*, 1932, 569.

2. Salts with divalent and trivalent anions give a slightly lower value, and salts with organic anions a higher value, explained as due to alteration in the ionic radius with change in co-ordination number.

3. The mass susceptibility of a number of potassium salts has also been determined to obtain correcting constants for the anions.

4. The theoretical atomic susceptibility has been calculated from Slater's approximate wave functions and is compared with the experimental value, which is considerably lower, indicating a discrepancy between theory and experiment.

5. A value of the ionic radius 1.36 \AA.U. has been deduced from the experimental atomic susceptibility and is compared with the value 1.49 \AA.U. obtained from X-ray crystallography.

6. The Slater method as applied by Brindley has been used to determine the relative contributions of the positive and negative ions in the salts with single univalent anions and again indicates too high a theoretical value for the atomic susceptibility of the thallos ion.

7. Comparison of the atomic susceptibility of the thallos ion with those for mercury and the plumbous ion indicate that the discrepancy between theory and experiment is due to too high a value for the screening constants of the $5d$ and $6s$ levels, given by Slater's method.

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IONIC DIAMAGNETIC SUSCEPTIBILITY AND DIAMAGNETIC
CORRECTING CONSTANTS

IONIC DIAMAGNETIC SUSCEPTIBILITY AND DIAMAGNETIC CORRECTING CONSTANTS.

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The diamagnetic susceptibility of a polar salt may be considered as an additive function of the susceptibility of its ions, the ions being regarded as independent centres of diamagnetism, thus

$$\chi_{\text{M}} = \chi_{\text{cation}} + \chi_{\text{anion}}.$$

The contribution of the ions to the diamagnetism has been estimated by a variety of methods by different investigators from the experimentally determined molar susceptibilities of compounds. Starting from the alkali halides, the most strictly polar salts, tables of the diamagnetic

susceptibility of ions have been prepared. The literature shows a considerable divergence among the values proposed by different observers. Each investigator tends to employ his own standard set of values so that correlation of magnetochemical work is rendered difficult. It appears therefore that a comparative survey of the methods available is required, calculating the ionic diamagnetic susceptibilities from such trustworthy experimental data as is available. In this way an average set of ionic susceptibilities can be obtained.

There are two important reasons for establishing such a standard set of values. Firstly, to compare with the various theoretical values for the magnetic susceptibility of ions and secondly to obtain a set of ionic correcting constants for use in estimating the diamagnetic effect of such ions in work with paramagnetic molecules. For compounds of low paramagnetic susceptibility the diamagnetic correction is often of appreciable size so that as great a degree of accuracy as possible is desirable. A table of some of the ionic magnetic susceptibilities proposed by different authors is given in Bhatnagar's "Magnetism," page 142, and reference to this will show the considerable variation between the values. Although in a number of cases agreement is fair, in extreme cases (*e.g.*, Cs⁺) variations reach as much as ten units of molar susceptibility.* Stoner ("Magnetism and Matter," p. 272) has proposed a set of ionic correcting constants based on a method due to Brindley, and employing experimental measurements due to Kido, but it seems more justifiable to attempt to obtain an average set of values using as wide a range of methods and experimental data as possible. It will be seen from what follows, that when allowance is made for possible sources of error in the methods, and values are re-calculated using improved experimental results, an extraordinarily good agreement is found for the ionic susceptibilities of the alkali metal and halide ions by the different methods. From these, values for the other ions can be deduced wherever reliable experimental data is available. In many cases, however, such values can only be given approximately until further measurements are available so that possible sources of error in the measurements of individual compounds may be eliminated. Having obtained the ionic values a comparison can be made with the various theoretical ionic susceptibilities. Further, it is possible to make a comparison between the ionic susceptibility values and those for the atom combined in homopolar compounds.

The earliest estimates of atomic susceptibilities were due to Pascal^{1†} and are based on his measurements of the susceptibility of halogenated carbon compounds. Such compounds all contain a homopolar bond between the atom in question and the nearest carbon atom so that this bond effect will be included in the estimated susceptibility, as has been pointed out by Stoner and others. Pascal's atomic susceptibility values are, thus, those of the atom in its homopolar compounds and not the value for the free ion. Pascal has shown that there is a definite constitutive bond effect in many organic compounds and Gray² and his

* Throughout the paper, magnetic mass susceptibilities are expressed in units of Gram-Ionic, or Molar, Diamagnetic susceptibility, *i.e.*, $-X_M \times 10^6$.

¹ P. Pascal. A summary of references to Pascal's work is given in Stoner, "Magnetism and Matter," p. 496.

† A summary of these values will be found in the *International Critical Tables*, Vol. VI, p. 349.

² F. W. Gray and W. Cruickshank, *Trans. Far. Soc.*, 1491, 1935.

co-workers have supplied evidence that a single homopolar bond will have an appreciable depressing effect on the total molar susceptibility. Thus susceptibility values for halogen atoms derived from homopolar compounds will be lower than the corresponding ionic ones, while those for cations will in most cases be higher since they are derived from the halide value. Comparison of strictly ionic susceptibilities with Pascal's homopolar values gives the bond effect for each atom, i.e., the lowering of susceptibility of the ion on passing from the free ion to an atom held by a homopolar bond.

Ionic Susceptibilities for Halide and Alkali Metal Ions.

The first method employed here for calculating ionic susceptibilities does not appear to have been suggested previously. This is to estimate from Pascal's experimental susceptibilities of the halogen molecules a value for the ionic susceptibilities of the halide ions by making use of the ratio between theoretical and experimental susceptibilities. Slater's³ theoretical method for calculating magnetic susceptibilities is employed in preference to other theoretical methods, since, on the whole, for the medium range of atomic numbers it gives results in best agreement with experimental data. For the very light and very heavy ions there is considerable discrepancy between all the theoretical values and those found by experiment. Such discrepancy is, however, an absolute one and will not affect the ratio ion/atom.

By taking one half of the molecular susceptibility of the halogen molecules one obtains Pascal's homopolar atomic susceptibility of the

halogen atoms. This may be converted to a true ionic susceptibility by using the ratio $A/B = C/D$ where A = the theoretical atomic susceptibility corresponding to the above experimental value, and is obtained by taking one half of the theoretical magnetic susceptibility of the molecule. (Reference to "Magnetism and

TABLE I.

Halogen.	Theoretical Magnetic Mass Susceptibility.		Experimental Magnetic Mass Susceptibility.	
	Homopolar Atom. (A.)	Ion. (C.)	Homopolar Atom. (B.)	Ion. (D.)
Fluorine .	7.1	8.30	6.3	7.3(5)
Chlorine .	22.3	25.79	20.2	23.4
Bromine .	35.4	40.01	32.0	36.2
Iodine .	53.0	59.80	45.7	51.6

Matter" by Stoner, p. 467, will give details of the method for calculating a theoretical molecular susceptibility for the halogens); B = the experimental homopolar atomic susceptibility as above; C = the theoretical ionic susceptibility calculated by Slater's method; D = the required experimental ionic susceptibility. Table I shows in columns 2, 3 and 4 the values of A , B and C for the halogen atoms while column 5 gives the resulting value for D . This method is not applicable to the alkali metal ions.

Methods 2, 3 and 4.—Three methods due to Weiss⁴ are available for estimating ionic susceptibilities. The first of these corrects Pascal's atomic values for the homopolar bond effect by adding or subtracting a constant factor ± 3.0 units of molar susceptibility. In addition, from the evidence of refractivity data and its correlation with magnetic susceptibility data, he corrects for the deforming effect of adjacent ions in the compound. These values of Weiss are employed as they stand in

³ J. C. Slater, *Physic. Rev.*, 1930, 57.

⁴ P. Weiss, *J. Physique*, 1930, 1, 185.

the present paper, although it should be pointed out that the value of the bond effect for all ions is by no means constant. As will appear later, this effect increases with increasing atomic number of the ion. The values for the ionic susceptibilities of halide and alkali ions by this method are shown in Table II, column 2.

Accurate measurements of the diamagnetic susceptibilities of certain of the alkali halides have been made by Hocart⁵ and from these Weiss deduced ionic values for the halide and alkali metal ions concerned. Having shown that the hydrogen ion has an effective paramagnetism in solution of 1.2 units of molar susceptibility, he deduced a value for the ionic susceptibility of the chloride ion as a starting point, other values then following from this, with allowance as in the previous method for the deforming effect of adjacent ions. These values are shown in column 3 of Table II.

Yet another method due to Weiss⁸ makes use of Reicheneder's⁶ mea-

surements of the magnetic susceptibilities of the halogen acids from which the correction for the effective paramagnetism of the hydrogen ion gives the ionic susceptibilities of the halide ions. Experimental values for these acids have more recently been obtained by both Kido^{7a} and Farquharson⁸ and taking a mean of the values due to all three authors gives a slightly different figure for the ionic susceptibilities than that of Weiss. Table III gives the relevant data, the ionic susceptibilities for the halide ions being shown in the last column. The method is, of course, inapplicable to the alkali metals

TABLE II

Ion.	Gram-Ionic Susceptibilities.			
	Weiss-Pascal.	Weiss-Hocart.	Brindley-Hoare.	Kido.
Fluoride . . .	—	—	9.4	12.2
Chloride . . .	23.1	23.1	24.2	22.1
Bromide . . .	34.7	33.9	34.5	34.7
Iodide . . .	49.8	49.5	50.6	53.2
Lithium . . .	—	—	0.7	—
Sodium . . .	7.6	8.2	6.1	7.6
Potassium . . .	16.0	16.5	14.7	13.6
Rubidium . . .	24.3	—	22.0	27.2
Caesium . . .	41.0	—	35.1	41.0

TABLE III

Ion.	Molar Susceptibility Halogen Acid.				Gram-Ionic Susceptibility.
	Reicheneder.	Kido.	Farquharson.	Mean Value.	
Chloride . . .	21.9	21.9	23.0	22.3	23.5
Bromide . . .	32.5	34.6	31.4	32.8	34.0
Iodide . . .	50.2	(53.5)*	49.3	49.9	51.1

* Neglected as too high.

Methods 5 and 6.—A fifth and sixth method of estimating ionic susceptibilities are both due to Brindley, the latter in collaboration with Hoare. In the first of these methods Brindley⁹ improves on a method suggested by Joos and used by Ikenmeyer. The contribution to the

⁵ R. Hocart, *C. Rend.*, 1929, 1151.

⁶ K. Reicheneder, *Ann. Physik*, 1929, 58.

⁷ (a) K. Kido, *Sci. Rep. Tohoku Univ.*, 1932, 149; (b) *ibid.*, 1932, 288; (c) *ibid.*, 1932, 869.

⁸ J. Farquharson, *Phil. Mag.*, 1931, 283.

⁹ G. W. Brindley, *ibid.*, 786.

total susceptibility of anion and cation in ions of the inert gas configuration, *i.e.* NaF, KCl, RbBr and CsI, are considered by Joos to be inversely as the square of the nuclear charge. Brindley showed that a more accurate estimate is given by using the ratio $1/(Z-s)^2 : 1/(Z'-s')^2$, where Z and Z' are the respective nuclear charges and s and s' are the screening constants given by Slater's method for determining atomic susceptibilities. The appropriate values of Z , s and Z' , s' are employed for each electron shell, and using Slater's effective quantum numbers for the respective shells, Brindley estimated the proportion of the experimental susceptibility due to each ion from the expression:—

$$\chi_{\text{cation}} = \frac{\Sigma \bar{r}^2_{\text{cation}}}{(\Sigma \bar{r}^2_{\text{cation}} + \Sigma \bar{r}^2_{\text{anion}})}, \text{ where } \Sigma \bar{r}^2 = \frac{(n')^2(n' + \frac{1}{2})(n' + 1)}{(Z - s)^2}.$$

$\Sigma \bar{r}^2$ represents the electron density distribution summed for each electron shell, and n' = the effective quantum number of the shell. Values for the ionic susceptibility of the alkali and halide ions as well as others of inert gas configuration are obtained in this way. In the present paper Ikenmeyer's values have not been included, as they are not accurate enough for the present purpose. Experimental measurements of the molar susceptibility of the alkali halides of required configuration have up to date been made by Hocart,⁶ Kido,^{7a} Gray and Farquharson^{10a} Gray and Dakers^{10b} and by Brindley and Hoare.¹¹ Comparison of these values showed that those of Hocart and of Brindley and Hoare were in best agreement and these have been used in the present paper as more reliable than some of the others. The final ionic values given in columns 6 and 7 of Table IV thus vary slightly from those obtained by Brindley in his original paper on this method and also from those calculated by Stoner¹² from Kido's^{7a} experimental values. Further evidence for considering Hocart's and Brindley and Hoare's values as more reliable than those of other workers is considered later on in this paper. The values of $\Sigma \bar{r}^2$ required for this calculation are shown in columns 2 and 3 of Table IV, while the experimental halide values are shown in columns

TABLE IV

Inert Gas Configuration.	$\Sigma \bar{r}^2$.		Experimental Molar Susceptibilities.		Gram-Ionic Susceptibilities.	
	Cation.	Anion.	Hocart.	Brindley.	Cation.	Anion.
NaF	5.28	10.27	—	15.9	5.4	10.5
KCl	—	—	39.1	38.8	15.0	23.9
RbBr	32.03	49.73	—	56.4	22.2	34.3
CsI	50.09	74.19	—	85.7	34.6	51.1

4 and 5. The actual experimental figure for caesium iodide has had 3.1 units of susceptibility added to correct from 8-co-ordination to 6.

Subsequently to Brindley's first paper, Brindley and Hoare¹¹ proposed a slightly different set of standard ionic values based on careful experimental measurements of the susceptibilities of the crystalline salts of the alkali halides. Ionic values were deduced from these by assuming that in the case of the lightest ion of the series, lithium, the experimental susceptibility might be taken as the same as the theoretical, calculated

¹⁰ (a) Gray and Farquharson, *Phil. Mag.*, 1930, 191; (b) Gray and Dakers, *ibid.*, 1931, 81.

¹¹ Brindley and Hoare, *Proc. Roy. Soc.*, 1935, 325.

¹² Stoner, "Magnetism and Matter," p. 271.

by Slater's method. Since the theoretical value for this ion is small ($\chi_M = -0.72 \times 10^{-6}$) any small divergence between theoretical and experimental values will not appreciably influence the values for other ions derived from this starting point. This extensive investigation showed that slightly different ionic values for any one ion were obtained for crystalline salts of different co-ordination number, increasing co-ordination causing a slight fall in diamagnetism due to deformation of the outer electron orbits. Thus, in the case of caesium iodide the increase from the normal 6-co-ordination of the other alkali halides to 8-co-ordination was shown by Brindley and Hoare to be accompanied by a fall in susceptibility of 3.1 units on the total molar susceptibility. The ionic correcting constants obtained by Brindley and Hoare for salts of 6-co-ordination have been employed throughout this present paper as they are in closest agreement with ionic values obtained by the other methods. This method is open to the objection that the choice of lithium as standard is not an ideal one since for the very light ions it has been shown that the theoretical susceptibilities are considerably too low. It is not until the ions of atomic numbers of the order ten to eighteen are reached that the theoretical and experimental susceptibilities approach each other (see Fig. 5). Thus the use of the lithium ion as standard will make the susceptibilities of negative ions derived from it slightly too high but the error is not large since the susceptibility of the lithium ion is itself so small. Table II, column 4 shows the relevant figures for ionic susceptibilities obtained by this method.

Method 7.—Kido⁷ has more recently suggested another approach to the problem. From a large number of measurements of the molar susceptibilities of polar salts he has plotted curves in which salts in the same group of the periodic table with a common anion are compared. When the molar susceptibility is plotted against the number of electrons in the cation for series with the same anion Kido finds that a series of straight lines result. In this way the alkali halides give a set of parallel straight lines. By extrapolation to the value effective atomic number 0, he deduces a value for the anion assuming that the susceptibility of the hydrogen ion can be taken as zero, *i.e.*, the extrapolated value is that corresponding to the acid H^+A^- and taking H^+ as zero gives the anion value required. This method is open to two sources of error, for as Weiss has shown, the effective paramagnetism of the hydrogen ion should be allowed for in estimating ionic susceptibilities and, even more important, it can be shown that the smoothing out of the susceptibility values to a straight line is not justified. Not only are the experimental susceptibilities not a linear function of the number of electrons in the cation or anion, but the theoretical susceptibilities themselves show a definite divergence from a linear form. This point is discussed more fully later. The magnitude of the error introduced in this way is for most ions not large, so that Kido's values are included in calculating the present average values. Column 5 of Table II shows Kido's values.

Summary of Results by foregoing Methods.

Comparison of the ionic values in the last columns of Tables I, III and IV with those in Table II shows that for the chloride, bromide and iodide ions these methods give a remarkably good agreement so that a satisfactory mean can be calculated for these three ions. Kido's value for the iodide ion has been omitted from the values used as being obviously too high. Thus an average for these ions results as follows:—

Ionic susceptibility	$\text{Cl}^- = 23.4 \pm 1.3$	(mean of 7 values).
" "	$\text{Br}^- = 34.6 \pm 1.6$	(mean of 7 values).
" "	$\text{I}^- = 50.6 \pm 1.6$	(mean of 6 values).

For the fluoride ion, data is more limited and agreement not so good and it again appears likely that Kido's value of 12.2 is too high. A mean of the remaining values gives:—

Ionic susceptibility $F^- = 9.1 \pm 1.8$ (mean of 3 values).

The data for the alkali ions is also rather restricted and agreement is not as close as for the first three halide ions, but the following mean values result:—

Ionic susceptibility $Na^+ = 7.0 \pm 1.7$ (mean of 5 values).
 " " $K^+ = 15.1 \pm 1.4$ (mean of 5 values).
 " " $Rb^+ = 22.8 \pm 1.5$ (mean of 3 values).
 " " $Cs^+ = 37.9 \pm 3.3$ (mean of 4 values).

Kido's values have again been neglected in calculating the susceptibilities of the rubidium and caesium ions as being much higher than the other values.

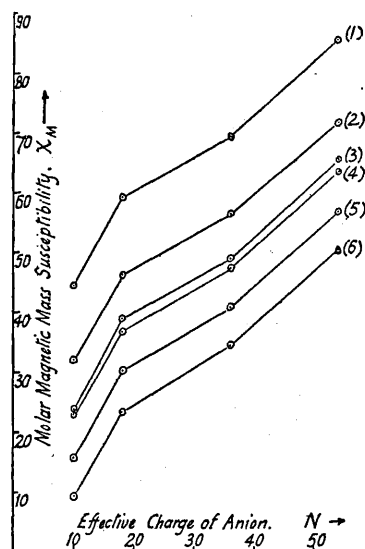


FIG. 1.—Experimental susceptibilities of alkali halides and the halide ions plotted against effective charge of anion.

- (1) Caesium salts (Brindley and Hoare).
- (2) Rubidium salts (Brindley and Hoare).
- (3) Potassium salts (Brindley and Hoare).
- (4) Ammonium salts. (This Laboratory.)
- (5) Sodium salts (Brindley and Hoare).
- (6) Mean experimental susceptibilities for halide ions (present paper).

Since the alkali values are only given by some of the methods and the agreement is not as close as is desirable it was considered advisable to use the summarised halide values to obtain a more accurate set of values for the alkali ions. This was done by means of a graphical method introduced to eliminate individual experimental errors in the susceptibility measurements used. If the experimental susceptibilities for the alkali halides obtained by the various authors mentioned previously are plotted against the effective atomic number of the anion it at once becomes apparent that the values of Brindley and Hoare and of Hocart are for the most part the most satisfactory. For the halide series of the alkali metals these authors' results give graphs which, although not linear throughout, are parallel over the corresponding section on passing from one halide value to the next (see Fig. 1). Values of other observers in many cases showed deviations from this parallel relationship. This graphical representation thus serves as an excellent check on the accuracy of the experimental figures as well as a means of smoothing out any individual deviations for a given compound. Plotting below the halide salt values the above mean values for the halide ion gives the susceptibilities for the

various alkali ions from the average distance between the graphs for the corresponding parallel sections. The values obtained in this way are likely to possess considerably greater accuracy than those based on individual measurements. The graphical values result as follows:—

$$\text{Na}^+ = 6.6, \quad \text{K}^+ = 14.7, \quad \text{Rb}^+ = 22.2, \quad \text{Cs}^+ = 35.0.$$

A mean of these graphically obtained values and the original set gives a final set of alkali ionic values proposed as the most accurate that can at present be obtained:—

Ionic susceptibility	$\text{Na}^+ = 6.8.$	
" "	$\text{K}^+ = 14.9.$	
" "	$\text{Rb}^+ = 22.5.$	
" "	$\text{Cs}^+ = 35.0.*$	

The ionic susceptibility of the lithium ion, being small, is difficult to estimate since the possible deforming factors in the crystalline salts will have their maximum effect. Brindley and Hoare, recognising this deformation in the experimental values, employed the value $\text{Li}^+ = 0.7$, assuming agreement between theoretical and experimental susceptibilities. Since, however, the theoretical susceptibility becomes increasingly lower than the experimental for the lighter ions it is likely that this is too low a value. Brindley's inert gas configuration method of finding ionic susceptibilities although not directly applicable can be modified for this case. By calculating an ionic value for the lithium ion from the salts LiF , LiCl , LiBr , where the ions are of unequal configuration, and extrapolating back to the symmetrical structure (*i.e.* the hypothetical LiX , where X would have a structure similar to the H^- ion and thus LiX would correspond to twice the helium configuration), it is possible to obtain a value for the lithium ion. This method gives an ionic susceptibility for Li^+ from lithium bromide = 0.565, from the chloride = 0.598, from the fluoride = 0.766, whence, plotting these figures against the atomic number of the inert gas configuration attained in each compound and extrapolating back, a value for the lithium ion of ionic susceptibility $\text{Li}^+ = 1.2$, with an uncertainty of some 0.2 units, is obtained.

This value is confirmed by using the new fluoride ion value and Brindley and Hoare's lithium fluoride experimental value, which is the least likely to suffer from deforming effects owing to the more nearly equal size of the two ions than in other compounds. Since the experimental susceptibility of lithium fluoride is 9.1 a value for $\text{Li}^+ = 1.0$ results from this method. The values of the other lithium halides cannot be similarly used, for the distortion produced by the unequal size of anion and cation makes it impossible to obtain a value. It is proposed provisionally to take 1.0 as the most likely value for the ionic susceptibility of the lithium ion.

Ionic Susceptibilities of Other Ions.

These new ionic values can be employed to obtain ionic susceptibility values for other ions provided that polar salts are used and the susceptibility is assumed additive. Stoner in "Magnetism and Matter," page 272, has given a set calculated by him from Kido's measurements of salts, using the halide and alkali metal ionic values obtained by Brindley's first method. Kido⁷ has also suggested a number of values from his own measurements but for the reasons already given it is proposed to attempt to obtain values of greater accuracy. In the various cases now considered for which ionic values are suggested an average of the best experimental values has been taken to avoid errors of individual experimentors and

* The two high values of 41.0 have been omitted in calculating this mean, since the graph supports the lower values.

wherever possible the graphical means of smoothing out individual discrepancies, due to the deforming factors already referred to, have been used. In this way values for the ionic susceptibilities of the univalent nitrate, oxyhalogen and cyanide series of negative ions have been calculated and for the positive ammonium and thallium ions. The data used is that due to Kido, to the present author and some unpublished work being completed in these laboratories by Miss M. E. Bedwell. Since correcting constants are frequently needed for the commoner polyvalent anions the values for some of these are included in the present paper. It should be noted, however, that such values are only strictly applicable for these ions in combination with univalent cations. Brindley has pointed out that on passing from univalent to divalent cations the susceptibility of the anion does, in the case of some salts, become modified, e.g., the effective susceptibility of the halide ions in the alkaline earth halides is less than in the alkali series. It is proposed to consider the necessary modifications to be introduced in the present values when combined with polyvalent cations in a subsequent paper.

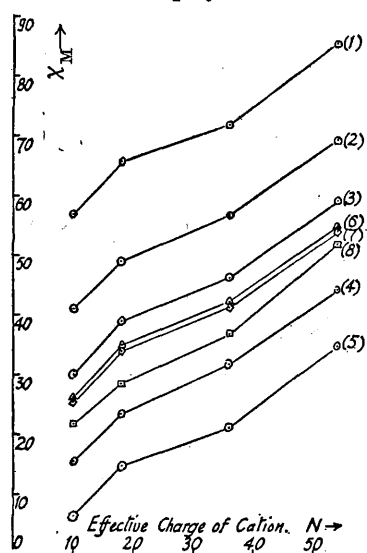


FIG. 2.—Experimental susceptibilities of alkali salts and the alkali ions plotted against effective charge of cation.

- (1) Alkali iodides (Brindley and Hoare).
- (2) Alkali bromides (Brindley and Hoare).
- (3) Alkali chlorides (Brindley and Hoare).
- (4) Alkali fluorides (Brindley and Hoare).
- (5) Alkali ions—Mean experimental susceptibilities (present paper).
- (6) Alkali sulphates (various authors).
- (7) Alkali nitrates (various authors).
- (8) Alkali carbonates (various authors).

The method of calculating the ionic susceptibilities in this section is as follows:—

Nitrate Ion.—The available experimental values for nitrates are those due to Kido¹⁰ who has measured the susceptibilities of the nitrates of the alkali metals and nitric acid. On plotting these values against the number of electrons in the anion they do not fall on the simple straight line which Kido suggested, but if similarly plotted between Brindley and Hoare's¹¹ corresponding values for the alkali fluorides and chlorides (see Fig. 2, curve 7) do, over the range sodium to rubidium, run parallel with the halide graphs. This gives evidence for the reliability of these values for determining the susceptibility of the nitrate ion. Kido's experimental value of 22.7 for lithium nitrate is not included since the value it gave for the nitrate ion was considerably higher than the mean obtained from the graphical method. From the graph the mean susceptibility of the nitrate ion is:—

$$\text{Ionic susceptibility } \text{NO}_3^- = 18.9.$$

Kido's own value of 20.1 is probably too high, due to including the lithium value and to considering the graph as a straight line. It may be noted

in passing that this graph may be used to give an estimate of the susceptibility of caesium nitrate, a salt whose susceptibility has not up to the present been measured. The probable value for the susceptibility of this salt, corrected to 6-co-ordination, is 54.2 units of susceptibility.

Ammonium Ion.—A mean value for the susceptibility of this ion from Kido's experimental susceptibilities of the ammonium halides is far from satisfactory. A far better mean is given by the revised values obtained in this laboratory by Miss M. E. Bedwell. These not only give a closer agreement to the mean but on plotting between the values for the sodium and potassium ions (in Fig. 1, curve 4) show a similar parallel relationship which is by no means obtained with Kido's figures. Table V summarises the data employed, including the value for ammonium nitrate. The figures give a mean of 13.4 while the graph, without the nitrate value, gives 13.2, so that the mean value for the ionic susceptibility of the ammonium ion can be taken as 13.3 units.

TABLE V.

Salt.	Molar Susceptibility.		Gram-Ionic Susceptibility.	
	Kido.	Bedwell.	Kido.	Bedwell.
NH ₄ F .	24.5	23.0	15.4	13.9
NH ₄ Cl .	34.2	36.7	10.8	13.3
NH ₄ Br .	47.4	47.0	12.8	12.4
NH ₄ I .	66.0	64.0	15.4	13.4
NH ₄ NO ₃ .	33.6	32.6	14.7	13.7
	Kido.	Trew.	Kido.	Trew.
NaClO ₃ .	37.8	—	31.0	—
KClO ₃ .	—	44.3	—	29.4
KBrO ₃ .	53.2	54.1	38.3	39.2
KIO ₃ .	65.8	65.9	50.9	51.0
KClO ₄ .	45.1	48.1	30.2	33.2
KIO ₄ .	67.0	—	52.1	—

The Oxyhalogen Ions.—Kido^{7c} and the present author¹³ have obtained values for the molar susceptibilities for several of the alkali salts of the chlorate, bromate, iodate, perchlorate and periodate ions which, except for the perchlorate ion, are in agreement. Here Kido's value is rather lower (see Table V). In all cases, except this

latter, a mean of the values is taken, giving the following ionic susceptibility values: ClO₃⁻ = 30.2, BrO₃⁻ = 38.8, IO₃⁻ = 51.0, ClO₄⁻ = 33.2 and IO₄⁻ = 52.1. Further confirmation of these values was obtained by plotting the susceptibility of the potassium and thallium chlorates, bromates and iodates against the number of electrons in the anion as in Fig. 3 when two parallel curves result, which are almost straight lines. From these the average difference IO₃⁻ - BrO₃⁻ = 11.3 and BrO₃⁻ - ClO₃⁻ = 10.1, whence, if the value for the chlorate ion is taken as 30.2, that for the bromate becomes 40.4 and for the iodate 51.7. While the iodate ion value is thus in fair agreement that for the bromate ion suggests that Kido's value for sodium bromate may be somewhat too low. A final mean for these three ions of ClO₃⁻ = 30.2, BrO₃⁻ = 39.8 and IO₃⁻ = 51.4 is suggested as being the most satisfactory.

An interesting point may be noted in this graph in that the usual points of inflection in the halide-effective atomic number graphs are so smoothed out by the addition of three oxygen atoms in the negative ion as to be almost missing, *i.e.* the three oxyhalides lie almost on a straight line, although the slight depression at the bromate ion is still noticeable.

¹³ Trew, *Trans. Faraday Soc.*, 1936, 1658.

Thus the anion behaves as a large compound ion in this series of compounds. This effect may be expressed as a bond depression due to a reduction of the spread of the electron density by the halogen oxygen bond. An estimate of the magnitude of this can be made from Pascal's atomic susceptibility value for the oxygen atom in combination, and this depression may be used to check the suggested susceptibility values for the perchlorate and periodate ions for which only limited data are available. It is reasonable to suppose that all four halide-oxygen bonds will have the same effect in depressing the susceptibility. Thus we have:—

$$\text{Ionic susceptibility Cl}^- = 23.4, \text{ClO}_3^- = 30.2.$$

Therefore the value for 3O-atoms = 6.8. But Pascal gives for the O-atom 4.6, whence the value for 3O- = 13.8.

Hence the bond depression per Cl—O bond = (13.8 - 6.8) = 2.3. An exactly similar reasoning gives the depression for the Br—O bond = 2.9, and the I—O bond = 4.3. Values for the susceptibility of the

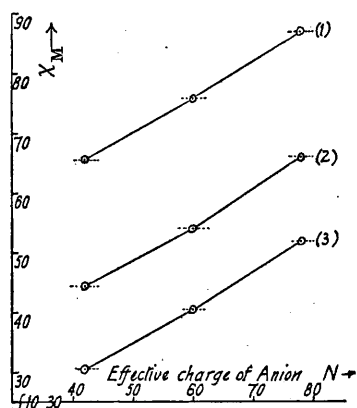


FIG. 3.—Oxyhalide salts of potassium and thallium plotted against effective charge of anion.

- (1) Thallium salts (present author).
- (2) Potassium salts (Kido and present author).
- (3) Mean experimental susceptibilities of oxyhalide ions.

perchlorate and periodate ions can then be estimated from these bond depressions as follows:—

$$\begin{aligned} \text{Ionic susceptibility ClO}_4^- &= (\text{Ionic susceptibility ClO}_3^- + \text{susceptibility O}^-) - \text{Depression Cl—O} \\ &= (30.2 + 4.6) - 2.3 \\ \therefore \text{ClO}_4^- &= 32.5. \end{aligned}$$

Similarly the value for $\text{IO}_4^- = 51.7$. The agreement with the values obtained previously is thus remarkably good and the ionic susceptibilities $\text{ClO}_4^- = 32.0$ and $\text{BrO}_4^- = 51.9$ are therefore proposed for these ions.

Thallium Ion.—With these values available it is possible to revise that for the thallium ion published in a previous paper.¹³ From the mean of the values for the fluoride, chloride, iodide (the latter corrected by adding on 3.1 to change from eight to six co-ordination), nitrate, chlorate, bromate and iodate salts of thallium given there, a mean ionic susceptibility value for the thallium ion of $\text{Tl}^+ = 35.6$ is now obtained on the basis of these revised correcting constants. A confirmation of this figure can be obtained from Fig. 3, since the Tl^+ and K^+ graphs are separated by a distance of 21.0 units. Whence, from the value 14.9 for the potassium ion, that of 35.9 results for the thallium ion. A mean value of $\text{Tl}^+ = 35.7$ may finally be taken.

Cyanide, Cyanate and Thiocyanate Ions.—Ionic susceptibilities for these three ions have been given by the present author in a previous paper¹³ but these will require modification to bring into line with the

new values. Taking the above mean for the thallium ion the previously published values for these salts of thallium gives $\text{CN}^- = 13.3$, $\text{CNO}^- = 19.8$ and $\text{CNS}^- = 31.0$. These may be compared with the corresponding homopolar values due to Pascal,¹ namely, $\text{CN}^- = 10.8$, $\text{CNO}^- = 16.2$ and $\text{CNS}^- = 26.6$. Kido^{7, 8} has published values for the three ions based on measurements of some of the alkali cyanides, cyanates and thiocyanates. These values ($\text{CN}^- = 16.6$, $\text{CNO}^- = 23.9$ and $\text{CNS}^- = 37.5$) are considerably higher than the present ones and rather higher than seems reasonable than those of Pascal. It was therefore felt desirable to re-measure the susceptibilities of the alkali salts of these ions and as a preliminary a value was obtained using recrystallised A.R. potassium cyanide, which was tested and found to have a negligibly small iron content. A molar susceptibility = 27.2 was found. Subtracting the ionic susceptibility, 14.9, of the cation gives $\text{CN}^- = 12.8$ in reasonably close agreement with the value 13.3 obtained from the thallium salt. It thus appears likely that Kido's figures are too high. This is further supported by the difference between the homopolar and heteropolar values for this series, *i.e.* for $\text{CN}^- = 2.0$, $\text{CNO}^- = 3.6$ and $\text{CNS}^- = 4.4$, which are of the same order as those for the halide ion series. The values $\text{CN}^- = 13.0$, $\text{CNO}^- = 19.8$ and $\text{CNS}^- = 31.0$ are provisionally suggested for these three ions.

Divalent Anions.

Passing to divalent anions, values are proposed for the sulphate and carbonate ions.

Sulphate Ion.—Here it was found necessary to re-measure the molar susceptibilities of sodium and ammonium sulphates since Kido's values for these salts appeared too low, and, in addition, the susceptibilities of rubidium and caesium sulphate were measured, no previous value being recorded for these salts. Values were obtained as follows:—

$(\text{NH}_4)_2\text{SO}_4 = 67.0$; Na_2SO_4 (calculated from the decahydrate) = 52.4;
 $\text{Rb}_2\text{SO}_4 = 84.8$; and $\text{Cs}_2\text{SO}_4 = 110.3$.

These values, together with Brindley and Hoare's value¹¹ for lithium sulphate, Kido's value for potassium sulphate and the present author's for thallium sulphate, are plotted in Fig. 2, taking one half the molar susceptibility since two alkali cations are involved. The graph, Fig. 2 (6), falls extraordinarily satisfactorily between that for the chloride and fluoride ions, following exactly the same parallel relationship as do the halide ions. From the graph a mean value $\text{SO}_4^{2-} = 40.1$ can be obtained. It is not possible to assign a satisfactory value to the univalent acid sulphate ion HSO_4^- since the susceptibility of the potassium salt only has been measured. From this salt, for which the molar susceptibility is 49.8, we get $\text{HSO}_4^- = 34.9$, considerably lower than for the divalent ion. Further investigation of the susceptibility of other bisulphates is needed here, since this drop in susceptibility of more than 5 units is out of proportion.

Carbonate Ion.—For this ion the available molecular susceptibilities do not give as good an agreement as for the sulphate ion. However, plotting the experimental values of the alkali carbonates due to Pascal and Kido and the thallium salt values of the present author give, as before, a graph appreciably parallel to that for the other anions, when one half of the molar susceptibility is used. (See Fig. 2 (8).) Pascal's value for caesium carbonate appears from the graph to be anomalous and re-measurement of the susceptibility of this compound appears indicated. From the graph a mean value for the susceptibility of the carbonate ion $\text{CO}_3^{2-} = 29.5$ results.

Attempts to obtain values for the susceptibility of other ions such as PO_4^{3-} , AsO_4^{3-} were not proceeded with as the available experimental data

did not give any consistent values and it is obvious that further experimental measurements on salts of these anions is required. The possible

modifying influence of water of crystallisation and covalency of the molecule may also have to be allowed for here, *i.e.* the additive law may no longer hold for these more complex salts.

It may be useful at this point to summarise the new ionic values proposed, together with the Pascal homopolar values which correspond (Table VI.).

TABLE VI.

	Heteropolar or Ionic Susceptibility.	Homopolar (Pascal's) Susceptibility.
F ⁻ . . .	9.1	6.3
Cl ⁻ . . .	23.4	20.1
Br ⁻ . . .	34.6	30.6
I ⁻ . . .	50.6	44.6
Li ⁺ . . .	1.0	4.2
Na ⁺ . . .	6.8	9.2
K ⁺ . . .	14.9	18.5
Rb ⁺ . . .	22.5	27.2
Cs ⁺ . . .	35.0	41.0

Values derived from above—

No ₃ ⁻ . . .	18.9	14.2
ClO ₃ ⁻ . . .	30.2	—
BrO ₃ ⁻ . . .	39.8	—
IO ₃ ⁻ . . .	51.4	—
ClO ₄ ⁻ . . .	32.0	—
BrO ₄ ⁻ . . .	51.9	—
CN ⁻ . . .	13.0	10.8
CNO ⁻ . . .	19.8	16.2
CNS ⁻ . . .	31.0	26.6
SO ₄ ⁼ . . .	40.1	33.6
CO ₃ ⁼ . . .	29.5	22.2
NH ₄ ⁺ . . .	13.3	—
Tl ⁺ . . .	35.7	—

show a marked deviation from linearity and any attempt at smoothing out to a straight line is unjustified.

A further interesting comparison may be made with the inert gases. The sum of the anion and cation values for ions of the same inert gas configuration, or the sum of the corresponding alkali and halide atomic values of Pascal (given in the foregoing table) each gives the values for the electronic isomers corresponding to twice the inert gas structures. The mean values of the above molecular susceptibility are plotted in the uppermost curve (Fig. 4, curve 1(b)). It should be noted that the sum of the ionic values with that of the homopolar values is in extremely close agreement and shows the satisfactory nature of the present ionic values. Immediately below this curve are plotted (Fig. 4, curve 1(a)) the values for the experimental susceptibilities of the inert gases multiplied by two to bring to the same scale. (The values for the first three of these are due to Wills and Hector (Stoner, "Magnetism and Matter," p. 202) while the last two are as given in Klemm's "Magnetochemie," p. 145). It will be noted that the graph for the inert gas susceptibility follows the same general course as the previous ones but falls very slightly below that for the sum of the positive and negative atoms or ions; being almost exactly parallel with the latter as might be expected. The unequal nature of the charge in the isomer MX, *i.e.* (N - 1) and (N + 1) renders the total susceptibility slightly greater than where the two atomic centres are symmetrical. This is in agreement with

Discussion of Results.

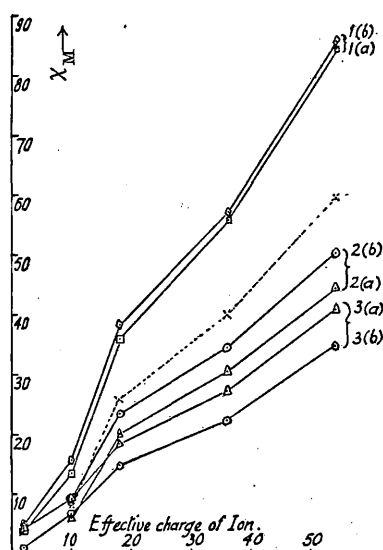
(1) Comparison with Theoretical Values.—Since some authors have attempted to show that a linear relationship exists between experimental ionic susceptibilities of the same series when plotted against the effective atomic number of the ion, it is useful to plot these values for the halide and alkali ions. In Fig. 4 the ionic susceptibilities of halide and alkali ions just obtained have been plotted, together with Pascal's corresponding values for the homopolar atom. All four curves are of the same type but

theory, since in the formula for the theoretical susceptibility a fall of one unit in N in the halide ion makes a relatively larger addition to $\Sigma\bar{r}^2$ than the lowering produced by the corresponding increase in N for the alkali ion.

To pass to a comparison of these experimental values with those obtained theoretically, Klemm in "Magnetochemie" gives graphs showing the course of the theoretical susceptibility-atomic number curve for alkali, halide and inert gas ions which show precisely similar deviations from linearity as the experimental curves. Klemm plots the theoretical values due to Angus¹⁴ which represent a slight modification of the Slater method. In Angus' method the s and p electrons for the same principal electron shell are considered separately in calculating the screening constants for the shell. The net result is to give rather lower theoretical susceptibility values which for the ions beyond potassium are in closer agreement with the experimental values. For

FIG. 4.—Experimental atomic and ionic susceptibilities of alkalis, halides and inert gases.

- (1a) Inert gas susceptibilities.
 - (1b) Sum of halide and alkali susceptibilities both homopolar and heteropolar.
 - (2a) Halide ion susceptibilities, homopolar (Pascal).
 - (2b) Halide ion susceptibilities, heteropolar (present paper).
 - (3a) Alkali ion susceptibilities, homopolar (Pascal).
 - (3b) Alkali ion susceptibilities, heteropolar (present paper).
- Dotted curve. Theoretical values of Slater for comparison.



convenience of reference, the curve of the Slater theoretical values for the halide ions has been plotted on Fig. 4 (dotted curve). From this the similarity in shape between experimental and theoretical curves may be noted and in addition the fact that the theoretical curve rises more sharply than the experimental after atomic number 10. The theoretical curves for the alkali ions, the homopolar atoms and the inert gases show similar relationships to the corresponding experimental curves. The general form of these theoretical graphs is dependent on the Langevin equation for the diamagnetic susceptibility of a spherically symmetrical system, *i.e.* $\chi_A = -\frac{e^2 L}{6mc^2} \Sigma\bar{r}^2$, where $\Sigma\bar{r}^2$ is as defined under Brindley's

first method of calculating ionic susceptibilities. The change in the slope of the curve on passing from one ion to the next will be determined by the change in values of $\Sigma\bar{r}^2$ for all the shells. The net difference, in passing from one ion to the next in the series is thus made up of a positive and a negative increment, since the contributions of inner

¹⁴ Angus, *Proc. Roy. Soc.*, 1932, 569.

shells becomes progressively less as that of additional outer shells is added. Even where the number of added electrons is the same, *i.e.* in passing from Cl to Br and from Br to I, an analysis of the constituents of Σr^2 shows that these two factors are not the same. Thus an analysis of the constituents of Σr^2 brings out the real nature of the change in slope of the susceptibility-effective atomic number curve and shows that the non-linear nature of the curve is a theoretical necessity. The present survey bringing out similar effects in the experimental results

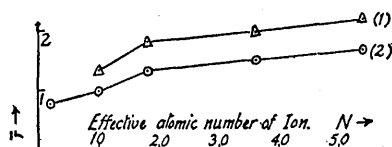


FIG. 4b.—Goldschmidt's ionic radii for alkali and halide ions plotted against effective charge of ion.

- (1) Halide ions.
(2) Alkali ions.

shows that in this respect experimental data supports the theory. Additional experimental evidence is supplied, if needed, by Fig. 4 (b), where Goldschmidt's¹⁵ ionic radii, derived from crystal structure data, for halide and alkali ions are plotted and show a similar type of deviation.

It is generally recognised that on the whole the theoretical susceptibilities are too high when compared with the experimental, the main deviations between experiment and theory occurring for the heavier ions where the theoretical values become progressively too high. (See

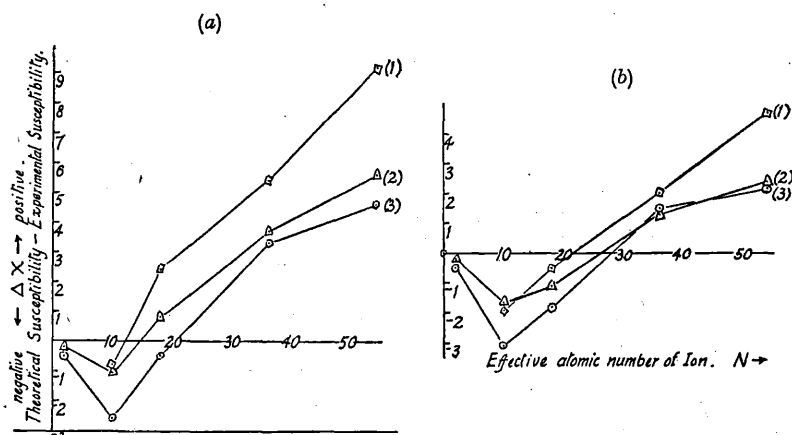


FIG. 5.—Deviations between theoretical and experimental susceptibilities.

- (a) Slater theoretical values { (1) Halide series.
(2) Inert gas series.
(3) Alkali series.
(b) Angus theoretical values { (1) Halide series.
(2) Inert gas series.
(3) Alkali series.

Stoner, "Magnetism and Matter," p. 272.) Klemm, however, suggests that any deviation between theory and experiment is not a systematic one but may be due to experimental error, especially since frequently there is a difference in the values obtained by different workers. In view of this opinion it was thought useful to plot the deviations between theoretical and experimental susceptibilities for the alkali, inert gas and halide ions, for both the Slater and Angus theoretical susceptibilities. Fig. 5 (a) and (b) shows these curves and indicates that the deviations are, contrary to Klemm's view, of a quite systematic nature. Thus,

¹⁵ Goldschmidt, *Trans. Faraday Soc.*, 1929, 253.

whichever theoretical susceptibilities are used, there is at first a fairly close agreement between theoretical and experimental values. The theoretical then falls below the experimental, reaching its minimum value at configuration $N = 10$, and then progressively rises with increasing values of N . The curves for the different ions are similar in type. The Slater values give best agreement for values of $N = 12-20$, while those of Angus are in better agreement for values of $N = 20-28$. On the whole, these curves support Stoner's opinion that Angus's separation of the "s" from the "p" electrons, in calculating the values, is not justified, since the Slater curves show the most systematic deviations. The deviations for heavier ions may be partly ascribed to the fact that experimental measurements never even approximate to the ideal condition of the free ion in empty space for which the theoretical calculations are made. Thus, as Brindley and others have pointed out, the limitation on the spread of the electron density for outer shells would lower the actually measured susceptibilities below the theoretical value. This effect is likely to become progressively larger, although not necessarily proportionately so as the volume of the ionic shell increases. That this is at least a partial explanation of the results is suggested by the gradual fall in susceptibility observed by Brindley and Hoare in compounds of increasing co-ordination number. It is further probable that for the elements of the alkali and halide groups agreement between theoretical and experimental susceptibilities would be reached could the experimental measurements be made for a single free ion in empty space, since Brindley and Hoare's results extrapolate back reasonably well to the Hartree theoretical value, as these authors have pointed out. This may not, however, be the case for all ions. The results obtained by the present author for the univalent thalious ion, where the experimental susceptibility is only a little more than half the theoretical value, suggests that in ions with the inert pair of electrons some other factor must be at work to produce the large discrepancy between experiment and theory.

(2) **Comparison of Heteropolar Values with Pascal's Homopolar Values.**—A useful comparison may be made for alkali and halide ions between Pascal's homopolar atomic susceptibility values and the present ionic values, thus giving a measure of the effect of converting a covalent to a polar bond. It will be noted from Table VI by subtracting corresponding values that the bond effect increases for the heavier ions. Plotting this bond increase or depression against N , the effective atomic number of the ion, shows in Fig. 6 the remarkably symmetrical nature of this effect, similar curves being obtained for halide and alkali ions over the corresponding sections. The general shape of these graphs and the gradual increase in bond effect on passing from lighter to heavier ion is in agreement with theory since the argument outlined before to explain the general form of the susceptibility-atomic number curve holds for these deviation curves. Furthermore, one electron makes a more marked contribution to the susceptibility in the higher shells, since the expression for Σr^{-2} contains several squared terms and thus the increasing bond effect is accounted for. The corresponding curve for the difference between theoretical homopolar and heteropolar values, derived by plotting the difference between the second and third columns of Table I (see Fig. 6 (1)) follows a similar course although some anomaly occurs at the fluoride ion. It may be remembered that only limited experimental data was

available for this ion and some correction in homopolar or heteropolar value may be needed. Fig. 6 further shows that Weiss's assumption that the Pascal atomic values can be corrected for the homopolar bond

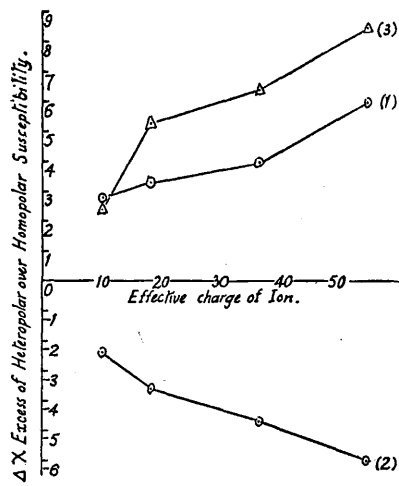


FIG. 6.—Excess of heteropolar over homopolar susceptibilities.

- (1) Halide ions.
- (2) Alkali ions.
- (3) Theoretical values halide ions.

effect by addition or subtraction of the factor ± 3.0 units of susceptibility is only approximately true for the lighter members of the series and a considerably greater correction is required for the heavier members. Fig. 6 summarises conveniently the extent of this bond effect for the univalent ions under consideration.

Summary.

1. Ionic diamagnetic susceptibility values for simple univalent ions of Periodic Table Groups I and VII, have been calculated. These may be used as correcting constants. These are mean values based on a survey of all the methods available, for calculating ionic susceptibility values, which have been critically discussed. A graphical method of checking experimental values, and deducing ionic correcting constants is introduced. Table VI gives the values proposed as the most satisfactory. Additional values for other univalent ions and some commoner divalent ions have been deduced from these, using a graphical means of smoothing out individual experimental errors.

2. The relationship between theoretical and experimental ionic susceptibilities for ions of related series has been considered graphically, showing that theoretical values follow substantially the same general form as experimental ones, but the relationship is not a linear one. The deviations between theoretical and experimental values have been discussed and it is shown graphically that, contrary to some opinions, such deviation is quite systematic.

3. The relationship between experimental values for the same atom in homopolar and heteropolar combination has been considered for the halide and alkali ions and it is shown that the bond effect due to the homopolar bond is, for the simple ions considered, not constant, but rises in a regular manner with increasing effective atomic number of the ion. The value for ions of the same effective atomic number is approximately of the same order of magnitude.

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THE DIAMAGNETIC SUSCEPTIBILITY OF SOME ALKYL AND ARYL HALIDES.

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In a previous paper¹ a comparison was made between the diamagnetic susceptibilities of homopolar and heteropolar halogen atoms in chemical compounds, that is, between the atomic susceptibilities of halogen atoms obtained by Pascal from the molar magnetic mass susceptibilities of halogen-containing compounds, and the ionic susceptibility of the halogen ion in its typically polar compounds such as those with the alkali metals. During the course of that investigation, it was noted that there are considerable variations in the magnetic susceptibility values obtained by different investigators for the simpler halogen substituted derivatives of saturated aliphatic and aromatic hydrocarbons. In addition there were some gaps in the values for these compounds considered as a series. It was shown (*loc. cit.*) that a graphical method could be employed as a considerable guide to the reliability of experimental magnetic susceptibility values for related series of compounds in the same physical state. For the methyl and ethyl halides and the monosubstituted halogen derivatives of benzene, not only were there several differing values reported for experimental susceptibilities, but on plotting the observed molar susceptibility of the compound against the effective atomic number of the halogen atom, a wide divergence from the characteristic graphical relationship was found among members of a related series.

The importance of securing more accurate data for the diamagnetic susceptibility of organic compounds has recently, and since this work was initially undertaken, been stressed by Professor Sugden² and by W. R. Angus.³ Professor Sugden draws attention to the lack of agreement between experimental values for the magnetic susceptibilities of various compounds obtained by different workers and different methods.

Benzene and acetone represent the only two liquids other than water for which any really satisfactory range of investigations has been made by a large number of workers, and even here the extreme values differ by some 1.5%. Sugden points out that this uncertainty forms the principal difficulty in making any detached analysis of the relation between diamagnetism and chemical constitution, and obscures the causes of the divergences that exist between theoretical and experimental diamagnetic susceptibility values, a divergence that has also been pointed out in previous papers from this laboratory.

In view of the above, we have carried out measurements of the susceptibilities of those compounds which showed the widest discrepancies (see Table I for individual members), and which could be prepared or obtained readily.

In addition, some improvements in experimental technique for the determination of mass susceptibility by the modified Gouy method previously described⁴ have been devised. The method described below is suitable for liquids only, but in this limited case, eliminates several sources of error inherent in the original method.

¹ Trew, *Trans. Faraday Soc.*, 1941, **37**, 476.

² Sugden, *9th Liversidge Lecture, J.C.S.*, 1943, 328.

³ Angus and Hill, *Trans. Faraday Soc.*, 1943, **39**, 185.

⁴ Trew and Watkins, *ibid.*, 1933, **30**, 1310.

TABLE I.*

Compound.	Mass Susceptibility. $-\chi \times 10^6$ at 20° C.	Molar Mass Susceptibility. $-\chi_M \times 10^6$.	Boiling Point (°C.)		Density (D_4^{20}).		Refractive Index (n_D^{20}).	
			Obs. val.	Lit. val.	Obs. val.	Lit. val.	Obs. val.	Lit. val.
C_6H_5Cl <i>a</i>	0.6218 ± 0.0008	69.95	132	132 <i>d</i>	1.107	1.1066 <i>d</i>	1.5252	1.52479 <i>d</i>
C_6H_5Br <i>a</i>	0.5030 ± 0.0011	78.92	156	155.6 <i>d</i>	1.497	1.497 <i>e</i>	1.5601	1.560 <i>e</i>
C_6H_5I <i>a</i>	0.4476 ± 0.0011	91.30	188	188.45 <i>d</i>	1.832	1.832 <i>e</i>	1.6200	1.621 <i>e</i>
$CHBr_3$ <i>a</i>	0.3253 ± 0.0005	82.22	149.5	149.5 <i>d</i>	2.890	2.890 <i>e</i>	1.5980	1.598 <i>g</i>
CHI_3 <i>b</i>	0.2974 ± 0.0071	117.1	M.P. 119	119 <i>d</i>	—	—	—	—
CCl_4 <i>a</i>	0.4340 ± 0.0011	66.77	76.8	76.74 <i>d</i>	1.595	1.595 <i>e</i>	1.46110	1.4607 <i>e</i>
CBr_4 <i>c</i>	0.2826 ± 0.0014	93.73	M.P. 91	90.1 <i>d</i>	—	—	—	—
C_2H_5Br <i>a</i>	0.5020 ± 0.0007	54.74	38	38.4 <i>d</i>	1.430	1.4307 <i>d</i> 1.4555 <i>f</i>	1.4252	1.42386
C_2H_5I <i>a</i>	0.4394 ± 0.0009	68.53	72	72.3 <i>d</i>	1.933	1.933 <i>e</i>	1.5141	1.513 <i>f</i>
C_6H_6 <i>a</i>	0.7020 ± 0.0007	54.79	80	80.08	0.87897	0.8788 <i>e</i>	1.5012	1.50165 <i>d</i>
CH_3COCH_3 <i>a</i>	0.5866 ± 0.0010	34.05	—	—	0.7915	0.7915 <i>e</i>	1.3589	1.35886 <i>e</i>

* In column 1, (a) refers to susceptibility measurements made on the liquid, (b) to measurements on solutions containing from 11 % to 20 % of iodoform, and (c) to measurements on the solid.

In columns 5, 7 and 9, (d) refers to Heilbron's *Dictionary*, (e) to the International Critical Tables, (f) to Landolt-Börnstein, and (g) to the Chemical Catalog Co.

Experimental.

Whenever possible, specimens of a single substance from different sources were examined. In all cases the specimens were subjected to rigorous purification by freezing, drying, redistillation in all-glass apparatus, or repeated recrystallisation, and the purity tested by reference to accepted standards of refractive index, density, and boiling or melting point. The specimens were also tested by means of thioglycollic acid for the presence of traces of iron, and shown to be free from this impurity. Determinations of the refractive index (sodium D line at 20° C.) were made using the Abbé refractometer, by Dr. D. M. Simpson, to whom the thanks of the authors are due. The results obtained, and a comparison with the values available in the literature are tabulated in Table I, columns 2-9.

The Gouy balance and method used for determining magnetic susceptibility have been described previously,⁴ but a number of special points for ensuring greater precision have since been adopted. Using the D.C. mains current of 220 volts, with a sensitive ammeter and variable rheostat in series with the magnet coils, experiments were carried out to determine the best current strength at which to work, and it was found that at 2.8 amp. a maximum diamagnetic thrust was obtained on the specimen. Hence it was decided to work at a current strength of 3 amp. as being sufficiently low to prevent undue heating of the coils, but safely within the region at which the coils were saturated, thus ensuring a constant field at the lower end of the specimen. Experiments with fields below the saturation point showed that slight variations in the current caused small but measurable variations in pull, and hence it was considered most satisfactory to work just within the region of maximum field. When the pole pieces were 1.25 cm. apart and the current strength 3.0 amp. the field was 5290 gauss. Although a maximum field of 7000 gauss was obtainable using a smaller pole gap, it was found that this necessitated using a smaller volume of specimen, and the errors introduced by this more than neutralised the advantages of the higher field.

An average length of 7 cm. was used for most specimens since at 6 cm. above the centre of the pole pieces of the magnet the field was zero.

In the Gouy method of determining magnetic mass susceptibility

when the top of the specimen is in zero field and the bottom is in field H_1 , the susceptibility is given by:—

$$10^6\chi = \frac{\alpha F}{W} + \frac{10^6 K_{\text{air}} V}{W}$$

where χ = mass susceptibility of specimen, F = force on the specimen in mg., W = weight of material in g., K = the specific susceptibility of air = 0.0294×10^{-6} , and V = the volume in c.c.; $\alpha = \frac{2l \times 10^6 \times 981}{H_1^2 \times 1000}$ and is a constant for the apparatus using a given field and constant length l of specimen.

It is usual to calibrate the apparatus with specimens of known susceptibility in order to determine α , the balance constant. In order, however, to eliminate possible sources of error in filling susceptibility tubes to a constant mark, and from possible fluctuations in α , a modification of the usual method was employed. Consecutive readings were made of the pull or thrust on the tube filled with air, with the standard liquid of known susceptibility, and with the liquid under investigation, using the same tube and suspension wire each time (platinum wire of diameter 0.004 in. was found most satisfactory).

$$\text{Since } 10^6\chi = \frac{\alpha F}{W} + \frac{0.0294V}{W} \quad \dots \quad (1)$$

where F is the resultant pull on the liquid under investigation, and the other terms are as before,

$$10^6\chi = \alpha F/W + 0.0294/d \text{ where } d = \text{density of specimen} = W/V.$$

Hence for liquid A: $10^6\chi_A = \alpha F_A/W_A + 0.0294/d_A$
 or $10^6\chi_A = \alpha F_A/Vd_A + 0.0294/d_A$ where V = volume of specimen to mark.

Similarly for standard liquid B: $10^6\chi_B = \alpha F_B/Vd_B + 0.0294/d_B$

$$\text{whence } \frac{10^6\chi_A - 0.0294/d_A}{10^6\chi_B - 0.0294/d_B} = F_A d_B / F_B d_A \quad \dots \quad (2)$$

Substituting the measured values of F_A and F_B , the densities d_A and d_B of the specimens at the temperature of the experiment, and the known value of χ_B , gives χ_A , whence

$$10^6\chi_A = (10^6\chi_B - 0.0294/d_B) F_A d_B / F_B d_A + 0.0294/d_A \quad \dots \quad (3)$$

The above method eliminates the errors referred to, the only measured quantities being the forces F_A and F_B which can be measured to within 0.2%. An accurate thermometer between the poles of the magnet was used to record the temperature at which experiments were carried out.

In considering the most suitable standards to use for diamagnetic susceptibility measurements, preliminary calibration of the balance and determination of the balance constant was carried out using pure paramagnetic substances as advocated by Sugden for general work with the Gouy balance. In later work with almost exclusively diamagnetic substances it was considered better to use as a standard, some pure diamagnetic substance whose susceptibility was accurately known, since the large paramagnetic pulls are of an entirely different order of magnitude from the diamagnetic measurements being carried out. For precision work it was decided not to use solid substances as the standard, as there may be small errors introduced in packing the material homogeneously in the tube.

Water, benzene, and acetone are the three substances whose susceptibility has been most reliably determined. Of these, water seems at first sight to be the best standard owing to its high susceptibility. Difficulties in obtaining and maintaining water in a high degree of purity make it less suitable as a standard than either benzene or acetone, provided that accepted standard values for these liquids can be obtained. In the case

of the latter two liquids, Sugden² has tabulated a large number of available susceptibility values. These figures show that though there is very fair average agreement, some of the values tend to be about a high mean value of -0.712×10^{-6} , whereas some tend to come considerably lower about a mean of -0.702×10^{-6} , for benzene. Acetone also shows a similar divergence of values. Angus and Hill,³ using pure nickel chloride as standard, have recently published results for benzene in which agreement was obtained with the lower values. The discrepancy between individual values appears to be in part due to the use of different initial standards by different investigators. A careful redetermination of the susceptibility of benzene and of acetone was therefore carried out on the basis that the susceptibility of water = -0.720×10^{-6} ; and using pure conductivity water as standard, results in agreement with the lower figure of -0.702×10^{-6} for benzene were obtained. Similarly for acetone the lower figure is confirmed (see Table I). Hence the values are suggested as the most satisfactory standards for diamagnetic susceptibility work:—

χ acetone . . .	-0.5866×10^{-6}
χ benzene . . .	-0.7020×10^{-6}
χ water . . .	-0.7200×10^{-6}

It may further be observed that much apparent difference in absolute values could be avoided if agreement could be reached by different workers on a suitable common standard. Both benzene and acetone are satisfactory as they can be obtained in a very high degree of purity. The benzene used in the present investigation was a Kahlbaum specimen whose boiling point and refractive index indicated it to be of a very high degree of purity (see Table I). The acetone used was of analytical purity and had been dried for a month over K_2CO_3 . The susceptibility value for benzene being established in terms of water as standard, the benzene was used as the standard liquid for subsequent susceptibility measurements.

Of the substances measured in this investigation the only one which presented any difficulty was iodoform, and its susceptibility had not previously been recorded, probably because it is the only one of the series in the solid state. Attempts were made to measure the susceptibility of the tightly packed solid powder, but these had to be discontinued as the fine light flakes could not be packed into a homogeneous solid rod of material, and widely varying susceptibility results were obtained owing to unequal packing. Search was then made for a suitable solvent, but in many cases rapid darkening was observed due to the liberation of iodine. Ethyl iodide, one of the liquids being investigated, was found to be the most useful solvent, the solution not darkening appreciably in a time sufficient for susceptibility readings to be made. Even after some darkening had occurred, no appreciable alteration in the susceptibility was obtained.

Results.

The results obtained for the molar mass susceptibilities of acetone, benzene, and the eleven other substances measured are shown in Table I, column 3. Each result is the mean of six closely agreeing values, and the maximum deviation is recorded in each case. All values are relative to conductivity water $\chi = -0.720 \times 10^{-6}$.

It will be noted that the result obtained for benzene, the substance for which the most recent comparative results are available, is in excellent agreement with that obtained by Angus and Hill³ (0.702_3). The value for bromobenzene is in good agreement with that of Bhatnagar, Nevgi and Khanna⁵ (0.505 at $20^\circ C.$) but those for benzene and chlorobenzene are considerably lower than those obtained by these three authors (0.712 for benzene, and 0.644 for chlorobenzene at $20^\circ C.$). The value for carbon

⁵ Bhatnagar, Nevgi and Khanna, *Z. Physik*, 1934, 89, 506.

tetrachloride is in fairly good agreement with that of Rao and Govindarajan⁶ for this compound (0.438 at 20° C.).

In Fig. 1 (a) the above experimental results for χ are plotted, together with values due to Pascal⁷ for those compounds which were not measured but are needed to complete the series. The relationships between the susceptibilities of the mono-, di-, tri-, and tetrahalides of the methane

series are shown against the effective atomic number of the halogen atom. Fig. 1(a) shows values for the di-, tri-, and tetrahalides of methane, the upper curve of each pair representing the Pascal theoretical susceptibilities without constitutive correcting constants; *i.e.* the sum of Pascal's atomic susceptibility values⁸ for carbon and the four halogen atoms, corrected to bring to the modern standard for water. The lower curve of each pair represents the experimental values. Fig. 1(b) represents the similar curves for the monohalides of methane, ethane, and benzene, but since accurate values for ethyl chloride and methyl bromide are not available the shape of the curves including these two compounds can only

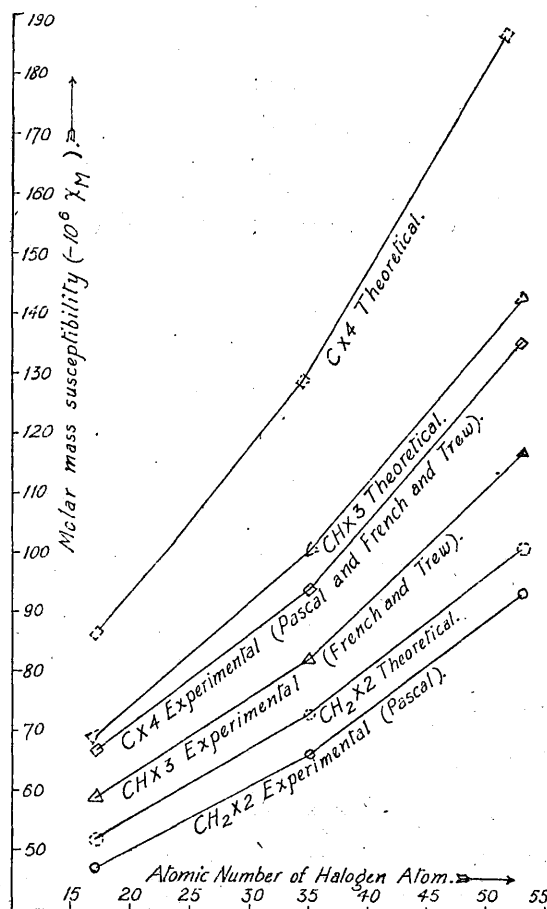


FIG. 1 (a).

be given tentatively and are represented on the graphs by broken lines. In each case the sum $\Sigma\chi_A$ of the susceptibilities for the constituent atoms, but without constitutive correcting constants for linkings, is plotted close to the experimental curve. The constitutive constants for the linkings were omitted as it was considered that if individual experimental determinations by Pascal were slightly incorrect in certain cases, these would influence the values of his constitutive constants, and one of the objects

⁶ Rao and Govindarajan, *Proc. Indian Acad. Sci. A*, 1942, 15, 35.

⁷ Pascal, *Ann. Chimie*, 1910, 19, 5.

⁸ Pascal, *Compt. rend.*, 1911, 152, 862.

of this investigation was to resurvey the whole question of the causes of deviation between the theoretical susceptibilities and the experimental values.

At the bottom of Fig. 1(b) the characteristic curve for the homopolar halogen atoms using Pascal's atomic susceptibility values for these, is given. The Pascal theoretical curves are mainly included for the purpose of comparison with the slope of the experimental curves, for which they afford an excellent check.

Discussion of Results.

The values obtained in the present investigation all fall on curves which have the characteristic inflexion point found for the homopolar halogen atoms. Pascal's value for the susceptibility of methyl bromide must obviously be considerably too high as it falls far from the characteristic curve and above the corresponding value for ethyl bromide obtained both by Pascal and by the authors. No value was available for ethyl chloride,

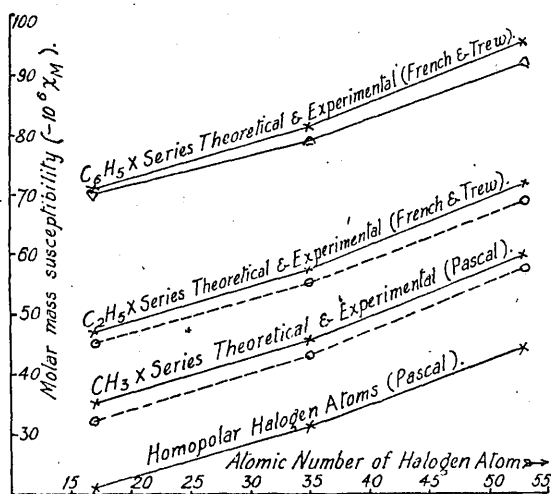


FIG. 1(b).

aryl halide series is more divergent. There is in fact a slight divergence in the case of the ethyl halides, but it is very small and hardly shows up graphically. These divergences are in agreement with Pascal's assignment of larger constitutive correcting constants to bromo-, and iodo-compounds than to chloro-compounds. The curves for the di-, tri- and tetrahalogen series show increasingly greater divergences from the Pascal atomic susceptibility curves—a fact already pointed out by Pascal himself.⁷

The present value for iodoform completes the trihalogen series curve—Fig. 1(a)—and it will be noted that the general shape fits in well with that of the other curves.

A study of Pascal's two papers^{7, 8} dealing with the alkyl halides, shows that he fully recognised the anomalous nature of these compounds. He attributed the susceptibility deviations to constitutive effects within the molecule, ascribed in part to the interaction of hydrogen and halogen, producing an effect comparable to the formation of a double bond with consequent lowering of the molar susceptibility; and partly, in polyhalogen compounds, to an interhalogen interaction also serving to lower the dia-

its susceptibility not yet having been measured. We were, under present conditions, unable to obtain a specimen of these two substances whose high volatility would, in any case, render susceptibility measurement difficult by the available apparatus. Hence a provisional value from the graph is suggested for methyl bromide of $-10^6 \chi_M = 42.7$, and for ethyl chloride of $-10^6 \chi_M = 45.0$.

The curves for the monohalides of methane and ethane run fairly parallel with the theoretical curves, whereas the

magnetism. Pascal made no general comparative survey of his results for the alkyl halides as a whole, being more concerned to consider anomalous susceptibility values for various specific cases, and he derived constitutive correcting constants to allow for the above effects for various types of halogen-carbon linkings in the molecules. The results obtained in this present investigation bring out certain additional points. For methyl and ethyl halides the graph of the deviations of the experimental susceptibility values from the Pascal additive values plotted against the atomic numbers of the halogen atoms indicates that some correction may be needed in Pascal's constitutive constants. Figs. 2(a) and 2(b) represent the deviation curves obtained in this way. The deviations were calculated from the difference between the experimental susceptibility values given in Table II, column 7, and the sum of the individual atomic susceptibilities (Table II, column 2) as calculated by Pascal's method.* The sum of Pascal's atomic

* I.C.T., Vol. VI, p. 349, gives the Pascal atomic and atomic group susceptibilities.

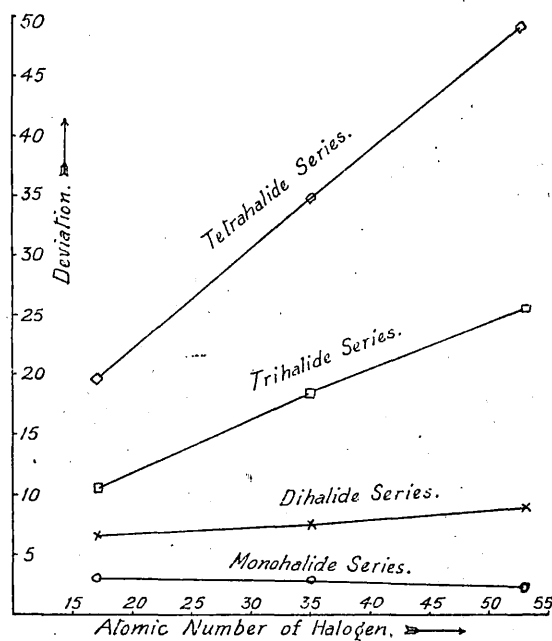


FIG. 2(a).

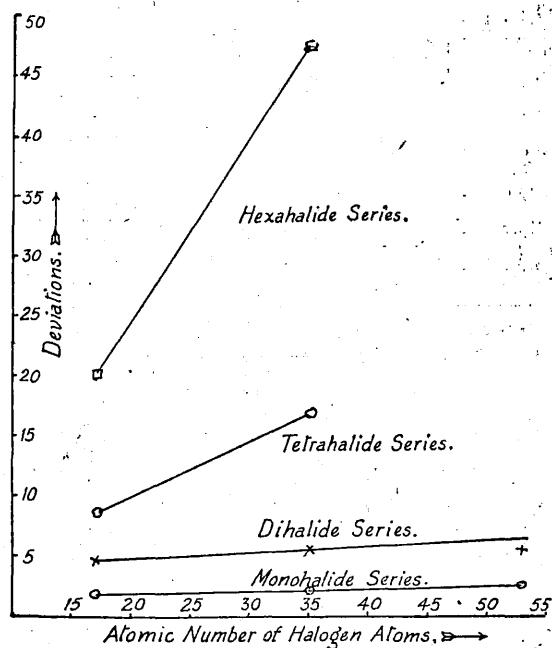


FIG. 2(b)

susceptibilities represents the molar susceptibility of the compound without allowance for constitutive effects within the molecule.

A number of interesting points may be noted from the deviation curves. For both methyl and ethyl monohalides the very slight deviation indicates that there is only a very small constitutive effect of between two and three units of atomic susceptibility, an effect that is appreciably the same for chloro-, bromo- and iodo-compounds. This constitutive effect was considered by Pascal to be due to the interaction of hydrogen and halogen within the molecule serving to lower the diamagnetism, but he derived his constitutive constants from investigations of the higher alkyl halides,⁸

TABLE II.*
COMPARISON OF EXPERIMENTAL AND THEORETICAL MAGNETIC SUSCEPTIBILITIES.

1 Compound.	- 10 ⁶ χ _M Theoretical.						7 Expt.
	2 Pascal Σχ _A .	3a Pauling	3b Pauling.	4 Gray and Cruickshank.	5 Slater.	6 Angus.	
CH ₄ . . .	17.7	19.4	[#] 19.8	17.7	18.7	17.2	16 <i>xc</i>
CH ₃ Cl . .	34.9	39.5	40.0	—	36.2	32.5	32.0 <i>a</i>
CH ₂ Cl ₂ . .	52.1	59.4	60.7	46.6	53.8	47.9	46.6 <i>a</i>
CHCl ₃ . . .	69.2	79.3	81.1	61.4	71.4	63.3	{ 58.8 <i>b</i> 58.3 <i>a</i>
CCl ₄ . . .	86.4	99.6	101.5	75.9	88.9	78.6	66.8
CH ₃ Br . .	45.4	61.1	62.1	—	49.0	45.0	42.8 <i>a</i>
CH ₂ Br ₂ . .	73.1	102.6	104.6	68.1	79.4	72.7	65.9 <i>a</i>
CHBr ₃ . . .	100.7	144.2	147.1	93.5	112.2	100.5	82.2 <i>c</i>
CBr ₄ . . .	128.4	185.8	189.7	118.9	140.2	128.3	93.7 <i>c</i>
CH ₃ I . . .	59.4	83.7	85.0	—	66.2	61.3	57.2 <i>a</i>
CH ₂ I ₂ . . .	101.1	147.9	150.5	97.0	113.8	105.3	93.5 <i>a</i>
CHI ₃ . . .	142.7	212.1	215.9	136.8	161.3	149.4	117.3 <i>c</i>
CI ₄ . . .	184.4	276.3	281.3	176.2	208.9	193.5	135.6 <i>a</i>
C ₂ H ₅ Cl . .	46.8	54.1	55.0	44.0	50.1	45.0	45.0 <i>xc</i>
C ₂ H ₅ Br . .	57.2	75.8	77.1	54.8	62.9	57.4	55.5 <i>c</i>
C ₂ H ₅ I . . .	71.2	99.4	100.0	69.2	80.1	73.7	68.5 <i>c</i>
C ₆ H ₅ Cl . .	70.7	93.9	{ 99.6 <i>e</i> 95.0 <i>f</i>	{ 87.9 <i>e</i> 51.5 <i>f</i>	86.7	75.7	69.9 <i>c</i>
C ₆ H ₅ Br . .	81.2	115.6	{ 121.6 <i>e</i> 117.0 <i>f</i>	{ 98.7 <i>e</i> 62.2 <i>f</i>	99.5	88.1	78.9 <i>c</i>
C ₆ H ₅ I . . .	95.2	138.2	{ 144.4 <i>e</i> 139.9 <i>f</i>	{ 113.0 <i>e</i> 76.6 <i>f</i>	116.7	104.4	91.3 <i>c</i>

* In columns 3b and 4 two different values are given for the theoretical susceptibilities of the benzene derivatives; (*e*) refers to the internal ionic form, and (*f*) to the benzenoid form.

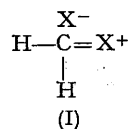
Of the experimental values (*a*) are those given by Pascal, (*c*) those of the present paper, and (*b*) a previously recorded value given by Trew. Values marked *x* are extrapolated ones.

which give a value of 3.07 for the linking >C-Cl , and 4.08 for the corresponding bromo-, and iodo-compounds. The above deviation curves indicate that for the first two members of the alkyl series the constitutive effect is rather lower (*i.e.* deviations of 2.9 for methyl chloride, 2.6 for methyl bromide, and 2.2 for methyl iodide, and 1.76, 1.75, and 2.72 for ethyl chloride, bromide, and iodide respectively). The deviations are very nearly constant for all three types of compounds.

In the case of the dihalide deviation curves it will be noted that the constitutive effect due to the halogen-hydrogen interaction is approximately double that in the monohalide series, and in addition the curves show a small but systematic rise in deviation on passing from chloro- to iodo-

compounds. Here, in addition to the small halogen-hydrogen interaction, there is the possibility of a halogen-halogen interaction; a deformation of the halogen atomic fields due to a polarisation effect with consequent lowering of diamagnetism. This effect, as the curves show, is greater for iodine than for bromine and chlorine, in agreement with the theoretical view of the greater polarisability of the iodine atom. The rapidly increasing slopes of the deviation curves for the tri- and tetrahalide series for the methyl compounds, and the incomplete tetrahalide and hexahalide curves for the ethyl compounds show that this polarisation effect increases with the introduction of more halogen atoms into the molecule. The straight line character of the deviation curves indicates the systematically additive nature of these deviations which are proportional to the atomic number of the halogen producing them. From the graphs, constitutive correcting constants could be derived for the various types of linkings with one or more halogen atoms present, but since these will obviously depend on the number of halogen atoms present and will be modified if hydrogen atoms are also present in the molecule, the attempt to deduce such constants is probably of no great value. The graphical representation of the general trend of these effects seems of more use and fully supports Pascal's suggestion made on a more restricted field of material, of two superposed effects within molecules of this type. The larger effect is, however, not the halogen-hydrogen interaction, but the polarisation effect due to the influence of halogen on halogen.

An interesting point in connection with this very much greater depression of magnetic susceptibility obtained when two or more halogen atoms are present is found in Pauling's views⁹ on the possible resonance forms of the alkyl halide molecules. He points out that in a methyl halide with only one halogen atom the possibility of resonance to the double-bonded structure is prevented as there are only four orbitals available for bond formation. With two or more halogen atoms present, however, resonance to molecules of the type (I) may occur. Thus the halogen-hydrogen interaction in monohalogen compounds is not to be ascribed to double-bond formation, and the depression, in any case, small, is more likely to be due to a general limiting of the electron spread in the molecule with the introduction of the halogen. With the addition of more halogen atoms the possible resonance to the form indicated above would tend to produce the very considerable lowering of diamagnetism associated with the double bond (*i.e.* a maximum of 5.47 per complete double bond according to Pascal's determinations). Thus it is of interest that in the dihalide series the deviation for the most deformed molecule CH_2I_2 (which would be expected to show the greatest double bond forming tendency) is 8.6 susceptibility units, which is greater than that of the monoiodo-compound CH_3I by 6.4 susceptibility units, a figure of the same order of magnitude as that given by Pascal for the double bond. The very much greater magnitude of the deviation for the tri- and tetrahalide series, however, indicates that polarisation of the halogen atoms themselves must also be a cause of lowering of diamagnetism.



When the curves for the susceptibility of the aryl halides are considered (Fig. 1 (b)) an additional effect not found with the alkyl halides is noted. These show a lowering of molar susceptibility of the same order of magnitude as the monohalogen compounds of methane and ethane, but unlike the alkyl compounds, there is a definite increase in the deviation in passing from aryl chloride to iodide. Thus it would appear that a larger benzene constitutive correcting constant should be employed for the aryl bromides and iodides than for the aryl chlorides. This result is in line with evidence from the dipole moments. While the monosubstituted methyl halides all have approximately the same dipole moment, 2.14,

⁹ Pauling, *Nature of the Chemical Bond*, 1942, 217.

2.15 and 2.13, there is a fall in moment in the aryl halides from 1.56 to 1.38. Whether the fall in moment is due to a shortening in distance between the carbon and halogen or to a lessening of the charge Δe , the effect from both causes would produce a fall in the diamagnetic susceptibility. Shortening of the linking would cause decrease in the electron spread and lowering of susceptibility, while decrease in the effective charge Δe would cause a lowering of susceptibility since it has been pointed out¹ that homopolar atoms have a susceptibility some three units lower than heteropolar ones.

Comparison with Theoretical Susceptibilities.

A number of methods for calculating theoretical molar mass susceptibilities are available, all based on the classical formula :—

$$\chi = \frac{-e^2}{6mc^2} \sum \bar{r}^2$$

but differing in the method of arriving at the value of \bar{r}^2 . Thus van Vleck¹⁰ and Pauling¹¹ have developed one method of obtaining the value of \bar{r}^2 whence

$$\chi = -0.807 \times 10^{-6} \int_0^{\infty} r^2 (dz/dr) dr.$$

Using the most accurate values for the physical constants involved including the value 0.5292×10^{-8} cm. for a_0 ¹², we have calculated the theoretical susceptibilities by this method. The values are tabulated in Table II, column 3a, while in column 3b have been included values obtained by allowing for the unequal sharing of charges in the molecule as in the Gray and Cruickshank method which is discussed below. It will be noted that the unequal sharing of charge causes the susceptibility to be slightly higher, but the effect is small and does not mask the fundamental disagreement between theoretical and experimental values.

It is generally considered that the Pauling method gives susceptibilities which are too high, and a method due to Slater¹³ using modified values for screening constants in calculating \bar{r}^2 gives susceptibility values which are considerably lower. These are summarised in column 5 of Table II. These values, as in the other cases, are considerably too high for the heavier molecules. Angus¹⁴ suggested that theoretical susceptibility values could be brought into closer agreement with experimental values by taking the *s* and *p* electrons separately in calculating the screening constants. Values calculated by this method using Angus's atomic susceptibility values are given in column 6 of Table II.

None of these methods can be strictly applied to a non-symmetrical molecule, neither is allowance made for bond effects in the molecule, and hence such effects may partially explain the high values obtained theoretically. The only system available so far, for calculation of bond effects is that of Gray and Cruickshank¹⁵ who found it gives excellent agreement for a number of simple organic compounds. It was therefore considered useful to extend this method to this series of halogen compounds. In all cases their bond depressions, where available, have been used, but values for the halogen-carbon link were not available and have therefore been calculated in each case from the monomethyl halides where

¹⁰ Van Vleck, *Physic. Rev.*, 1928, **31**, 587.

¹¹ Pauling, *Proc. Roy. Soc. A*, 1927, **114**, 181.

¹² R. T. Birge, August 1941. See Taylor and Glasstone, *Physical Chemistry*, Vol. I, p. 21, and Appendix.

¹³ Slater, *Physic. Rev.*, 1930, **36**, 57.

¹⁴ Angus, *Proc. Roy. Soc. A*, 1932, **136**, 569.

¹⁵ Gray and Cruickshank, *Trans. Faraday Soc.*, 1935, **31**, 1491.

there is no possibility of interhalogen interaction. These theoretical values are given in Table II, column 4.

It will be noted in general, that of the methods which do not take into account the bond depressions, that of Angus gives results which are on the whole closest to the experimental susceptibilities of the present paper and of other recent work in this field. Even here, as with the other methods, theoretical values for compounds with more than one halogen atom present are higher than the experimental, an effect obviously due to the halogen-halogen interaction previously discussed. In the Gray and Cruickshank method, where bond depressions have been included, a similar result is obtained. Agreement is fair for the lower members of the series, but as before, an increasing divergence between theoretical and experimental values occurs as more halogen atoms are added. Attempts to evaluate bond depressions for the Slater and Angus methods also resulted in a divergence for the polyhalides though of a smaller magnitude.

It is therefore in question whether any standard set of bond depressions for such types of compounds can be evaluated, and it is probable that no general scheme can be evolved to bring the theoretical and experimental susceptibilities into alignment until exact theoretical calculations are available for the halogen-halogen polarisation.

Summary.

1. Modifications are described in the Gouy method of measuring magnetic susceptibilities in precision work with liquids, details of the experimental conditions leading to the maximum degree of accuracy being given.

2. The suitability of various substances for use as standards is discussed, and the advantages of agreement among different workers on a common substance for this purpose, with an accepted susceptibility value is stressed.

3. Results for the determination of the susceptibilities of various alkyl and aryl halides are given, and where such measurements have not been possible in a given series, a value for the susceptibility is suggested from the graphical relationships.

4. A theoretical discussion on the significance of the results follows, and it has been shown that there is an increasing divergence between the experimental susceptibility values and the theoretical values calculated by any of the different methods available, with increasing number of halogen atoms in the molecule. The importance of this phenomenon which appears to be due to the polarisation effect of one halogen on another, and which was first noted by Pascal, has been confirmed.

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DIAMAGNETIC SUSCEPTIBILITY OF AMMONIUM COMPOUNDS

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The diamagnetic mass susceptibility of the ammonium halides in solution and in the solid state has been determined, and values for the gram ionic susceptibility of the ammonium ion in various co-ordination states have been deduced, using the appropriate anionic correcting constants. The molar susceptibility and co-ordination number show a linear relationship for each halide, and extrapolation gives values of molar susceptibility for the free ions. Measurements have also been made on nine further compounds of ammonium, and an estimate of the susceptibility of the ammonium ion has been made in those cases where data are available.

Comparison of the experimental figures with those calculated theoretically indicates that the extrapolated experimental figures for free ions are in closest agreement with theoretical values calculated by Slater's method.

The systematic investigation of the diamagnetic susceptibility of polar compounds has been undertaken by a number of workers in recent years. In 1932 Kido¹ measured the magnetic susceptibility of certain alkali and ammonium salts. He noted a linear relationship between molar magnetic mass susceptibility and the number of electrons in the cation for the series of alkali salts with the same anion, and a similar relationship for the halide series with the same cation. From these results he deduced values for the ionic mass susceptibility of alkali and halide ions but made no attempt to allow for variation of co-ordination numbers in the salts concerned. Later Brindley and Hoare^{2, 3, 4} carried out a systematic investigation of the diamagnetic susceptibility of the alkali halides showing that slightly greater values for the susceptibility of the salts were obtained in the dissolved state than in the solid state. This conclusion was supported by the subsequent work of Flordal and Frivold⁵ and of Fahlenbrach.⁶ Brindley and Hoare also derived values for the ionic susceptibility of anions and cations in different co-ordination states, investigating the influence of adjacent ions upon the ion concerned. More recently Klemm⁷ has suggested values for a large number of ionic susceptibility constants, in which he has made corrections for the co-ordination effects, while Frivold and Olsen⁸ have made similar corrections in the case of the alkali halides. On theoretical grounds Klemm⁷ and Trew⁹ independently have pointed out that the ionic susceptibilities of a related series e.g. alkali metal or halogen ions should not be a linear function of the number of electrons in the ion, but should be related to the numerical periodicity of the electron shells of the ions concerned.

¹ Kido, *Sci. Rep. Tohoku Imp. Univ.*, 1932, **21**, 149, 288, 869; 1933, **22**, 835.

² Brindley and Hoare, *Proc. Roy. Soc. A*, 1935, **152**, 342.

³ Brindley and Hoare, *ibid.*, 1937, **159**, 395.

⁴ Brindley and Hoare, *Trans. Faraday Soc.*, 1937, **33**, 268.

⁵ Flordal and Frivold, *Ann. Physik*, 1935, **23**, 425.

⁶ Fahlenbrach, *ibid.*, 1935, **24**, 485.

⁷ Klemm, *Z. anorg. Chem.*, 1941, **246**, 347.

⁸ Frivold and Olsen, *Avhandl. Norsk. Vidensk. Akad.*, 1940, **2**, 16.

⁹ Trew, *Trans. Faraday Soc.*, 1941, **37**, 476.

Kido's apparently linear results would seem to arise mainly from a neglect of co-ordination effects.

Less attention has been paid to salts of ammonium than to those of the alkali metals and there is considerable variation in the results of different investigators. The present work was undertaken to investigate the general additivity relationships for the ammonium salts, and to study the influence of co-ordination upon the susceptibility of the ammonium ion.

Experimental

Preparation of Compounds.—Wherever possible A.R. materials were used and these were further purified by careful recrystallisation. The compounds were especially examined for ferromagnetic impurities, iron, nickel and cobalt, and only materials giving negative reactions were used for the magnetic measurements. In all cases, as a further test of purity, the anion content of the compounds was determined and material rejected for which duplicate analyses varied by more than 0.2 % from the theoretical amount. All specimens were carefully dried before use.

Measurement of Susceptibility.—Magnetic susceptibility measurements were carried out at room temperature, using a modified Gouy method, precautions being taken to eliminate various sources of error and obtain concordant results as described in previous papers.^{10, 11}

Results

Tables I(a) and (b) summarise the results obtained for the diamagnetic susceptibility of the ammonium halides in the solid state and in aqueous solution, and of the other salts investigated. The values in solution were calculated, assuming additivity, from the relationship

$$\chi_{\text{measured}} = w_1\chi_{\text{solvent}} + w_2\chi_{\text{solute}}$$

where w_1 and w_2 are weights per cent. of solvent and solute respectively. The last column shows the susceptibility values obtained by other investigators, where these are available.

TABLE I.—DIAMAGNETIC MASS SUSCEPTIBILITY OF AMMONIUM COMPOUNDS *

(a)

Compound	State	Co-ordination Number	$-10^6 \cdot \chi_M$	$-10^6 \cdot \chi_M$ (literature)
NH ₄ F *	Solid	4	23.0 ± 0.04	24.5 ¹
	Solution 16.9 %	4	23.5 ± 0.11	—
NH ₄ Cl *	Solid	8	36.7 ± 0.21	34.2, ¹ 35.7, ¹² 36.2 ¹³
	Solution 16.8 %	4	38.5 ± 0.16	—
NH ₄ Br	Solid	8	47.0 ± 0.30	47.4, ¹ 46.7, ¹² 46.2 ¹³
	Solution 16.7 %	4	49.8 ± 0.30	—
NH ₄ I *	Solid	6	64.4 ± 0.15	66.0, ¹ 69.5, ¹² 64.1 ¹³
	Solution 16.8 %	4	66.4 ± 0.16	—

The % composition of solutions refers to grams solute per 100 g. solution.

* The experimental data for the ammonium halides (with the exception of the bromide), in the solid state have been previously published⁹ but are included here for the purposes of detailed discussion in relation to co-ordination number.

¹⁰ Trew and Watkins, *Trans. Faraday Soc.*, 1933, 29, 1310.

¹¹ French and Trew, *ibid.*, 1945, 41, 439.

¹² Duchemin, *Compt. rend.*, 1931, 199, 571.

¹³ Dinsdale and Long, *Proc. Leeds Phil. Soc.*, 1937, 3, 270.

(b)

Compound	State	$-10^6 \cdot \chi_M$	$-10^6 \cdot \chi_M$ (literature)
NH ₄ NO ₃ *	Solid	32.6 ± 0.16	33.6 ¹
	Solution 14.1 %	38.9 ± 0.27	
NH ₄ VO ₃	Solid	-8.1 ± 0.23	-14.04, ¹⁴ -14.04 ¹⁵
NH ₄ OH	Solution 35 %	31.5 ± 0.15	—
(NH ₄) ₂ SO ₄	Solid	67.0 ± 0.70	75.4, ¹⁶ 63.2 ¹²
(NH ₄) ₂ SO ₃ · H ₂ O	Solid	70.3 ± 0.67	—
(NH ₄) ₂ S ₂ O ₃	Solid	75.1 ± 0.59	—
(NH ₄) ₂ CrO ₄	Solid	-1.0 ± 0.38	—
(NH ₄) ₂ Cr ₂ O ₇	Solid	-37.8 ± 0.75	—
(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	Solid	163.1 ± 0.84	—

Discussion

The experimental figures for the susceptibility of the ammonium halides in Table I(a) are in good agreement with previously published values,^{1, 12-16} the closest agreement being with the most recent results, those of Dinsdale and Long.¹³ It will be noted that the values for the susceptibilities of salts in solution are slightly higher than the corresponding values for the solid state. This result is in agreement with the observations of Brindley and Hoare²⁻⁴ for the alkali halides and was explained by them as due to the reduction in the co-ordination number of the ions when in the dissolved state. In order to investigate this effect more fully, values for the susceptibility of salts containing the ammonium ion in various states of co-ordination have been calculated from the experimental figures of Table I.

For strongly polar salts, such as the alkali halides, it can be assumed that the molar diamagnetic susceptibility is solely made up of the sum of the ionic susceptibility values for the anion and the cation, provided that the ions are in the same co-ordination state. This assumption has been shown to hold for the salts of the alkali halides and thus should be applicable to the ammonium salts. In the crystalline state the co-ordination number of the ammonium ion is known for the various halides, and for large ions in solution can be taken as four.¹⁷ The experimental molar susceptibility thus represents the sum of the susceptibility values for the cation and anion in the particular co-ordination state of the crystal in question, and values for other states require to be calculated. This can be done by a method similar to that used by Brindley and Hoare³ for the alkali ions, using the values given by them for the susceptibility of halide ions in various co-ordination states. From the experimental molar susceptibilities, complete sets of values can thus be obtained for the four ammonium halides in four-, six-, and eight-fold co-ordination. Table II (columns 2-5) shows the values obtained in this way. The detailed calculation by which the figures were obtained for co-ordination number eight provides an illustration of the method involved. Subtracting the values³ for the susceptibility of the chloride and bromide ions in eight-fold co-ordination from the respective experimental molar susceptibilities (Table I) gives a value for the susceptibility of the ammonium ion in eight-fold co-ordination, thus: *

¹⁴ Ray Chaudhuri, *Indian J. Physics*, 1936, 10, 245.

¹⁵ Meyer, *Ann. Physik*, 1899, 68, 325.

¹⁶ Gray and Farquharson, *Phil. Mag.*, 1930, 10, 191.

¹⁷ Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

* All molar and ionic diamagnetic susceptibility values quoted in the text are given in c.g.s. units $\times (-10^6)$, and paramagnetic values in c.g.s. units $\times 10^6$.

DIAMAGNETIC SUSCEPTIBILITY

$$\chi_{\text{NH}_4\text{Cl}^{(8)}} - \chi_{\text{Cl}^{-(8)}} = \chi_{\text{NH}_4^{+(8)}} \quad \text{and} \quad \chi_{\text{NH}_4\text{Br}^{(8)}} - \chi_{\text{Br}^{-(8)}} = \chi_{\text{NH}_4^{+(8)}}$$

$$36.7 - 22.9 = 13.8 \quad \quad \quad 47.0 - 33.4 = 13.6$$

whence a mean value of $\chi_{\text{NH}_4^{+(8)}} = 13.7$ is obtained.

TABLE II.—THEORETICAL, EXPERIMENTAL AND DERIVED DIAMAGNETIC SUSCEPTIBILITIES ($-10^6\chi$) FOR THE AMMONIUM ION AND SALTS WITH VARIOUS CO-ORDINATION NUMBERS

C.N. = Co-ordination number. Values in brackets are the derived values. Addition of the corresponding values for the singly charged halide ion, in each case, gives the figures in columns 7-9.

	Experimental and Derived Values $\times (-10^6)$ c.g.s.					Theoretical Values $\times (-10^6)$ c.g.s.		
	Crystal C.N.8	Crystal C.N.6	Crystal C.N.4	Aqueous Solution C.N.4	Extrapol. Value C.N.zero	Method of Pauling	Method of Slater	Method of Angus
NH_4^+	13.7	13.8	—	14.2	14.5	15.1	15.0	13.9
NH_4F	(22.4)	(23.2)	23.0	23.5	(24.6)	23.2	23.1	21.0
NH_4Cl	36.7	(38.0)	—	38.5	(40.7)	44.1	40.3	36.3
NH_4Br	47.0	(48.3)	—	49.8	(52.3)	69.1	54.3	49.0
NH_4I	(62.5)	64.4	—	66.4	(70.2)	95.1	73.6	68.1

The theoretical figures were calculated as follows. In the ammonium ion the unit positive charge is considered as divided approximately equally among the five atoms,³⁰ each having a resultant charge of about $+0.2$. Using the theoretical susceptibility values for atoms with whole number charges which have been calculated by the Pauling,²⁵ Slater,²⁷ and modified Slater (Angus)²⁸ methods, we have, in terms of $-10^6\chi$ the following values:

	Pauling		Slater		Angus	
N^{+1}	0.2×5.91	1.2	0.2×5.36	1.1	0.2×4.67	0.9
N^0	0.8×8.28	6.6	0.8×7.93	6.3	0.8×6.73	5.4
H^{+1}	$4 \times 0.2 \times 0$	0.0	$4 \times 0.2 \times 0$	0.0	$4 \times 0.2 \times 0$	0.0
H^0	$4 \times 0.8 \times 2.273$	7.3	$4 \times 0.8 \times 2.370$	7.6	$4 \times 0.8 \times 2.370$	7.6
	$\therefore \chi_{\text{NH}_4^+} = 15.1$		$\therefore \chi_{\text{NH}_4^+} = 15.0$		$\therefore \chi_{\text{NH}_4^+} = 13.9$	

From this figure, calculated values for the molar susceptibilities of the two remaining halides, ammonium fluoride and iodide with co-ordination number eight can be obtained by addition of the values for these anions with that co-ordination number:

$$\chi_{\text{NH}_4^{+(8)}} + \chi_{\text{F}^{-(8)}} = \chi_{\text{NH}_4\text{F}^{(8)}} \quad \text{and} \quad \chi_{\text{NH}_4^{+(8)}} + \chi_{\text{I}^{-(8)}} = \chi_{\text{NH}_4\text{I}^{(8)}}$$

$$13.7 + 8.7 = 22.4 \quad \quad \quad 13.7 + 48.8 = 62.5$$

Similar calculations give the remaining figures in Table II (columns 2-5). The value for the fluoride ion with co-ordination number eight is not given by Brindley and Hoare. For the sake of completing the data on the ammonium ion, a value for the fluoride ion in eight-fold co-ordination, could this be realised, was estimated by assuming a percentage change on passing from co-ordination number six to eight of the same order as for the chloride ion. It will be seen that the average change in molar susceptibility for a change in co-ordination number of two units is 3%. This may be compared with a similar figure of about 4% for the caesium halides obtained by Brindley and Hoare.²

Values for the ionic susceptibility of the ammonium ion with various co-ordination numbers follow from the experimental results. Thus,

subtracting the value for the susceptibility of the halide ion in the appropriate state, $\chi_{\text{NH}_4^+(\text{s})} = 13.7$ from the chloride and bromide measurements, and $\chi_{\text{NH}_4^+(\text{s})} = 13.8$ from the iodide measurement. Values for the susceptibility of the ammonium ion in the dissolved state calculated by means of Brindley and Hoare's suggested values for halide ions in solution⁴ are not, however, satisfactory. Thus, if the values $\chi_{\text{F}^-}(\text{dissolved}) = 10.3$, $\chi_{\text{Cl}^-}(\text{dissolved}) = 25.1$, $\chi_{\text{Br}^-}(\text{dissolved}) = 36.4$ and $\chi_{\text{I}^-}(\text{dissolved}) = 54.2$ are subtracted from the measured susceptibility values, the susceptibility of the ammonium ion in solution follows, namely $\chi_{\text{NH}_4^+(\text{dissolved})} = 13.2$ from the fluoride measurement, 13.4 from the chloride, 13.4 from the bromide and 12.2 from the iodide, all values lower than those in the solid state with higher co-ordination number. An alternative method for assessing the contribution of the ammonium ion to the total susceptibility in the dissolved state, that is not dependent on the absolute magnitude of the halide ion contribution, is to assume that the same proportional contribution of the total susceptibility is made by anion and cation whether in the solid state or in solution.

The ratio

$$\frac{\chi_{\text{NH}_4^+(\text{dissolved})}}{\chi_{\text{NH}_4\text{X}(\text{dissolved})}} = \frac{\chi_{\text{NH}_4^+(\text{cryst.})}}{\chi_{\text{NH}_4\text{X}(\text{cryst.})}}$$

(where NH_4X signifies the halide salts) will give the required value for $\chi_{\text{NH}_4^+(\text{dissolved})}$ since $\chi_{\text{NH}_4^+(\text{cryst.})}$ is as given above for the six- and eight-fold co-ordination states; the values for the susceptibility of the salt in solution and in the solid state are as in Table I and hence $\chi_{\text{NH}_4^+(\text{dissolved})}$ follows. This method gives $\chi_{\text{NH}_4^+(\text{dissolved})} = 14.5$ from the chloride, 14.4 from the bromide and 13.8 from the iodide, representing a mean value of 14.2 for the susceptibility of the ammonium ion with co-ordination number four in the dissolved state. This value is higher than that obtained for the six- and eight-fold co-ordination states and hence is in line with the general trend of increase in susceptibility with fall in co-ordination number. This method for obtaining a value for $\chi_{\text{NH}_4^+(\text{dissolved})}$ is supported by the application of an equation relating the diamagnetic susceptibility of an ion in solution to that in the solid state, proposed recently by Lee.¹⁸ Pointing out that the transfer of an ion from the crystalline state to solution involves the two factors of an increase in susceptibility due to a release of the ion from a strong field in which mutual deformation occurs, and a counter effect of a deformation of some of the water molecules due to the introduction of an ion into their vicinity, which will of course lower the susceptibility of the solution, he suggests a relationship $-\chi_s = a_1(-\chi_c) - b_1$, where $-\chi_s$ and $-\chi_c$ are the ionic susceptibilities in solution and the solid state respectively expressed in 10^6 c.g.s. units and a_1 and b_1 are constants. For univalent anions and cations, $a_1 = 1.09$ and $b_1 = 1.0$. Lee shows that this relationship holds to within ± 0.3 unit of susceptibility for the alkali and halide ions. Applying this to the present data and taking $\chi_{\text{NH}_4^+(\text{cryst.})} = 13.7$, the calculated value for $\chi_{\text{NH}_4^+(\text{dissolved})} = 13.9$ in good agreement with the experimental value of 14.2 obtained above, on the assumption that the proportional change in susceptibility is the same for each univalent ion on transferring from the solid state to the dissolved state. Thus the susceptibility of the ammonium ion in solution is 14.0 rather than 16 units of susceptibility tentatively suggested by Brindley and Hoare.⁴

If the susceptibility values of Table II (columns 2-5) are plotted against the appropriate co-ordination number of the salt in question the points lie on five straight lines, one for the ammonium ion and one for each

¹⁸ Lee, *J. Chinese Chem. Soc.*, 1945, 12, 81.

halide, a result similar to that for the alkali halides. Extrapolation of the straight lines to zero co-ordination number gives the values shown in column 6 of Table II. These may be taken to represent the susceptibility values for the free ion in the case of ammonium, and for the state of zero co-ordination number for the salts, i.e. a state in which the co-ordination effects have been eliminated. These susceptibility values may be compared with theoretical values.

It has already been pointed out⁹ that on plotting the experimental results for the solid halides of Table I against the effective charge of the anion, a graph results which shows the periodicity expected from the change in number of electrons in the electron shells of the anion on passing from fluoride to iodide, and that this graph is reasonably parallel with those for the alkali salts. A slight deviation from the parallel relationship occurs with ammonium iodide and fluoride due to the difference in co-ordination number of the ammonium ion in these salts from that in the chloride and bromide.

In Table I(b) where the co-ordination number data are inadequate, the values for the susceptibility of the ammonium ion were calculated in those cases where data for the anionic contribution to the susceptibility were available, although no allowance could be made for change in co-ordination number. A value of $\chi_{\text{NH}_4^+} = 13.7$ was obtained for the susceptibility of the ammonium ion in the nitrate and $\chi_{\text{NH}_4^+} = 13.5$ in the sulphate, using the anionic values suggested previously.⁹ These values are in good agreement with that obtained from the halide series showing that any change in co-ordination number has only a small effect. Since no experimental anionic values were available for the thiosulphate, chromate, and dichromate ions, these were estimated from recent experimental measurements on the sodium and potassium salts of these anions by subtracting the cationic contributions.* The considerable variation in the experimental susceptibility values of different investigators for the same salt make the conclusions rather uncertain, but the results are

* The method of calculation is as follows :

$\chi_{\text{Na}_2\text{S}_2\text{O}_3} = 61.8$,¹⁹ whence subtracting twice $\chi_{\text{Na}^+} = 6.8$ ⁹ gives $\chi_{\text{S}_2\text{O}_3^{2-}} = 48.2$.

Correspondingly from $\chi_{\text{K}_2\text{S}_2\text{O}_3} = 75.9$,²⁰ subtracting twice $\chi_{\text{K}^+} = 14.9$ ⁹ gives $\chi_{\text{S}_2\text{O}_3^{2-}} = 46.1$, giving a mean $\chi_{\text{S}_2\text{O}_3^{2-}} = 47.2$. This, subtracted from the experimental figure for ammonium thiosulphate in Table I(b), gives the value $\chi_{\text{NH}_4^+} = 14.0$. Kido's¹ figure for the susceptibility of sodium thiosulphate trihydrate was not used in this calculation since if the full value for the susceptibility of the three molecules of water of crystallisation is subtracted it gives a very much lower value for the susceptibility of the anion than either of the other two values used.

(2) The paramagnetic susceptibility of sodium chromate is $\chi_{\text{Na}_2\text{CrO}_4} = 19.4$,²¹ and $\chi_{\text{Na}_2\text{CrO}_4} = 11.0$,²² whence the paramagnetic susceptibility $\chi_{\text{CrO}_4^{2-}} = 33.0$ and 24.6, subtracting twice $\chi_{(\text{dia.})\text{Na}^+}$. Similarly from the paramagnetic values for the susceptibility of $\text{K}_2\text{CrO}_4 = 4.0$,^{22, 23} and 0.0,²¹ the paramagnetic susceptibility $\chi_{\text{CrO}_4^{2-}} = 25.8$, 25.8, 29.8, giving a mean of the five values of $\chi_{\text{CrO}_4^{2-}} = 27.8$ for the paramagnetic susceptibility of the chromate ion, and hence $\chi_{(\text{dia.})\text{NH}_4^+} = 13.4$ from the data for ammonium chromate in Table I.

(3) Similarly the values available for the paramagnetic susceptibility of potassium dichromate are $\chi_{\text{K}_2\text{Cr}_2\text{O}_7} = 37.9$,²⁴ 54.0,²¹ 31.8,¹⁴ 15.0,²² whence the paramagnetic value $\chi_{\text{Cr}_2\text{O}_7^{2-}} = 64.5$ follows as a mean value, giving $\chi_{(\text{dia.})\text{NH}_4^+} = 13.4$.

¹⁹ Pascal, *Compt. rend.*, 1921, 173, 712.

²⁰ Farquharson, *Phil. Mag.*, 1932, 14, 1003.

²¹ Gray and Dakers, *ibid.*, 1931, 11, 297.

²² Tilk and Klemm, *Z. anorg. Chem.*, 1939, 240, 355.

²³ Trew, *Trans. Faraday Soc.*, 1936, 32, 1655.

²⁴ Endo, *Sci. Rep. Tohoku Imp. Univ.*, 1925, 14, 479.

included as they give a value for the susceptibility of the ammonium ion of the same order of magnitude as that derived from the halide salts. Thus $\chi_{\text{NH}_4^+} \approx 14.0$ from the thiosulphate measurement and 13.4 from both chromate and dichromate.

Comparison of Theoretical and Experimental Diamagnetic Susceptibilities.—A number of methods for calculating theoretical diamagnetic susceptibilities have been proposed,²⁵⁻²⁸ and have been frequently discussed so that details need not be given here. The theoretical susceptibilities for the ammonium ion, calculated by the methods of Pauling,²⁵ Slater,²⁷ and Angus,²⁸ are summarised in Table II (columns 7-9). Following the method originally applied by Gray and Cruickshank,²⁹ allowance has been made for the partial shift in charge, due to unequal sharing of electrons as determined from dipole measurements. The theoretical values for the susceptibilities of the halides have been calculated assuming that the linkings between the ammonium and halide ions are completely polar. It will be seen that for the ammonium ion itself, the theoretical molar susceptibility calculated by Angus' method, $\chi_{\text{NH}_4^+} = 13.9$, agrees most closely with the experimental value, $\chi_{\text{NH}_4^+} = 13.6-13.8$, for the ion in combination with univalent anions in solid crystals. The values obtained when the experimental susceptibilities of the salts are extrapolated to co-ordination number zero are in closest agreement with susceptibilities calculated by Slater's method in which semi-empirical rules for obtaining the screening constants in the ions are used.

An increasing divergence between theoretical and experimental susceptibilities occurs as the effective atomic number of the salt increases, a result similar to that found for the alkali and other salts.^{9, 23, 31} For all the halides except the fluoride, calculations by Pauling's method give, as in these other cases, theoretical susceptibilities which are higher than the experimental for salts of heavier ions. When, however, as in Slater's method of calculating atomic and ionic susceptibilities, modified screening constants are used for the *N*-shell of electrons and beyond, the resultant theoretical susceptibility is brought very much closer to that for the salt corrected for the co-ordination effects, as a comparison of column 6 with column 8 of Table II will show. Angus' further suggestion that the contribution of *s* and *p* shells of electrons to the susceptibility should be computed separately, brings the final calculated molar susceptibility below the experimental values corrected for co-ordination effects, and so would appear unjustified by the experimental results.

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²⁵ Pauling, *Proc. Roy. Soc. A*, 1927, 114, 181.

²⁶ Hartree, *Proc. Camb. Phil. Soc.*, 1928, 89, 111; *Proc. Roy. Soc. A*, 1933, 141, 282.

²⁷ Slater, *Physic. Rev.*, 1930, 36, 57.

²⁸ Angus, *Proc. Roy. Soc. A*, 1932, 136, 569.

²⁹ Gray and Cruickshank, *Trans. Faraday Soc.*, 1935, 31, 1491.

³⁰ Pauling, *Nature of the Chemical Bond* (1940).

³¹ Brindley, *Phil. Mag.*, 1931, 13, 786.

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THE DIAMAGNETIC SUSCEPTIBILITY OF SOME
SUBSTITUTED ETHYL MALONATES

THE DIAMAGNETIC SUSCEPTIBILITY OF SOME SUBSTITUTED ETHYL MALONATES

BY C. M. FRENCH AND V. C. TREW

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A modified technique has been evolved for the more precise measurement of magnetic susceptibility by the Gouy method. The diamagnetic susceptibilities of a number of substituted ethyl malonates have been measured, and a considerable variation in the magnitude of the CH_2 increment within this series has been found, although certain regularities appear to exist. The absolute value of the CH_2 increment in this series of compounds is higher than that in many simple homologous series previously investigated.

A comparison of the experimental molar mass susceptibilities with those calculated by the method of Pascal indicates the presence of both ketonic and partially enolic forms in ethyl malonate and the monosubstituted esters. This magnetic evidence is supported by evidence from molar refractivity data.

Measurements of the magnetic mass susceptibility of a number of compounds in different homologous series have led to the conclusion that, at least with the higher members of some series, there is a constant increment in the diamagnetic susceptibility for every additional CH_2 group. The exact magnitude of this increment has, nevertheless, been the subject of considerable controversy, and investigations in various laboratories have resulted in the quotation of values of 11.355,¹ 11.48,² 11.64,³ 11.69,⁴ and more recently 11.36.⁵ These and subsequent values represent c.g.s. units $\times 10^6$. Actual mass susceptibility values are of course diamagnetic. The constancy of this increment seems most marked in relatively simple homologous series such as open chain monocarboxylic acids and esters, and simple aldehydes, ketones and alcohols, but is less regular for more complex compounds. Thus although Pacault,⁶ investigating four methyl and heptyl substituted benzacridines, obtained increments of 11.3, 12.6 and 11.3, Bonino and Manzoni-Ansidei⁷ in similar measurements on

¹ Bhatnagar, Mitra and Tuli, *Phil. Mag.*, 1934, 18, 449.

² Cabrera and Fahlenbrach, *Anales soc. española fis. quim.*, 1934, 32, 543.

³ Farquharson and Sastri, *Trans. Faraday Soc.*, 1937, 33, 1472.

⁴ Angus and Hill, *Trans. Faraday Soc.*, 1943, 39, 185.

⁵ Broersma, *J. Chem. Physics.*, 1949, 17, 873.

⁶ Pecault, *Ann. Chim.*, 1946 (xii), 1, 527.

⁷ Bonino and Manzoni-Ansidei, *Ber.*, 1943, 76, 553.

pyrrole homologues obtained increments varying from 9.54 to 14.1. Farquharson and Sastri⁸ in the alicyclic series, found increments of 12.83, 15.32 and 9.76 for each successive CH_2 addition on passing from cyclopropane carboxylic acid to cyclohexane carboxylic acid.

It has been emphasized that even where constancy is obtained, the absolute value of the CH_2 increment may not be the same in all homologous series, and Angus and Hill⁴ have illustrated this effect by reference to the apparently lower value for the susceptibility of the CH_2 group in aldehydes as compared with that in ketones. Furthermore, it has been suggested that even where the transition from one member of a homologous series to the next higher member involves no structural alteration other than that involved in the replacement of a hydrogen atom by a methyl group, nevertheless the rest of the molecule, or some active group in it, may exercise an appreciable influence on the magnitude of the CH_2 increment. This influence will be most apparent in the lower members of simple series. Here active groups form a considerable part of the whole molecule and will be in close proximity to any replaceable hydrogen atom. In higher members of a series such active groups will have a smaller influence upon the susceptibility of the molecule. Finally it may be noted that isomerides do not always have identical magnetic susceptibilities, as has been shown with a number of different compounds.⁴ It appeared therefore of interest to investigate compounds in which an active methylene group is partly or completely substituted. Such a series is found in the ethyl esters of malonic acid and the substituted malonic acids. An additional interest lies in the number of possible structural alternatives (ketonic and enolic forms together with a number of resonance forms) in some of the substituted malonic acid esters and in ethyl malonate itself, with their possibly different values of magnetic susceptibility.

Experimental

All the malonates used in this investigation were purified by distillation under reduced pressure through an all-glass apparatus, using a well-lagged

TABLE I

Substance	Boiling Point		Refractive Index (n_D^{20})		Density (d_4^{20})		Specific Suscept. $-\chi_s \times 10^6$
	°C	Press. (mm.)	Obs. Val.	Lit. Val.	Obs. Val.	Lit. Val.	
Ethyl malonate	101.5	30.5	1.41363	1.41428 ⁹ 1.4112 (n_D^{25}) ¹⁰	1.05496	1.0550 ⁹ 1.0490 (d_4^{25}) ¹⁰	0.5721
Ethyl diethylmalonate	117.5	21	1.42474	1.4141 (n_D^{25}) ¹⁰	0.98762	0.9982	0.6492
Ethyl butylmalonate	127	23	1.42291	1.4226 ¹¹	0.97639	0.9749	0.6442
Ethyl ethylpropylmalonate	121	22	1.42435	—	0.97846	—	0.6619
Ethylethylbutylmalonate	133	20	1.42834	—	0.97287	—	0.6683
Ethyl phenylmalonate	142	22	1.49126	—	1.09593	—	0.6017
Ethyl benzylmalonate	176	21	1.48709	—	1.07493	—	0.6172
Ethyl methylphenylmalonate	177	42	1.49034	—	1.07488	—	0.6121

fractionating column packed with small glass helices. A number of separate fractions were collected, and those middle fractions were used for which a constant value of refractive index was obtained. In view of the paucity of physical data on the substituted ethyl malonates, the boiling points at the pressures employed are recorded in Table I.

⁸ Farquharson and Sastri, *Trans. Faraday Soc.*, 1937, **33**, 1474.

⁹ Weissberger and Proskauer, *Organic Solvents* (Clarendon Press, 1935).

¹⁰ Pearson, *J. Amer. Chem. Soc.*, 1949, **71**, 2212.

¹¹ Mumford and Phillips, *J. Chem. Soc.*, 1950, 75.

The refractive indices of the malonates were measured at 20°C by means of a Pulfrich refractometer, using the *D* line of the sodium spectrum, and these, together with the densities, are also recorded in Table I.

The magnetic susceptibilities were measured by the Gouy method using a modification of a balance previously described.¹² An air-cooled electromagnet of 12,000 turns and cobalt-steel pole pieces was employed. A 1 cm. pole gap was maintained using a cylindrical brass distance piece fitted between the conical-shaped poles. The distance piece was pierced above the poles to allow passage of the susceptibility tube centrally between the pole gap, and a second circular aperture, which could be viewed by a telescope, enabled exact alignment to be made of the base of the tube in the region of maximum field. This adjustment was made by reference to illuminated cross-marks fixed to the back and front of the distance piece. The region of constant field between the poles was found to be 0.2 cm. above and below the mid-point of the pole faces. A maximum current of 5 A could be employed with the magnet, but to reduce the heating effect to a minimum it was found most satisfactory to carry out measurements at lower amperages. Three slightly different values of the current of 1.8, 2.0 and 2.2 A were used, giving respectively fields of 7,000, 7,180 and 7,390 gauss. The ammeter scale and pointer were viewed by a telescopic attachment and, by means of a variable resistance, the pointer was maintained at one of the exact readings noted above during the time the magnet was switched on. The length of the specimen was carefully adjusted so that the upper level was in a region of zero field. The weighings were carried out by means of a short beam balance to which the susceptibility tube was attached by means of a Nylon suspension thread. This was found to be more satisfactory than a platinum suspension being less influenced by minor variations in humidity of the atmosphere. Benzene was used as the standard for reasons previously discussed.¹²

The susceptibilities were in all cases calculated by means of the equation:¹²

$$10^6 \chi_A = \left(10^6 \chi_B - \frac{0.0294}{d_B} \right) \frac{F_A d_B}{F_B d_A} + \frac{0.0294}{d_A}$$

where the subscript B refers to the standard liquid benzene ($\chi_B = -0.702 \times 10^{-6}$) and A to the liquid under investigation. *F* is the thrust on the specimen and *d* its density.

Results

The results of the measurements of magnetic susceptibility are shown in Table I, the specific susceptibilities in column 8 representing the mean of several (usually 6) closely agreeing values, the maximum variation being ± 0.0010 susceptibility units. The values of the molar mass susceptibilities are shown in Table II, column 2.

TABLE II

Substance	Molar Mass Susceptibilities ($-\chi_M \times 10^6$)					Molar Refractivities			
	Expt. Val.	Max. Expt. Error	Calculated Values Pascal Method			Expt.	Calculated		
			Form I	Form II	Form III		Form I	Form II	Form III
Ethyl malonate . . .	91.62	± 0.16	93.10	91.43	87.68	37.91	37.78	38.77	39.77
Ethyl diethylmalonate .	140.41	± 0.22	143.62	—	—	55.96	56.37	—	—
Ethyl butylmalonate . .	139.32	± 0.22	143.12	139.37	—	56.39	56.37	57.37	—
Ethyl ethylpropylmalonate . .	152.43	± 0.23	155.48	—	—	60.10	61.02	—	—
Ethyl butylethylmalonate . .	163.27	± 0.24	167.34	—	—	64.66	65.66	—	—
Ethyl phenylmalonate . .	142.15	± 0.24	145.80	142.65	—	62.46	61.92	62.91	—
Ethyl benzylmalonate . .	154.45	± 0.25	159.78	156.03	—	66.98	66.56	67.56	—
Ethyl methylphenylmalonate . . .	153.21	± 0.25	158.16	—	—	67.36	66.56	—	—

¹² French and Trew, *Trans. Faraday Soc.*, 1945, 41, 439.

Discussion

Only slight comparison with other experimental values is possible. The only compound of this series which appears so far to have been measured is ethyl malonate itself. The only previously recorded values are 91.50,⁵ which is in close agreement with that now presented, 93.60,¹³ and 92.56.¹⁴ In the case of the last of these values, purification had been effected by distillation at atmospheric pressure, and consequently at a temperature nearly 100° C higher than that in the present investigation, and it is possible, therefore, that some slight decomposition may have taken place. In this connection it is of interest that a specimen of ethyl malonate purified by the same method as used in the earlier investigation gave a molar mass susceptibility of 92.52.

The experimental values were compared with values calculated using Pascal's atomic and constitutive susceptibility constants corrected for the present accepted value for the susceptibility of water of -0.720×10^{-6} , and also with those calculated theoretically by the methods of Slater,¹⁵ Angus,¹⁶ Pauling,¹⁷ and Gray and Cruickshank.¹⁸ The values obtained

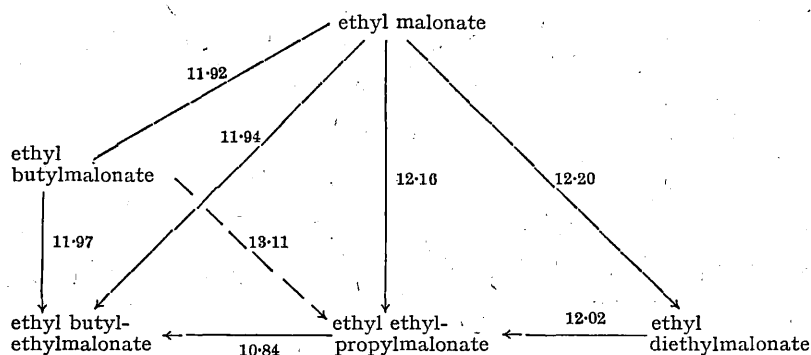


FIG. 1.

(The figures indicate the experimental value for the CH₂ increment in the corresponding transition.)

by Angus's method are 10-15 % higher than the experimental values, and the methods of Slater and Pauling yield even higher values, all three methods indicating an identical susceptibility for the different tautomers and resonance forms, and a constant increment in the magnetic susceptibility for each additional CH₂ group. The experimental values obtained in this investigation show a higher figure for this increment than is usually found in the more simple homologous series. Although a constant value for the increment is not obtained, certain regularities may clearly be detected as shown in Fig. 1.

It appears that with the lower members of the aliphatic series, the magnitude of the CH₂ increment depends very largely on the size of the group replacing one or both of the methylenic hydrogen atoms, and is inversely related to this quantity, since in transitions from ethyl malonate an average increment of 11.94 is obtained when one substituent is a butyl radical, 12.16 when it is the smaller propyl radical, and 12.20 for the even smaller ethyl group. With compounds containing aromatic substituents,

¹³ Pascal, *Ann. Chim. Physique*, 1912, 25, 289.

¹⁴ French, *Trans. Faraday Soc.*, 1947, 43, 356.

¹⁵ Slater, *Physic. Rev.*, 1930, 36, 57.

¹⁶ Angus, *Proc. Roy. Soc. A*, 1932, 136, 569.

¹⁷ Pauling, *Proc. Roy. Soc. A*, 1927, 114, 181.

¹⁸ Gray and Cruickshank, *Trans. Faraday Soc.*, 1935, 31, 1491.

it may be observed that the value of the increment in one case is 11.06 and in the other 12.30, but the number of compounds available for investigation in this series was insufficient for any general conclusion to be reached.

Calculation of the magnetic susceptibilities of the substituted ethyl malonates from Pascal's atomic and constitutive constants recently revised by Pacault, gives different values for the tautomeric forms I, II and III (Fig. 2), as shown in columns 4, 5 and 6 of Table II. Where both methylenic hydrogen atoms have been substituted by an alkyl or aryl group, only the tautomeric form I can exist with ethyl diethylmalonate and ethyl ethylpropylmalonate. Here the experimental susceptibilities are approximately three units lower than the calculated values, which may be explained by contributions from the resonance forms. These cannot be evaluated by this method. The experimental value for ethyl butylmalonate is 3.8 units lower than that calculated for the purely ketonic structure, suggesting a significant contribution from the partially enolic form of type II (Fig. 2) with its lower susceptibility value.

When the groups substituting the methylenic hydrogen atoms are of sufficient size so that the effect of the activating group at a distant part of the molecule is relatively weak, it would be expected that the CH_2 increment would approximate closely to the value obtained for simple

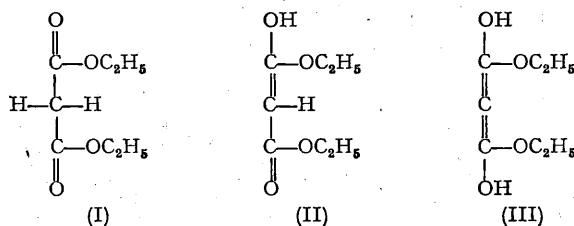


FIG. 2.

(The above structures will represent the substituted ethyl malonates on replacement of the methylenic hydrogen atoms by the appropriate radicals.)

open chain compounds. The experimental value for the susceptibility of ethyl butylethylmalonate, while much lower than that calculated by the Pascal-Pacault method although no enolic form is possible here, results in a value for the CH_2 increment between this compound and ethyl butylmalonate which is much closer to the simple open chain value, than that for the increment between compounds with smaller substituents. The low value for the magnetic susceptibility of ethyl butylethylmalonate may again be due to contributions of the resonance form.⁵

With ethyl malonate it is unlikely that form III with its two adjacent double bonds would make any appreciable contribution to the equilibrium state. This conclusion is supported by the experimental value which lies between the calculated values for forms I and II, and does not therefore necessitate a contribution from form III with its very low susceptibility.

The experimental value for ethyl methylphenylmalonate, for which the ketonic form alone is possible, is 4.95 units lower than the calculated value, due possibly again to contributions from other resonance forms. With ethyl benzylmalonate the difference between the experimental value and that calculated for the ketonic form is even greater (5.33 units), indicating a significant contribution from the partially enolic structure with its lower susceptibility. Comparison between the experimental and calculated values for the susceptibility of ethyl phenylmalonate suggests that both ketonic and partially enolic structures contribute to the equilibrium condition of this compound also.

Gray and Cruickshank's method of evaluating magnetic susceptibility also takes account of tautomeric forms, and further enables values for certain of the resonance structures to be calculated. These theoretical values in general give support to the conclusions reached by the Pascal-Pacault method. Since, however, it is not possible to calculate values for all the important resonance structures by Gray and Cruickshank's method, the latter cannot satisfactorily be used to assess the contribution made by the various forms to the equilibrium condition.

It is of interest to note also that conclusions reached by comparison between experimental values and those calculated by Pascal-Pacault's method are largely supported by evidence from molar refractivities. In Table II, column 7, are recorded the experimental values for this property. In columns 8, 9 and 10 are those calculated for the various tautomeric forms I, II and III, using bond refractivities recently published by Vogel.¹⁹ In view of the fact that contributions from polar forms (which cannot be evaluated by this method) would lower the calculated value of the molar refractivity, the difference between the experimental and calculated values for the three disubstituted ethyl malonates, where both substituents are alkyl groups, is to be expected, the experimental value being low compared with the calculated value in each instance. For all the monosubstituted derivatives, including those containing a phenyl radical, the experimental value is somewhat higher than that calculated for the ketonic form, indicating in each case a significant contribution from the partially enolic form with its higher molar refractivity, in general agreement with the data from magnetic susceptibility measurements. The contribution of the purely enolic form of ethyl malonate cannot be evaluated from the molar refractivity although the results do not necessitate any significant contribution from this structure. The high value for the molar refractivity of ethyl methylphenylmalonate compared with the calculated value remains an anomaly.

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¹⁹ Vogel, Cresswell, Jeffery and Leicester, *Chem. and Ind.*, 1950, 358.

**THE DIAMAGNETIC SUSCEPTIBILITY OF SOME ALKYL
BENZENES AND HIGHER ALIPHATIC HYDROCARBONS**

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The diamagnetic susceptibility of the normal alkyl benzenes and the normal paraffins from octane to undecane and a number of branched chain isomers has been measured and the magnitude of the CH₂ increment has been shown to have the value

$$- 10^6 \chi_M(\text{CH}_2) = 11.69.$$

There is, however, a marked "end effect" in the normal paraffin series tending to produce a lower increment between earlier members of the series. The chain branching increment has been found to have the values of 1.37, 2.33 and 3.04 molar susceptibility units for one, two and three branches respectively. With increased number of branches it appears to increase to a more-or-less constant value.

The magnetic data have been correlated with changes in density, refractive index, molecular volume and refraction. No simple relation exists between the various properties, but increase in molecular volume can explain the end effect and certain of the enhanced values of diamagnetism on chain branching. The results are discussed in relation to Pascal's atomic susceptibility constants and values for the molar susceptibility of characteristic groups are suggested to take account of chain branching.

Within recent years the diamagnetic susceptibilities of homologous series of organic compounds have been investigated by a number of authors;^{1, 2, 3} for a number of such series the molar diamagnetic susceptibility increment for the CH₂ group has been shown to be sensibly constant within the series. It has been found, however, that small deviations occur in the susceptibilities of isomeric compounds due both to chain branching and to positional isomerism. The hydrocarbon series of compounds is the simplest type in which to study the nature of the CH₂ increment. Broersma⁴ has published a detailed study of the diamagnetism of some of the earlier members of the aliphatic hydrocarbon series, together with a few members of the alkyl benzene series. The ranges studied by him are complementary to the present range which is one that ensures that any special effect due to end groups, which may influence the susceptibility increment, will tend to be minimized. The magnitude of the isomer effect is small and thus especially pure materials have been employed and precautions taken to obtain results of high accuracy in the magnetic measurements.

EXPERIMENTAL

The pure materials used for this work, kindly supplied by Prof. E. E. Turner, F.R.S., Dr. Bryce-Smith,⁵ Miss G. M. Owen⁶ and the Institute of Petroleum, were refractionated and physical measurements made as rapidly as possible thereafter. The purity of the various compounds was checked by determination of the densities and refractivities and comparison of these with the more reliable literature values.⁷ (Corrected boiling points and methods of preparation and purification will be found in ref. (5) and (6).)

For the magnetic measurements certain improvements were made to increase the accuracy of the modified Gouy method described previously.⁸ A maximum field strength in the pole gap of 9500 gauss was used which gave a thrust 15 mg in excess of the thrust on the tube alone, on a water column of approximately 1 cm² cross-section, and 8 cm long. The field strength was varied, and the thrusts on the specimen under investigation for fourteen different fields over the range 7000 to 9500 gauss were determined. The balance

was calibrated for each of the fields used, with both benzene and water, and a plot of thrust against amperage was made for both standards and the substance investigated. Random errors in individual readings could thus be detected. Reproducibility of readings from one complete determination to another, on the same specimen, was generally within 0.2%. Deviations were never greater than 0.3%. When necessary, measurements were repeated until satisfactory reproducibility of this order was obtained. An additional degree of accuracy was obtained in studying the isomer effect by plotting the thrusts against amperage for the various isomers on the same graph as that for the straight chain member. For the fourteen field strengths used, the water/benzene susceptibility ratio was found to be 1.025 ± 0.001 which gave a specific susceptibility for benzene of 0.7023 when that of water was taken as 0.7200 (e.m.u. per g $\times -10^6$). All susceptibilities were calculated from the usual relationship:

$$\left(\chi_A - \frac{K}{d_A}\right) / \left(\chi_s - \frac{K}{d_s}\right) = \frac{F_A d_s}{F_s d_A},$$

giving χ_A in e.m.u. of susceptibility per gram, $\times -10^6$. The volume susceptibility $K_{(\text{air})} = 0.0294$ e.m.u. $\times 10^6$; χ_s , d_s and F_s are the mass susceptibility, density and thrust for the standard substance, and χ_A , d_A and F_A are the corresponding values for the compound under investigation. The thrusts are expressed in mg.

The densities and refractive indices were measured at $20^\circ \pm 0.004^\circ$ C. Densities were determined with a 2 ml Ostwald-type pycnometer, all weighings being corrected for the buoyancy effect, and the results reduced to vacuum. The readings were reproducible to ± 0.00003 g/ml. The refractive indices were measured with a calibrated Pulfrich refractometer, individual measurements being reproducible to ± 0.00002 .

RESULTS

In table 1 are recorded the densities, molecular volumes, refractive indices, molar susceptibilities and refractions for the two series of compounds studied, together with the available literature values for the molar susceptibilities. The densities and refractive

TABLE 1.—MOLAR DIAMAGNETIC SUSCEPTIBILITY AND OTHER PHYSICAL PROPERTIES

compound	d_4^{20}	$V_m = M/d_4^{20}$	n_D^{20}	$[R_D]^{20}$	$-10^6 \chi_M^*$	literature values $-10^6 \chi_M$
<i>(a) alkyl benzenes</i>						
benzene	0.87883	88.88	1.50119	26.19	54.85	54.75 ³ 54.85, ² etc.
toluene	0.86683	106.20	1.49691	31.10	65.46	66.11 ⁴ 66.10 ² 65.60 ³ 64.99 ⁹ 65.6 ¹⁰
ethyl benzene	0.86709	122.34	1.49577	35.75	77.37	77.20 ⁴ 77.31 ³
<i>p</i> -xylene	0.86106	123.20	1.49579	36.00	76.97	76.78 ⁴ 76.91 ³
<i>n</i> -propyl benzene	0.86200	139.33	1.49186	40.44	89.24	
4-phenyl but-1-ene	0.88153	149.85	1.50748	44.64	93.49	
<i>n</i> -butyl benzene	0.86017	155.92	1.48975	45.09	100.79	
<i>isobutyl</i> benzene	0.85345	157.15	1.48657	45.20	101.81	
<i>n</i> -amyl benzene	0.85904	172.46	1.48827	49.74	112.55	
1-phenyl-2-methyl butane	0.86072	172.11	1.48906	49.71	113.53	
<i>n</i> -hexyl benzene	0.85830	188.93	1.48698	54.37	124.23	
1-phenyl-4: 6: 6-tri- methyl heptane	0.85591	255.13	1.48268	72.82	173.90	
<i>(b) aliphatic hydrocarbons</i>						
octane	0.70349	162.33	1.39812	39.20	96.47	96.63 ⁴ 94.85 ¹³
nonane	0.71725	178.81	1.40550	43.85	108.00	108.13 ⁴ 104.45 ¹³
4-methyl octane	0.72260	177.48	1.40678	43.67	109.63	
decane	0.72990	194.93	1.41177	48.48	119.74	119.51 ⁴
4-methyl nonane	0.73222	194.31	1.41185	48.33	121.39	
2: 6-dimethyl octane	0.72764	195.54	1.41056	48.50	122.54	
undecane	0.74055	211.06	1.41697	53.08	131.84	
2: 4-dimethyl nonane	0.73849	211.65	1.41576	53.08	134.68	
3: 4-dimethyl nonane	0.75119	208.07	1.42143	52.81	134.70	
4: 5-dimethyl nonane	0.75120	208.07	1.42142	52.81	134.52	

* all molar susceptibilities χ_M are expressed in c.g.s. units of magnetic susceptibility multiplied by -10^6 throughout.

indices are given as criteria of purity, and are in good agreement with other recent literature values where these are available.⁷ Agreement is especially close with the recent values of Forziatti and Glasgow and co-workers.¹¹ Furthermore, if the densities and refractive indices are plotted against the number of carbon atoms in the compound, values for both properties for the straight chain series fall on regular curves from which branched chain isomers of similar type exhibit deviations in a systematic manner. It will be noted that where other values are available for the molar susceptibilities there is good agreement with the present ones. The one unsaturated hydrocarbon was included for comparison with the butyl benzenes.

THE CH₂ INCREMENT.—The mean value of the CH₂ susceptibility increment was determined graphically by plotting the molar susceptibility values against number of carbon atoms in the alkyl chain in the alkyl benzene series and against total number of carbon atoms in the hydrocarbon series. The mean CH₂ increment was then found from the slope of the graph and also by the intercept method of Farquharson and Sastri.¹² Owing to a slight tendency for the increment to fall off in the lower members of the aliphatic series the intercept was taken at C₇ for this series. For the alkyl benzene series the value of $\chi_{M(\text{CH}_2)} = 11.70$ was obtained from the slope, and 11.685 from the intercept, using the relationship

$$\chi_{M(\text{CH}_2)} = (\chi_{M(n)} - \chi_{M(\text{intercept})})/n.$$

($\chi_{M(n)}$ is the molar susceptibility for a hydrocarbon with n carbon atoms in the side chain).

Similarly, for the aliphatic series the value from the slope was 11.71 and from the intercept 11.68 using the relationship

$$\chi_{M(\text{CH}_2)} = (\chi_{M_n} - \chi_{M_{C_7}})/(n - 7).$$

Thus, a mean value of 11.69 was obtained for the molar susceptibility increment for the CH₂ group. It will be seen from table 1 that a similar increment occurs in such branched chain compounds of similar structure as have been measured, e.g. the susceptibility difference between 4-methyl octane and 4-methyl nonane is 11.76 and between *isobutyl* benzene and 1-phenyl-2-methyl butane is 11.72. The value 11.69 is in excellent agreement with that of 11.68 obtained by Angus, supporting his figure for the CH₂ increment in homologous series. It is rather higher than that deduced by Broersma (11.36) from his measurements on the lower members of the saturated aliphatic hydrocarbon series, over the C₅ to C₈ range, on account of a considerable end effect which only becomes negligible by the time the C₈ members are reached. A similar effect is observed for both the refractive index and density and hence must affect the molecular volume, a property which may be expected to influence the molar susceptibility. This is dealt with in a later section.

In the alkyl benzenes the constant value of the CH₂ increment is observed very much earlier in the series. The present figures also confirm the observation of Angus³ that the increment (10.61) between benzene and toluene is anomalously low but that a normal, or even slightly excessive value (11.91) is found between toluene and ethyl benzene. Density and refractive index show a similar trend. Apart from the end effect no evidence has been found for any significant difference in the value of the CH₂ increment in these two series of normal hydrocarbons.

DISCUSSION

THE CHAIN BRANCHING EFFECT.—Molar susceptibilities of branched chain compounds are higher than those of straight chain compounds. The effect is dependent upon the number of branches in the isomer, in agreement with previous observations,^{3, 4, 14} although estimates of the size of the effect by different authors have varied. Table 2 showing the magnitude of the chain-branching effect has been compiled from the molar mass susceptibility values obtained for the aliphatic hydrocarbons in the present investigation and those of Broersma, together with one set of figures given by Angus.³ The chain branching increment is largest for a single branch, the successive effects of later branching becoming less. If the mean figures for this increment (one branch 1.4, two branches 2.3 and three branches 3.0 molar susceptibility units) are plotted against number of branches they lie on a curve passing through the origin, and showing a tendency to approach a limiting figure of some 4 units of molar susceptibility for a chain of six branches or more.

In the alkyl benzene series (see table 1) a rather lower value is found for a single branch (mean of three values 0.74 unit). The one example (1-phenyl-4:6:6-trimethyl heptane) of a chain with three branches in this series can only be compared with an extrapolated figure for decyl benzene (170.8), derived graphically, but the value of the increment so obtained (3.1) is in agreement with

TABLE 2.—THE CHAIN BRANCHING EFFECT

	one branch.		two branches			three branches		
	$-10^6\chi_M$	Δ^*	hydrocarbon	$-10^6\chi_M$	Δ^*	hydrocarbon	$-10^6\chi_M$	Δ^*
aliphatic hydrocarbons								
<i>n</i> -pentane	63.05(a)		—	—	—	—	—	—
2-methyl butane	64.40(a)	1.35						
<i>n</i> -hexane	74.05(a)		2 : 2-dimethyl butane	76.24(a)	2.19	—	—	—
2-methyl pentane	75.26(a)	1.21						
3-methyl pentane	75.52(a)	1.47	2 : 3-dimethyl butane	76.22(a)	2.17			
<i>n</i> -heptane	85.24(a)		2 : 2-dimethyl pentane	86.97(a)	1.73	2 : 2 : 3-trimethyl butane	88.36(a)	3.12
2-methyl hexane	86.24(a)	1.00	2 : 3-dimethyl pentane	87.51(a)	2.27			
			2 : 4-dimethyl pentane	87.48(a)	2.24			
<i>n</i> -octane	96.47(b)		2 : 3-dimethyl hexane	98.77(a)	1.98	2 : 2 : 3-trimethyl pentane	99.86(a)	3.25
3-methyl heptane	96.63(a)	1.45						
3-ethyl hexane	97.99(a)	1.14	3 : 4-dimethyl hexane	99.06(a)	2.52	2 : 2 : 4-trimethyl pentane	98.34(a)	2.73
	97.68(c)		2 : 5-dimethyl hexane	98.15(a)	1.61	2 : 3 : 4-trimethyl pentane	99.68(c)	3.07
<i>n</i> -nonane	108.00(b)							
4-methyl octane	108.13(a)	1.56						
	109.63(b)							
<i>n</i> -decane	119.74(b)		2 : 6-dimethyl octane	122.54(b)	2.91			
4-methyl nonane	119.51(a)	1.76						
	121.39		3 : 4-dimethyl nonane	134.70(b)	2.86			
<i>n</i> -undecane	131.84(b)		4 : 5-dimethyl nonane	134.52(b)	2.68			
			2 : 4-dimethyl nonane	134.68(b)	2.84			

* The differences (Δ) due to chain-branching are derived by subtraction of the susceptibility value for the normal hydrocarbon from that of the branched-chain isomer, except in the case of *p*-cymene where the comparison is with the *iso*-compound. (a) Broersma's values; (b) values of present paper; (c) Angus' values.³

the corresponding value in the aliphatic series. Broersma⁴ and Manzoni-Ansidei¹³ found additional evidence for a further modification in molar susceptibility due to positional isomerism. This effect is, however, even smaller than that due to chain branching and barely lies outside the range of experimental uncertainty of the figures at present available. Attempts to make a quantitative estimate of it appear premature.

CORRELATION WITH OTHER PHYSICAL PROPERTIES.—Bhatnagar,¹⁴ Angus and Hill² and Angus³ have found evidence of some correlation between the magnetic susceptibility and other properties. From studies on various normal and *iso*-alcohols and acids it has been suggested that the more diamagnetic isomeride

has the lower value of boiling point, density and refractive index. So far as density and refractive index are concerned the present data appear to support this in only a few cases, i.e. for normal and *isobutyl* benzene, decane and 2:6-dimethyl octane, and undecane and 2:4-dimethyl nonane. In all other cases the relationship with the other physical properties appears to be considerably more complex as is shown by the variations in density with chain branching.

If the densities of the relevant C_5 to C_{11} hydrocarbons are considered in relation to those of the normal series, certain systematic variations may be noted. Hydrocarbons with a single branch in the 2-carbon position show lower, and those with a single branch in the 3 or 4 carbon position show higher densities than normal, the variations being systematic over the range C_5 to C_{11} . Similarly, compounds with two branches in the 2:2, 2:4, 2:5, and 2:6 carbon positions have densities lower, and in the 2:3, 3:4 and 4:5 positions higher, than normal.* The molecular volume (M/d_4^{20}) varies in the converse sense. Refractive indices vary similarly with the density. Thus, since deviations in density and refractive index are always in the same sense, the molar refractions in table 1 show little indication of the chain branching effect.

In all these cases, however, the magnetic susceptibility chain branching increment is positive and cannot be explained solely by enhanced molecular volume. Huggins,¹⁵ Platt,¹⁷ and Wiener¹⁸ have considered systematic variations in a number of properties of hydrocarbons on chain branching (boiling points, molecular volumes, etc.) and suggest that the contribution of a given C—C or C—H bond is modified by its position and by the number and nature of radicals or other groups attached to it. While no estimate can as yet be made of the magnitude of the position effect from the magnetic data, the general increase in susceptibility on chain branching, irrespective of the direction of the change in molecular volume, seems to point to some other factor, such as modification in charge distribution within the molecule, as a contributor to the changes in susceptibility.

The end effect observed in the magnetic measurements on the straight chain aliphatic hydrocarbons, may be compared with a similar effect found for the molecular volumes by Huggins,¹⁵ on plotting against the number of carbon atoms in the chain. The earlier values show a marked departure from the linear relationship which holds for later members. This is apparent from the molecular volume figures in table 1 when supplemented by the values of 115.20, 130.70 and 146.60 for normal pentane, hexane and heptane respectively, calculated from Broersma's data. The molecular volume graph begins to approach a linear relationship only at about the eighth member of the series. Huggins proposed the general formula

$$V_m = 29.97N_{CH_3} + 16.49N_{CH_2} + (29.0/n_C)$$

for the molecular volumes of the normal paraffins, where the first and second terms represent the contributions to the molecular volume of the CH_3 and CH_2 groups in the molecule and the last term is a correction for the end effect, n_C being the total number of carbon atoms. The present results and those of Broersma satisfy this relationship well. If the value of the increase in molecular volume due to the end effect is calculated (i.e., $V_m(\text{expt}) - [29.97N_{CH_3} + 16.49N_{CH_2}]$) and plotted against the number of carbon atoms, the curve so obtained is of a similar shape to the corresponding molar susceptibility deviation curve, both curves approaching linearity in the same region in the hydrocarbon series (fig. 1). The molar susceptibility deviation curve is obtained from the relationship

$$\Delta\chi_M = [n\chi_C + (n+2)\chi_H] - \chi_M(\text{expt}),$$

where the term in brackets represents χ_{M_F} the calculated molar susceptibility derived from Pascal's atomic susceptibility constants for carbon (6.00) and

* generalizations drawn from density data of Forziatti and co-workers,¹¹ Broersma⁴ (from his volume and mass susceptibility figures) and the present investigation, see also (7).

hydrogen (2.93). The end effect which is the cause of Broersma's abnormally low CH_2 increments thus appears to be produced by the enhanced molecular volume in these earlier members of the series.

GROUP SUSCEPTIBILITY INCREMENTS.—The experimental susceptibilities of both series of compounds fall consistently below the sum of the Pascal atomic constants¹ for the carbon and hydrogen atoms as illustrated by fig. 1 for the hydrocarbon series. Even after allowance has been made for the end effect as discussed above, the Pascal constants are rather too high. The experimental susceptibility increment for the CH_2 group stabilizes at the value 11.69, while that of Pascal is 11.86. An increasing divergence between the two values would thus be expected, irrespective

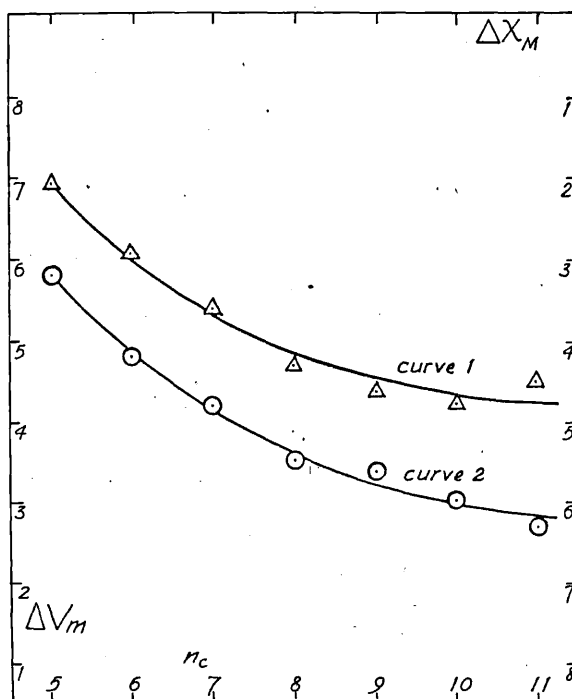


FIG. 1.—Deviations in molar volume and molar susceptibility for normal paraffin hydrocarbons. Curve 1, molar susceptibility deviations ($\Delta\chi_M$); curve 2, molar volume deviations (ΔV_m).

of any end effect. Furthermore, the Pascal atomic susceptibility constants give no indication of the chain branching effect, there being no constitutive constants on this system for bonds in saturated hydrocarbon compounds.

Broersma has suggested revised values for certain of the atomic susceptibility constants based on his experimental measurements, in which allowance has been made for the different types of carbon linkages in the molecule, but these are dependent upon his value for the CH_2 increment, which is influenced by the end effect. The assumption, moreover, of constant atomic susceptibility values unmodified by the nature of the compound, even when this is of a simple type, such as a hydrocarbon, is, as suggested by Angus and Hill,² open to question. It thus appears useful to approach the problem of susceptibility increments from a different standpoint. Since the total molar susceptibility can be expressed by a formula of the type

$$\chi_M = n_1\chi_{M(-\text{CH}_3)} + n_2\chi_{M(>\text{CH}_2)} + n_3\chi_{M(\geq\text{C}-\text{H})} + n_4\chi_{M(<\text{C}<)} + \Sigma\chi_a$$

in which the groups $-\text{CH}_3$, etc., are bonded only to carbon atoms, and the last term is a constitutive correction for positional isomerism, it is possible from the molar susceptibility figures in table 2 to derive values for the contribution to the susceptibility of groups other than the CH_2 group, in simple molecules of this type. From the molar susceptibilities of the normal hydrocarbons heptane to undecane the mean susceptibility contribution of the group $-\text{CH}_3$ is 13.21 ± 0.15

(mean of five values), while the value for the $(\text{C})-\overset{\text{(C)}}{\underset{\text{(C)}}{\text{C}}}-\text{H}$ group, derived from com-

pounds with only one branch on a given carbon atom, is 11.36 ± 0.30 (mean of fifteen values). There follows a mean value for the $(\text{C})-\overset{\text{(C)}}{\underset{\text{(C)}}{\text{C}}}-(\text{C})$ group of

10.40 ± 0.40 . Only hydrocarbons with seven carbon atoms or more were used to calculate these figures, as the end effect may influence earlier members. Although based on the rather limited data available at present, it is of some interest that these increments show the same type of non-linear transition from one to the next as was found by Gibling¹⁶ to hold for the parachor increments

when similarly expressed, namely, $[P]$ for $(\text{C})-\text{CH}_3 = 55.2$, $(\text{C})-\text{CH}_2 = 39.8$,

$(\text{C})-\text{CH} = 27.2$ and for $(\text{C})-\overset{\text{(C)}}{\underset{\text{(C)}}{\text{C}}}-(\text{C}) = 2.4$. As this effect is related to molecular

volume, the parallel seems significant.

A further confirmation of the CH_3 value was obtained from the alkyl benzene series. The intercept (3.07) on the graph of molar susceptibility of the normal paraffin hydrocarbons, plotted against number of carbon atoms, represents twice the susceptibility contribution of the additional hydrogen atom in a CH_3 group. The intercept on the graph of molar susceptibility of the alkyl benzenes, plotted against number of carbon atoms in the side chain represents the susceptibility contribution of $\text{C}_6\text{H}_5 + \text{H}-$. Since this hydrogen represents that of the end methyl group in the aliphatic series, the subtraction of 1.54 from the intercept value 54.08 gives the contribution of the C_6H_5 group in the alkyl benzenes. Using this value and that for CH_2 a further estimate was made of the contribution of the $-\text{CH}_3$ group to the total susceptibility from the alkyl benzenes (13.24, five values). The final mean for the susceptibility contribution of the $-\text{CH}_3$ group is 13.22 (mean of ten values). Similar calculations from *isobutyl* benzene and 1-phenyl-2-methyl butane, give the values 11.25 and 11.28, which, with the previous values, yield a final mean for the contribution of the $\text{C}-\text{H}$ group of 11.35 (seventeen values).

The next step would appear to be the substitution of these values in more complex types of compounds to determine whether they remain constant. If so, further extensions to cover other groups may be made which can be used to study possible end effects and group interaction effects. The values suggested above may need modification as more data on long series of compounds become available, and a further extension to include position isomerism should later become possible.

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