EXPERIMENTAL STUDIES ON THE MASS SUSCEPTIBILITY OF THE AMMONIUM AND SUBSTITUTED AMMONIUM IONS.

Thesis presented for the Degree
of Doctor of Philosophy.

\- by -

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June, 1941.

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Abstract.

"Experimental Studies on the Mass Susceptibility of the Ammonium & Substituted Ammonium Ions."

by M.E.Bedwell.

The present research was intended to establish a reliable value for the gram-ionic mass susceptibility of the ammonium ion, since the values obtained by various workers are not in close agreement. The specific susceptibilities of a large number of ammonium compounds have been measured, using the modified Gouy method. The molecular mass susceptibility of each compound has been calculated by multiplying the specific susceptibility by the molecular weight, and from the resulting values the correcting constant for anion was subtracted, giving the gram-ionic susceptibility of the ammonium ion in combination with univalent and divalent anions, and in solution. Deviations were found to occur in the two latter cases. A similar procedure has been adopted for the substituted ammonium compounds. Measurements on the ammonium halides in solution, and in the solid crystalline state, show a linear relationship between molecular susceptibility and coordination number, and mean values of the gram-ionic susceptibility of the sulphate and lower fatty acid anions have been found in alkali metal and ammonium salts. Several anionic correcting constants have been proposed on the basis of the experimental results. A series of susceptibility/atomic number graphs have been plotted, showing the relation between the experimental results and those calculated by theoretical means. In almost every case theory has been confirmed by experiment. The values of bond depressions were found inapplicable in a number of cases, owing to the uncertainty of which of several resonance formulae is the most satisfactory. The gram-atomic susceptibility of the oxygen atom in sulphur- and chromium-oxyacids has been determined, and a mean value of the susceptibility of the CH_2 group agreeing closely with that of Pascal, has been found from several homologous series of compounds. Measurements on electronic and position isomers have confirmed the results of Bhatnagar and his co-workers.

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(5) THEORETICAL DISCUSSION:

(1) INTRODUCTION

The object of the present research was the determination of the magnetic mass susceptibilities of certain derivatives of ammonium and substituted ammoniums, from which the gram-ionic mass susceptibility of the ammonium ion and also the substituted ammonium ions were deduced. The relationship of the susceptibility of the ammonium ion to those of the alkali-metal ions was determined; the latter group of ions has already been widely investigated, whereas the ammonium salts have not.

The substituted ammonium compounds were also investigated, in order to study the effects of the substitution on the ionic susceptibility. Information was also desired on bond effects, coordination effects etc. as modifying influences on the susceptibility.

All results were checked where possible by theoretical methods, taking resonance formulae into account, and the experimental results were compared with those of other workers.

The results were considered from the point of view of the CH_2 value, obtained by difference from successive members of some homologous series; also from the point of view of the variation of susceptibility with coordination number. The susceptibility of isomers was considered, and the relation between the sodium, potassium and ammonium salts of some organic fatty acids, and also between the halides, was discussed.

The effect of bond depression on the contribution of the oxygen atom to molecular susceptibility, was considered in the series S_2O_n, SO_n, Cr_2O_n, CrO_n, and the experimental results were considered from the point of view of bond depressions in connection with resonance formulae.

The value of the susceptibility of the ammonium ion was used to obtain improved values for the susceptibilities of anions in certain of its polar salts; in these cases the values were previously rather uncertain, owing to a lack of experimental data.

Work of a similar nature has been done previously by:-

Sugden (1) on silver and copper compounds

Spencer & Hollens (2) on cadmium compounds

Trew (3) on thallous compounds

Ikenmeyer (4) on the alkali metal halides

Brindley & Hoare (5,6,7,8) on alkali metal and alkaline earth halides

Kido (9,10,11,12) on acids, alkali metal and alkaline earth salts; silver, zinc, cadmium and mercury salts

Angus & Farquharson (13) on beryllium compounds

(2) EXPERIMENTAL

(i) Preparation and Analysis of Substances

The compounds to be investigated were obtained as pure as possible from Harrington Bros. or British Drug Houses Ltd.

The susceptibility of the substances of "Analar" purity was measured without further purification, after testing for ferromagnetic impurities by the reactions enumerated below.

The "Pure" substances were analysed, first qualitatively in order to ascertain the nature of the impurities present. In particular, tests were made for the presence of ferromagnetic impurities (e.g. iron, cobalt, nickel) using the following sensitive reactions:-

IRON: Purple colour is given on adding an ammoniacal aqueous solution of thioglycollic acid to the test solution. (Sensitive to I part in 5,000,000.)

NICKEL: Red colour is given when an ammoniacal alcoholic solution of α-benzildioxime (in the proportions 0.2 gm. α-benzildioxime to 950 cc. alcohol and 50 cc. conc. ammonia) is added to an ammoniacal test solution. (Sensitive to 1 part in 1,000,000.)

COBALT: Orange colour is given on adding a solution of α-nitroso β-naphthol (prepared by dissolving 0.2 gm. α-nitroso β-naphthol in 100 cc. cold glacial acetic acid, diluting with

100 cc. hot water and filtering.) together with dilute caustic soda and a little ammonium chloride to the test solution. (Sensitive to 1 part in 100,000.)

The results of the tests are given in Section (8).

The "Pure" substances were then analysed quantitatively, determining the percentage of the anion present in the case of salts of ammonium. In the case of ammonium bromide and ammonium dichromate, the salts were first purified by recrystallisation from hot water and then analysed. In the other cases, the salts were too unstable to allow of purification by recrystallisation or sublimation.

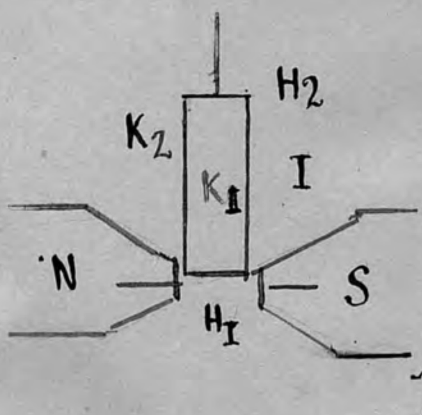
The organic derivatives were purified by various methods enumerated in Section (8).

(ii) Measurements of Susceptibilities

We employed the modified Gouy method, (14) in which the pull on a specimen suspended in a non-homogeneous magnetic field was weighed by means of a chemical balance.

The method was based on the principle that all substances experience a force in a non-homogeneous magnetic field; there is a tendency for diamagnetic substances to move away from the field of greatest intensity, and for para- and ferromagnetic substances to move towards it. The apparatus was arranged so that the force was in a direction vertically upwards or downwards, according as to whether the substance was of a diamagnetic or paramagnetic nature respectively.

In the accompanying diagram:-



K_1 = volume susceptibility of substance
K_2 = " " " medium
H_1 = maximum field at centre of magnet (position of base of cylinder.)
H_2 = maximum field at top of cylinder
I = length of column of substance in cm.
N,S = north and south poles of electromagnet.
A = area of cross-section of substance in $cm.^2$
F = force upwards or downwards in dynes
μ_1 = permeability of material
μ_2 = permeability of medium (e.g. air.)

∴ The force on a material of permeability μ_1 in a medium of permeability μ_2 is given the expression:-

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

Since $\mu = (I + 4\pi K)$, $F = \frac{1}{2}(K_1 - K_2).A.(H_1^2 - H_2^2)$

$$\text{i.e. } K_1 = [2F/A(H_1^2 - H_2^2)] + K_2$$

Since χ = mass susceptibility = K/d (where d = density of column) and d = w/IA, it follows that:-

$$\chi = [2Fl/W(H_1^2 - H_2^2)] + K_2 IA/W$$

Where W = weight of column. If K_2 = volume susceptibility of air = $0.03 . 10^6$, then we have that:-

$$10^6 . \chi = \frac{2Fl}{W(H_1^2 - H_2^2)} + \frac{0.03.lA}{W}$$

When 1 is sufficiently large, H_2 becomes zero, and we assume this condition to hold in the experiment. Also, for a given length of column and aperture between the pole pieces, the length of the column 1 and the fields H_1 and H_2 are constant. Hence:-

$$\chi . 10^6 = \frac{\alpha F}{W} + \frac{0.03.lA}{W}$$

$\alpha = 21/H_1^2$ = a constant for the apparatus.

Since lA = V = volume, it follows that:-

$$\chi . 10^6 = \frac{F + 0.03.V}{W}$$

For convenience, F was measured in mgms., l in cm., V in cc., and W in gms., α was expressed in C.G.S. units

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

In addition to measurements on the powdered solid material, the specific susceptibility of the ammonium halide salts was measured in aqueous solution. It was necessary to take into consideration two opposing factors in deciding on the most suitable concentration to be used. Firstly, a solution containing too small a concentration of solute would cause considerable error in measurement. However, if the solution was too concentrated, the additivity law could not strictly be applied to the solute molecules, owing to the field effects of ions and molecules, of both solvent and solute, on each other; these effects are negligible in dilute solution but more marked in concentrated solution owing to the proximity of the ions and molecules.

In addition, the formula by which the specific susceptibility of the pure solute could be calculated from that of the solution, did not take into account any interaction effects between solvent and solute. Hence a solution of medium concentration was ideal; the concentration chosen was approximately 17%. The same concentration was employed in each case so that any interaction effects were eliminated, comparatively.

The specific susceptibility of the solvent χ_S , was calculated from that of the solution χ_{sol} using the equation:-

$$\chi_{sol} = c\chi_s + (I - c)_w$$

where χ_w = specific susceptibility of <u>pure</u> water (although this may be questioned. Brindley & Hoare (8)); c = concentration of solute. The same equation was used in the case of ammonia solution.

The apparatus is shown in Plate I (p.11) and diagram I (p.12).

The magnetic field was generated by means of an electromagnet having a coil of 20,000 turns. A current of 3 amperes at 200 volts was maintained, which was controlled by means of a variable rheostat connected in series with the coil, and registered by an ammeter also in series. Two pole switches were also connected in series which facilitated rapid make and break of the circuit. A maximum field of 5,000 gauss was produced.

The weighing was conducted by means of a very sensitive balance of the Bunge type with a short beam. The balance was mounted above the electromagnet, so that the centre of a circular hole in the base beneath the left hand arm was in a vertical line with the centre of the gap between the pole pieces. The left hand scale pan was replaced by a light aluminium support carrying a disc with a hook at its lower side. The hook carried a fine platinum wire (0.04" diameter), attached at its lower end to a brass stirrup.

From the stirrup the tube containing the substance to be investigated was supported by two glass arms sealed at about 1·5 cm. from the top. The tube was of glass having a low magnetic susceptibility, and was about 11.0 cm. in length, and about 0.6 cm. in diameter. It was essential that the bottom of the tube was level with the centre of the pole pieces, and that the tube hung vertically between the pole pieces.

The tube was etched with a fine calibration line about 7.0 cm. from the bottom. It was thoroughly cleaned with chromic acid to remove magnetic impurities adhering to it, and dried by rinsing it out with ether and passing a current of air into it. The open end was closed by a cork, or for deliquescent substances a ground glass stopper.

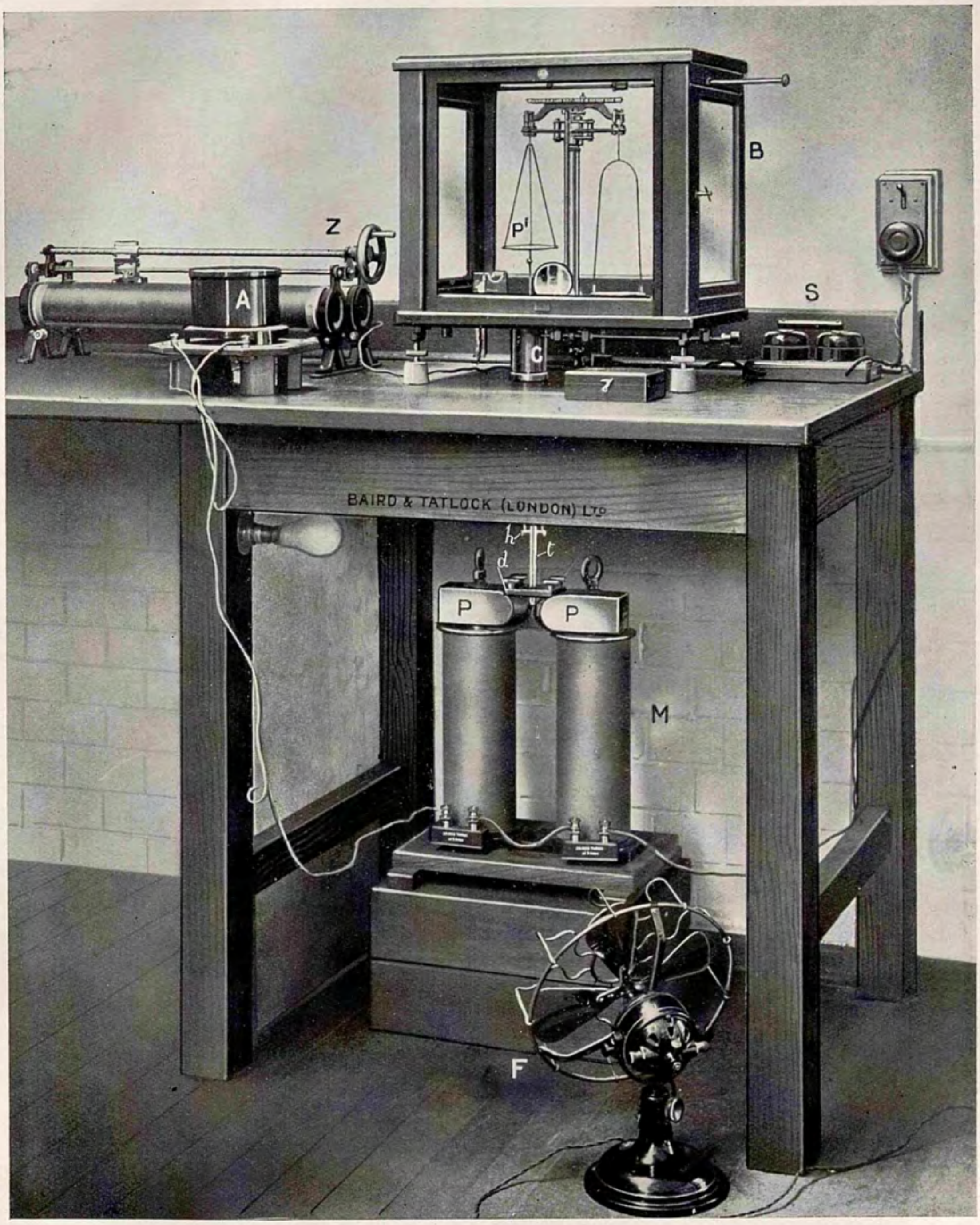
The substance under investigation was a pure liquid, solution or solid, and perfect dryness was essential. The substance was dried in a desiccator unless dehydration occurred, in which case it was dried in the air (or in an inert atmosphere if it was unstable in contact with air.) Solids were finely powdered in a mortar and then packed tightly and uniformly into the tube, being hammered down with a flat ended rod of slightly smaller diameter than the interior of the tube.

The tube was filled to the calibration mark with the specimen to be measured, so that approximately the same volume of substance was used for all measurements.

All weights were determined to 0.01 mgm. in the usual manner by oscillations, the scale being read through a lens.

KEY TO PLATE I

A	Ammeter
B	Balance
C	Copper tube which protects suspension from draughts
F	Electric fan
M	Coils of electromagnet
P	Pole pieces of electromagnet
P'	Pan of balance which carries a hook from which the platinum suspension hangs
S	Double switch (two pole switches)
Z	Rheostat
d	Distance-piece
h	Copper stirrup
t	Specimen tube


Z
A
B
P'
S
C
z
BAIRD & TATLOCK (LONDON) LTD
h
d
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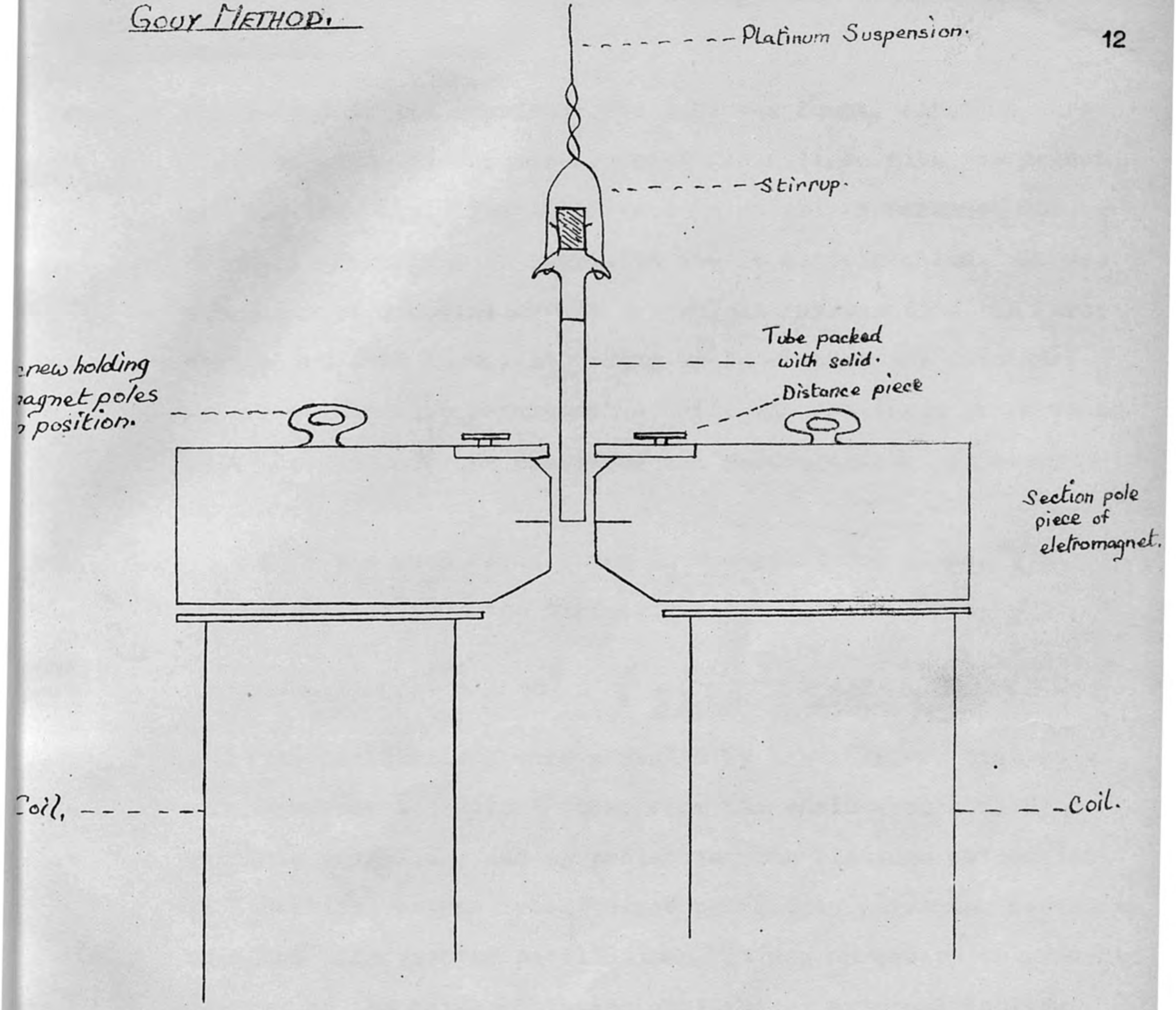
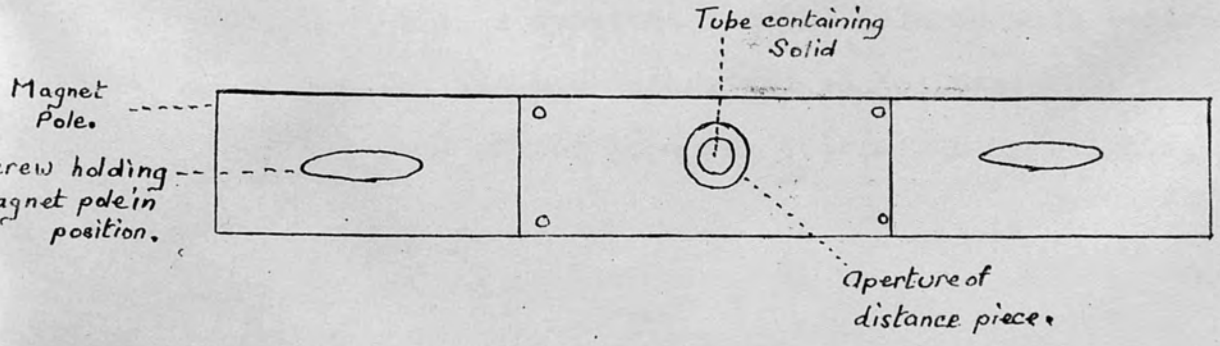
P
M
F

GOUY METHOD.



Vertical Section.



Horizontal Section.

The weight of the substance and tube was found, first in zero field and then in the experimental field (i.e. with the magnet off and then on). The difference in weight represented the force of attraction or repulsion due to magnetisation. It was necessary to subtract or add the weight representing the force due to the tube alone, according as to whether the substance was diamagnetic or paramagnetic. (If the net force was greater than the original the substance was paramagnetic; if less, diamagnetic.)

From the mean force F due to the substance alone, χ was calculated from the expression:-

$$\chi . 10^6 = \frac{\alpha F}{W} + \frac{0.03.V}{W}$$

The oscillations were affected by draughts, so that it was necessary to exclude these from the whole apparatus by suitable screening, and by protecting the platinum suspension by a vertical copper tube. Since convection currents, caused by heating, affected the oscillations, it was necessary to prevent heating of the coil. This was achieved by external cooling with an electric fan and by exciting the field for short periods only.

α is a constant for the balance with a given experimental tube, and was determined as follows:-

The pull of the tube was determined by weighing the tube alone in air, with the magnet off and then on. The experiment was repeated with the tube filled up to the mark with a pure substance of known magnetic susceptibility. Both benzene and acetone were employed.

The volume of the tube V up to the mark was determined by filling it with distilled water and weighing. The temperature was recorded and the corresponding density of water found from tables, thus enabling us to calculate V.

α was calculated separately using benzene and acetone, from the equation:-

$$\alpha = \frac{[W.\chi 10^6 - 0.03.V]}{F}$$

The mean value of α was subsequently employed. The results for tube 2 are shown below. α was determined by a similar method for the other tubes employed.

Pull of tube 2

	Magnet Off.	Magnet On.	Pull. (negative)
(a)	6.24 mgm.	5.55 mgm.	0.69 mgm.
(b)	6.26 mgm.	5.53 mgm.	0.73 mgm.
(c)	6.45 mgm.	5.65 mgm.	0.80 mgm.
(d)	6.21 mgm.	5.49 mgm.	0.72 mgm.
(e)	6.14 mgm.	5.47 mgm.	0.67 mgm.
(f)	6.10 mgm.	5.41 mgm.	0.69 mgm.

∴ Mean Pull = 0.72 mgm. Mean Weight = 7.48612 gm.

Constant of the Balance for Tube 2.

V x 0.03 = 0.090

(I) Pull of Tube 2 + Benzene

	Magnet Off	Magnet On	Pull (negative)	Mean Pull (negative)	Mean Weight
(a)	7.75 mgm.	2.50 mgm.	5.25 mgm.	5.28 mgm.	10.13778 gm.
	7.78 mgm.	2.50 mgm.	5.28 mgm.		
	7.80 mgm.	2.48 mgm.	5.32 mgm.		
(b)	7.01 mgm.	1.80 mgm.	5.21 mgm.	5.23 mgm.	10.13707 gm.
	7.12 mgm.	1.91 mgm.	5.21 mgm.		
	7.08 mgm.	1.81 mgm.	5.27 mgm.		
(c)	9.18 mgm.	3.89 mgm.	5.29 mgm.	5.37 mgm.	10.13912 gm.
	9.18 mgm.	3.77 mgm.	5.41 mgm.		
	9.00 mgm.	3.60 mgm.	5.40 mgm.		

∴ Mean Pull = -5.29 mgm.

∴ Net Pull = -4.57 mgm. (Benzene alone)

Mean Weight = 10.13799 gm.

∴ Net Weight = 2.65187 gm. (Benzene alone.)

$$\therefore = \frac{-(2.65187.0.716)-(0.090)}{-4.57}$$

$$= 0.43540$$

Pull of Tube 2 (after benzene measurement)

	Magnet Off.	Magnet On.	Pull (negative)
(a)	8.44 mgm.	7.66 mgm.	0.78 mgm.
(b)	7.43 mgm.	6.58 mgm.	0.85 mgm.
(c)	6.00 mgm.	5.21 mgm.	0.79 mgm.
(d)	6.26 mgm.	5.52 mgm.	0.74 mgm.
(e)	7.23 mgm.	6.47 mgm.	0.76 mgm.
(f)	7.48 mgm.	5.72 mgm.	0.76 mgm.

∴ Mean Pull = -0.78 mgm.

Mean Weight = 7.48656 gm.

(II) Pull of Tube 2 + Acetone

	Magnet Off	Magnet On	Pull (negative)	Mean Pull (negative)	Mean Weight
(a)	9.20 mgm.	5.07 mgm.	4.13 mgm.	4.13 mgm.	9.87920 gm.
	9.17 mgm.	5.01 mgm.	4.16 mgm.		
	9.19 mgm.	5.08 mgm.	4.11 mgm.		
(b)	5.51 mgm.	1.53 mgm.	3.98 mgm.	4.10 mgm.	9.86539 gm.
	5.48 mgm.	1.33 mgm.	4.15 mgm.		
	5.17 mgm.	1.00 mgm.	4.17 mgm.		
(c)	5.80 mgm.	1.53 mgm.	4.27 mgm.	4.24 mgm.	9.88573 gm.
	5.66 mgm.	1.45 mgm.	4.21 mgm.		
	5.45 mgm.	1.21 mgm.	4.24 mgm.		

∴ Mean Pull = -4.16 mgm.

∴ Net Pull = -3.38 mgm. (Acetone alone)

Mean Weight = 9.87677 gm.

∴ Net Weight = 2.39021 gm. (Acetone alone)

$$\therefore \quad \alpha = \frac{-(2.3902 \,.\, 0.716)-0.090}{-\,3.38}$$

$$= 0.43762$$

TABLE 1a

Specific Susceptibilities of Ammonium and Substituted Ammonium Compounds

(1) Ammonia (Solution)
($35\%\ NH_3\ ^{W}/W$)

Pull of tube 4 = -0.56 mgm.

$a = 0.39257$

V . 0.03 = 0.091

	Pull (negative) Tube + material	Mean Pull (negative) Tube + material	Pull (negative) material alone	Weight of Material	$-\chi \cdot 10^6$
(a)	6.08 mgm. 6.03 mgm. 6.15 mgm.	6.09 mgm.	5.53 mgm.	2.68018 gm.	0.780
(b)	6.00 mgm. 6.25 mgm. 6.09 mgm.	6.11 mgm.	5.55 mgm.	2.68603 gm.	0.781
(c)	6.29 mgm. 6.08 mgm. 6.08 mgm.	6.15 mgm.	5.59 mgm.	2.69306 gm.	0.785

Mean Value = $-0.783 \cdot 10^{-6}$

$\therefore \chi$ solute . 10 = $-0.900 \cdot 10^{-6}$

(2) Ammonium Fluoride. NH_4F

Pull of tube 1 = -0.37 mgm.

$\alpha = 0.92737$

v . 0.03 = 0.096

	Pull (negative) Tube + material	Mean Pull (negative) Tube + material	Pull (negative) material alone	Weight of Material	$-\chi . 10^6$
(a)	1.89 mgm.	1.89 mgm.	1.52 mgm.	2.10696 gm.	0.624
	1.88 mgm.				
	1.90 mgm.				
(b)	1.89 mgm.	1.89 mgm.	1.52 mgm.	2.11019 gm.	0.623
	1.89 mgm.				
(c)	1.90 mgm.	1.90 mgm.	1.53 mgm.	2.14598 gm.	0.616
	1.86 mgm.				
	1.93 mgm.				

Mean Value = $-0.621 . 10^{-6}$

(3) Ammonium Chloride. NH_4Cl

Pull of tube 1 = -0.58 mgm. (i) Pull of tube 1 = -0.30 mgm. (ii)

$a = 0.41315$ $a = 0.92737$

$V . 0.03 = 0.096$ $v . 0.03 = 0.096$

Tube No.		Pull (negative) Tube + material	Mean Pull (negative) Tube + material	Pull (negative) material alone	Weight of Material	$-\chi . 10^6$
I (i)	(a)	5.58 mgm. 5.65 mgm. 5.63 mgm.	5.62 mgm.	5.04 mgm.	2.88120 gm.	0.690
	(b)	5.46 mgm. 5.68 mgm. 5.63 mgm.	5.59 mgm.	5.01 mgm.	2.86669 gm.	0.688
I (ii)	(c)	2.48 mgm. 2.46 mgm. 2.53 mgm.	2.49 mgm.	2.19 mgm.	2.84240 gm.	0.681

Mean Value = $-0.686 . 10^{-6}$

(4) Ammonium Bromide. NH_4Br

Pull of tube I = -0.58 mgm.

α = 0.41315

V . 0.03 = 0.096

	Pull (negative) Tube + Material	Mean Pull (negative) Tube + Material	Pull (negative) Material alone	Weight of Material	$-\chi \cdot 10^6$
(a)	5.72 mgm. 5.60 mgm. 5.62 mgm.	5.65 mgm.	5.07 mgm.	4.20821 gm.	0.475
(b)	5.94 mgm.	5.94 mgm.	5.36 mgm.	4.38647 gm.	0.483
(c)	6.10 mgm. 6.10 mgm. 6.09 mgm.	6.10 mgm.	5.52 mgm.	4.53977 gm.	0.481

Mean Value = $- 0.480 \cdot 10^{-6}$

(5) Ammonium Iodide. NH_4I

Pull of tube 4 = -0.56 mgm.

a = 0.39257

v . 0.03 = 0.091

	Pull (negative) Tube + Material	Mean Pull (negative) Tube + Material	Pull (negative) Material alone	Weight of Material	$-\chi . 10^6$
(a)	6.24 mgm. 6.19 mgm.	6.22 mgm.	5.66 mgm.	4.92290 gm.	0.433
(b)	6.15 mgm. 6.14 mgm.	6.15 mgm.	5.59 mgm.	4.69518 gm.	0.448
(c)	6.07 mgm. 6.11 mgm. 6.06 mgm.	6.08 mgm.	5.52 mgm.	4.62137 gm.	0.449

Mean Value = $-0.443 . 10^{-6}$

(6) Ammonium Nitrate. NH_4NO_3

Pull of tube I = -0.58 mgm. (i) Pull of tube I = -0.31 mgm. (ii)

α = 0.41315 α = 0.92737

v . 0.03 = 0.096 v . 0.03 = 0.096

Tube No.		Pull (negative) Tube + Material	Mean Pull (negative) Tube + Material	Pull (negative) Material alone	Weight of Material	$-\chi \cdot 10^6$
I (i)	(a)	4.62 mgm. 4.72 mgm. 4.61 mgm.	4.65 mgm.	4.07 mgm.	3.90712 gm.	0.407
	(b)	4.48 mgm. 4.46 mgm. 4.44 mgm.	4.46 mgm.	3.88 mgm.	3.71717 gm.	0.405
I (ii)	(c)	1.87 mgm. 1.87 mgm.	1.87 mgm.	1.56 mgm.	3.29888 gm.	0.408

Mean Value = $-0.407 \cdot 10^{-6}$

TABLE 1b

Specific and Molecular Susceptibilities of Ammonium and Substituted Ammonium Compounds

Formula of Compound	$-\chi \cdot 10^6$	$-\chi_M \cdot 10^6$	Temp. °C
Ammonia (Solution)			
NH_4OH	0.900	31.54	15.5
Monovalent Salts			
NH_4F	0.621	23.00	18.4
NH_4Cl	0.686	36.70	20.0
NH_4Br	0.480	47.02	17.0
NH_4I	0.441	63.94	20.0
NH_4NO_3	0.407	32.58	19.0
NH_4VO_3	-0.069	-8.07	20.0
Divalent Salts			
$(NH_4)_2SO_3 \cdot H_2O$	0.524	70.32	28.7
$(NH_4)_2SO_4$	0.507	66.97	17.0
$(NH_4)_2S_2O_3$	0.507	75.15	15.9
$(NH_4)_2S_2O_8$	0.490	111.82	14.0
$(NH_4)_2CrO_4$	-0.066	-1.00	19.0
$(NH_4)_2Cr_2O_7$	-0.150	-37.82	16.0

Formula of Compound	$-\chi . 10^6$	$-\chi_M . 10^6$	Temp. °C
Complex Salts			
$(NH_4)_6Mo_7O_{24}.4H_2O$	0.132	163.1	19.0
Salts of Organic Acids			
$(COONH_4)_2H_2O$	0.582	82.70	20.0
$HCOONH_4$	0.504	31.79	26.8
CH_3COONH_4	0.561	43.24	17.3
$C_2H_5COONH_4$	0.599	54.58	19.8
Organic Derivatives			
$\alpha\ -(C_{10}H_5NH_2)$	0.557	79.71	15.0
$\beta\ -(C_{10}H_5NH_2)$	0.556	79.56	18.9
$C_6H_4.CH_3NH_2$(meta)	0.689	73.79	20.8
$C_6H_4.CH_3NH_2$(para)	0.693	74.29	17.3
$NH_2OH.HCl$	0.639	44.41	19.5
$2NH_2OH.H_2SO_4$	0.480	78.78	23.0
$N_2H_4.HCl$	0.650	44.53	18.6
$N_2H_4.H_2SO_4$	0.487	63.36	25.0
$N_2H_4.H_2O$	0.710	35.55	17.0
$C_6H_5NHNH_2.HCl$	0.656	94.86	17.0

Formula of Compound	$-\chi \cdot 10^6$	$-\chi_M \cdot 10^6$	Temp. °C
$C_6H_5NH(CH_3)$	0.689	94.86	20.5
$C_6H_5NH(C_2H_5)$	0.709	85.94	19.0
$C_6H_5N(CH_3)_2$	0.709	85.94	19.5
$C_6H_5N(C_2H_5)_2$	0.731	108.99	24.0
$CH_3NH_2 \cdot HCl$	0.689	46.59	25.0
$NH(CH_3)_2 \cdot HCl$	0.719	58.64	17.5
$N(CH_3)_3 \cdot HCl$	0.735	70.26	20.0
$NH(C_2H_5)_2 \cdot HCl$	0.742	81.34	17.3
$N(C_2H_5)_4Cl$	0.735	121.80	18.0
$N(CH_3)_4Br$	0.561	86.40	21.7
$N(C_2H_5)_4Br$	0.623	130.95	20.3
$N(CH_3)_4I$	0.502	100.95	20.0
$N(C_2H_5)_4I$	0.567	145.85	19.2
NH_4F (solution)	0.705	23.54	19.3
NH_4Cl "	0.719	38.47	21.0
NH_4Br "	0.508	49.76	22.0
NH_4I "	0.458	66.41	18.6
NH_4NO_3 "	0.680	34.86	16.5
$HCOONa \cdot H_2O$	0.474	40.07	20.3
C_2H_5COONa	0.513	49.25	15.6

Formula of Compound	$-\chi \cdot 10^6$	$-\chi_M \cdot 10^6$	Temp. °C
HCOOK	0.392	32.92	19.2
C_2H_5COOK	0.503	56.50	21.0
$Na_2SO_4 \cdot IOH_2O$	0.565	182.05	20.5
Rb_2SO_4	0.318	84.80	16.6
Cs_2SO_4	0.306	110.33	20.1

(3) RESULTS

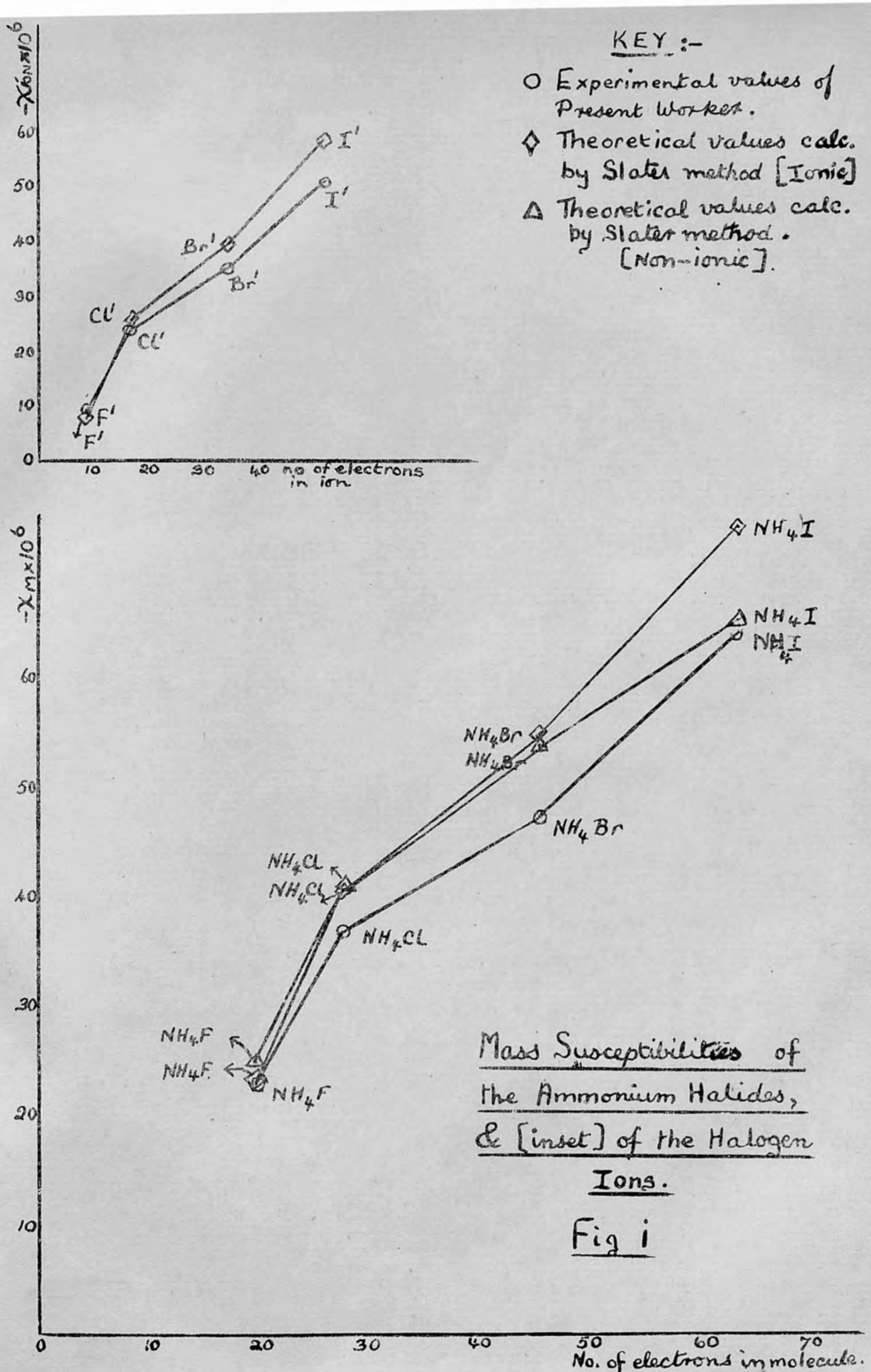
The results are shown in detail in Table 1A (pp. 18 - 23) Table 1b gives the mean value of the specific mass susceptibility χ_S obtained in the former table, and the molecular mass susceptibility χ_M calculated from χ_S , where:-

$$\chi_S \, M = \chi_M$$

M being the molecular weight of the compound. The temperature at which the measurements were conducted is shown in column 4. The results are tabulated according to the valency of the negative radical in the case of ammonium salts of inorganic acids, and the salts of organic acids are tabulated separately, with the corresponding salts of sodium and potassium at the end of the table.

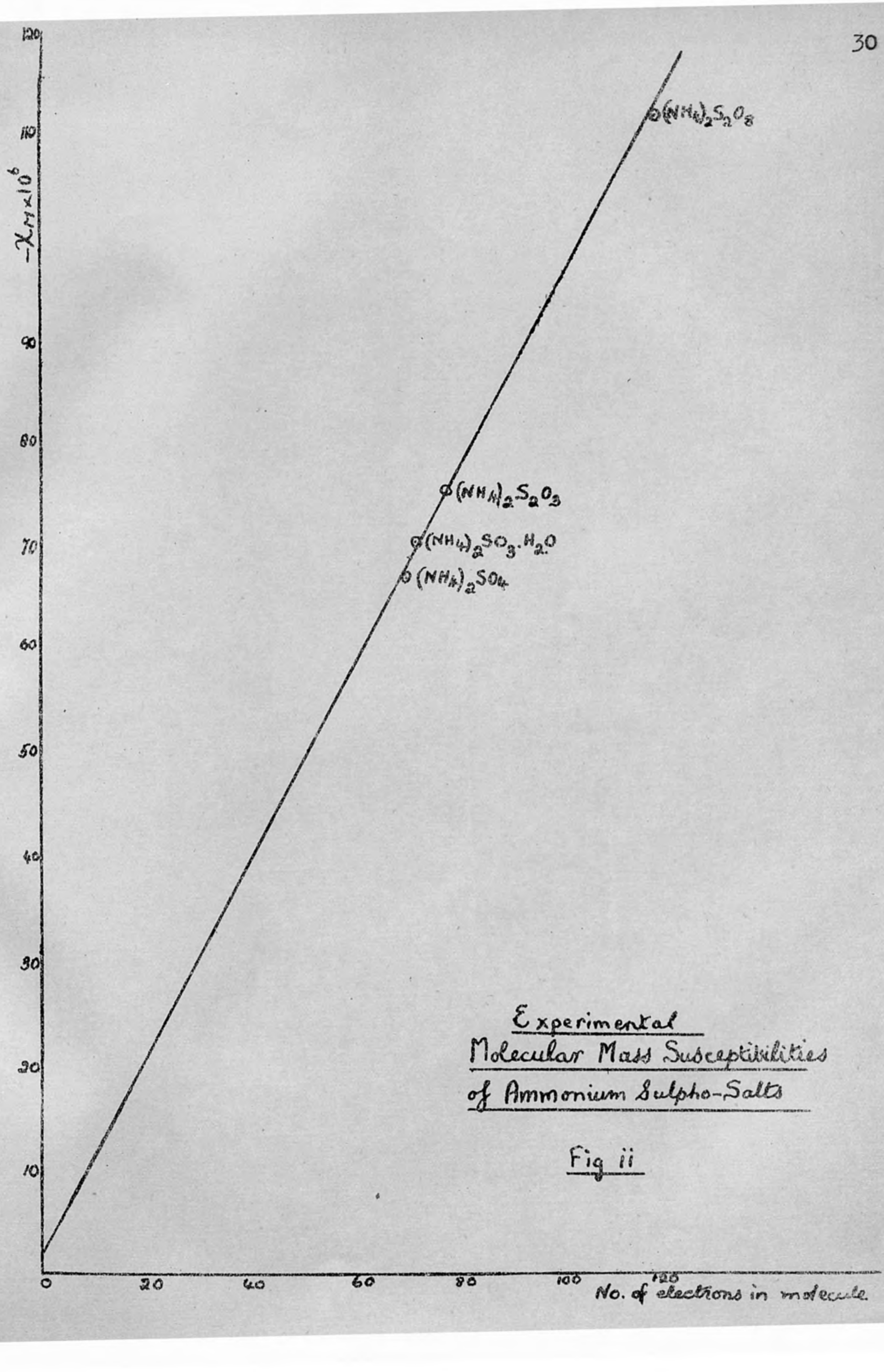
The remaining organic compounds are grouped together separately according to type.

Graphs i-vii, (pp. 29 - 35) show the curves obtained by plotting the value of $_M$ against the total number of electrons in the compound considered. The curves obtained were linear, except in those cases involving the halogen anions (i.e. the ammonium and substituted ammonium halides in graphs i and v respectively. The curves are discussed in detail in Section IV of the theoretical discussion, p. 97).



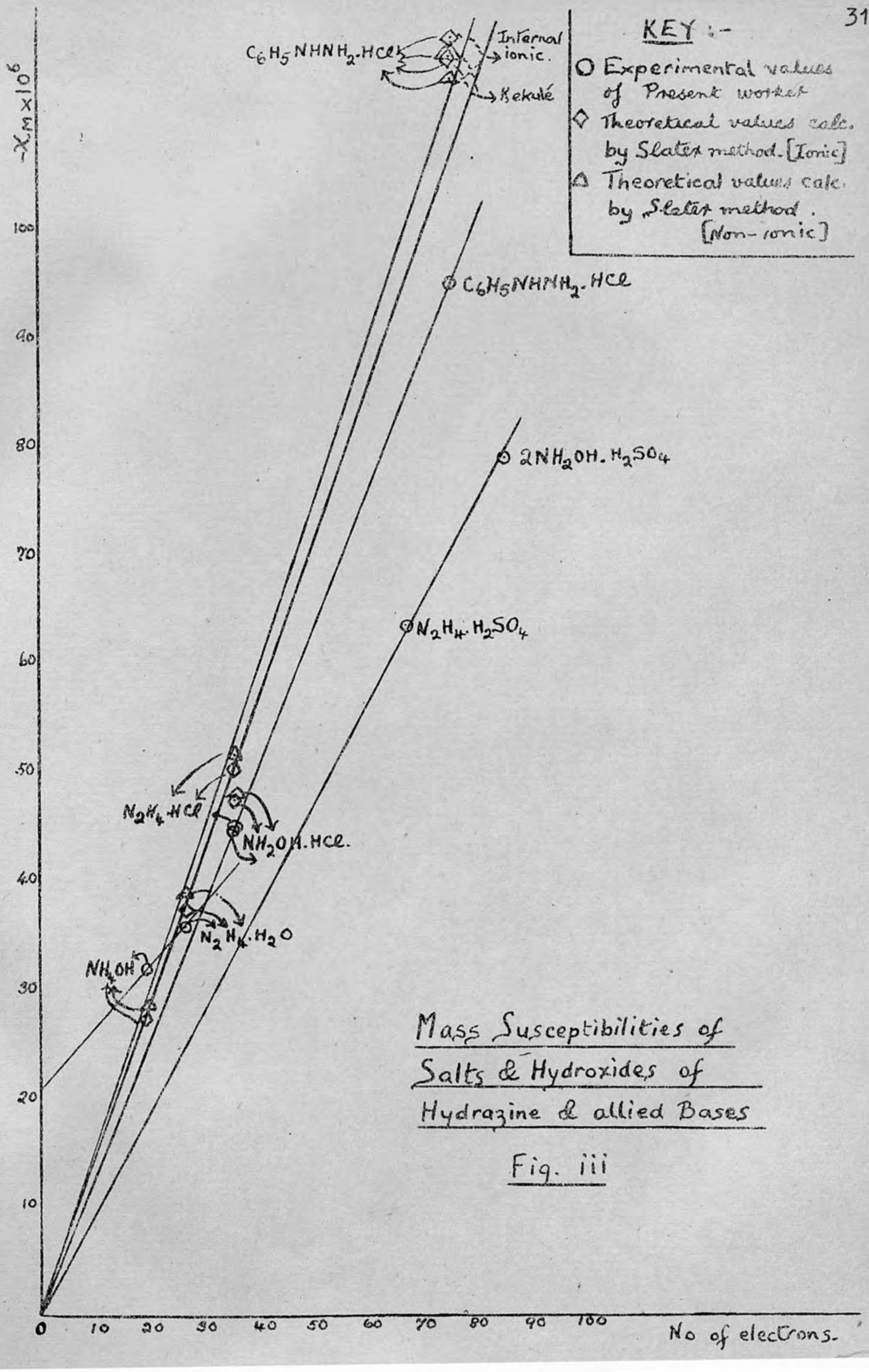
Mass Susceptibilities of the Ammonium Halides, & [inset] of the Halogen Ions.

Fig i



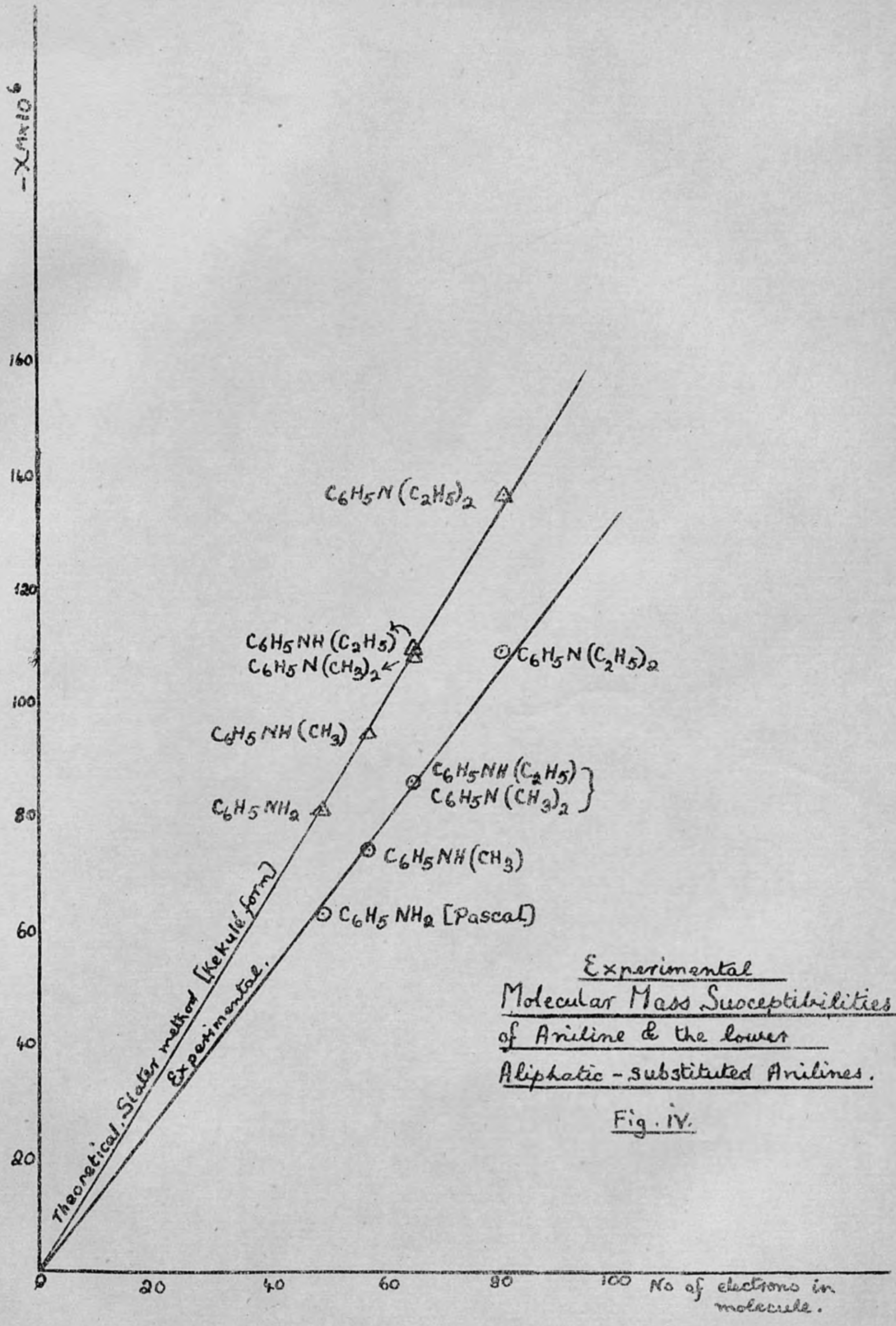
Experimental Molecular Mass Susceptibilities of Ammonium Sulpho-Salts

Fig ii



Mass Susceptibilities of Salts & Hydroxides of Hydrazine & allied Bases

Fig. iii



Experimental Molecular Mass Susceptibilities of Aniline & the lower Aliphatic-substituted Anilines.

Fig. IV.

KEY:–

○ Experimental [Present Worker]

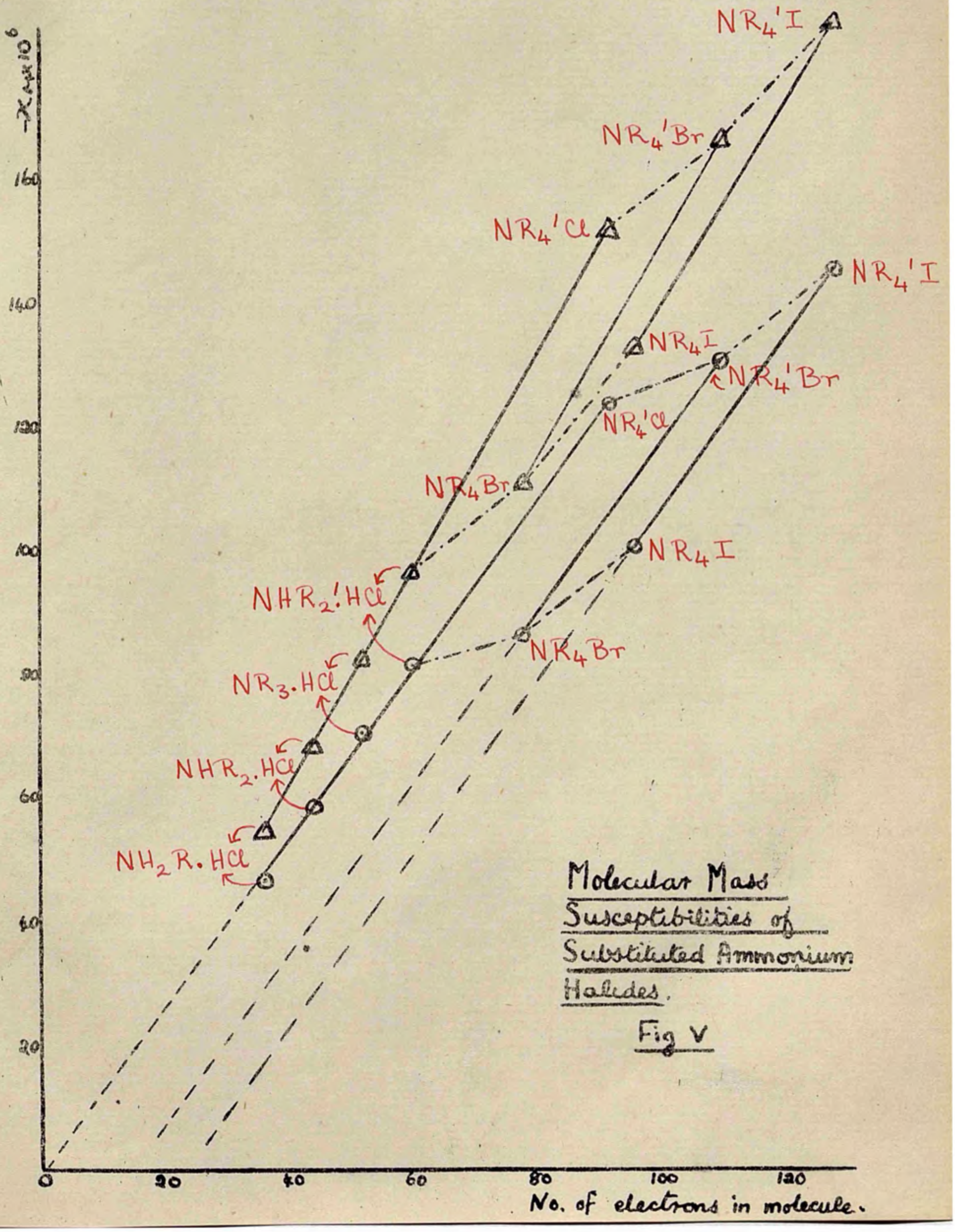
Δ Theoretical. Slater method. [Ionic.]

—— Curve for salts with common anion.

–·–· Curve for salts with common cation.

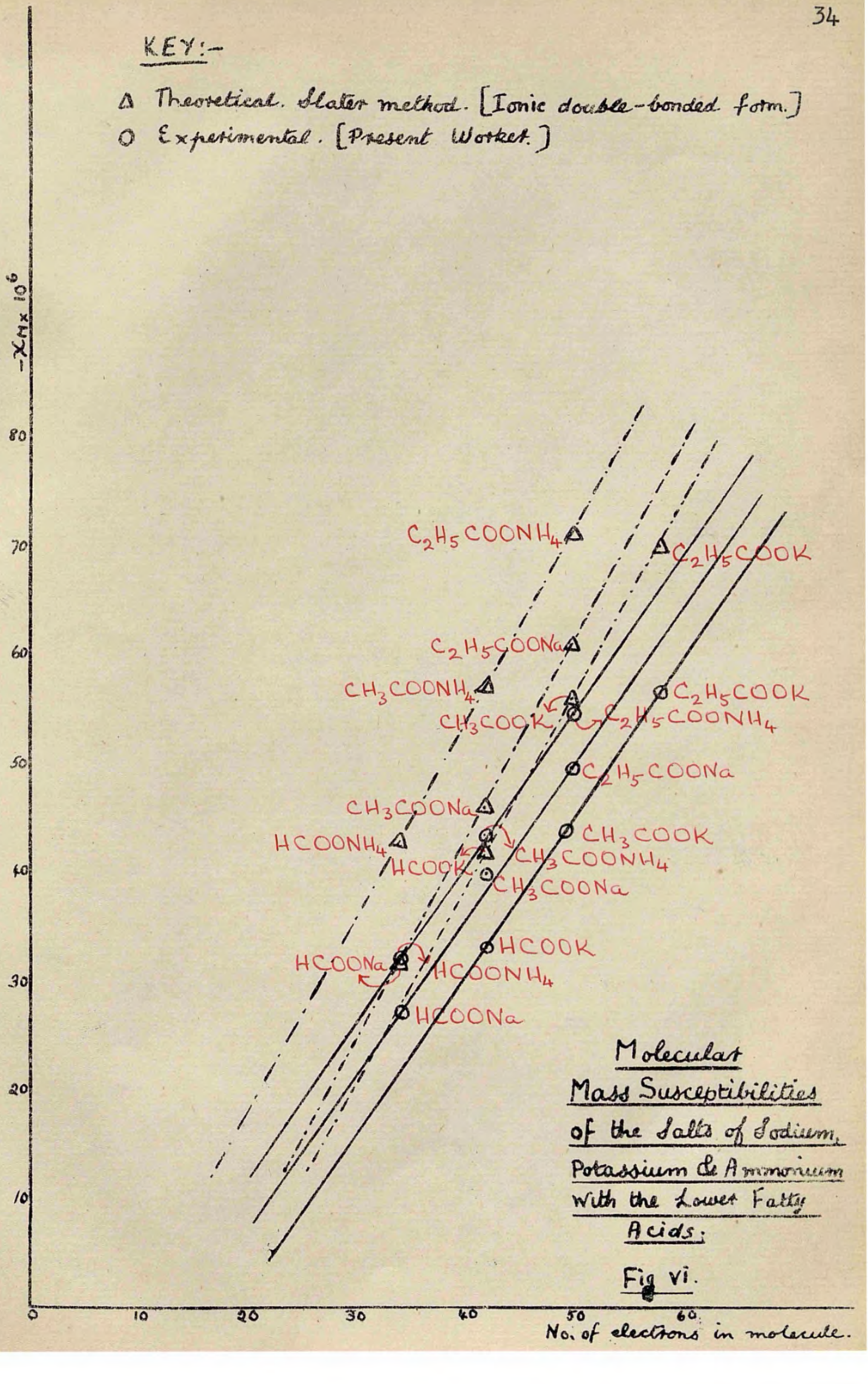
R = CH_3.

R′ = C_2H_5.



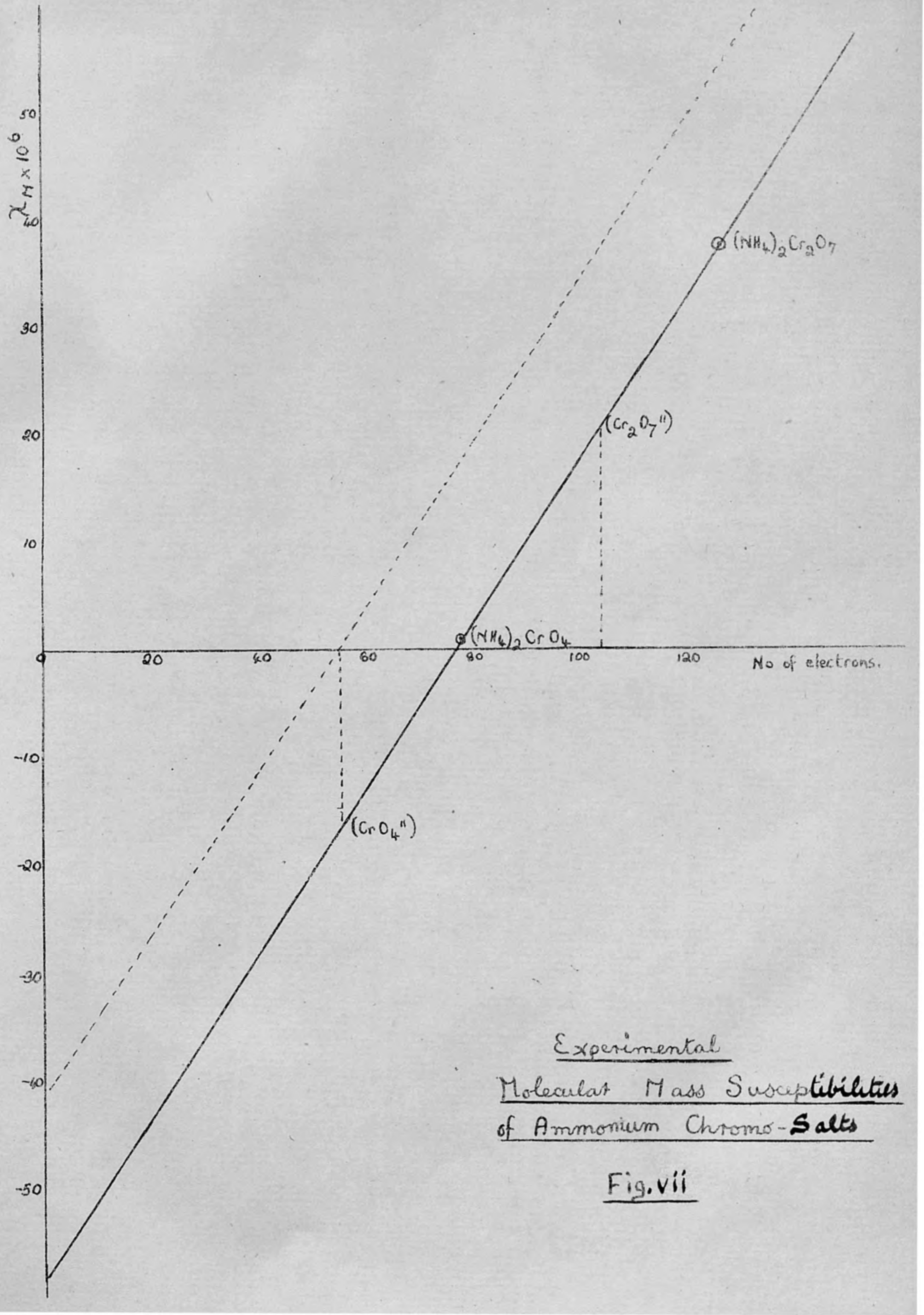
Molecular Mass Susceptibilities of Substituted Ammonium Halides.

Fig V



Molecular Mass Susceptibilities of the Salts of Sodium, Potassium & Ammonium with the Lower Fatty Acids.

Fig vi.



Experimental

Molecular Mass Susceptibilities of Ammonium Chromo-Salts

Fig. vii

(4) DISCUSSION OF RESULTS

(I) Experimental Results of Other Workers

The molecular mass susceptibility of the compounds under consideration, obtained by other workers, are collected in Table 2. Agreement with the present values is fairly close for the majority of compounds, but there is divergence in the case of sodium sulphate, hydrochlorides of di- and tri-methylamine, tetramethylammonium iodide, ammonium persulphate, ammonium acetate, and ammonium vanadate.

The present values were checked theoretically where possible. (Section I of the theoretical discussion).

The temperature of observation is given in the last column of Table 2.

TABLE 2

Values of Molecular Mass Susceptibilities Previously Published.

$(\chi_M \cdot 10^6)$

Substance.	$-\chi_M \cdot 10^6$	Observer	Reference No.	Temp. °C.
NH_4OH	27·3	Kido	9	26
	35·09	Farquharson	15	-
	38·56	Pascal	18	16
NH_4F	24·5	Kido	9	25
NH_4Cl	34·2	Kido	9	11
	35·7 ± 0·47	Farquharson	15	-
NH_4Br	47·4	Kido	9	12
	46·71	Farquharson	15	-
NH_4I	66·0	Kido	9	12
	69·48	Farquharson	15	-
NH_4NO_3	33·6	Kido	9	11
NH_4VO_3	-19·1	Perrakis	16	17 & 45
	+14·04	Meyer	17	15
$(NH_4)_2SO_4$	63·2	Kido	9	14
$(NH_4)_2S_2O_8$	100·3	Kido	11	21
CH_3COONH_4	42·9	Kido	9	23
$NH_2OH.HCl$	42·45 ± 0·39	Farquharson	15	-
$N_2H_4.HCl$	40·90 ± 0·27	Farquharson	15	-
$m\text{-}C_6H_4CH_3NH_2$	72·97	Bhatnagar & Mathur	19	40

Substance.	$-\chi_M . 10^6$	Observer	Reference No.	Temp. °C.
$C_6H_5NH(CH_3)$	82·74	Bhatnagar & Mathur	20	-
	74·41	Pascal	21	Room
$C_6H_5NH(C_2H_5)$	87·14	Bhatnagar & Luther	22	-
	85·92	Pascal	21	Room
$C_6H_5N(CH_3)_2$	79·34	Bhatnagar & Luther	22	-
	86·12	Pascal	21	Room
$NH_2CH_3.HCl$	44·45 ± 0.39	Farquharson	15	-
$NH(CH_3)_2.HCl$	53·32 ± 0·28	Farquharson	15	-
$N(CH_3)_3.HCl$	64·27 ± 0·51	Farquharson	15	-
$N(CH_3)_4Br$	87·21 ± 0·46	Dakers	23	-
$N(CH_3)_4I$	105·0 ± 0·88	Dakers	23	-
$N(C_2H_5)_4I$	152·6 ± 0·31	Dakers	23	-
$Na_2SO_4.IOH_2O$	170·85	Meslin	24	

(II) Susceptibility of the Ammonium and Substituted Ammonium Ions.

The ionic susceptibility of the ammonium and substituted ammonium ions was obtained by three distinct methods:-

- (a) From the experimental results,
- (b) Graphically, by extrapolation of experimental curves,
- (c) Theoretically.

(a) From the experimental values of χ_M were subtracted the experimental values of χ_{anion} concerned. The latter, obtained by various workers, are shown in Table 3. This method assumed that the additivity law held rigidly, i.e. that:-

$$\chi_a + \chi_c = \chi_M$$

where χ_a = ionic susceptibility of anion; χ_c = ionic susceptibility of cation; χ_M = molecular susceptibility of compound.

The method assumes that the compound is completely polar in the solid crystalline state and in solution; otherwise the additivity law is probably invalid. Many of the compounds measured were at least partially covalent or coordinated. According to Sidgwick (25) ammonium and substituted ammonium salts are almost invariably anhydrous," as one would expect, since in ammonium the nitrogen is covalently saturated and the hydrogen attached to it can only act as acceptor under very exceptional circumstances. None of its salts with simple monobasic acids are hydrated and when we find a salt with a

Table 3

Experimental Gram-Ionic Mass Susceptibilities of Anions due to Various Workers.

$(-\chi_{ion} \cdot 10^6)$

Anion	Brindley (26)	BRINDLEY (7)				Kido (12)	Weiss, Hocart (27)	Weiss, Pascal (27)	Mean of preceding	Trew (28)
		CN6	CN8	CN6,3	CN8,4					
F^-	-	9·4	-	9·2±·2	8·6±·1	12·2	-	-	10·4	9·1
Cl^-	24·0	24·2	22·9	-	21·7±·1	22·1	23·1	23·1	23·04	23·4
Br^-	37·5	34·5	33·4	-	30·1±·1	34·7	33·9	34·7	34·4	34·6
I^-	55·7	50·6	48·8	-	47·5±·1	53·2	49·5	49·8	51·76	50·6
Li+	0·7	0·7	-	-	-	1·6	-	-	1·1	1·2
Na+	5·2	6·1	-	-	-	7·6	8·2	7·6	6·9	6·8
K +	13·5	14·6	-	-	-	13·6	16·5	16·0	14·4	14·9
Rb+	24·0	22·0	-	-	-	(27·2)	-	24·3	23·4	22·5
Cs+	36·8	35·1	33·8	-	-	(41·0)	-	38·0	35·9	35·0
NO_3-	-	-	-	-	-	20·1	-	-	-	18·9
OH^-	-	-	-	-	-	8·5	-	-	-	-
$CH_3CO_2^-$	-	-	-	-	-	32·0	-	-	-	-
SO_4^{--}	-	-	-	-	-	39·0	-	-	-	40·3
SO_3^{--}	-	-	-	-	-	36·5	-	28·8*	-	-
$S_2O_3^{--}$	(39·7) (51·42) -	(34·5)[1] (49·62)[2] -	- - -	- - -	- - -	(39·5) (46·62) 43·0	(30·7) (45·42) -	(31·7) (46·62) 49·90*	(34·9) (48·02) -	(33·9) (48·22) -
$S_2O_8^{--}$	(73·28) (75·4) -	(71·08)[3] (73·2)[4] -	- - -	- - -	- - -	(73·08) (75·2) 75·5	(67·28) (69·4) -	(68·28) (70·4) -	(71·48) (73·6) -	(70·48) (72·6) -
CrO_4^{--}	(-27·0)	(-29·2)[5]	-	-	-	(-27·2)	(-33·0)	(-32·0)	(-29·6)	(-28·6)
$Cr_2O_7^{--}$	- (-64·95) (-81·0)	- (-67·15)[6] (-83·2)[7]	- - -	- - -	- - -	- (-65·15) (-81·2)	- (-70·95) (-87·0)	- (-69·95) (-86·0)	- (-67·45) (-82·8)	** (-33·5) (-66·5) (-82·6)

* Pascal corrected homopolar value.
** Trew (29)
C.N = Coordination number.

dibasic acid is hydrated we may take it as evidence of hydration of the anion."

Examples of this are:- Oxalate - IH_2O

Sulphite - IH_2O

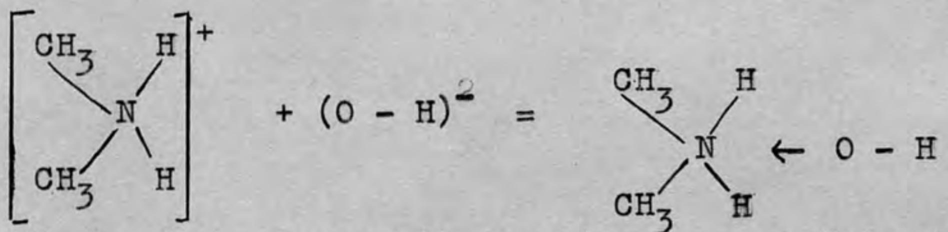
The remaining salts measured were unhydrated, except hydrazine hydrate $N_2H_4.H_2O$ which is a normal compound since the nitrogen is not covalently saturated in hydrazine.

Since the theoretical equation (due to Langevin), given in Section I of the theoretical discussion was originally deduced for the magnetic mass susceptibility of polar compounds consisting of two mononuclear spherically symmetrical ions such as $Na\cdot$ and Cl^-, it cannot strictly apply to any other type of compound. In the hydrated compounds mentioned above, the coordination of water affects the ionic susceptibility of anion and cation, since it changes the radius of the molecule. The attraction of the water molecules by the nucleus causes the molecule to contract, but the net effect is an increase in radius due to the water shell, and hence the individual ionic susceptibilities will be affected, since they depend on the ionic radius. (Method (c) below).

Other hydrated salts measured were $Na_2SO_4.IOH_2O$ and $CH_3COONa.3H_2O$ (the latter was measured by Kido). The sulphate ion can be di-hydrated, but it seems unlikely that the sodium ion is eight-coordinated with water, in sodium sulphate.

In the calculations it was assumed that the ionic susceptibilities of the ions in the molecule, and the molecular susceptibility of the water of crystallisation were all additive, and as has been shown, this introduces a slight error owing to the coordinate nature of the water.

The hydroxides of ammonium and substituted ammoniums, are relatively weak bases, except for the tertiary substituted ammonium hydroxides which have no hydrogen atom attached to the nitrogen atom and so the cation cannot pass over into the covalent form by coordinating a molecule of water. This can and does occur in the other cases since they have at least one hydrogen atom attached to the central nitrogen atom, e.g. Dimethyl ammonium hydroxide:-



Similarly the corresponding salts can pass into the covalent form by coordinating a molecule of acid on to the hydrogen of the cation, and, in fact, the salts are chiefly covalent, whereas those of the tetra-substituted ammoniums are entirely polar, having no hydrogen atom available for coordination.

The values of susceptibility measured in solution contained a slight error due to the hydrolysis of the ammonium halides in water. Ammonium hydroxide itself was measured in very concentraded solution, and was present chiefly in the covalent form. In covalent compounds the spherical symmetry of the component systems is distorted, and the Langevin equation does not strictly apply.

In addition to covalency and coordination, forces in crystals and solutions caused by the attraction and repulsion of ions for molecules of solvent or other ions, tend to modify the susceptibility of the ions concerned.

Table 3 gives values for the ionic susceptibility of the halogen ions, alkali metal ions and some polyatomic ions. The methods employed in deducing these values from experimental measurements of the susceptibilities of salts may be criticised. [Trew. (28)]

The figures in brackets were obtained indirectly from the sodium or potassium salts, assuming the additivity law, and subtracting the different values for the sodium or potassium ions given in the table. The key to the table is given below:-

1.	$K_2S_2O_3$	Observer:-	Kido (11)
2.	$Na_2S_2O_3$	"	Pascal (30)
3.	$K_2S_2O_8$	"	" "
4.	$K_2S_2O_8$	"	Farquharson (31)
5.	K_2CrO_4	"	Gray & Dakers (32)
6.	$K_2Cr_2O_7$	"	Endo (33)
7.	$K_2Cr_2O_7$	"	Gray & Dakers (32)

The ionic correcting constants due to Trew (28) (last column of Table 3) represent a mean value of other workers with modifications, and they were considered to be the most reliable. They agreed closely with those of Brindley (26).

Table 4 gives the values for the ionic susceptibility of the ammonium and substituted ammonium ions obtained with the aid of Tables Ib and 3. The figures in brackets correspond to those in brackets in Table 3. The figures for ammonium do not differ appreciably, although those in brackets are the least reliable. The ionic susceptibility of ammonium in the salts with organic fatty acids is abnormally high, probably owing to the covalent nature of these compounds.

The value for ammonium in ammonium bromide was found to be anomalously low. Trew (29) found this to be the case with thallous ion in thallous bromide. The reason for the anomaly does not seem clear. Ammonium bromide was measured after recrystallisation both from aqueous and alcoholic solutions, and the measurements agreed within the limits of experimental error. If the correcting constants of Weiss & Hocart, or Brindley (7) were employed, the value for ammonium was brought into line with the other halide values.

The new ionic correcting constants of Trew give a mean value for the susceptibility of the ammonium ion in combination with the univalent ions $F^{\cdot}$, $Cl^{\cdot}$, $NO_3^{\cdot}$, of:-

$$-\chi_{NH_4^{\cdot}} \cdot 10^6 = \underline{13{\cdot}56}$$

For combination with divalent anions, the values obtained from the sulphate using the Trew correcting constant, and from the value of sodium thiosulphate (Pascal) with the Trew correcting constant for sodium and the present value of ammonium

TABLE 4 24

Experimencal Gram-Ionic Mass Susceptibilities of the Ammonium and Substituted Ammonium Ions using Values for Anions shown in Table 3. $(-\chi_{ion}\cdot 10^6)$

Cation in Compound	Brindley (26)	BRINDLEY. (7)				Kido (12)	Weiss, Hocart (27)	Weiss, Pascal (27)	Mean of preceding.	Trew (28)
		CN6.	CN8.	CN6,3	CN8,4					
NH_4^+										
NH_4OH	-	-	-	-	-	23·04	-	-	-	-
NH_4F	-	-	-	-	14·40	10·80	-	-	12·60	13·90
NH_4Cl	12·70	-	13·80	-	-	14·60	13·60	13·60	13·66	13·30
NH_4Br	9·52	-	13·62	-	-	12·32	13·12	12·32	12 58	12·42
NH_4I	8·24	13·34	-	-	-	10·74	14·44	14·14	12·18	13·24
NH_4NO_3	-	-	-	-	-	12·48	-	-	12·48	13·70
$(NH_4)_2SO_4$	-	-	-	-	-	13·99	-	-	13·99	13·34
$(NH_4)_2SO_3$	-	-	-	-	-	10·45	-	14·27	10·45	-
$CH_3CO_2NH_4$	-	-	-	-	-	11·24	-	-	11·24	-
$(NH_4)_2S_2O_3$	(17·73)	(20·33)	-	-	-	(17·83)	(20·23)	(21·73)	(20·13)	(20·93)
	(11·87)	(12·76)	-	-	-	(14·47)	(14·87)	(14·47)	(13·57)	(13·48)
	-	-	-	-	-	16·07	-	12·63	-	-
$(NH_4)_2S_2O_8$	(19·27)	(20·37)	-	-	-	(19·37)	(22·27)	(21·77)	(20·17)	(21·01)
	(18·21)	(19·31)	-	-	-	(18·31)	(21·21)	(20·71)	(19·11)	(19·91)
	-	-	-	-	-	18·16	-	-	-	-
$(NH_4)_2CrO_4$	(-13·0)	(-14·1)	-	-	-	(-14·1)	(-16·0)	(-15·5)	(-14·4)	(-14·7)
	-	-	-	-	-	-	-	-	-	(-17·2)
$(NH_4)_2Cr_2O$	12·57)	(-14·67)	-	-	-	(-13·67)	(16·57)	(16·07)	(-13·9)	(-15·27)
	(-21·59)	(-22·69)	-	-	-	(-21·69)	(-24·59)	(24·09)	(-22·49)	(-23·29)

Cation in Compound	Brindley (26)	BRINDLEY. (7)				Kido (12)	Weiss, Hocart (27)	Weiss Pascal (27)	Mean of pre-ceding.	Trew (28)
		CN6.	CN8.	CN6,3	CN8,4					
$\underline{N_2H_5^+}$										
$N_2H_4.HCl$	20·53	-	-	-	-	22·43	21·43	21·43	21·50	21·13
$N_2H_4.H_2O$	-	-	-	-	-	(27·05)	-	-	-	
$\underline{NH_3OH^+}$										
$NH_2OH.HCl$	20·41	-	-	-	-	22·31	21·31	21·31	21·38	21·01
$2NH_2OH.H_2SO_4$	-	-	-	-	-	19·89	-	-	-	
$\underline{C_6H_5NHNH_3^+}$										
$C_6H_5NHNH_2.HCl$	70·86	-	-	-	-	72·76	71·76	71·76	71·83	71·46
$\underline{CH_3NH_3^+}$										
$CH_3NH_2.HCl$	22·59	-	-	-	-	24·49	23·49	23·49	23·56	23·19
$\underline{(CH_3)_2NH_2+}$										
$(CH_3)_2NH.HCl$	34·64	-	-	-	-	36·54	35·54	35·54	35·61	35·24
$\underline{(CH_3)_3NH.+}$										
$(CH_3)_3N.HCl$	46·26	-	-	-	-	48·16	47·16	47·16	47·23	46·86
$\underline{(CH_3)_4N+}$										
$(CH_3)_4NBr$	48·90	-	-	-	-	51·70	52·50	51·70	51·73	51·62
$(CH_3)_4NI$	45·25	-	-	-	-	47·75	51·45	51·15	48·99	50·35
$\underline{(C_2H_5)_2NH_2+}$										
$(C_2H_5)_2NH.HCl$	57·34	-	-	-	-	59·24	58·24	58·24	58·31	57·94
$\underline{(C_2H_5)_4N+}$										
$(C_2H_5)_4NCl$	97·80	-	-	-	-	99·70	98·70	97·80	98·76	98·40
$(C_2H_5)_4NBr$	93·45	-	-	-	-	96·25	97·05	96·25	96·55	96·35
$(C_2H_5)_4NI$	90·15	-	-	-	-	92·65	96·35	96·05	94·09	95·25

thiosulphate, together gave a mean figure of:-

$$-\chi_{NH_4^{\circ}} \,.\, 10^{6} = \underline{13{\cdot}41}$$

The agreement between the values for the ammonium ion obtained using the anionic correcting constants which were calculated either directly or indirectly (shown in Table 3), and the mean value for the ammonium ion in combination with the uni- or divalent anion, was improved in certain cases if Pascal's homopolar value for the susceptibility of the anion was corrected to give the heteropolar value.

For instance, Pascal's homopolar value for the sulphate ion (30) is $-33{\cdot}6 \times 10^{-6}$, whereas the heteropolar value is $-40{\cdot}1 \times 10^{-6}$, giving a difference $\Delta\chi = -6{\cdot}5 \times 10^{-6}$. Pascal's homopolar value for the sulphite ion is $-22{\cdot}3 \times 10^{-6}$, and so if $\Delta\chi$ was assumed to be the same as before, the corrected heteropolar value would be $-28{\cdot}8 \times 10^{-6}$, giving a value for the ammonium ion of $-14{\cdot}27 \times 10^{-6}$, which was in better agreement with the mean value of $-13{\cdot}41 \times 10^{-6}$ than was the figure $-10{\cdot}45 \times 10^{-6}$ which was calculated using Kido's anionic correcting constant.

The value of $\Delta\chi$ probably differed slightly for the two anions, since the sulphite ion was the smaller of the two, but $\Delta\chi$ would be less rather than more for the sulphite ion, so that the value of the susceptibility of the ammonium ion would agree less closely with the mean value, than did the assumed value.

The mean value for the ammonium ion given previously, was less in combination with divalent anions than with monovalent anions. This would be expected since the doubly charged anions would affect the cation to a greater extent than the singly charged anion, as regards the electron distribution of the atom, causing a decrease in atomic radius, and consequently of ionic susceptibility of the ammonium ion. The change in interatomic distance due to the double charge is not large, owing to the intrinsic repulsion between adjacent ions varying as a high inverse power of their separation. The divalent ions concerned are strongly repelled by each other owing to their double charge and the size of the molecule is not altered appreciably, so the decrease of susceptibility of the cation cannot be attributed to this cause.

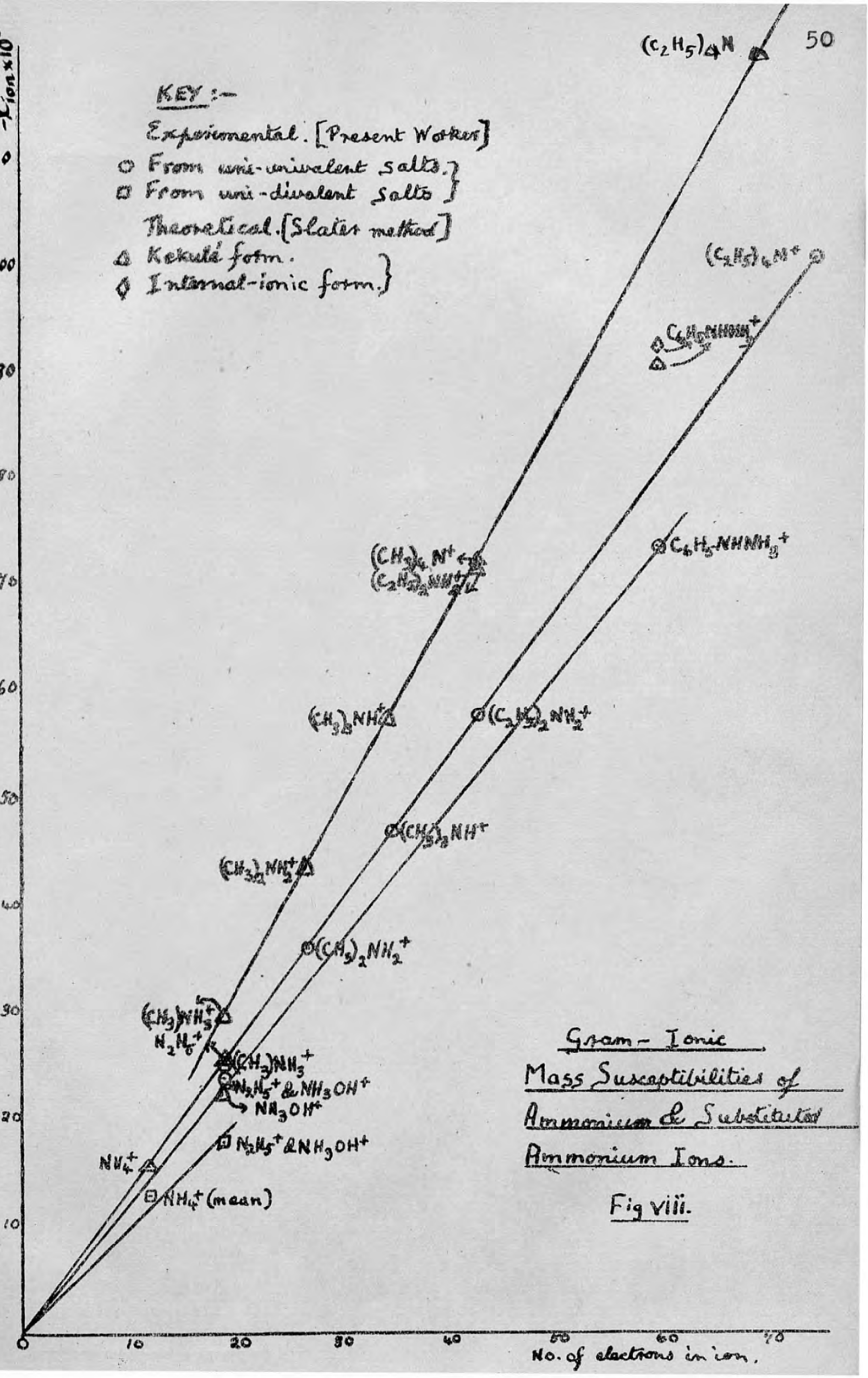
(b) The second method of obtaining the susceptibility of the ammonium and substituted ammonium ions, consisted in extrapolating the straight line curves obtained experimentally, to the appropriate ion containing a known number of electrons. This method has been employed by Kido (9) but he includes the anomalous halide curves, assuming them to be linear. (Trew (28)). In the present case it was not found possible to employ the linear portions of the halide curves.

In general it was found, as before, that the ionic susceptibility of the cation was less in divalent salts than in univalent salts, as would be expected. The resulting values are shown in Table 11, and Graph viii (p. 50) shows the curves obtained by plotting the ionic susceptibilities against the corresponding number of electrons in each ion. The ions lie on a series of linear curves; the ammonium hydrazine, and hydroxylamine ions lie on two lines, one for monovalent, and one for divalent salts, the latter having the lesser slope corresponding to smaller susceptibilities. Both pass through the origin.

The organic ions lie on a separate line of greater gradient which also passes through the origin. The theoretical values for the ions given in the table and the graph are considered under Method (c) and Section IV of the discussion.

(c) The third method of obtaining the susceptibility of the ammonium and substituted ammonium ions is a theoretical one, and is discussed under Section (I) of the theoretical discussion.

Finally, the value of the gram-ionic susceptibility of the ammonium ion obtained by the present worker was compared with those of other workers. Kido (9) gives a value of $-12{\cdot}4 \cdot 10^{-6}$, considering only uni-univalent salts. Brindley and Hoare (26) give a value of $-13{\cdot}5.10^{-6}$ for the solid crystalline state, and 16 for the dissolved state, although they state that the latter figure is somewhat approximate; it is much higher than the corresponding values obtained in the present work, as shown in Table 7. Their crystal value agrees closely with the



Gram - Ionic Mass Susceptibilities of Ammonium & Substituted Ammonium Ions.

Fig viii.

present value of $-13{\cdot}56.10^{-6}$ for the ammonium ion in its uni-univalent salts, whereas the corresponding value of Kido is much lower than the present value.

Considering the accuracy of Brindley and Hoare's measurements as compared with those of Kido (discussed by Trew (49)), it seems likely that the value of the gram-ionic susceptibility of the ammonium ion lies between $-13{\cdot}5$ and $-13{\cdot}6.\ 10^{-6}$, in uni-univalent salts; but the present writer found the value for the dissolved ion to vary according to the salt measured, if the correcting constants for dissolved anions, due to Brindley and Hoare (26), which were employed in the calculations, were assumed to be correct.

If however Trew's anionic correcting constants were applied to the values obtained by the present writer for the ammonium halides in the dissolved state, a mean value for the gram-ionic susceptibility of the ammonium ion in the dissolved state, was found to be $-15{\cdot}12 \times 10^{-6}$, as is shown in the table below:-

All values $\times 10^{-6}$	F^-	Cl^-	Br^-	I^-	Mean value
NH_4^+	$-14{\cdot}44$	$-15{\cdot}07$	$-15{\cdot}16$	$-15{\cdot}81$	$-15{\cdot}12$

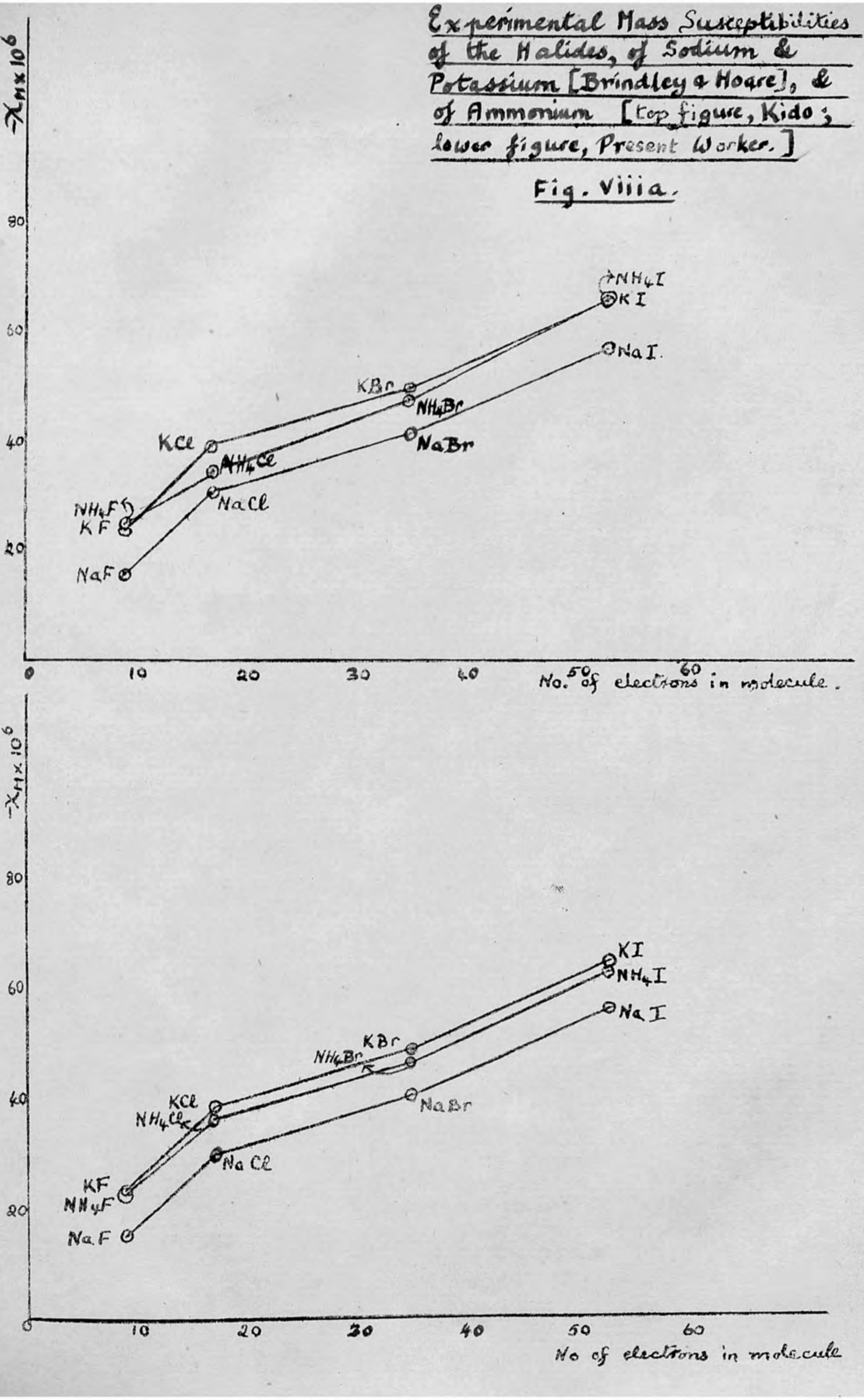
This value is nearer to Brindley's figure of -16×10^{-6} than the figure obtained by taking a mean of the values in column 6 of Table 7, omitting Kido's value; (i.e. $- 13{\cdot}06 \times 10^{-6}$).

(III) Relation of the Ammonium Halides to those of Sodium and Potassium.

It was suggested by Dr Trew that a graph should be plotted correcting the molecular susceptibilities of the halides of sodium, potassium and ammonium, with the number of electrons in the corresponding halagen ions. The result is shown in graph viiia, (page 53). For the sodium and potassium salts, the values of Brindley and Hoare (6) were employed, and for the ammonium salts the values obtained in the present work were employed. The halide curve for each positive ion had the same anomalous shape (the reason for which is discussed under the description of graph i in the case of the ammonium halides; similar reasoning would apply to the sodium and potassium salts). Moreover, the corresponding linear sections of each curve are practically parallel, except for the fluoride/chloride portions.

Trew (28) has shown that the results of Brindley and Hoare are remarkably consistent, and the above parallelism applies also to the halides of rubidium and caesium, so that the halide curve for ammonium would be expected to have the form which it was found to take, and not a linear form as Kido found (9). Hence the results of Brindley and Hoare served as a check on those of the present work. The anomalous values for the fluorides were probably due to the small radius of the fluoride ion, Experimental Mass Susceptibilities of the Halides, of Sodium & Potassium [Brindley & Hoare], & of Ammonium [top figure, Kido; lower figure, Present Worker.]

Fig. viiia.



which would cause the cations to be brought into specially close proximity, and their intrinsic repulsions would affect the interatomic distances in the molecules, so that the values differed from those calculated by adding the appropriate radii. A similar explanation was offered by Brindley and Hoare (6) to account for the discrepancies in the susceptibility values of lithium chloride and bromide, and sodium iodide.

In the present instance, if the calculated values for ammonium fluoride and iodide in 8-fold coordination (Table 5) were employed, so as to bring those two salts into line with ammonium chloride and bromide which were measured in the 8-coordinated solid crystalline state, the deviations from parallelism were found to be practically negligible.

TABLE 5

Decrease of Molecular Susceptibility with Increase of Coordination Number. $(-\chi_M \cdot 10^6)$

Substance	Salts in Solution. C.N 4.	Difference	NaCl type crystals C.N.6	Difference	CsCl type crystals. C.N.8.
NH_4F	23·00*(ZnO type) 24·50† 23·54	0.26 1·76 0·80	22°74	0·24	22·50
NH_4Cl	38·47	0·93	37·54	0°84	36·70*
NH_4Br	49·76	1·92	47·84	0·82	47·02*
NH_4I	66·41	2·47	63·94*	1·34	62·60

$*$ = Experimental Value for Salt

$\dagger$ = Kido (9)

C.N.= Coordination number.

(IV) Relation of Susceptibility to Coordination Number.

Brindley and Hoare have investigated the susceptibility of a number of substances, including the alkali metal and alkaline earth halides, both in solution and in the crystalline state. (8) They have deduced from their results the gram-ionic susceptibility of a number of ions in solution, and have also studied the variation of the susceptibility of chlorides, bromides, and iodides of caesium and rubidium. These salts, in common with all other uni-univalent salts, have a coordination number of 4 in solution, according to Bernal and Fowler (34); in the crystalline state they have a coordination number of 8, and their susceptibilities in 6-fold coordination can be calculated from the susceptibilities of the ions in the rock salt type of structure. Brindley and Hoare found a decrease in susceptibility with increase of coordination number.

This relationship was investigated in the present work in the case of the ammonium halides, and the results shown in Table 5 confirm the observations of Brindley and Hoare, and show that the inverse relationship is probably a general one. On page 57 is shown the method of calculation of the molecular susceptibility of the salts in n-fold coordination number, where n is different from the actual value exhibited in the crystal.

The coordination numbers of the actual salts were obtained from the figures quoted by Wyckoff (35), and in order to calculate the susceptibility of the salts in n-fold coordination,

Method of Calculation of Molecular Susceptibility of Salts having a coordination number different from that of the actual one.

$(-\chi \,.\, 10^6)$

Substance	C. N. of Salt Required	Suscep. of Anion of C.N. Required (Brindley)	Suscep. of Salt of C.N. Required containing NH_4^+	Suscep. of Anion of C.N. Required (Brindley)	Suscep. of NH_4^+ of required C.N.	Required value of Suscep. of Salt.
NH_4F	6	F^- 9·4	NH_4I 63·94	I^- 50·6	13·34	22·74
NH_4F	8	F^- 8·7a	NH_4Cl 36·70	Cl^- 22·9	13·80	22·50
NH_4Cl	6	Cl^- 24°2	NH_4I 63°94	I^- 50·6	13·34	37·54
NH_4Br	6	Br^- 34·5	NH_4I 63·94	I^- 50·6	13·34	47·84
NH_4I	8	I^- 48·8	NH_4Cl 36·70	Cl^- 22.9	13·80	62·60

a. $-\chi_M \times 10^6$ of NaF = 15·6 (Hoare) (5)

$-\chi_{Na_{\text{Brindley}}} \times 10^6$ = 6·9 (mean value used since value for C.N. 8 unknown)

Suscep. = susceptibility.

59
graph

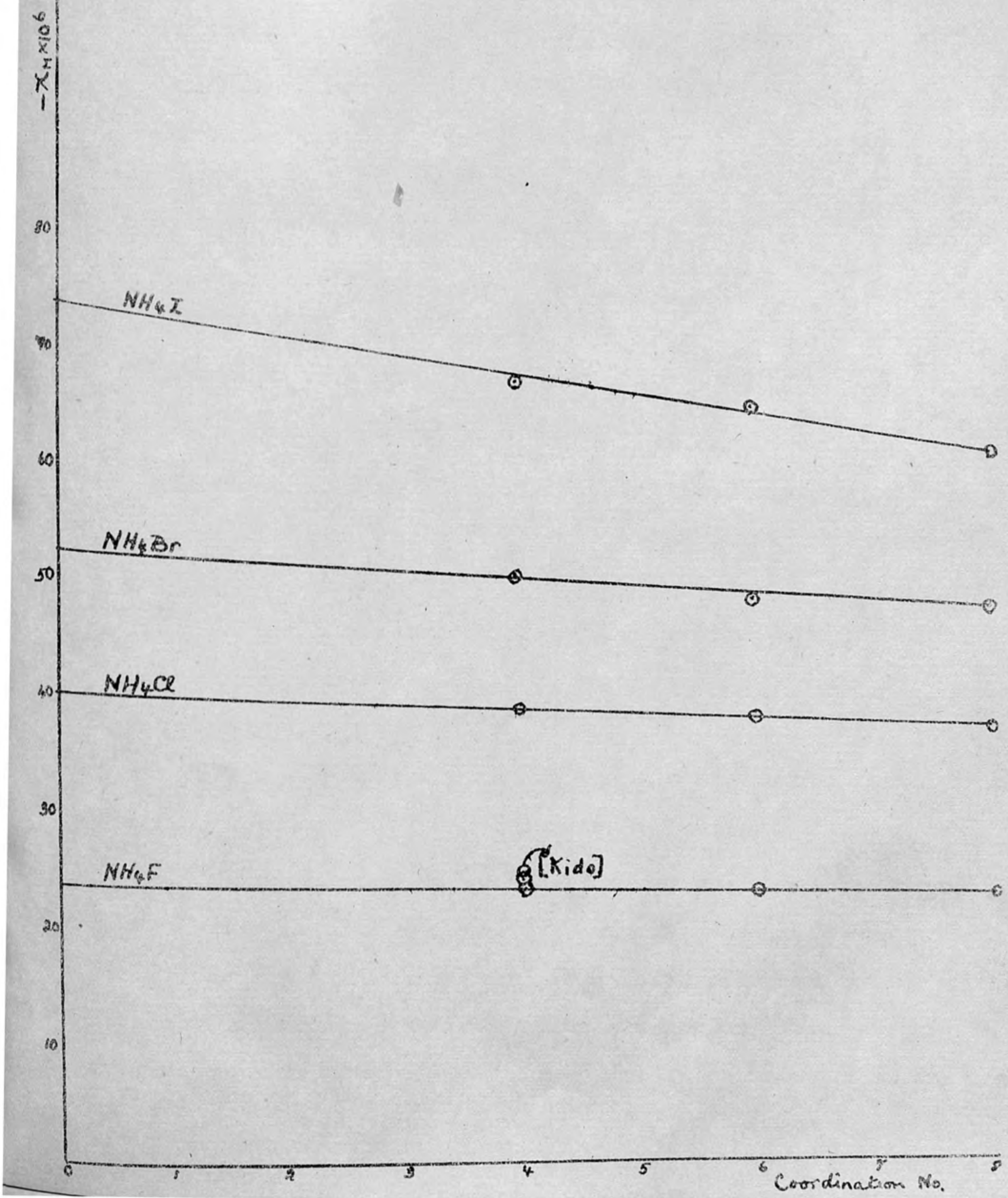
the susceptibility of the halide anion of coordination number n was obtained from the list given by Brindley and Hoare (7). The susceptibility of ammonium for coordination number n was obtained from that of a halide salt of coordination number n by subtracting the susceptibility of the halide anion of coordination number n, given in the aforementioned list. The sum of the susceptibilities of ammonium and halide ion gave the required susceptibility (column 7).

The figures in the Difference columns in Table 5 increase in passing down the series of halides, corresponding to a similar increase in the case of the halogen ions. (Table 7). If, however, the results were plotted on a graph connecting coordination number and molecular susceptibility, (Graph ix, p. 59), they were seen to fall approximately on four straight lines, each of which represented a different halide of ammonium. On extrapolating each line to the ordinate which corresponded to C.N. = 0, the value of the molecular susceptibility of each halide in 0-fold coordination was obtained. This represented the condition of free ions, which was the condition for which the theoretical values of molecular susceptibility were calculated.

Table 6 shows the value of susceptibility for the condition of free ions, obtained graphically and by the theoretical method of Slater described on p.73 (both ionic and non-ionic values being given.) The graphical values for the fluoride and iodide

Susceptibility & Coordination Number of the Ammonium Halides.

Fig. IX



lay between the theoretical ionic and non-ionic values, whereas the graphical values for the bromide and chloride lay slightly below either of the theoretical values. However the agreement was thought to be sufficiently close in all cases to justify the assumption of linear forms for the curves.

TABLE 6

Molecular Susceptibility of the Ammonium Halides for the Condition of Free Ions. $(-\chi_M \times 10^6)$

Substance.	Suscep. from Extrapolation of χ /C.N. curve.	Theoretical Suscep. by Slater Method.	
		Ionic Value.	Non-Ionic Value.
NH_4F	23·60	23·34	24·82
NH_4Cl	40·00	40·46	40·64
NH_4Br	52·40	54·49	53·67
NH_4I	73·60	73·81	70·25

The linear forms of the curves could all be represented by an equation of the type:-

$$y = mx + c$$

where y = Molecular Susceptibility of the ammonium halide; x = Coordination Number; m = tangent to the slope of the line; c = intercept of the line on the x axis. The quantity m, which was negative, increase on passing up the series from fluoride to iodide, and represented the rate at which the susceptibility of each compound increased with decreasing coordination number.

The increase in m in passing up the series of halides corresponded to the increase in the Difference columns in Table 5 mentioned previously. Brindley and Hoare (8) have attributed this difference Δ_χ (between the molecular susceptibility of a substance in aqueous solution, and in the crystalline state, regardless of coordination number) to the tighter binding of the ions in a solid crystal than in solution where water molecules are the binding agents. This, together with the larger number of ions surrounding any ion in a solid crystal than in solution, i.e. the larger coordination number of the compound in a solid crystal than in solution, will give a positive value for Δ_χ. (as was found in the present instance) since the susceptibility of the free ions will be diminished more in the solid crystalline state than in solution.

The same reasoning would apply to a substance which existed (actually or hypothetically) as crystals of different coordination number; the susceptibility would be greater for crystals of smallest coordination number; i.e. Δ_χ would again be positive, as was found in the present instance.

Brindley and Hoare state that the above is true only in the case of large ions (of which the halogens and ammonium are examples). The effect of the solute ions <u>on</u> the surrounding water molecules is a minimum for solutions of large ions, whereas it is well marked if the solute ions are small (e.g. H^+)

and perhaps doubly charged (e.g. Br^{++}), and determines the nature of $\Delta\chi$; the crystal and solution forces referred to previously are neglibly small, since the actual susceptibilities are small.

Since for large ions such as those considered by the present worker, the value of $\Delta\chi$ was dependent solely on solution and crystal forces, a linear relationship between susceptibility and coordination number might be expected. No deviations were found which might be accounted for by the relative weakness of solution forces compared with crystal forces.

Table 7, column 3, gives the mass susceptibility of the ammonium ion in halide salts of different coordination numbers, using Brindley's correcting constants for the halogen ions with corresponding coordination numbers.

TABLE 7

Experimental Gram-Ionic Mass Susceptibility of the Ammonium Ion in Solution (C.N.4) and in Crystals of Various Coordination Numbers. $(-\chi_{ion}\cdot 10^6)$

Salt	Suscep. of Anion in Salt.[i]	Suscep. of NH+ in Salt.	C.N. of Salt	Suscep. of Anion in Solution[ii]	Suscep. of NH_4^+ in Solution.	C.N. of Solution.
NH_4F	9·1[iv]	13·90	4	10·3	14·20[iii] 13·24	4
NH_4Cl	22·9	13·80	8	25·1	13·37	4
NH_4Br	33·4	13·62	8	36·4	13·36	4
NH_4I	50·6	13·34	6	54·2	12·21	4

i. Brindley and Hoare (7)
ii. " " (8)
iii. Kido (9)
iv. Trew (28)

The value for the fluorine ion in salts having a coordination number 4, is given by Brindley only for combination with a divalent (alkaline-earth) cation, and consequently the Trew value for the ion was used in the calculation. The values for the ammonium ion given in column 3 have thus been corrected for the coordination effects (except in the case of ammonium fluoride) and the values are seen to be in fairly good agreement.

Column 6 gives corresponding values for the susceptibility of the ammonium ion in solutions of halide salts, in all of which it has a coordination number 4. (Bernal and Fowler (34)). These figures, like those in column 3 decrease from fluoride to iodide, the present value for the fluoride being excepted, and for each compound the solution value for the ammonium ion is less than the solid crystal value, which would not be expected from comparison with the results for Brindley for ions of different coordination numbers.

The value for ammonium obtained from that of the iodide in solution was approximately a whole unit lower than the other values in the same column, which are seen to be in good agreement.

Ranganadham and Qureshi (36) have recently measured the magnetic mass susceptibilities of solutions of sodium and potassium nitrates for different concentrations, covering a wide range, and the results, plotted graphically, give susceptibility/concentration curves showing systematic deviations from the linear form. Their results for the two salts in the dissolved state are as follows:-

$$NaNO_3 \quad -\chi_M \cdot 10^6 = 23{\cdot}86$$
$$KNO_3 \quad -\chi_M \cdot 10^6 = 31{\cdot}62$$

By taking the Trew experimental correcting constants for the sodium and potassium ions, instead of the theoretical values which they employed, the two values for the gram-ionic susceptibility of the nitrate ion are found to be $-17{\cdot}06.10^{-6}$, and $-17{\cdot}02.10^{-6}$ respectively from sodium and potassium nitrates. This value is lower than the Trew value of $-18.9\ 10^{-6}$ for the nitrate ion in the solid state, as would not be expected, since the deforming forces in solution tend to be weaker than in the crystalline state.

In the course of the present work the susceptibility of ammonium nitrate was measured both in the solid state and in solution. Using a mean value for the ammonium ion in solution (Table 7) of $-15{\cdot}12\ .10^{-6}$, the gram-ionic susceptibility of the nitrate ion in solution was found to be $-19{\cdot}74.10^{-6}$.

Using the value for ammonium in uni-univalent solid crystalline salts, $-13{\cdot}56 \times 10^{-6}$, the gram-ionic susceptibility of the nitrate ion in the solid crystalline state was found to be $-19{\cdot}02 \times 10^{-6}$, which was smaller than the solution value, as was to be expected from theoretical considerations.

The concentration of the solution measured was one for which no deviations from linearity occurred in the Ranganadham curves for the sodium and potassium salts.

TABLE 8

Gram-Ionic Susceptibility of some Fatty Acid Anions and the Sulphate Ion. $(-\chi_{ion}\cdot 10^6)$

Source of χ_{anion}		Suscep. of $HCOO^-$	Suscep. of CH_3COO^-	Suscep. of $C_2H_5COO^-$	Suscep. of SO_4^{--}
Exptl.	Na salt	20·30	$32{\cdot}8^{i}$	42·45	38·75
	K salt	18·02	$30{\cdot}1^{i}$	41·60	40·45
	NH_4 salt	18·23	29·68	41·02	40·15
Theoret. Slater method.	Kekulé form	27·52	41·80	55·88	-
a) Ionic	Intern. Ionic	27·11	41·29	55·35	-
b) Non-ionic.	From NH_4 salt.				
	Kekulé form	29·98	43·42	57·49	-
	Intern. Ionic	27·40	41·53	55·62	-

(V) Molecular Susceptibilities of the Sodium, Potassium, and Ammonium Salts, of the lower Fatty Acids and Sulphuric Acid. Gram-ionic Susceptibility of the Sulphate Ion.

In Table 8 is given a list of the values of gram-ionic susceptibility of the ions:- formate, acetate, propionate, and sulphate, obtained experimentally from measurements on the sodium, potassium and ammonium salts, (after allowing for water of crystallisation, the molecular susceptibility of which was subtracted from that of the salt, assuming the validity of the additivity law). The Trew value for the cation in each salt was subtracted from the experimental salt value, assuming the additivity law, and the resultant values for each anion in different salts, were compared.

The values marked i are those due to Kido (9). The values for the anions (except SO_4--) in the non-ionic salt forms, could only be calculated theoretically in the case of the ammonium salts owing to lack of available data. The values for the anions were deduced by subtracting the theoretical value for ammonium (Slater method, page 73) from the theoretical salt values. The theoretical values for the sulphate ion could not be calculated owing to lack of available data.

It will be seen from Table 8 that the values for the fatty acid anions obtained from the experimental results agree fairly closely. From the results, mean values were calculated to be:-

$$-\chi_{HCOO^-} \cdot 10^6 = 18{\cdot}95$$

$$-\chi_{CH_3COO^-} \cdot 10^6 = 30{\cdot}96$$

$$-\chi_{C_2H_5COO^-} \cdot 10^6 = 41{\cdot}69$$

The theoretical values were considerably higher (but see(5) Section II on bond depressions).

The values of molecular susceptibility of the sulphates of ammonium, sodium, rubidium and caesium [obtained in the present work and shown in Table 1a], and Pascal's value for potassium sulphate ($-70{\cdot}25.10^{-6}$), were employed to calculate the gram-ionic susceptibility of the sulphate ion, using the anionic correcting constants of Trew (except ammonium, for which the present value from uni-divalent salts was used) and assuming the validity of the additivity law. The results are shown below:-

All values $.10^{-6}$	NH_4+	Na+	K+	Rb+	Cs+	Mean Value.
SO_4--	-40•15	-38•75	-40•45	-39•80	-40•33	-39•90

The mean value was close to the tentative value of Trew [$-40{\cdot}3 \,.\, 10^{-6}$]

TABLE 9

Gram-ionic Susceptibilities of some Anions in Salts of Ammonium with Inorganic Acids. $(-\chi_{\text{ion}} \cdot 10^6)$

Mono-valent Anion.	Susceptibility.	Di-valent Anion.	Susceptibility
F^-	9·44	SO_3^{--}	48·33
Cl^-	20·14	SO_4^{--}	40·15
Br^-	33·46	$S_2O_3^{--}$	30·53
I^-	50·38	$S_2O_8^{--}$	85·00
NO_3^-	20·11	CrO_4^{--}	-27·82
VO_3^-	-21·63	$Cr_2O_7^{--}$	-64·64

(VI) Gram-ionic Susceptibilities of some Anions in Salts of Ammonium with Inorganic Acids.

Table 9 gives the values of gram-ionic susceptibility of some inorganic anions which were found by subtracting the mean experimental value for ammonium obtained in the present work (Section II of the disuussion of results) from the experimental values of molecular susceptibility of the ammonium salts obtained in the present work. This method assumed the validity of the additivity law in the cases considered.

In the case of mono- and di-valent salts, respectively, the corresponding mean value for ammonium was employed. The experimental susceptibility of the vanadate and dichromate ions had not been measured previously.

(5) THEORETICAL DISCUSSION

(1) Theoretical Determination of Susceptibility.

There are three chief methods available for calculating the susceptibility of a monatomic ion on a theoretical basis, and they all involve formulae connecting the diamagnetic susceptibility with the charge distribution of a symmetrical atom or ion. The expression derived for the atomic diamagnetic susceptibility of a symmetrical atom or ion on the basis of the Larmour Theorem is due to Langevin (37):-

$$\chi_A = \frac{-e^2}{6mc^2} \sum_N \overline{r}^2 \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

the summation being extended over all the circumnuclear electrons. This formula holds on the quantum mechanical view, except that the value of $\overline{r}^2$ is different. Van Vleck (38) and Pauling (39) have independently calculated the value of $\overline{r}^2$ to be:-

$$\overline{r}^2 = a_o^2 \; \frac{n^2}{(Z)^2} \left[\frac{5n^2}{2} - \frac{3l(l + 1) - 1}{2} \right] \ldots\ldots \quad (2)$$

where Z = effective nuclear charge; a_o = radius of one quantum orbit of hydrogen $0{\cdot}528.10^{-8}$ cm.; n and l are the total and serial quantum numbers. If we substitute in equation (1) the value of $\overline{r}^2$ in equation (2) and give the physical constants the appropriate numerical values, the value of the diamagnetic susceptibility of a single electron is given by:-

$$\chi = -0{\cdot}790 \;.\; 10^6 \frac{n^2}{(\overline{Z})^2}\left[\frac{5n^2}{2} - \frac{31(1+I) - I}{2}\right] \ldots\ldots\ (3)$$

The result was obtained for a hydrogen-like atom having a single electron, but the result may be extended to atoms in general by substituting $(Z-S)^2$ for Z^2, and introducing suitable screening constants S for each n,l group of electrons. S was estimated by Pauling for different electron groups, and he calculated a number of susceptibilities for ions and atoms. Except for the rare gases his values are much higher than the experimental ones.

Gray and Farquharson (15) have obtained screening constants for various ions by interpolation from those of Pauling, and have calculated the susceptibility of ions differing in stages of two electrons from those of Pauling.

Stoner (40) has applied Hartree's determination of space-charge distribution (41) in a symmetrical atom or ion by a self-consistent field method. The radial charge density in electron units per unit radial distance = dZ/dr. The total number of electrons in an atom or ion = total charge = $\int_0^\infty (dZ/dr)dr$

$$\overline{r}^2 = \int_0^\infty r^2(dZ/dr)dr \Big/ \int_0^\infty \frac{r^2(dZ/dr)dr}{(dZ/dr)dr}$$

and hence, substituting for $\overline{r}^2$ and the numerical values of the physical constants in equation (I), the value of ths susceptibility of the atom or ion is obtained:-

$$\chi = -0{\cdot}790 \;.\; 10^6 \int_0^\infty r^2(dZ/dr)dr.$$

As in the Pauling method the theoretical values are muchhigher than the experimental ones, although this method is the most accurate of the three. However Slater's method of approximate wave function (42) has more simple application (the Hartree distributions in application suffer from the inevitable disadvantages of numerical solutions) and the susceptibilities calculated by Brindley using this method (26) give the most consistent agreement with observed values, especially for atoms and ions of large radius.

Slater employed the fact, shown by Zener (43) that the θ and ϕ parts of the wave equation can in certain cases be neglected, the significant part being the radial part of the wave function, which for a single electron is:-

$$\psi = r^{n^{+}-I} e^{-(Z-S/n^{*}r)}$$

where r is expressed in atomic units a_0, n^{*} = effective quantum number; (Z-S) = effective nuclear charge. The value of $\overline{r}^2$ obtained by integrating the wave function is given by:-

$$\overline{r}^2 = \frac{(n^{*})^2 \; (n^{*} + \tfrac{1}{2}) \; (n^{*} + I)}{(Z-S)^2}$$

and hence the diamagnetic susceptibility of each electron in a group is given by:-

$$\chi = -0{\cdot}790 \, . \, 10^{-6} \, \frac{(n^{*})^2 (n^{*} + \tfrac{1}{2})(n^{*} + I)}{(Z-S)^2}$$

Slater gives rules for the evaluation of n^{*} and S for any electron group, and he divides the electrons into groups as follows:-

Is; 2s, p; 3s,p; 3d; 4s,p;4d; 4f; 5s,p; etc.

Angus has modified the method by considering s and p sub-groups separately, which gives slightly lower values for susceptibility than those calculated by the Slater method(44).

The values of N^{+2}, N^{o}, H^{-I}, H^{o}, C^{+I}, C^{-I}, O^{+I}, O^{-I}, F^{o}, Cl^{o}, Br^{o}, I^{o}, were calculated in the present work both by the Slater and modified Slater methods, and $Na+^{I}$, and K^{+I}, by the modified Slater method. The theoretical values of ionic susceptibility are collected in Table 10, where the values of the present work are shown in brackets. All Slater and modified Slater values have been corrected by 0·790/0·807, in accordance with the new value of a_o given previously. The values shown in brackets under the Pauling method were obtained in the present work by interpolation from known values, as shown in Graph X (page 75).

Theoretical Ionic Diamagnetisms
(Gray & Farquharson's Calculation by Pauling Method)

Fig. X

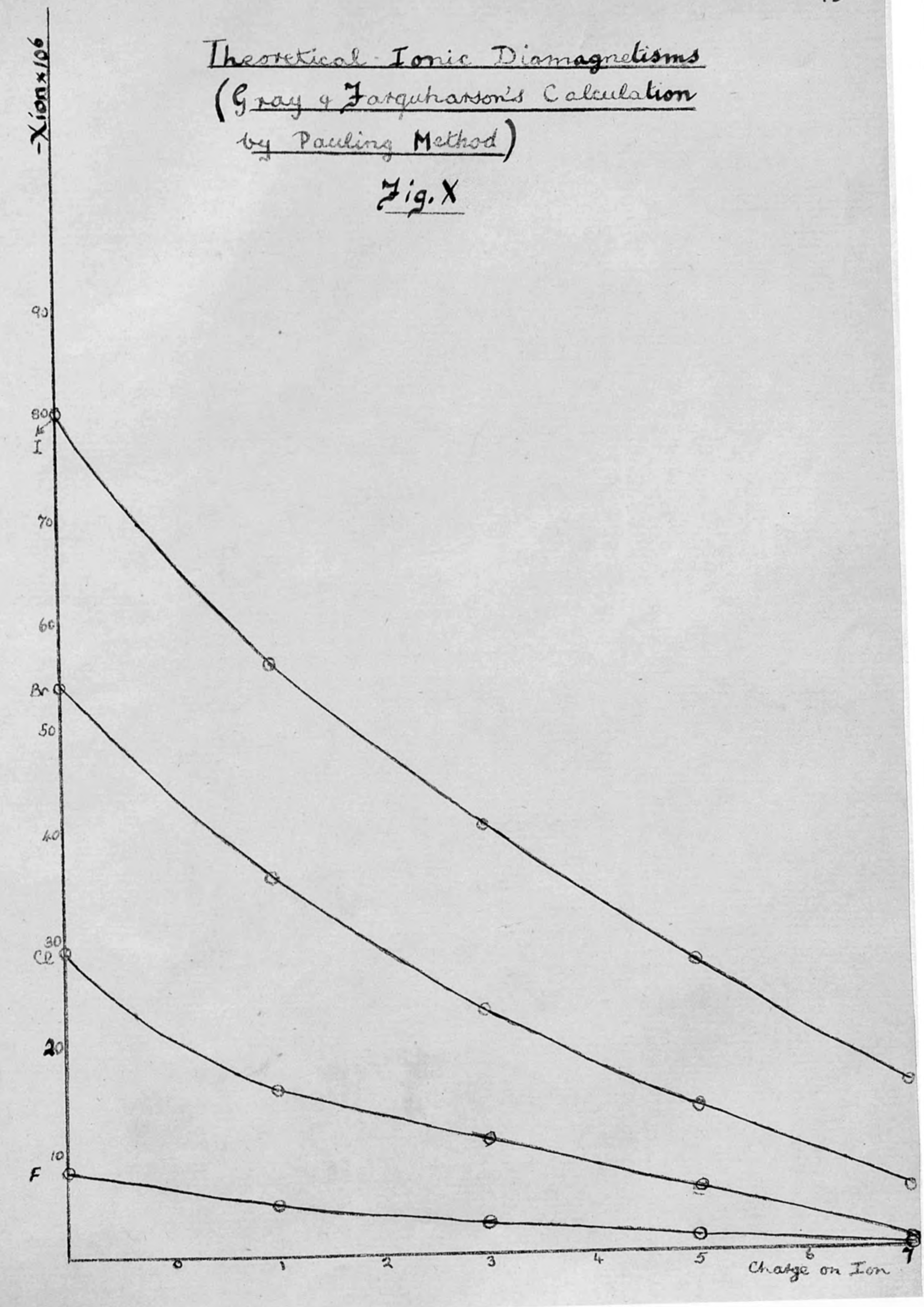


TABLE 10

Theoretical Values of Gram-Ionic Mass Susceptibility.

$(-\chi_{ion}\cdot 10^{6})$

Ion.	Suscep. Gray & Cruikshank. Pauling method.	Suscep. Angus, Slater method.	Suscep. Angus, modified Slater method.	Ion.	Suscep. Gray & Cruikshank. Pauling method.	Suscep. Angus, Slater method.	Suscep. Angus, modified Slater method.
H^{+1}	0	0	0				
H^{0}	2·273	(2·370)	(2·370)	N^{-1}	11·45	11·39	9·56
H^{-1}	7·954	(9·680)	(9·680)	N^{-2}	15·76	–	–
				N^{-3}	21·89	23·44	19·54
C^{+4}	0·15	0·15	0·15	O^{+6}	0·08	0·08	0·08
C^{+3}	1·90	–	–	O^{+5}	0·86	–	–
C^{+2}	4·23	3·14	3·14	O^{+4}	1·90	1·41	1·41
C^{+1}	6·64	(5·53)	(5·02)	O^{+3}	2·74	–	–
C^{0}	9·96	9·12	7·67	O^{+2}	3·91	3·52	3·10
C^{-1}	14·69	(14·23)	(11·63)	O^{+1}	5·32	(5·01)	(4·48)
C^{-2}	21·56	22·02	17·76	O^{0}	7·09	6·96	6·02
C^{-3}	32·00	–	–	O^{-1}	9·40	(9·40)	(8·14)
C^{-4}	48·78	55·46	44·69	O^{-2}	12·66	12·87	11·01
N^{+5}	0·11	0·11	0·11	S^{+6}	1·4	1·38	1·28
N^{+4}	0·21	–	–	S^{+4}	–	5·62	5·52
N^{+3}	2·72	2·08	2·08	S^{+2}	–	11·87	10·76
N^{+2}	4·12	(3·46)	(3·18)	S^{0}	–	21·49	18·91
N^{+1}	5·91	5·36	4·67	S^{-2}	–	36·62	31·94
N^{0}	8·28	(7·93)	(6·73)				
F^{+7}	0·063	0·059	0·059	I^{+3}	40·53	30·49	29·30
F^{+5}	1·52	1·05	1·05	I^{+1}	57·27	42·20	39·70
F^{+3}	2·95	2·49	2·26	I^{0}	(66·30)	(49·05)	(46.35)
F^{+1}	4·98	4·67	4·12	I^{-1}	80·00	58·60	54·20
F^{0}	(6·50)	(6·20)	(5·42)	Na^{+1}	4·2[i]	4·1[ii]	(3·6)
F^{-1}	8·10	8·13	7·10	K^{+1}	16·7[i]	14·10[ii]	(12·8)
Cl^{+7}	1·20	1·16	1·10				
Cl^{+5}	5·71	4·39	4·32				
Cl^{+3}	10·92	8·96	8·21				
Cl^{+1}	18·19	15·57	13·89				
Cl^{0}	(20·06)	(19·88)	(17·69)				
Cl^{-1}	29·0	25·25	22·38				
Br^{+7}	6·00	6·80	6·73				
Br^{+5}	13·74	11·67	11·59				
Br^{+3}	23·09	18·18	17·30				
Br^{+1}	35·81	27·00	25·80				
Br^{0}	(44·05)	(32·66)	(30·10)				
Br^{-1}	(54·00)	39·28	35·09				
I^{+7}	17·00	15·30	15·19				
I^{+5}	27·68	21·81	21·70				

In order to calculate the ionic susceptibility of a polyatomic ion or molecule, it is not sufficient to take the sum of the values for the component ions given in Table 10. Knowledge of the magnitude of the dipole moment of an individual link, (Sidgwick (25)), enables us to calculate the distribution in the molecule of the residual charges due to the unequal sharing of the linked electrons.

$\triangle e$ = moment/d (d = distance between the nuclei
$\triangle e$ = residual charge)

$$\therefore \frac{\triangle e}{e} = F$$

expressed in terms of the charge e on one electron ($4{\cdot}77 \ . \ 10^{10}$) Sidgwick gives the values of F for a number of links, and by using them together with the data for the whole number charges in Table 10, the susceptibility of a polyatomic ion or molecule can be calculated. The results calculated for the present work for anions, cations, and molecules are given in Tables 12, 11, and 13 and 14. In the two latter the ionic values are those representing the sum of values for the component ions given in Tables 12 and 11. The Non-Ionic values are those calculated for the molecules, assuming covalent and coordinate linkages throughout. The Ionic values assume that the law of additivity was valid in the cases concerned.

Gray and Cruikshank (45) have observed that the assumption of fractional charges is fully in agreement with the statistical view of sub-molecular structure, and that the

TABLE 11

Gram-Ionic Mass Susceptibilities of Ammonium and Substituted Ammonium Ions obtained Graphically and Theoretically.

$(-\chi_{ion} \cdot 10^6)$

Cation	Susceptibility extrapolated from exptl. Graph.			THEORETICAL SUSCEPTIBILITIES.		
				Pauling method.	Slater method.	Mod.Slater method.
NH_4^+	12·7 (Graph ii,p.30) 12·3 (Graph vii, p.35)			15·53	15·21	13·91
$N_2H_5^+$	23·5 (Chloride) (Graph iii,p. 31) 17·3 (Sulphate) (Graph iii, p. 31)			26·52	24·95	23·25
NH_3OH^+	23·5 (Chloride) (Graph iii, p. 31) 17·3 (Sulphate) (Graph iii, p. 31)			22·47	22·02	19·83
$C_6H_5NHNH_3^+$	73·3 (Graph iii, p. 31)			96·00[i] 98·01[ii]	90·36[i] 92·23[ii]	79·46[i] 80·80[ii]
NH_4^+ Organic Salts.	— (Graph vi, p. 34)			15·53	15·21	13·91
	(Graph v, p. 33)					
	Cl	Br	I			
$CH_3NH_3^+$	24·7	-	-	30·96	29·05	26·37
$(CH_3)_2NH_2^+$	35·5	-	-	45·10	43·03	38·94
$(CH_3)_3NH^+$	46·5	-	-	59·94	57·01	51·52
$(CH_3)_4N^+$	-	38·8	27·1	75·62	71·78	64·77
$(C_2H_5)_2NH_2^+$	57·4	-	-	74·89	71·04	64·02
$(C_2H_5)_4N^+$	100·05	82·3	71·6	141·11	127·30	114·25

i. Kekulé form.
ii. Internal-ionic form.

TABLE 12

Gram-Ionic Mass Susceptibilities of some Anions

(Theoretical) $-\chi_{\text{ion}} \cdot 10^6$.

Anion.	Resonance Structure.	THEORETICAL SUSCEPTIBILITIES		
		Pauling method.	Slater method.	Mod. Slater method.
OH^-	-	12·05	12·17	10·67
$HCOO^-$	Double-bonded	28·44	27·52	24·02
	Internal-ionic	28·03	27·11	23·86
CH_3COO^-	Double-bonded	43·52	41·80	36·71
	Internal-ionic	43·05	41·29	36·49
$C_2H_5COO^-$	Double-bonded	58·32	55·88	49·25
	Internal-ionic	57·96	55·35	49·21
$(COO)^{--}$	Double-bonded	52·03	50·20	43·27
	Internal-ionic	45·46	43·46	37·90
NO_3^-	Form i	32·21	31·75	27·40
	" ii	32·74	32·39	28·00

TABLE 13

Theoretical Values of Molecular Mass Susceptibility of the Ammonium and Substituted Ammonium Compounds which exist in Resonating Forms.

$(-\chi_M \cdot 10^6)$

Compound	Resonance Structure.	Ionic Form.			Non-ionic Form.		
		Pauling method.	Slater method.	Mod. Slater method.	Pauling method.	Slater method.	Mod. Slater method.
$(COONH_4)_2$	Double-bonded	83·09	80·62	71·09	85·50		
	Internal-ionic	76·52	73·88	65·72	81·94	80·43	72·40
$HCOONH_4$	Double-bonded	43·97	42·73	37·93	45·88	45·19	39·98
	Internal-ionic	43·56	42·32	37·77	43·30	42·61	38·46
CH_3COONH_4	Double-bonded	59·05	57·01	50·62	60·11	58·63	52·57
	Internal-ionic	58·58	56·50	50·40	58·30	56·74	51·14
$C_2H_5COONH_4$	Double-bonded	73·85	71·09	63·16	75·00	72·70	65·11
	Internal-ionic	73·49	70·56	63·12	73·23	70·83	63·88
$HCOONa$	Double-bonded	32·64	31·62	27·62	-	-	-
	Internal-ionic	32·23	31·21	27·46	-	-	-
CH_3COONa	Double-bonded	47·72	45·90	40·31	-	-	-
	Internal-ionic	47·25	45·39	43·09	-	-	-
C_2H_5COONa	Double-bonded	62·52	60·08	52·75	-	-	-
	Internal-ionic	62·16	59·45	52·81	-	-	-
$HCOOK$	Double-bonded	45·14	41·62	36·82	-	-	-
	Internal-ionic	44·73	41·21	36·66	-	-	-
CH_3COOK	Double-bonded	60·22	55·90	49·51	-	-	-
	Internal-ionic	59·75	55·39	49·29	-	-	-
C_2H_5COOK	Double-bonded	75·02	69·98	62·05	-	-	-
	Internal-ionic	74·66	69·45	62·01	-	-	-
$C_6H_5NHNH_2 \cdot HCl$	Kekulé	125·00	115·61	101·84	121·76	115·78	102·58
	Internal-ionic	127·01	117·48	103·18	121·83	113·99	100·65
$C_6H_5NH_2$	Kekulé	-	-	-	85·57	80·40	70·45
	Internal-ionic	-	-	-	84·78	79·71	69·20
$C_6H_5NH(CH_3)$	Kekulé	-	-	-	100·20	94·19	82·87
	Internal-ionic	-	-	-	99·64	93·69	81·95
$C_6H_5N(CH_3)_2$	Kekulé	-	-	-	114·98	107·95	95·29
	Internal-ionic	-	-	-	114·44	107·67	94·63
$C_6H_5HN(C_2H_5)$	Kekulé	-	-	-	115·06	109·17	96·16
	Internal-ionic	-	-	-	114·71	107·95	94·79
$C_6H_5N(C_2H_5)_2$	Kekulé	-	-	-	144·81	136·10	120·30
	Internal-ionic	-	-	-	144·20	135·81	119·86
$C_6H_4 \cdot CH_3 \cdot NH_2$	Kekulé	-	-	-	100·51	94·50	83·10
	Internal-ionic	-	-	-	-	-	-

TABLE 14.

Theoretical Values of Molecular Mass Susceptibility of the Ammonium and Substituted Ammonium Compounds. $(-\chi_M \cdot 10^6)$

Compound.	Ionic Form			Non-ionic Form.		
	Pauling method.	Slater method.	Mod. Slater method.	Pauling method.	Slater method.	Mod. Slater method.
NH_4F	23·81	23·34	21·01	24·84	24·82	23·63
NH_4Cl	44·53	40·46	36·29	40·81	40·64	37·04
NH_4Br	69·53	54·49	49·00	64·68	53·67	50·63
NH_4I	96·53	73·81	68·11	86·80	70·25	66·17
NH_4OH	27·58	27·38	24·58	28·61	28·44	24·42
$N_2H_4.HCl$	56·07	50·20	45·63	51·80	51·37	46·40
$N_2H_4.H_2O$	38·57	37·12	33·92	39·60	38·72	35·83
$NH_2OH.HCl$	52·02	47·27	42·21	47·75	47·63	42·95
$NH_2CH_3.HCl$	60·51	54·30	48·75	55·55	54·48	49·49
$NH(CH_3)_2.HCl$	74·65	68·28	61·32	70·38	68·46	62·07
$N(CH_3)_3.HCl$	89·49	82·26	73·90	85·23	82·43	74·64
$NH(C_2H_5)_2.HCl$	104·44	96·29	86·40	100·26	97·62	87·14
$N(CH_3)_4Br$	129·62	110·96	99·86	-	-	-
$N(CH_3)_4 1$	156·62	130·28	118·97	-	-	-
$N(C_2H_5)_4Cl$	170·66	152·55	136·63	-	-	-
$N(C_2H_5)_4Br$	195·11	166·58	149·34	-	-	-
$N(C_2H_5)_4 1$	222·11	185·90	168·45	-	-	-

significance is that the atom has two whole-numbered charges for certain proportions of the time, i.e. there is a series of resonant systems.

In addition to these resonant systems, many substances exist in two or more definite resonant forms possessing different structures. The proportions of time occupied by each form can be estimated by comparing the experimental molecular susceptibility of the compound with the theoretical value calculated by the above method, after correcting the latter for bond depression values (i.e. the amount by which the experimental susceptibility for each bond is less than the theoretical quantity). Gray and Cruikshank (45) have determined a number of bond depressions, and used their results to determine the resonant forms of benzene, naphthalene, acid carboxyl group, the ortho-alkyl ureas, water, alcohol, and hydrogen peroxide.

The method has also been applied by Clow and Thompson (46) in connexion with the resonance of urea and its derivatives, and also (47) in connexion with the resonance of organic sulphur compounds.

Tables 12 and 13 give the theoretical values for some anions and compounds, respectively, calculated from the available data for various resonant structures. Pauling (48) discusses these structures in detail, and those for the nitrate ion are given in (5) Section II, together with those for the acid carboyxl ion, substituted anilines and naphthylamine.

TABLE 15

Application of Bond Depressions to the Resonant Forms of the Lower Fatty Acid Salts of Ammonium, and the Corresponding Anions. (Molecular Susceptibility $-\chi_M \cdot 10^6$)

Substance	Form	Expt. Mol. Stand		% time cpd. exists in each form of different Suscep.		Mean Theor. Mol. dia.	Exptl Mol. dia.
		Double-bonded (D)	Internal ionic (I)	D	I		
Ammonium formate	Non-ionic	30·63	37·91	83·85	16·15	31·79	31·79
Ammonium acetate	"	41·82	49·87	82·40	17·60	43·24	43·24
Ammonium propionate	"	53·67	61·76	88·75	11·25	54·48	54·48
Formate	Ion	15·71	25·16	72·36	27·64	18·32	18·32
Acetate	"	27·75	37·14	79·48	20·52	29·68	29·68
Propionate	"	39·51	49·01	84·15	15·85	41·02	41·02
Ammonium oxalate	Non-ionic	54·08	70·24	3·13	96·87	69·73	69·73
Oxalate	Ion	25·65	38·60	?	?	42·61	42·61

(II) Bond Depressions in Connection with Resonance Forms.

Gray and Cruikshank (45) have interpreted the difference which is found between the theoretical molecular susceptibility of a compound, calculated by the method of Part (4) of Section (II)c. of this thesis, which is a summation for free ions, i.e. theoretical molecular standard. [Theor. Mol. Stand.],

and the experimentally observed value, i.e. experimental molecular diamagnetism [Expt. Mol. Dia.], as being due to bond depressions in the molecule, i.e.:-

Expt. Mol. Dia. = Theor. Mol. Stand $-\sum$ Bond Dep.... (1).

Using Pascal's experimental figures, they have calculated a series of bond depressions of diamagnetism, from equation (2), and have employed their results in connection with the resonance forms of various compounds, using equation (2):-

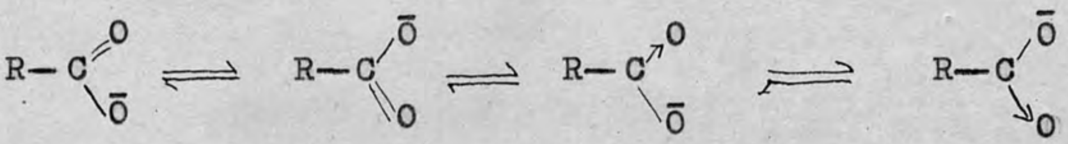
Expt. Mol. Stand. = Theor. Mol. Stand $-\sum$ Bond Dep.... (2)

The experimental molecular standard [Expt. Mol. Stand.] above, was calculated in the first place from the sum of Pascal's experimental atomic standards plus Pascal's corrections, and hence equation (3) holds only for substances which have constitutions similar to those of the substances from which he derived his standards:-

Expt. Mol. Stand. = Expt. Mol. Dia. .... (3)

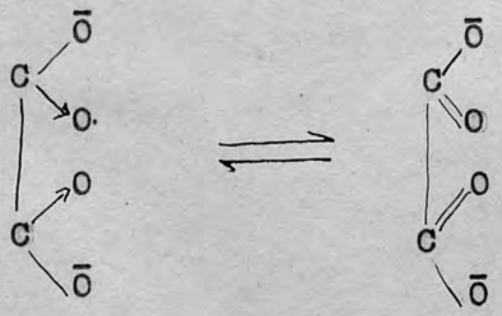
In most cases equation (3) does not hold, and by comparing the value of Expt. Mol. Stand. obtained from equation (2), with the value of Expt. Mol. Dia. obtained experimentally, it is possible to predict the type of chemical constitution of a compound.

Clow and Thompson have applied the method to the resonance forms of urea and its derivatives (46), and organic sulphur compounds (47), and Table 15 shows its application to the resonance forms of salts of ammonium with fatty acids, and the corresponding anions. The various resonance structures which may be attributed to these compounds and ions are derived from that of the acid carboxyl ion which is shown below. Gray and Cruikshank (45) give structures (1) and (3) only, whereas Pauling (48) includes also structure (2); structure (4) was suggested tentatively by the present writer as a further spatial possibility. The two double-bonded forms (1) and (2) have the same magnetic susceptibility, as have the internal-ionic structures (3) and (4):-



(1) (2) (3) (4)

Since the oxalic acid anion contains two acid carboxyl groups, the number of resonance possibilities is greatly increased. Table 15 only includes the theoretically calculated values for the two extreme forms shown below: (2) is entirely double-bonded, and (3) entirely internal-ionic, as regards the second carbon-oxygen bond:-



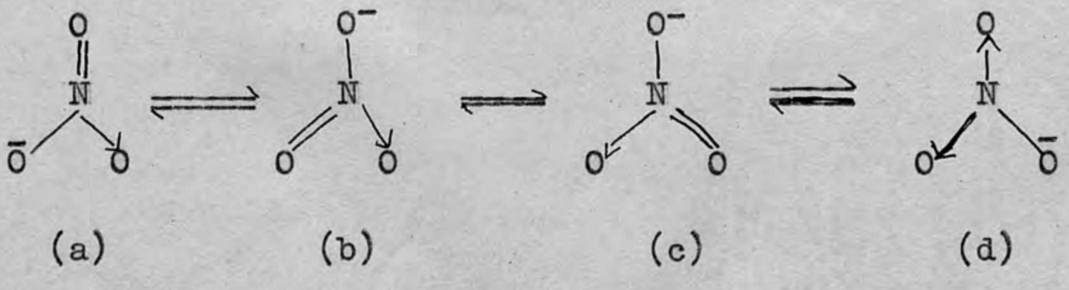
(1) (2)

Both (1) and (2) can exist in various spatial forms, but all the forms of type (1) have the same magnetic susceptibility, which is different in value from that of all the forms of type (2).

The sodium, potassium and ammonium salts were assumed to resonate between structures similar to those of the corresponding fatty acid anions. Columns 5 and 6 of Table 15, which give the percentage of time for which the compound or ion exists in each form of different susceptibility, shows that the values differ for the various compounds and ions. Gray and Cruikshank (45) found for acetic acid [50% D; 50%I.]

The concept of bond depressions did not appear to hold in the case of non-polar ammonium oxalate; the corrected theoretical values were both lower than the experimental value. It seems possible that this was due to the uncertainty of which resonant forms were actually existent.

For the nitrate ion, according to Pauling (48), the possibilities are:-

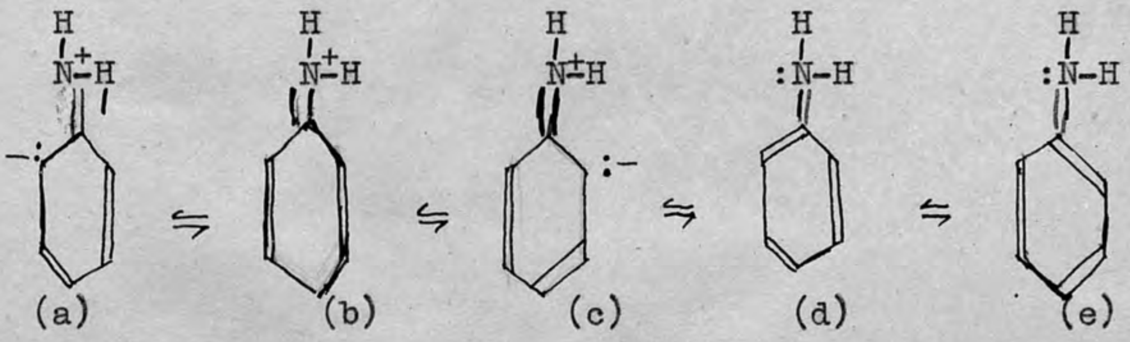


Of these, (a), (b), and (c) have the same susceptibility type (i) and (d) has a different susceptibility (type ii). Table 16 gives a corresponding data for the nitrate ion, and the bond depression values were found to hold in this case.

TABLE 16

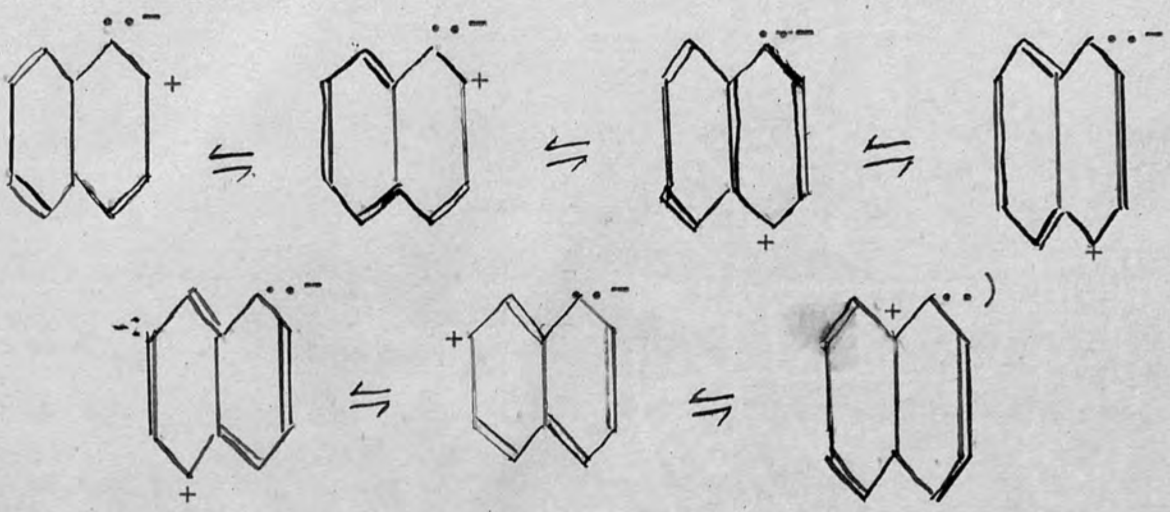
Substance	Form	Expt. Mol. Stand.		% time cpd. exists in each form of diff. suscep.		Mean Theor. Mol. Dia.	Exptl Mol. Dia.
		Type (i)	Type (ii)	(i)	(ii)		
Nitrate	Ion	29.64	15.73	23.64	76.36	19.02	19.02

Table 13 deals with the theoretical molecular susceptibility of resonating molecules. Pauling (48) gives the following resonant forms for aniline, and the substituted anilines and phenylhydrazine hydrochloride would be similar:-

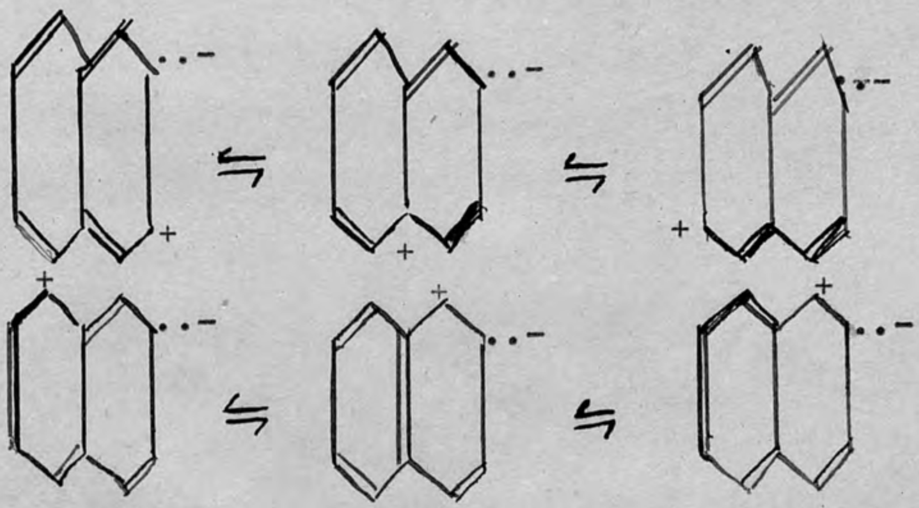


The first three forms are internal-ionic and the last two Kekulé (double-bonded). All five forms are represented by two values for the susceptibility of the molecule; an internal-ionic and a Kekulé value respectively.

According to Pauling, α-naphthylamine exists in seven resonating forms:-



whereas the β-compound exists in six resonant forms:-



The substituent group is attached to the carbon atom with the negative sign. All these eleven forms are represented by the same value of susceptibility (i.e. type (a)) except the last α-form and the second β-form, for which a second value is necessary (i.e. type (b)).

Table 16a shows that the bond depression values did not appear to hold for aniline, and hence would not hold for the substituted anilines and phenylhydrazine hydrochloride. If however the whole of the benzene ring is supposed to have an internal-ionic form in resonance with the Kelulé form as Gray and Cruikshank have suggested in the case of benzene itself, it is seen that the values of bond depressions obtained by them may be applied to this case. Aniline would then exist in the following resonating forms:-

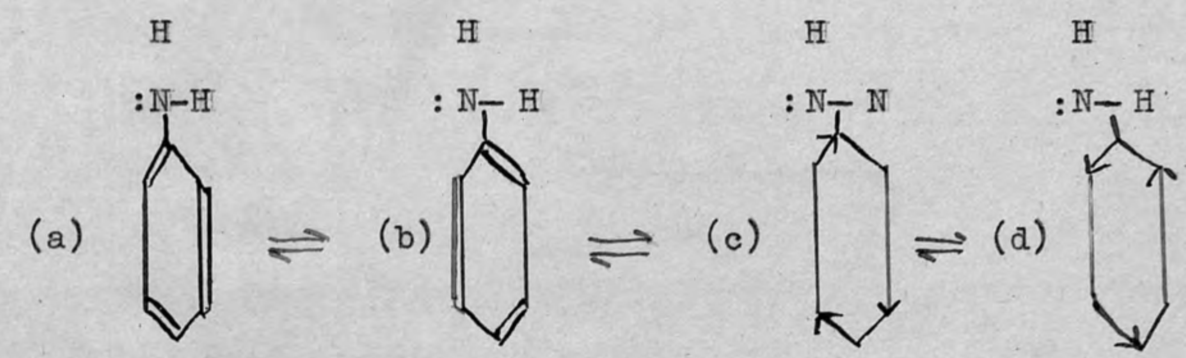
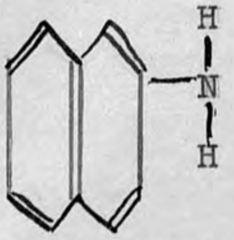


TABLE 16a

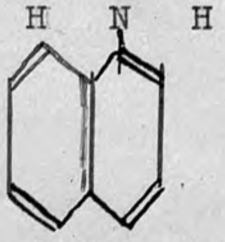
(Molecular Susceptibility $-\chi_M \cdot 10^6$)

Substance	Structure proposed by:-	Expt. Mol. Stand. Types			% time cpd. exists in each form of different susceptibility.		Mean Theor. Mol Dia.	Exptl Mol. Dia.
Aniline		Double-bonded (D)	Internal ionic (I)	Internal ionic (I)	D	I(Mean)		
	Pauling	45·56	52·29	-	?	?	62·40	62·40
	Gray	45·56	(c) 70·58	(d) 81·85	45·01	54·99	62·40	62·40
			Mean =	76·22				
Naphthylamine α and β		(a)	(b)	-	(a)	(b)		Mean of α & β
	Pauling	73·13	73·19	-	?	?	79·64	79·64
	Gray	(1) 100·48	(2) 100·56	(3) 100·42	(1) ?	(2), (3) Mean ?	79·64	79·64
		Kekulé (K)	-	-	(K)	-		
	-	64·33	-	-	?	?	79·64	79·64

Both the Pauling values for naphthylamine were found to be lower than the experimental value, and the normal Kekulé-type value were lower:-

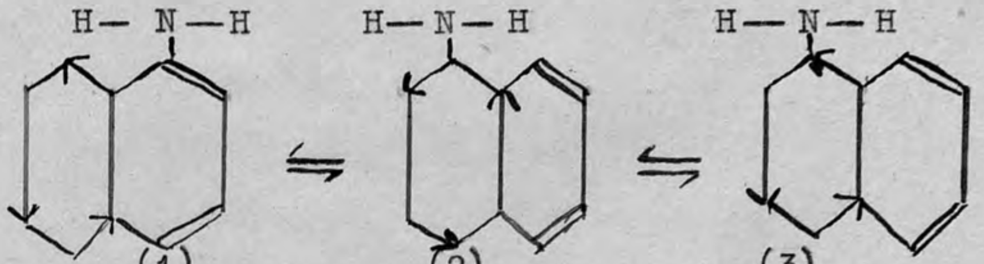


β-Naphthylamine



α-Naphthylamine

If resonance structures were postulated similar to those proposed by Gray and Cruikshank for naphthalene itself, it is seen from the table that all the susceptibility values calculated theoretically and corrected for bond depressions (Columns 3, 4 and 5) are much higher than those obtained experimentally. It seems likely, therefore, that a suitable choice of resonant forms would give a calculated value coincident with the experimental one. The Gray and Cruikshank type resonating structures for α-naphthylamine would be:-



(1) (2) (3)

Each form (1), (2) and (3) has a different susceptibility and includes various mirror-image forms. The corresponding susceptibility values of the β-form in all the resonating types considered are identical with that of the α-form.

It is possible that the concept of bond depressions may not be justified. Moelwyn-Hughes (49) has drawn attention to the fact that the bond length for the C — H bond and others varies in different compounds, being a function of the remainder of the molecule; hence the susceptibility of the bond will be affected, so that it does not seem justifiable to assume additivity of bond depressions, the values of which were all originally obtained from a consideration of various different types of compound, mostly of a simple nature.

TABLE 17

Gram-Ionic Susceptibility (Experimental) of $S_2O_n^{--}$, $Cr_2O_n^{--}$,
SO_n^{--}, CrO_n^{--}

Ion^{--}	$-\chi_{ion}\cdot 10^6$		$-\Delta\chi_{ion}\cdot 10^6$	
	Kido	Present	Kido	Present
S_2O_3	43·0	49·75	9·2	-
S_2O_4	52·2	-	7·0	-
S_2O_5	59·2	-	2 x 7·5	5 x 7·34
S_2O_7	73·9	-	1·6	-
S_2O_8	75·5	86·42		-
SO_3	36·5	31·95	2·5	9·62
SO_4	39·0	41·57		
CrO_4	-	-25·60	-	-11·22
Cr_2O_7	-	-62·42		

(III) Bond Depression Effect in the Series, S_2O_n, Cr_2On, SO_n, CrO_n.

Just as the value of the susceptibility of the CH_2 group (page103) was found to decrease on passing up the homologous series of the aliphatic substituted ammonium chlorides, the experimental rate of decrease being much greater than the theoretical rate, owing to screening effects of the adjacent atoms and ions, so, in the same way, the "oxygen difference" between successive members of a series of oxyacidic anions would be expected to decrease in passing up the series. Kido's figures, shown in column 4 of Table 17, show this to be the case in the series S_2O_n. For similar reasons, a smaller "oxygen difference" would be expected between the molecular susceptibilities of ions $S_2O_3^{--}$ and $S_2O_8^{--}$, than between the molecular susceptibilities of ions SO_3^{--} and SO_4^{--}, since the two latter ions are the least complex and screening effects should be less in the latter instance, so that the decrease in the susceptibility of the oxygen atoms should be less. This was found to be the case, as regards the results of the present worker, but Kido's values of "oxygen difference" ($\Delta\chi_{ion}$ in Column 4 of the table), are somewhat irregular, and the value of $-\Delta\chi_{ion} \cdot 10^6$ between SO_3^{--} and SO_4^{--} appears to be too small.

Kido (11) gives the values shown in Columns 2 and 4 of Table 17, and mentions the fact that Soné, in his magnetic research on the nitric oxides, found a constant difference of $-\Delta\chi \cdot 10^6 = 9{\cdot}8$, Kido's maximum value is 9·2. The maximum value obtained by the present worker was 9·62, which is closer to Soné's value. This value represents the effect on the molecular susceptibility caused by the combination of an oxygen atom, for the condition of small screening effects.

The "oxygen difference" calculated by the present writer between the ions $S_2O_3^{--}$, and $S_2O_8^{--}$, was rather small, possibly owing to the complex nature of the latter ion, and the correspondingly large screening effects, compared with those lower down the series $S_2O_n^{--}$.

The "oxygen difference" between CrO_4^{--}, and $Cr_2O_7^{--}$, was calculated by subtracting twice the value of the susceptibility of the former ion from the susceptibility of the latter ion. Owing to screening effects and different arrangements of atoms within the ions CrO_4^{--} and $Cr_2O_8^{--}$, (the latter being unknown), the "oxygen difference" calculated was rather too small, but even so, probably greater than was found in the sulphur series (i.e. $< 11{\cdot}22$ compared with $9{\cdot}62$). The inference was, that in passing up a group of the periodic table, the "oxygen difference" increases with increasing nuclear charge on the central atom of corresponding oxyacidic anions.

Theoretically, the oxygen atom should contribute an amount to the susceptibility of a compound as given by Pascal's value of $-\chi_{o} \cdot 10^6 = 4{\cdot}61$. In the several series considered above, the value was much greater, and the difference must be attributed to bond depression due to the homopolar bond.

(IV) Susceptibility of the Ammonium and Substituted Ammonium Compounds.

Comparing the tables 1b and (13 and 14) it is seen that in practically every case the theoretical molecular susceptibility exceeded the experimental value for the same substances. This was also found true for the individual ions (Tables 4, and 11 and 12).

The theoretical and experimental values agreed more closely for ions and molecules of low atomic weight and simple form, such as the halides of ammonium, ammonium hydroxide, and the ions ammonium, hydrazine, and hydroxylamine. For these ions and molecules the additivity law is approximately true, as is borne out by the agreement. For the simpler molecules the covalent form gives a theoretical value differing little from the value for the polar salt, but wider deviations occur for the more complicated molecules such as diethylamine hydrochloride.

The values decreased in the order; Pauling, Slater, modified Slater, and the latter agreed most closely with the experimental values. Ammonium hydroxide was anomalous in that the experimental value exceeded the theoretical ones. This was probably due to the presence of free ammonia in the solution. In section IV of the discussion of results, it is shown that extrapolation of Susceptibility/Coordination number curves to C.N. = 0, gives values for the susceptibility of the ammonium halides for free ions agreeing closely with the theoretical Slater values.

The theoretical values of the molecular susceptibility of the compounds measured, both ionic and non-ionic, calculated by the Slater method, were plotted on the graphs with the experimental figures. The Slater figures gave the best agreement with experiment for many of the simpler ions such as hydroxylamine, and the lighter monatomic ions such as those lower in the series of halogen and alkali metal ions, and so they were regarded as being the best values to compare graphically with the experimental results. Considering the curves in detail (p. 29 - 35):-

(i) Halides of Ammonium.

The anomalous shape of the experimental curve was borne out by theory, the two curves having a similar form. The experimental curve for Trew's values for the halogen ions, and the corresponding theoretical curve (corrected Slater values) had a similar form to the former curves, showing that the anomaly occurred in the halogen ion itself. It is due to the grouping of electrons in the orbits, shown below:

F^- 2, 8
Cl^- 2, 8, 8.
Br^- 2, 8,18, 8.
I^- 2, 8,18,18, 8.

F^- and Cl^- are similar, and Br^-, I^- similar, but since the first member of each pair has a smaller nuclear charge than the second member, the effective radii of the orbits are different, and the susceptibility of the ions will not vary in a linear manner. Hence there is no reason why the curve should be linear or the F/Cl, Br/I portions parallel.

Alone of the three portions the Br/I portion if extrapolated passes through the origin, and this line was not found to give a reasonable value for the ammonium ion.

(ii) Ammonium Sulpho-salts.

The ammonium sulpho-salts yielded experimental values of susceptibility which lay on a linear curve, the latter giving on extrapolation a value for the susceptibility of the ammonium ion which was smaller than the value $-13{\cdot}56 \times 10^{-6}$ (page 44) owing to the divalent nature of the sulpho-acid ions, as was explained in Section IIa of the discussion of results. Data was not available for calculation of the corresponding theoretical values.

(iii) Salts and Hydrates of Hydrazine and Allied Bases.

The Slater values for the theoretical susceptibility of hydrazine hydrate were both a little higher than the experimental figure, but the latter coincided with a combination of the modified Slater ionic and non-ionic figures in suitable proportions. By assuming a certain percentage of NH_3 in the ammonium hydroxide an experimental figure for the molecular susceptibility could be found which was identical with a combination of the Slater ionic and non-ionic figures in suitable proportions.

The experimental values for the hydrazine- and similar hydrochlorides lay on a linear curve with hydrazine hydrate, and the sulphates of hydrazine and hydroxylamine were assumed to lie in a linear curve of smaller gradient than the first. Insufficient data was available for calculation of the theoretical susceptibilities of the sulphates, but those of the hydrochlorides lay approximately on a straight line with ammonium hydroxide and hydrazine hydrate.

(The theoretical ionic susceptibility of the hydroxylamine ion was slightly smaller than the experimental value. The reverse should have held, since crystal forces tend to diminish the susceptibility of an ion in a solid crystal. However, the difference was small and did not arise if the Pauling value was considered). All the curves passed through the origin.

(iv) Substituted Anilines.

The substituted anilines also yielded a linear graph, and the theoretical graphs for the Kekulé and Internal-ionic forms were straight lines, of gradient steeper than that of the first line.

(v) Substituted Ammonium-Halides.

The theoretical and experimental curves for the substituted ammonium halides were of a form exactly similar to those of the ammonium halides in Graph 1. This would be expected, since the anomaly lay solely in the anion. Here again the experimental values represented a check on the theoretical ones.

The chloride, bromide and iodide curves were parallel, and the lines joining the values for the chloride and bromide, or bromide and iodide of the same cation were parallel for different cations (the lines shown dotted). This applied to both experimental and theoretical curves. Tetramethylammonium chloride was not measured, but diethylamine hydrochloride which is isomeric with it, was measured, and the line joining it with tetramethylammonium bromide was found to be parallel to the corresponding line for the ethyl compounds. The experimental curve passed through the origin but the theoretical curve did not.

(vi) Sodium, Potassium and Ammonium Salts of some Organic Fatty Acids.

The experimental values of the susceptibility of the formate, acetate, and propionate of sodium, potassium and ammonium lay on parallel straight lines, one for each cation, and the theoretical curves were of the same form, thus being confirmed by the experimental results. None of the curves passed through the origin.

(vii) Ammonium Chromo-salts.

The curve on which the molecular susceptibilities of ammonium chromate and ammonium dichromate lay was assumed, by analogy with the previous curves, to have a linear form. The susceptibility of the ammonium ion could not be found directly by extrapolation of the curve, owing to the paramagnetism of the anions. The apparent susceptibility of the chromate and dichromate ions was given by the ordinates of the two points on the line whose abscissae corresponded to the number of electrons in the respective ions, The results were as follows:-

Salt	Exptl. Suscep. $+\chi_M \cdot 10^6$	Anion Apparent Suscep. $+\chi_{ion} \cdot 10^6$	$2NH_4^{\cdot}$ Apparent Suscep. $+\chi_{ion} \cdot 10^6$
$(NH_4)_2CrO_4$	1·00	−15·90	16·90
$(NH_4)_2Cr_2O_7$	37·82	21·00	16·82

Since the addition of $2NH_4^{\cdot}$ to the anion to form a salt represents an average addition of +16·86 to the ordinate of a point of the line, a line drawn parallel to the first at an ordinate distance of +16·82, gave the value of the susceptibility of $2NH_4^{\cdot}$ at the point whose abscissa corresponded to 22 electrons which is the number of electrons in $2NH_4^{\cdot}$; viz. $-24 \cdot 6 \, . 10^{-6}$.

Considering Graph viii (page 50) (Ammonium and Substituted Ammonium Ions), the theoretical values lay on straight lines corresponding to the experimental ones (Section IIb of the Discussion of Results) but of slightly steeper gradient. The line for ammonium and the organic substituted ammoniums did not pass through the origin, nor did the line containing the values for ammonium, hydrazine and hydroxylamine. The similar forms of experimental and theoretical curves served as a check on the theoretical values.

(V) Susceptibility of the CH_2 Group.

Pascal (21) has determined the difference in molecular susceptibility between successive members of various homologous series. This difference gives the value of the susceptibility of the CH_2 group. Pascal's mean value corrected to conform with the modern standard for water ($-0{\cdot}72.10^{-6}$) is $-11{\cdot}86.10^{-6}$. All his figures given in the present tables have been similarly corrected. Table 18 gives some values of the susceptibility of the CH_2 group obtained in the present work for the series:- Aniline and the toluidines; aniline and the substituted anilines; ammonium and substituted ammonium halides; fatty acid salts of ammonium, sodium and potassium, respectively. The corresponding theoretical values are also shown, where sufficient data was available for the calculations.

From the results in Table 18 mean values of the susceptibility of the CH_2 group were found to be as follows:-

Mean Value $-\chi_{CH_2} \times 10^6$ (Experimental) = $11{\cdot}25$

" " " " (Theoretical) = $\left\{\begin{array}{l} 15{\cdot}03 \text{ (Pauling)} \\ 14{\cdot}07 \text{ (Slater)} \\ 12{\cdot}59 \text{ (Modified Slater)} \end{array}\right.$

The experimental value for CH_2 only varied slightly and in no definite direction in passing up the series of aniline and the substituted anilines, whereas it decreased regularly in passing up the series of hydrochlorides of substituted ammonias. (For the chloro, bromo- and iodo- salts of the above, the ammonium salt was found to be anomalous, probably on account of its semi-polar character).

The theoretical values of the susceptibility of CH_2 were in no definite order except the Slater values which increased regularly up the latter series, both for the ionic and non-ionic form of compound. A decrease up the series was found in the tetra-substituted salts of ammonium, except for the Pauling values where the reverse occurred.

These facts are illustrated graphically in figure xi, (page 106), in which the susceptibility of the CH_2 group is plotted against the mean number of electrons in the two successive members of a homologous series, which are concerned. The lower figure gives the curves for ammonium and substituted ammonium chlorides. The upper figure shows the curves for aniline and the substituted anilines and here it will be seen that the mean theoretical Kekulé curve (Slater method of calculation), has the same anomalous shape as the experimental curve, a fact which served as a check on the theoretical values.

In these two series and also the sets of sodium, potassium and ammonium salts of some fatty acids, the value of the susceptibility of the CH_2 group was found to decrease on passing up the series, the experimental rate of decrease being much greater than the theoretical rate (where an actual

TABLE 18

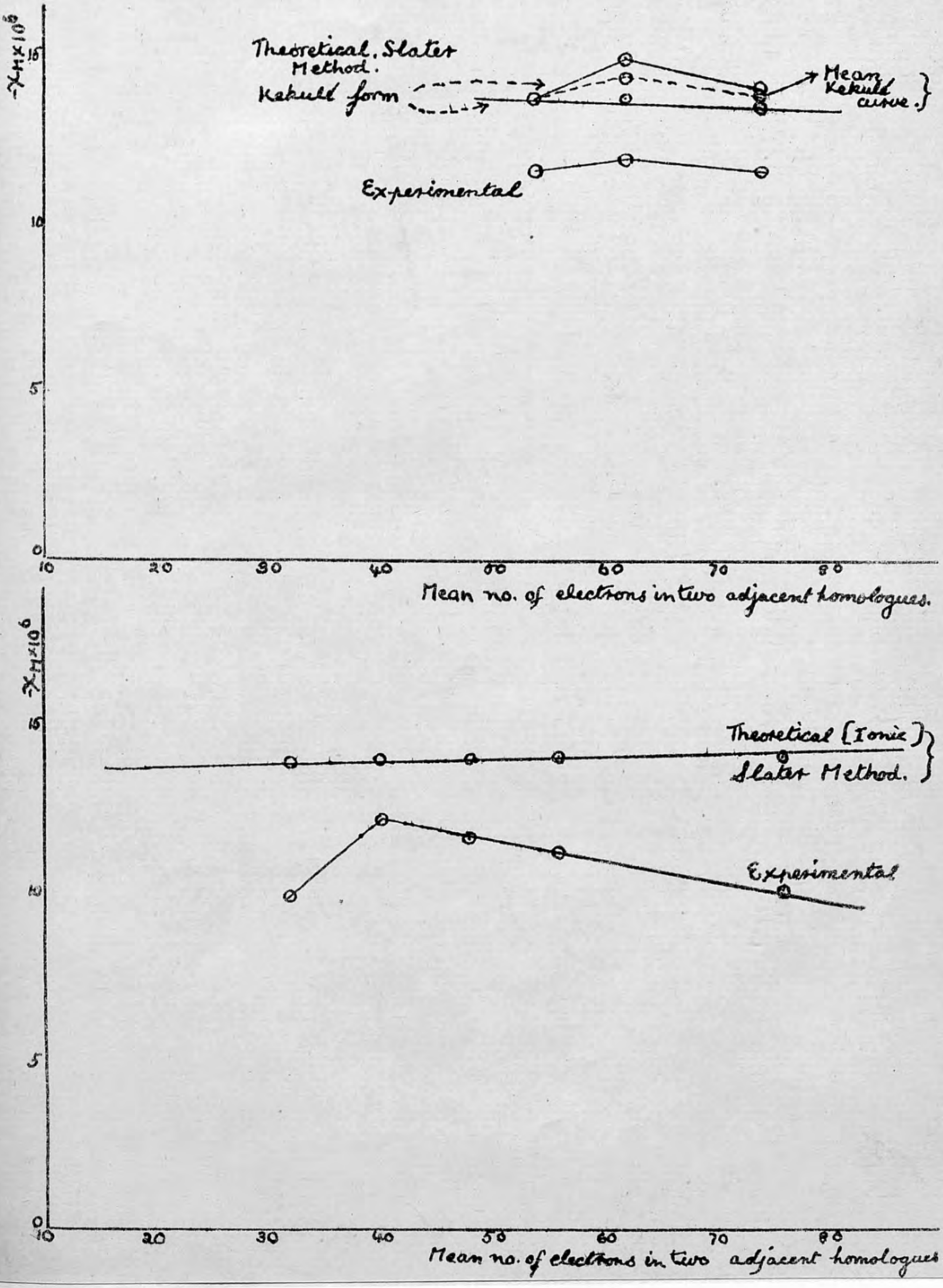
Mass Susceptibilities of CH_2 Group. $(-\chi_{group} \cdot 10^6)$

Compound	Suscep.	Exptl Suscep. of CH_2 group.	Theoretical Suscep. of CH_2 group.					
			Ionic Form			Non-ionic Form.		
			Pauling method.	Slater method.	Mod. Slater method.	Pauling method.	Slater method.	Mod. Slater method.
$C_6H_5NH_2$	62·40^{i}	12·68	-	-	-	14·94	14·10	12·65
o-$C_6H_4NH_2CH_3$	75·08	11·78	-	-	-			
m-$C_6H_4NH_2CH_3$	74·18	11·89	-	-	-			
p-$C_6H_4NH_2CH_3$	74·29							
$C_6H_5NH_2$	62·40^{i}	11·56	14·86	13·98	12·75	14·63	13·79	12·42
$C_6H_5NHCH_3$	73·96	11·98	14·80 15·07	13·98 14·26	12·68 12·84	14·78 14·85	13·76 14·98	12·32 13·29
$C_6H_5N(CH_3)_2$	85·94							
$C_6H_5NH(C_2H_5)$	85·94	11·53	14·88 14·75	14·07 13·93	12·62 12·04	14·92 14·88	14·08 13·47	12·51 12·07
$C_6H_5N(C_2H_5)_2$	108·99							
NH_4Cl	36·70	9·89	15·43	13·84	12·46	14·74	13·84	12·45
$NH_2CH_3.HCl$	46·59	12·05	14·14	13·98	12·57	14·83	13·98	12·58
$NH(CH_3)_2.HCl$	58·64	11·62	15·84	13·98	15·58	14·85	13·97	12·57
$N(CH_3)_3.HCl$	70·26	11·17	14·95	14·03	12·50	15·03	15·19	12·50
$NH(C_2H_5)_2.HCl$	81·43	10·09	16·47	14·07	12·55	-	-	-
$N(C_2H_5)_4.HCl$	121·80							
NH_4Br	47·02	9·85	15·02	14·12	12·72	-	-	-
$N(CH_3)_4Br$	86·40	11·14	16·47	13·88	12·37	-	-	-
$N(C_2H_5)_4Br$	130·95							
NH_4I	63·94	9·25	15·02	14·12	12·72	-	-	-
$N(CH_3)_4I$	100·95	11·23	16·47	13·88	12·37	-	-	-
$N(C_2H_5)_4I$	145·85							
$HCOONH_4$	31·79	11·45	15·08^{a} 15·02^{b}	14·28^{a} 14·18^{b}	12·69^{a} 12·63^{b}	14·23^{a} 15·00^{b}	13·44^{a} 14·13^{b}	12·59^{a} 12·68^{b}
CH_3COONH_4	43·24	11·34	14·80^{a} 14·91^{b}	14·08^{a} 14·06^{b}	12·54^{a} 12·72^{b}	14·89^{a} 14·93^{b}	14·07^{a} 14·09^{b}	12·54^{a} 12·74^{b}
$C_2H_5COONH_4$	54·58							
$HCOONa$	27·10	12·50	15·08^{a} 15·02^{b}	14·28^{a} 14·18^{b}	12·69^{a} 12·63^{b}	-	-	-
CH_3COONa	39·6^{ii}	9·65	14·80^{a} 14·91^{b}	14·08^{a} 14·06^{b}	12·54^{a} 12·72^{b}	-	-	-
C_2H_5COONa	49·25							
$HCOOK$	32·92	12·08	15·08^{a} 15·02^{b}	14·28^{a} 14·18^{b}	12·69^{a} 12·63^{b}	-	-	-
CH_3COOK	45·0^{ii}	11·50	14·80^{a} 14·91^{b}	14·08^{a} 14·06^{b}	12·54^{a} 12·72^{b}	-	-	-
C_2H_5COOK	56·50							

i. Pascal (21)
ii. Kido (12)

a. Double-bonded form.
b. Internal-ionic form.

Theoretical & Experimental Mass Susceptibility of the $-CH_2$ Group in Aniline & Substituted Anilines [top figure], and Chlorides of Ammonium & the Substituted Ammoniums [lower figure]. Fig XI.



increase was found in the series of ammonium and substituted ammonium chlorides). The anomalous increase in the middle of the curve for aniline and the substituted anilines was relatively less in the experimental curve than in the theoretical curve. For clarity, only the Kekulé theoretical curve is shown, but the Internal-ionic form curve has a similar form.

The reason was to be found in the screening effects of the adjacent ions and atoms on the CH_2 group or groups in the molecule. The effect would be such as to decrease the size of the CH_2 group and hence a decreasing contribution of the susceptibility of the CH_2 group to that of the molecule would be expected on passing up a series, since the screening effects would increase.

Since, however, the actual variations in the experimental and theoretical values of the susceptibility of the CH_2 group were relatively small, it was permissible to take a mean (as Pascal has done in the experimental case). None of the homologues considered were sufficiently high up in a series for undue distortion to occur.

TABLE 19

Molecular Mass Susceptibilities of some Aromatic Position Isomers. $(-\chi_M \cdot 10^6)$

Compound.	Suscep. Ortho	Suscep. Meta	Suscep. Para	Worker
Toluidine	$75\cdot08^{\mathrm{i}}$ $75\cdot65^{\mathrm{iii}}$	$73\cdot79^{\mathrm{ii}}$ $72\cdot97^{\mathrm{iii}}$	$74\cdot29^{\mathrm{ii}}$ -	i. Pascal (21) ii. Present Work. iii. Bhatnagar and Mathur. (19)
Cresyl Methyl Ether.	81·94	77·91	79·13	(Same Ref. as iii)
Phenetidine	101·1	-	95·86	"
Cresol	73·62	72·32	72·75	Bhatnagar, Mathur and Mal. (50)
Nitrotoluene	6·61	5·52	-	"
Chlorophenol	5·20	-	5·10	"
Naphthylamine	(α) 79·71	(β) 79·56	-	Present Work.

(6) Molecular Susceptibilities of some Aromatic Position Isomers, and Electronic Isomers.

(a) Aromatic Position Isomers.

Bhatnagar, Mathur and Mal (50) and Bhatnagar and Mathur (19) have discussed fully the subject of position isomers, both aliphatic and aromatic. In Table 19 are collected the values of molecular susceptibility of aromatic position isomers obtained experimentally by various workers, including the present worker.

In each case the ortho compound is seen to have the greatest susceptibility. This was confirmed by the values in the present work for meta- and para-toluidine and Pascal's value for ortho-toluidine. The two isomeric forms of a substituted naphthalene were also measured in the present work. (α- and β- nephthylamine) and the α-form, which corresponds to the orthoform of a di-substituted benzene, was found to have the greater susceptibility.

Bhatnagar and Mathur (19) have interpreted their results, (published both in this paper and (50)) on the basis of the electronic significance of valency bonds, the qualitative explanation being similar to that given by Stoner (51) Chap. XIV. They say that, in the case of aromatic position isomerides, although all the carbon atoms in the benzene ring are initially alike, the substitution of a hydrogen atom associated with any of the carbon atoms by, say, a group CH_3, causes the other carbon atoms in the ring to alter their character. The two carbon atoms adjacent to the one attached to the substituent group will have the maximum decrease in effective positive charge for combination with other atoms, owing to the proximity of the substituent group which has a greater positive charge than a hydrogen atom (all the bonds are non-polar).

Since in the ortho-position the two substituent groups are nearest together, their effective positive charges will be a minimum, and since the dimensions of shared orbits increase with decreasing effective positive charge on the nuclei concerned, and the susceptibility varies directly with the size of the orbits, (Langevin treatment), the ortho- compound should be more diamagnetic than the meta- or para- compounds. This is found experimentally to be the case.

Similar reasoning would apply to the case of the naphthalene di-substituted compounds i.e. the susceptibility of the α-cpd is greater and is confirmed by the results of the present work.

Bhatnagar and Mathur find that the differences in molecular susceptibility of ortho-, meta- and para-isomers (and others) cannot be attributed to differences in their molecular association. In this paper and paper (50) the relation is studied between these differences and physical properties, such as density, boiling-point, surface tension, refractive index and viscosity, molecular magnetic rotation and depolarisation factors, which are never exactly the same for the different isomers of the same substance. Toluidine (which they also measured) accords with their generalisation that the isomeride in a group which has the greatest susceptibility (i.e. the ortho-isomeride) has also the greatest molecular magnetic rotation, and the lowest boiling-point and molecular volume.

The actual figures are given in paper (19), for ortho- and meta-toluidine.

The corresponding data for α- and β- naphthylamine is given below:-

Substance	Molec. Mag. Suscep. $(-\chi_M . 10^6)$	Molec. Mag. Rotation.	Molecular Volume.	B.P. °C.
α-Naphthylamine	79·71	37·478(52)	163·9[i]	301·0[i]
β-Naphthylamine	79°56	35·700(52)	153·6[i]	306·1[i]

It is evident from this data that in the α-compound in the naphthlene series corresponds to the ortho-compound in the benzene series, as was to be expected on theoretical grounds, according to the interpretation of Bhatnagar and Mathur (loc. cit.)

As regards the meta- and para- compounds in the benzene series, Bhatnagar and Mathur (19) have noted that the meta-compound has a smaller susceptibility than the corresponding para-compound, in the case of cresol and cresyl-methylether. Also the two isomers differ in susceptibility by a far smaller amount than that by which either of them differs from the ortho-isomer. The value of the susceptibility of para-toluidine, measured in the present work, in conjunction with Pascal's value for the meta-compound (Table 19) confirmed the conclusions of Bhatnagar and Mathur. Their value for meta-toluidine appears to be rather low, and Pascal's value was considered to be more reliable, taken in conjunction with his value for the ortho-compound.

The physical data for the cresols, cresylmethylethers and toluidines given by Bhatnagar and Mathur, is given below for purposes of comparison. The data for para-toluidine has been added to complete the series:-

Substance	Molec. Mag. Suscep. ($-\chi_M \times 10^6$)	Molec. Mag Rotation.	Molecular Volume.	B.P. °C.
o-Toluidine	75·08	17·20 (52)	126·6	200·7[i]
m- "	73·79	16·21 (52)	128·1	203·3[i]
p- "	74·29	16·19 (52)	128·7 (53)	200·5[i]
o-Cresylmethylether	81·94	15·19	146·1	171·2
m- "	77·91	14·65	147·5	176·7
p- "	79·13	14·71	147·7	176·1
o-Cresol	73·62	13·382	121·5	190·8
m- "	72·32	12·869	123·5	202·0
p- "	72·75	12·776	123·5	201·0

(i. Taken from the International Critical Tables).

According to the interpretation of Bhatnagar and Mathur (loc. cit.), we should expect the meta-compound to have a susceptibility greater than that of the para-isomeride, since the carbon atom in the para-position is further from the ortho-carbon atom than is the carbon atom in the meta-position. Except in the case of the cresylmethylethers, the molecular magnetic rotation was seen to decrease in the order, ortho, meta, para, in the normal manner.

The boiling-points, however, were anomolous, but their order of magnitude corresponded (inversely) with that of the susceptibilities, except for the boiling-point of ortho-toluidine. The anomaly did not occur in the values of molecular volume, which appeared to be somewhat irregular, and in no definite order.

It seems possible that the apparent anomaly was due to the fact that all three isomers of each substance existed in several Kekulé and Internal-ionic resonating forms, so that no static picture of the molecule was adequate for the interpretation of its properties.

If one or several Internal-ionic forms, were postulated, which contained no double bonds in the benzene ring, the condition would be similar to that of cyclo-hexane, with modifications in the angles between bonds due to the charges on the carbon atoms in the ring. Applying the Sachs-Mohr theory of "bent" molecules to the present case, it would seem that, as in the case of cyclo-hexane, the valency angles for the carbon atoms in the ring were of magnitudes such that the strainless molecule would be bent, and the cis- and trans- bent forms would be in resonance.

It is conceivable that in either cis- or trans- form, the para- carbon atom in the ring would be relatively nearer to the ortho-carbon atom than the meta-carbon atom would be, and hence, on theoretical grounds, the susceptibility of the meta-compound would be less than that of the para-compound, but only a little less when the "flat" forms were also considered.

TABLE 20

Molecular Mass Susceptibilities of some Electronic Isomers. $(-\chi_M \cdot 10^6)$

Compound	Atomic No.	No of atoms.	Radius A.U.	K value	Suscep. exptl.	Suscep. calc. on equn (3)	Worker
I. Organic							
Methyl Acetate	40	11	1·263	13·79	39·78	41·8	Bhatnagar &
Propionic Acid	40	11	1·263	13·79	43·83	41·8	Mathur (20)
Isobutylaldehyde	40	13	1·305	14·7	47·45	47·56	"
Methylethyl-ketone	40	13	1·305	14·7	47·45	47·56	"
Ethyl Acetate	48	14	1·357	15·32	59·70	60·40	"
Butyric Acid.	48	14	1·357	15·32	61·13	60·42	"
Glycerine	50	14	1·323	16·04	56·12	53·3	"
Aniline	50	14	1·460	16·04	65·1	65·1	"
Anisol	58	16	1·532	16·305	72·79	72·79	"
Benzyl Alcohol	58	16	1·532	16·305	67·60	72·79	"
Cresol	58	16	1·532	16·305	71·17	72·79	"
Phenylhydrazine	58	16	1·505	16·305	67·82	70·21	"
Toluidine	58	17	1·534	16·32	88·69[i]	73·0	"
				16·82	74·24	74·10	Present Work
Methylaniline	58	17	1·534	16·32	82·74	73·0	Ref.(20)
				16·82	73·96	74·10	Present Work
Ethylaniline	66	20	1·601	18·34	89·3	89·4	Ref. (20)
				18·00	85·94	87·15	Present Work
Dimethylaniline	66	20	1·601	18·34	89·66	89·4	Ref. (20)
				18·00	85·94	87·15	Present Work
Methyl Benzoate	72	18	1·620	16·44	83·23	82·9	Ref. (20)
Phenyl Acetate	72	18	1·620	16·44	82·69	82·9	"
Ammonium Oxalate $C_2O_4(NH_4)_2 \cdot H_2O$	76	19	1·424	17·96	82·70	68·65	Present Work
Naphthylamine	76	20	1·718	18·00	79·64[ii]	100·25	"
Phenylhydrazine-hydrochloride.	76	18	1·674	17·93	94·86	94·86	"
II. Organic, Inorganic.							
Ammonium Acetate	42	12	1·244	14·77	43·24	43·24	Present Work
Ammonium Nitrate	42	9	1.140	13·27	32·58	32·58	"
Potassium Formate	42	5	2·147	3·77	32·92	32·92	"
III. Inorganic.							
Ammonium Hydroxide	20	7	0·881	12·20	31·54	17·86	"
Ammonium Fluoride	20	6	0·881	11·70	23·00	17·14	"
Sodium Fluoride	20	2	2·450	0·96	11·76	10·95	Ref. (20)
Magnesium Oxide	20	2	2·075	0·96	6·73	7·83	"
Sodium Chloride	28	2	2·825	1·5	23·98	22·94	"
Calcium Oxide	28	2	2·350	1·5	15·12	15·74	"
Hydroxylamine-hydrochloride	36	7	1·220	12·20	44·41	34·30	Present Work
Hydrazine-hydrochloride	36	8	1·226	12·70	44·53	36·00	"
Barium Oxide	64	2	2·750	2·1	18·4	21·55	Ref. (20)
Silver Chloride	64	2	2·825	2·1	40·13	31·99	"
Potassium Carbonate	68	6	2·675	6·0	76·02	81·57	"
Calcium Sulphate	68	6	1·922	6·0	51·73	43·00	"
Caesium Chloride	72	2	3·425	2·2	47·12	48·94	"
Potassium Iodide	72	2	3·475	2·2	51·46	50·35	"
Tellurous Acid	78	6	1·471	8·194	33·72	33·68	"
Zinc Sulphate	78	6	1·051	8·194	43·58	42·44	"

i. Mean of Values for meta and para compounds.
ii. Mean of Values for α and β compounds.

(b) Electronic Isomers.

Bhatnagar and Dhawar (54) have put forward an empirical equation from which the molecular susceptibility (χ_M) of the isomeric forms of a molecule may be calculated:-

$$\chi_M = -2{\cdot}83 \times 10^{10} \Sigma (K\bar{r}\ )^2 \ldots\ldots\ldots\ldots \quad (1)$$

where $\bar{r}$ represents the value of the radius of the molecule, and K is an arbitrary constant. This equation resembles the Langevin equation very closely:-

$$\chi_A = -2{\cdot}83 \times 10^{10} \sum_n \bar{r}^2 \ldots\ldots\ldots\ldots \quad (2)$$

where χ_A = gram-atomic susceptibility of a single atom, and $\bar{r}$ = atomic radius. Bhatnagar and Mathur (20), however, pointed out that $\bar{r}^{\ 2}$ is the mean square radius of the projected orbit in a plane perpendicular to the field, and the resemblance is closer if the mean square radius $(R)^2$ of the orbit itself is employed, i.e.:-

$$\chi_M = -2{\cdot}83 \times 10^{10} \times \tfrac{2}{3}k\ R^2 \ldots\ldots\ldots\ldots \quad (3)$$

In these two papers and in a later paper by Bhatnagar and Luther (22), the values of R^2 for a number of electronic isomers have been calculated by Bragg's method, whereby:

$$R = [r^{\ 3} + r_2^{\ 3} + \ \ldots\ldots\ldots\ ]^{\frac{1}{3}}$$

where r , r_2 .... are the radii of the constituent atoms in the molecule. Values of k have been calculated which give the best agreement with equation (3) for any particular set of isomers, using the experimental values of χ_M. They found that:-

(I) k had the same value for every pair of isomeric molecules.

(II) In the case of groups of electronic isomers with the same atomic number, the value of k increased with the number of atoms in the molecule.

(III) For groups of isomers having the same number of atoms in the molecule, k increased in value with the atomic numbers of the groups.

Consequently they attributed to k a fundamental significance.

Table 20 gives a list of data for electronic isomers studied by Bhatnagar and Dhawar (54) and Bhatnagar and Mathur (20), and the present worker. The contributions of Bhatnagar and Luther (22) have been omitted, since their results were only of a confirmatory nature and show no large discrepancies. The present values for the two sets of organic isomers, of which each member of a set contains the same number of atoms (toluidine and methylaniline; ethylaniline and dimethylaniline, respectively), differ from those of Bhatnagar and Mathur, but the group k values still agree with their generalisations (I) and (II).

In the other four sets of electronic isomers studied in the present work, the members differed in the number of constituent atoms, and the k values increased with the number of atoms in the molecule, confirming the second generalisation of Bhatnagar and Mathur for members of the same group. Their third generalisation was confirmed by the case of phenylhydrazine hydrochloride (measured in the present work), and methyl benzoate and phenyl acetate, measured by Bhatnagar and Mathur. All three substances had 18 atoms in the molecule, but the value of k for the first substance was large than for the two latter, corresponding to a higher atomic number in the former case.

It will be seen from the table that the present k values have been brought into line with those of Bhatnagar and Mathur, but in several cases wide divergences between the experimental and calculated values of molecular susceptibility were apparent, e.g. hydrated ammonium oxalate, naphthylamine, ammonium hydroxide. The equation appears to be more readily applicable to groups of isomers, each member of which contains the same number of atoms, than to those cases where the members differ as regards the number of constituent atoms.

(7) Table Ia (continued)

(7) Ammonium Vanadate. NH_4VO_3

Pull of tube 1 = 0·58 mgm.
α = 0·41315
V . 0·03 = 0·096

Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (positive) Material alone.	Weight of Material.	$+\chi \cdot 10^6$
(a) 0·14 mgm. 0·28 mgm. 0·07 mgm.	0·17 mgm.	0·41 mgm.	3·81835 gm.	0·070
(b) 0·16 mgm.	0·16 mgm.	0·42 mgm.	3·83754 gm.	0·070
(c) 0·21 mgm. 0·20 mgm. 0·18 mgm.	0·19 mgm.	0·42 mgm.	3·81767 gm.	0·067

Mean Value = $+ 0·069 \cdot 10^{-6}$

(Continued)

(8) Ammonium Sulphite. $(NH_4)_2SO_3.H_2O$

Pull of tube I = -0·66 mgm.

α = 0·41315

V . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi . 10^6$
(a)	4·98 mgm. 4·90 mgm.	4·94 mgm.	4·28 mgm.	3·13548 gm.	0·533
(b)	4·74 mgm. 4·74 mgm.	4·74 mgm.	4·08 mgm.	3·06483 gm.	0·519
(c)	4·75 mgm. 4·78 mgm. 4·85 mgm.	4·79 mgm.	4·13 mgm.	3·09294 gm.	0·521

Mean Value = $-0.524 . 10^{-6}$

(Continued)

(9) Ammonium Sulphate. $(NH_4)_2SO_4$

Pull of tube I = −0·58 mgm.

α = 0·41315

V . 0∘03 = 0·096

Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi.10^6$
(a) 5·12 mgm. 5·11 mgm.	5·12 mgm.	4·54 mgm.	3·57600 gm.	0·498
(b) 5·10 mgm. 5·07 mgm. 5·14 mgm.	5·10 mgm.	4·52 mgm.	3·48642 gm.	0·508
(c) 5·08 mgm. 5·07 mgm. 5·03 mgm.	5·06 mgm.	4·48 mgm.	3·41653	0·514

Mean Value = $-0{\cdot}507 \,.\, 10^{-6}$

(Continued)

(10) Ammonium Thiosulphate. $(NH_4)_2S_2O_3$

Pull of tube 4 = -0·56 mgm. Pull of tube 1 = -0·66 mgm.

a = 0·39257 a = 0·41315

v . 0·03 = 0·091 v . 0·03 = 0·096

Tube No.		Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material	$-\chi.10^6$
4	(a)	4·85 mgm.	4·85 mgm.	4·29 mgm.	3·20250 gm.	0·500
1	(b)	4·96 mgm. 5.02 mgm. 5·05 mgm.	5·01 mgm.	4·35 mgm.	3·37577 gm.	0·504
	(c)	5·18 mgm. 5·19 mgm. 5·08 mgm.	5·15 mgm.	4·49 mgm.	3·40456 gm.	0·517

Mean Value = $-0·507 .10^{-6}$

(Continued)

(11) Ammonium Persulphate. $(NH_4)_2S_2O_8$

Pull of tube 2 = -0·69 mgm.

a = 0·43222

V . 0·03 = 0·093

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi . 10^6$
(a)	5·34 mgm. 5·30 mgm.	5·32 mgm.	4·63 mgm.	3·85800 gm.	0·494
(b)	5·26 mgm. 5·23 mgm.	5·22 mgm.	4·53 mgm.	3·85029 gm.	0·483
(c)	5·39 mgm. 5·38 mgm. 5·35 mgm.	5·37 mgm.	4·68 mgm.	3·89858 gm.	0·494

Mean Value = $-0·490 . 10^{-6}$

(Continued)

(12) Ammonium Chromate. $(NH_4)_2CrO_4$

Pull of tube 2 = -0·75 mgm. Pull of tube 1 = -0·58 mgm.

α = 0·43651 α = 0·41315

V. 0·03 = 0·090 V . 0·03 = 0·096

Tube No.	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (positive) Material alone.	Weight of Material.	$+\chi . 10^6$
2	(a) 0·51 mgm. 0·21 mgm.	0·36 mgm.	0·39 mgm.	3·97642 gm.	0·065
	(b) 0·34 mgm.	0·34 mgm.	0·41 mgm.	3·98551 gm.	0·067
1	(c) 0·29 mgm. 0·03 mgm. 0·01 mgm.	0·11 mgm.	0·47 mgm.	4·39047 gm.	0·066

Mean Value = $+0·066 . 10^{-6}$

(continued)

(13) <u>Ammonium Dichromate.</u> $(NH_4)_2Cr_2O_7$

Pull of tube 1 =-0·58 mgm.

a = 0·41315

V . 0·3 = 0·096

	Pull (positive) Tube + material.	Mean Pull (positive) Tube + material.	Pull (positive) Material alone.	Weight of Material	$+\chi_{\circ}\ 10^{6}$
(a)	0·75 mgm. 0·75 mgm. 0·86 mgm.	0·79 mgm.	1·37 mgm.	4·36486 gm.	0·149
(b)	0·81 mgm. 0·80 mgm.	0·81 mgm.	1·39 mgm.	4·37638 gm	0·153
(c)	0·75 mgm. 0·75 mgm. 0·70 mgm.	0·73 mgm.	1·31 mgm.	4·31485 gm	0·148

Mean Value = $+\ 0{\cdot}150\ .\ 10^{-6}$

(Continued)

(14) <u>Ammonium Molybdate.</u> $(NH_4)_6Mo_7O_{24}.4H_2O$

Pull of tube 2 = -0•78 mgm.

α = 0•43651

V . 0•03 = 0.090

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi . 10^6$
(a)	2•73 mgm. 2•92 mgm. 2•90 mgm.	2•85 mgm.	2•07 mgm.	5•88157 gm.	0•138
(b)	2•58 mgm. 2•74 mgm. 2•55 mgm.	2•66 mgm.	1•88 mgm.	5•82673 gm.	0•125
(c)	2•54 mgm. 2•75 mgm. 2•98 mgm.	2•76 mgm.	1•98 mgm.	5•84867 gm.	0•132

Mean Value = $-0•132 .10^{-6}$

(Continued)

(15) Ammonium Formate. $HCOONH_4$

Pull of tube 1 = -0·66

α = 0·41315

V . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material	$-\chi . 10^6$
(a)	4·46 mgm. 4·46 mgm.	4·46 mgm.	3·80 mgm.	2·93249 gm.	0·505
(b)	4·56 mgm. 4·39 mgm. 4·40 mgm.	4·45 mgm.	3·79 mgm.	2·90532 gm.	0·505
(c)	4·44 mgm. 4·42 mgm.	4·43 mgm.	3·72 mgm.	2·91234 gm.	0·503

Mean Value = $- 0·504.10^{-6}$

(Continued)

(16) Ammonium Acetate. CH_3COONH_4

Pull of tube 4 = -0·56 mgm.

a = 0·39257

V . 0·03 = 0·091

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi \cdot 10^6$
(a)	4·73 mgm.	4·75 mgm.	4·19 mgm.	2·77168 gm.	0·561
	4·74 mgm.				
	4·77 mgm.				
(b)	4·68 mgm.	4·69 mgm.	4·13 mgm.	2·75058 gm.	0·557
	4·69 mgm.				
(c)	4·78 mgm.	4·81 mgm.	4·25 mgm.	2·79372 gm.	0·564
	4·88 mgm.				
	4·78 mgm.				

Mean Value = $-0{\cdot}561 \cdot 10^{-6}$

(Continued)

(17) Ammonium Propionate. $C_2H_5COONH_4$

Pull of tube 1 = −0·28 mgm.

α = 0·92737

v. 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	2·56 mgm. 2·56 mgm.	2·56 mgm.	2·28 mgm.	3·36969 gm.	0·598
(b)	2·59 mgm. 2·59 mgm.	2·59 mgm.	2·31 mgm.	3·41174 gm.	0·601
(c)	2·57 mgm. 2·60 mgm. 2·58 mgm.	2·58 mgm.	2·30 mgm.	3·40000 gm.	0·599

Mean Value = $-0{\cdot}599 . 10^{-6}$

(Continued)

(18) <u>Ammonium Oxalate.</u> $(COONH_4)_2H_2O$

Pull of tube 2 = -0·75 mgm.

α = 0·43651

V . 0·03 = 0·090

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi . 10^6$
(a)	5·14 mgm. 5·17 mgm. 5·13 mgm.	5·15 mgm.	4·40 mgm.	3·18098 gm.	0·571
(b)	5·25 mgm. 5·30 mgm. 5·32 mgm.	5·29 mgm.	4·54 mgm.	3·25660 gm.	0·582
(c)	5·44 mgm. 5·42 mgm. 5·42 mgm.	5·43 mgm.	4·68 mgm.	3·30095 gm.	0·592

Mean Value = $-0{\cdot}582 . 10^{-6}$

(Continued)

(19) <u>α-Naphthylamine.</u> $C_{10}H_7NH_2$

Pull of tube 1 = -0•63 mgm.

α = 0•41315

V. . 0•03 = 0•096

	Pull (negative) Tube + Material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material	$-\chi . 10^6$
(a)	4•14 mgm. 4•13 mgm. 4•14 mgm.	4•14 mgm.	3•71 mgm.	2•57974 mgm.	0•557
(b)	4•08 mgm. 4•20 mgm. 4•11 mgm.	4•13 mgm.	3•70 mgm.	2•57943 mgm.	0•556

Mean Value = $-0 \cdot 557 . 10^{-6}$

(Continued)

(20) β-Naphthylamine. $C_{10}H_7NH_2$

Pull of tube 5 = −0·62 mgm.

$a = 0{\cdot}41056$

V . 0·03 = 0·094

	Pull (negative) Tube + Material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	4·06 mgm. 4·01 mgm.	4·04 mgm.	3·42 mgm.	2·37803 gm.	0·551
(b)	4·04 mgm. 4·16 mgm.	4·10 mgm.	3·48 mgm.	2·37789 gm.	0·561
(c)	4·18 mgm. 4·15 mgm. 4·21 mgm.	4·18 mgm.	3·56 mgm.	2·46550 gm.	0·555

Mean Value = $-0{\cdot}556 . 10^{-6}$

(Continued)

(21) <u>Meta-Toluidine</u>. $C_6H_4CH_3NH_2$

Pull of tube 1 = -0·63 mgm.

α = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + Material.	Mean Pull (negative) Tube + Material.	Pull (negative) Material alone.	Weight of Material.	$-\chi.10^6$
(a)	5·99 mgm. 6·08 mgm. 6·03 mgm.	6·03 mgm.	5·40 mgm.	3·14725 gm.	0·678
(b)	6·11 mgm. 6·12 mgm. 6·09 mgm.	6·11 mgm.	5·48 mgm.	3·15062 gm.	0·688
(c)	6·37 mgm. 6·33 mgm. 6·33 mgm.	6·34 mgm.	5·71 mgm.	3·15888 gm.	0·700

Mean Value = $-0·689 .10^{-6}$

(Continued)

(22) <u>Para-Toluidine</u>. $C_6H_4CH_3NH_2$

Pull of tube 5 = -0·62 mgm.

a = 0·41056

V . 0·03 =0·094

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	4·99 mgm. 4·95 mgm.	4·97 mgm.	4·35 mgm.	2·49899 gm.	0·675
(b)	5·36 mgm. 5·25 mgm.	5·31 mgm.	4·69 mgm.	2·65862 gm.	0·689
(c)	5·34 mgm. 5·28 mgm. 5·28 mgm.	5·30 mgm.	4·69 mgm.	2·55924 gm.	0·714

Mean Value = $-0·693 . 10^{-6}$

(Continued)

(23) <u>Hydroxylamine Hydrochloride.</u> $NH_2OH.HCl$

Pull of tube 1 = -0·63 mgm.

α = 0·41315

V . 0·03 = 0·096

	Pull (negative) Tube + Material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	6·02 mgm. 5·97 mgm. 6·05 mgm.	6·01 mgm.	5·38 mgm.	3·30890 gm.	0·643
(b)	6·05 mgm. 6·12 mgm.	6·09 mgm.	5·46 mgm.	3·40136 gm.	0·635
(c)	6·02 mgm. 6·08 mgm.	6·05 mgm.	5·42 mgm.	3·36033 gm.	0·638

Mean Value = $-0·639 . 10^{-6}$

(Continued)

(24) Hydroxylamine Sulphate. $2NH_2OH.H_2SO_4$

Pull of tube 1 = -0·66 mgm.

α = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi \cdot 10^6$
(a)	5·23 mgm. 5·29 mgm.	5·26 mgm.	4·60 mgm.	3·77339 gm.	0·478
(b)	5·25 mgm. 5·25 mgm.	5·25 mgm.	4·59 mgm.	3·77258 gm.	0·477
(c)	5·29 mgm. 5·41 mgm.	5·35 mgm.	4·69 mgm.	3·79460	0·485

Mean Value = $-0{\cdot}480.10^{-6}$

(Continued)

(25) Hydrazine Hydrochloride. $N_2H_4.HCl$

Pull of tube 1 = −0·63 mgm.
α = 0·41315
V . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi . 10^6$
(a)	5·83 mgm. 5·83 mgm. 5·86 mgm.	5·84 mgm.	5·21 mgm.	3·18067 gm.	0·647
(b)	5·89 mgm. 5·82 mgm. 5·68 mgm.	5·80 mgm.	5·17 mgm.	3·14054 gm.	0·650
(c)	5·59 mgm. 5·86 mgm. 5·91 mgm.	5·79 mgm.	5·16 mgm.	3·08066 gm.	0·653

Mean Value = $-0\cdot650.\ 10^{-6}$

(Continued)

(26) Hydrazine Sulphate. $N_2H_4.H_2SO_4$

Pull of tube 1 =-0·66 mgm.

α = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	5·87 mgm. 5·78 mgm.	5·83 mgm.	5·17 mgm.	4·22277 gm.	0·483
(b)	5·98 mgm. 6·06 mgm.	5·96 mgm.	5·30 mgm.	4·25574 gm.	0·492
(c)	5·79 mgm. 5·93 mgm. 5·93 mgm.	5·88 mgm.	5·22 mgm.	4·25348 mg.	0·485

Mean Value = $-0·487.10^{-6}$

(Continued)

(27) Hydrazine Hydrate. $N_2H_4.H_2O$

Pull of tube 1 = -0·63 mgm.

a = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	6·38 mgm. 6·41 mgm. 6·41 mgm.	6·41 mgm.	5·78 mgm.	3·28818 gm.	0·697
(b)	6·56 mgm.	6·56 mgm.	5·93 mgm.	3·29000 gm.	0·715
(c)	6·50 mgm. 6·61 mgm. 6·63 mgm.	6·58 mgm.	5·95 mgm.	3·29135 gm.	0·718

Mean Value = $-0·710.10^{-6}$

(Continued)

(28) Phenylhydrazine Hydrochloride. $C_6H_5NHNH_2HCl$

Pull of tube 5 = -0·62 mgm.

$a = 0{\cdot}41056$

$v \,.\, 0{\cdot}03 = 0{\cdot}094$

	Pull (negative) Tube + Material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi . 10^6$
(a)	6·73 mgm. 6·73 mgm. 6·72 mgm.	6·73 mgm.	6·11 mgm.	3·66791 gm.	0·658
(b)	6·55 mgm. 6·66 mgm. 6·58 mgm.	6·60 mgm.	5·98 mgm.	3·64714 gm.	0·647
(c)	6·30 mgm. 6·16 mgm. 6.21 mgm.	6·22 mgm.	5·60 mgm.	3·31907 gm.	0·664

Mean Value = $-0{\cdot}656.10^{-6}$

(Continued)

(29) Monomethylaniline. $C_6H_5NH(CH_3)$

Pull of tube 1 = −0·65 mgm.

α = 0·41315

V . 0·03 = 0·096

	Pull (negative) Tube + Material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	6·13 mgm. 6·10 mgm.	6·12 mgm.	5·47 mgm.	3·15041 gm.	0·687
(b)	6·20 mgm. 6·13 mgm. 6·18 mgm.	6·17 mgm.	5·52 mgm.	3·15342 gm.	0·693
(c)	6·08 mgm. 6·09 mgm.	6·09 mgm.	5·44 mgm.	3·14425 gm	0·686

Mean Value = $-0{\cdot}689 .\ 10^{-6}$

(Continued)

(30) Monoethylaniline. $C_6H_5NH(C_2H_5)$

Pull of tube 1 = -0·65 mgm.

a = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	6·14 mgm. 6·23 mgm.	6·19 mgm.	5·54 mgm.	3·07338 gm.	0·714
(b)	6·18 mgm. 6·15 mgm.	6·17 mgm.	5·52 mgm.	3·07264 gm.	0·711
(c)	6·15 mgm. 6·10 mgm. 6.05 mgm.	6·10 mgm.	5·45 mgm.	3.07045 gm.	0·702

Mean Value = $-0{\cdot}709.10^{-6}$

(Continued)

(31) Dimethylaniline. $C_6H_5N(CH_3)_2$

Pull of tube 1 = -0·65 mgm.

α = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material	$-\chi \cdot 10^6$
(a)	6·08 mgm. 6·07 mgm.	6·07 mgm.	5·42 mgm.	3·05104 gm.	0·703
(b)	6·09 mgm. 6·10 mgm. 6·10 mgm.	6·10 mgm.	5·45 mgm.	3·05291 gm.	0·707
(c)	6·20 mgm. 6·18 mgm.	6·19 mgm.	5·54 mgm.	3·06310 gm.	0·716

Mean Value = $-0 \cdot 709 . 10^{-6}$

(Continued)

(32) **Diethylaniline.** $C_6H_5N(C_2H_5)_2$

Pull of tube 1 = -0·65

α = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	6·18 mgm. 6·18 mgm.	6·18 mgm.	5·53 mgm.	2·99186 gm.	0·732
(b)	6·18 mgm. 6·13 mgm.	6·16 mgm.	5·51 mgm.	2·99030 gm.	0·729
(c)	6·24 mgm. 6·23 mgm. 6·18 mgm.	6·22 mgm.	5·57 mgm.	3·00736 gm.	0·733

Mean Value = $-0·731.10^{-6}$

(Continued)

(33) Monomethylamine Hydrochloride. $CH_3HN_2.HCl$

Pull of tube 1 = -0·66 mgm.

α = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	4·74 mgm. 4·70 mgm.	4·72 mgm.	4·06 mgm.	2·30381 gm.	0·689
(b)	4·71 mgm. 4·71 mgm. 4·73 mgm.	4·72 mgm.	4·06 mgm.	2·30531 gm.	0·688
(c)	4·72 mgm. 4·76 mgm. 4·74 mgm.	4·74 mgm.	4·08 mgm.	2·31282 gm.	0·690
(d)	4·69 mgm. 4·79 mgm. 4·79 mgm.	4·76 mgm.	4·10 mgm.	2·32468 gm.	0·689

Mean Value = $-0·689 . 10^{-6}$

(Continued)

(34) <u>Dimethylamine Hydrochloride</u>. $(NH(CH_3)_2HCl$

Pull of tube 1 = -0·31 mgm.

$\alpha\beta$ = 0·92737

v .0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	2·18 mgm. 2·19 mgm. 2·22 mgm.	2·20 mgm.	1·89 mgm.	2·32777 gm.	0·712
(b)	2·34 mgm. 2·32 mgm.	2·33 mgm.	2·02 mgm.	2·44793 gm.	0·726
(c)	2·30 mgm. 2·28 mgm. 2·31 mgm.	2·30 mgm.	1·99 mgm.	2·43708 gm.	0·718

Mean Value = $-0·719.10^{-6}$

(Continued)

(35) Trimethylamine Hydrochloride. $N(CH_3)_3HCl$

Pull of tube 1 = -0·31 mgm.

a = 0·92737

v. . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) material alone.	Weight of Material.	$-\chi . 10^6$
(a)	2·05 mgm. 2·00 mgm.	2·03 mgm.	1·72 mgm.	2·02769 gm.	0·739
(b)	2·02 mgm. 1·96 mgm. 2·01 mgm.	2·00 mgm.	1·69 mgm.	1·99848 gm.	0·737
(c)	2·07 mgm. 1·90 mgm. 1·97 mgm.	1·98 mgm.	1·67 mgm.	1·99659 gm.	0·728

Mean Value = $-0·735 . 10^{-6}$

(Continued)

(36) Diethylamine Hydrochloride. $NH(C_2H_5)_2HCl$

Pull of tube 1 = -0·31 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi . 10^6$
(a)	1·87 mgm. 1·84 mgm.	1·86 mgm.	1·55 mgm.	1·80633 gm.	0·743
(b)	1·97 mgm. 1·97 mgm.	1·97 mgm.	1·66 mgm.	1·94518 gm.	0·743
(c)	1·97 mgm. 1·98 mgm.	1·98 mgm.	1·67 mgm.	1·96061 gm.	0·741

Mean Value = $-0{\cdot}742 . 10^{-6}$

(Continued)

(37) Tetraethylammonium Chloride. $N(C_2H_5)_4Cl$

Pull of tube 1 = -0·27 mgm.

α = 0·92737

v. 0·03 = 0·096.

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	2·36 mgm.	2·35 mgm.	2·08 mgm.	2·49452 gm.	0·735
	2·35 mgm.				
	2·35 mgm.				
(b)	2·39 mgm.	2·39 mgm.	2·12 mgm.	2·52061 gm.	0·740
	2·39 mgm.				
	2·38 mgm.				
(c)	2·38 mgm.	2·36 mgm.	2·09 mgm.	2·51544 gm.	0·730
	2·34 mgm.				

Mean Value = -0·735 . 10^{-6}

(Continued)

(38) Tetramethylammonium Bromide. $N(CH_3)_4Br$

Pull of tube 1 = -0·30 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	2·38 mgm. 2·32 mgm.	2·35 mgm.	2·05 mgm.	3·24037 gm.	0·557
(b)	2·41 mgm. 2·39 mgm. 2·42 mgm.	2·41 mgm.	2·11 mgm.	3·32613 gm.	0·559
(c)	2·40 mgm. 2·41 mgm.	2·41 mgm.	2·11 mgm.	3·26169 gm.	0·571

Mean Value = $-0·561.10^{-6}$

(Continued)

(39) Tetraethylammonium Bromide. $N(C_2H_5)_4Br$

Pull of tube 1 = -0·37 mgm.

a = 0·92737

v . 0.03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	2·65 mgm. 2·65 mgm. 2·62 mgm.	2·64 mgm.	2·27 mgm.	3·23703 gm.	0·605
(b)	2·62 mgm. 2·65 mgm. 2·62 mgm.	2·63 mgm.	2·26 mgm.	3·19740 gm.	0·608
(c)	2·64 mgm. 2·65 mgm. 2·63 mgm.	2·64 mgm.	2·27 mgm.	3·22707 gm.	0·605

Mean Value = $-0{\cdot}606 . 10^{-6}$

(Continued)

(40) <u>Tetramethylammonium Iodide.</u> $N(CH_3)_4I$

Pull of tube 1 = -0·43 mgm.

α = 0·92737

v . 0·03 = 0·096

(a)	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	2·86 mgm. 2·85 mgm.	2·86 mgm.	2·43 mgm.	4·28833 gm.	0·503
(b)	2·84 mgm. 2·85 mgm. 2·82 mgm.	2·84 mgm.	2·41 mgm.	4·27959 gm.	0·500
(c)	2·92 mgm. 2·90 mgm. 2·92 mgm.	2·91 mgm.	2·48 mgm.	4·37166 gm.	0·504

Mean Value = $-0·502 .10^{-6}$

(Continued)

(41) Tetraethylammonium Iodide. $N(C_2H_5)_4I$

Pull of tube 1 = -0·43 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of Material.	$-\chi . 10^6$
(a)	2·63 mgm. 2·65 mgm.	2·64 mgm.	2·21 mgm.	3·45853 gm.	0·565
(b)	2·66 mgm. 2·60 mgm. 2·65 mgm.	2·64 mgm.	2·21 mgm.	3·43841 gm.	0·568
(c)	2·63 mgm. 2·63 mgm.	2·63 mgm.	2·20	3·41761 gm.	0·569

Mean Value = $-0·567 . 10^{-6}$

(Continued)

(42) Ammonium Fluoride Solution.[16·86%]

Pull of tube 1 = −0·29 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	2·98 mgm. 2·98 mgm.	2·98 mgm.	2·69 mgm.	3·40137 gm.	0·706
(b)	2·95 mgm. 2·98 mgm.	2·97 mgm.	2·68 mgm.	3·40146 gm.	0·704
(c)	2·97 mgm. 2·96 mgm. 2·97 mgm.	2·97 mgm.	2·68 mgm.	3·39406 gm.	0·705

Mean Value = $-0{\cdot}705.10^{-16}$

$\therefore \chi_{\text{Solute}} = -0{\cdot}636.10^{-6}$

(Continued)

(43) Ammonium Chloride (16·82% solution).

Pull of tube 1 = -0·30 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	3·01 mgm. 3·01 mgm. 3·00 mgm.	3·01 mgm.	2·71 mgm.	3·34827 gm.	0·722
(b)	2·99 mgm. 2·99 mgm.	2·99 mgm.	2·69 mgm.	3·34807 gm.	0·717
(c)	3·04 mgm. 3·02 mgm. 3·01 mgm.	3·02 mgm.	2·72 mgm.	3·35795 gm.	0·722

Mean Value = $-0{\cdot}720\ .10^{-6}$

$\therefore \chi_{\text{Solute}} = -0{\cdot}719\ .10^{-6}$

(Continued)

(44) Ammonium Bromide (16·73% solution)

Pull of tube 1 = -0·43 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^{-}$
(a)	3·12 mgm. 3·10 mgm.	3·11 mgm.	2·68 mgm.	3·49690 gm.	0·683
(b)	3·12 mgm. 3·10 mgm.	3·11 mgm.	2·68 mgm.	3·49680 gm.	0·683
(c)	3·14 mgm. 3·13 mgm. 3·15 mgm.	3·14 mgm.	2·71 mgm.	3·50590 gm.	0·688

Mean Value = $-0{\cdot}685 \,.10^{-6}$

$\therefore \chi_{\text{solute}} = -0{\cdot}508.10^{-6}$

(Continued)

(45) Ammonium Iodide (16·82% solution)

Pull of tube 1 = -0·43 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	3·13 mgm. 3·11 mgm. 3·08 mgm.	3·11 mgm.	2·68 mgm.	3·53063 gm.	0·677
(b)	3·10 mgm. 3·11 mgm.	3·11 mgm.	2·68 mgm.	3·53731 gm.	0·675
(c)	3·11 mgm. 3·12 mgm. 3·08 mgm.	3·10 mgm.	2·67 mgm.	3·52810 gm.	0·675

Mean Value = $-0·676 . 10^{-6}$

$\therefore \chi_{\text{solute}} = -0·458 . 10^{-6}$

(continued)

(46) Ammonium Nitrate Solution [14·06%]

Pull of tube 1 = −0·28 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	2·89 mgm. 2·90 mgm.	2·90 mgm.	2·62 mgm.	3·39061 gm.	0·688
(b)	2·86 mgm. 2·86 mgm.	2·86 mgm.	2·58 mgm.	3·39058 gm.	0·676
(c)	2·85 mgm. 2·83 mgm. 2·83 mgm.	2·84 mgm.	2·56 mgm.	3·37155 gm.	0·676

Mean Value = $-0{\cdot}680.10^{-6}$

$\therefore \chi_{\text{Solute}} = -0{\cdot}436\ .10^{-6}$

(Continued)

(47) Sodium Formate. $HCOONa.H_2O$

Pull of tube 1 = −0·28 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	1·87 mgm. 1·86 mgm. 1·86 mgm.	1·86 mgm.	1·58 mgm.	2·90280 gm.	0·473
(b)	1·87 mgm. 1·83 mgm. 1·88 mgm.	1·86 mgm.	1·58 mgm.	2·89007 gm.	0·475
(c)	1·87 mgm. 1·89 mgm.	1·88 mgm.	1.60 mgm.	2·93176 gm.	0·473

Mean Value = $-0·474 .10^{-6}$

(Continued)

(48) Sodium Propionate. C_2H_5COONa

Pull of tube 1 = -0·27 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi . 10^6$
(a)	1·88 mgm. 1·81 mgm. 1·83 mgm.	1·84 mgm.	1·57 mgm.	2·63058 gm.	0·518
(b)	1·84 mgm. 1·83 mgm.	1·84 mgm.	1·57 mgm.	2·68083 gm.	0·508
(c)	1·87 mgm. 1·87 mgm. 1·86 mgm.	1·87 mgm.	1·60 mgm.	2·71404 gm.	0·512

Mean Value = $-0·513 . 10^{-6}$

(Continued)

(49) Potassium Formate HCOOK

Pull of tube 1 = -0·28 mgm.

a= 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	2·08 mgm. 2·05 mgm.	2·07 mgm.	1·79 mgm.	3·99023 gm.	0·393
(b)	2·05 mgm. 2·04 mgm. 2·08 mgm.	2·05 mgm.	1·77 mgm.	3·96038 gm.	0·391
(c)	2·10 mgm. 2·09 mgm. 2·10 mgm.	2·10 mgm.	1·82 mgm.	4·04404 gm.	0·392
(d)	2·05 mgm. 2·11 mgm. 2·09 mgm.	2·08 mgm.	1·80 mgm.	4·02761 gm.	0·391

Mean Value = $-0\cdot392 .10^{-6}$

(Continued)

(50) <u>Potassium Propionate.</u> C_2H_5COOK

Pull of tube 1 = -0°27 mgm.

α = 0°92737

v . 0·03 = 0°096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	2°19 mgm. 2·20 mgm.	2·20 mgm.	1·93 mgm.	3°37273 gm.	0°503
(b)	2°17 mgm. 2°19 mgm.	2°18 mgm.	1·91 mgm.	3°32038 gm.	0°505
(c)	2°14 mgm. 2°22 mgm. 2°18 mgm.	2°18 mgm.	1·91 mgm.	3·34083 gm.	0°502

Mean Value = $-0.503 .10^{-6}$

(Continued)

(51) Sodium Sulphate. $Na_2SO_4.IOH_2O$

Pull of tube 1 = -0·65 mgm.

a = 0·41315

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	5·68 mgm.	5·68 mgm.	5·03 mgm.	3·53099 gm.	0·561
	5·68 mgm.				
(b)	5·74 mgm.	5·74 mgm.	5·09 mgm.	3·54179 gm.	0·567
	5·74 mgm.				
(c)	5·54 mgm.	5·74 mgm.	5·09 mgm.	3·54157 gm.	0·567
	5·85 mgm.				
	5·82 mgm.				

Mean Value = $-0{\cdot}565 .10^{-6}$

(Continued)

(52) <u>Rubidium Sulphate</u>. Rb_2SO_4

Pull of tube 1 = -0·39 mgm.

α = 0·92737

V . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material.	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	2·16 mgm. 2·20 mgm. 2.23 mgm.	2·20 mg.	1·81 mgm.	4·96105 gm.	0·319
(b)	2·18 mgm. 2·19 mgm.	2·19 mgm.	1·80 mgm.	4·93675 gm.	0·318
(c)	2·17 mgm. 2·16 mgm.	2·17 mgm.	1·78 mgm.	4·92146 gm.	0·317

Mean Value = $-0{\cdot}318.10^{-6}$

(Continued)

(53) <u>Caesium Sulphate</u>. CO_2SO_4

Pull of tube 1 = -0·28 mgm.

α = 0·92737

v . 0·03 = 0·096

	Pull (negative) Tube + material.	Mean Pull (negative) Tube + material	Pull (negative) Material alone.	Weight of material.	$-\chi.10^6$
(a)	3·64 mgm.	3·65 mgm.	3·37 mgm.	9·17985 gm.	0·306
	3·68 mgm.				
	3·62 mgm.				
(b)	3·60 mgm.	3·61 mgm.	3·33 mgm.	9·70436 gm.	0·308
	3·61 mgm.				
(c)	3·58 mgm.	3·61 mgm.	3·33 mgm.	9·86995 gm.	0·303
	3·63 mgm.				
	3· 62mgm.				

Mean Value = $-0·306.10^{-6}$

(8) ANALYSIS OF THE COMPOUNDS UNDER INVESTIGATION

(1) Ammonium Bromide. NH_4Br

(Pure)

Qualitative Analysis. Impurities: trace of Na; SO_4''. $Mg^{\cdot\cdot}$

No Fe, Co, Ni, detectable.

Recrystallised once from hot water in a platinum dish, dried at the pump and then in an evacuated desiccator to prevent atmospheric decomposition.

Quantitative Analysis. (gravimetric) 25 cc. of a solution containing a known concentration of ammonium bromide were diluted to 300cc. and the cold solution made slightly acid with dilute nitric acid. A solution of silver nitrate was added slowly with constant stirring until the precipitate collected together, and further addition of the reagent caused no further precipitation. The mixture was heated to boiling, allowed to settle in the dark, filtered through a sintered crucible, and washed with water containing a little nitric acid until free from chloride; then twice with water to remove the nitric acid. The precipitate was dried at 130° to constant weight.

Results.

Weight of AgBr(A) = 0.2855 gm. (B) = 0.2840 gm.

Weight of NH_4Cl per 250 cc. = 1.4814 gm.

Weight of Br (found = 82.03% (A) 81.602% (B)

Weight of Br (calculated) = 81.60%

$\therefore$ Mean % Purity of NH_4Br = 100.27% (due probably to HBr impurity)

Recrystallised also once from 95% hot alcohol in which hydrolysis was negligible; dried rapidly at the pump, and in a desiccator in the dark to prevent decomposition.

Quantitative Analysis. (Gravimetric). The estimation was carried out as before.

Results.

Weight of AgBr (A) = 0.2725 gm. (B) = 0.2868 gm.

Weight of NH_4Br (A) = 0.1425 gm. (B) = 0.1500 gm.

Weight of Br (found) (A) = 81.38% (B) = 81.38%

Weight of Br (calculated) = 81.58%

$\therefore$ Mean % Purity of NH_4Br = 99.75%

(2) Ammonium Iodide. NH_4I

Qualitative Analysis. Impurities: trace of Na; K; SO_4'', NO_3 Al;$^{\cdot\cdot}$
No, Fe, Co, Ni, detectable.

Quantitative Analysis. (gravimetric). The iodide was estimated as silver iodide in a manner exactly similar to that employed in the estimation of ammonium bromide.

Results. Weight of AgI (A) = 0.2961 gm. (B) = 0.2946 gm.
Weight of NH_4I per 250 cc. = 1.8371 gm.
Weight of I (found) = 87.10% (A). 86.69% (B).
Weight of I (calculated) = 87.52%.

∴ Mean Purity of NH_4I = <u>99·29%.</u>

(3) Ammonium Chromate. $(NH_4)_2CrO_4$

Qualitative Analysis. Impurities: trace of Na; K; SiO_3'', NO_3'.
$Mg^{\cdot\cdot}$ No Fe, Co, Ni detectable.

Quantitative Analysis. (gravimetric). The chromate was estimated as barium chromate in a manner exactly similar to that employed in the estimation of ammonium bichromate.

Results.

Weight of $BaCrO_4$ (A) = 0·4653 gm. (B) = 0·4620 gm.

Weight of $(NH_4)_2CrO_4$ = 3.0321 gm.

Weight of CrO_4 (found) = 70.26% (A) 69.76% (B).

Weight of CrO_4 (calculated) = 76.26%

∴ Mean % purity of $(NH_4)_2CrO_4$ = <u>91.88%.</u>

(4) Ammonium Dichromate. $(NH_4)_2Cr_2O_7$

(Pure Cryst)

Qualitative Analysis. Impurities: trace of $Na^{\bullet}$, $K^{\bullet}$, Cl', SiO_3'', Fe(very faint), no Co, Ni, detectable.

Recrystallised twice from hot water in a platinum dish, dried at the pump and then in a desiccator. On testing, it was found to be free from iron.

Quantitative Analysis. (gravimetric) 25 cc. of a solution containing approximately 0.1 gm. of chromium as ammonium bichromate were diluted to 300 cc. and made weakly acid with acetic acid. The solution was treated at the boiling temperature with a 10% solution of barium acetate added drop by drop, and was heated on a water bath until the precipitate settled. Complete precipitation was tested for by adding a little more reagent. The mixture was allowed to settle and cool, and was then filtered through a sintered crucible. The precipitate was washed with hot water until free from barium, and dried at 130° to constant weight.

Results

Weight of $BaCrO_4$(A) = 0.2924 gm. (B) = 0.2926 gm.
Weight of $(NH_4)_2Cr_2O_7$ = 1.4625 gm.
Weight of Cr_2O_7 (found) = 85.21%.(A). 85.27%.(B)
Weight of Cr_2O_7 (calculated) = 85.704%

$\therefore$ Mean % Purity of $(NH_4)_2Cr_2O_7$ = 99.49%

(5) Ammonium Sulphate. $(NH_4)_2SO_3.H_2O$

(Cryst. Freshly ppd)

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable.

Recrystallisation was not attempted owing to the instability of the salt, but it was dried in a desiccator before use since it was very deliquescent.

Quantitative Analysis. (volumetric) Finkener-Rose (55), Volhard (56), Raschig (57). About 0.8 gm. of ammonium sulphite were weighed out accurately into a 500 cc. conical flask, and 175 cc. of standard iodine solution were rapidly added. The excess of iodine was titrated against standard sodium thiosulphate solution using starch solution as indicator. The iodine solution was previously standardised against the sodium thiosulphate solution using the same indicator.

Results

Normality of $Na_2S_2O_3$ = 0.10014 N

Titration value of $Na_2S_2O_3$ = 23.68 cc.

∴ Normality of I_2 = 0.094798 N

Titration value of $Na_2S_2O_3$ = 17.80 cc.(A) 18.65 cc.(B)

∴ No. of ccs. of $I_2 \equiv (NH_4)_2SO_3.H_2O$ = { 156.20 cc. (A)
{ 155.31 cc. (B)

∴ No. of gms of SO_2 in solution = { 0.35348 gm.(A)
{ 0.35156 gm.(B)

No. of gms. of $(NH_4)_2SO_3.H_2O$ weighed out = (0.7511 gm. (A)
(0.7487 gm. (B)

~~∴ Weight of SO_2 (found) = 47.07% (A). 46.96% (B).~~
~~Weight of SO_2 (calculated) = 47.76%~~

~~∴ Mean % Purity of $(NH_4)_2SO_3.H_2O$ = 98.42%.~~

$\therefore$ Weight of SO_2 (found) = 47.07%(A). 46.96%(B).

Weight of SO_2 (calculated) = 47.76%

$\therefore$ Mean % Purity of $(NH_4)_2SO_3.H_2O$ = <u>98.42%</u>

(6) Ammonium Thiosulphate. $(NH_4)_2S_2O_3$

(Laboratory Reagent)

Qualitative Analysis. Impurities

No Fe, Co, Ni, detectable

Quantitative Analysis. (volumetric). 25 cc. portions of standard iodine solution were titrated against a solution containing about 5.0 gms. of ammonium thiosulphate per 250 cc. using starch solution as indicator. The iodine solution was previously standardised using standard sodium thiosulphate solution, with the same indicator.

Results

Normality of $Na_2S_2O_3$ = 0.10028 N.

Titration value of $Na_2S_2O_3$ = 23.45 cc.

$\therefore$ Normality of I_2 = 0.094028 N.

Titration value of $(NH_4)_2S_2O_3$ = 19.02 cc.

$\therefore$ Normality of $(NH_4)_2S_2O_3$ = 0.12888 N.

$\therefore$ No. of gms. of S_2O_3 in solution = 3.6124 gm.

No. of gms. of $(NH_4)_2S_2O_3$ weighed out = 4.8618 gm.

$\therefore$ Weight of S_2O_3 (found) = 74.30%

Weight of S_2O_3 (calculated) = 75.63%

$\therefore$ Mean % Purity of $(NH_4)_2S_2O_3$ = 98.24%

(7) Ammonium Molybdate. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$

(Pure Cryst)

Qualitative Analysis. Impurities: trace of $Na^{\cdot}$, $K^{\cdot}$, $Mg^{\cdot\cdot}$ $NO_3^{\prime}$
No Fe, Co, Ni, detectable.

Qualitative Analysis. (gravimetric) 200 cc. of a solution containing approximately 0.1 gm. of ammonium molybdate were heated to boiling and maintained near boiling point over a small flame. From a burette a solution of lead acetate was added (4 gm. of lead acetate and 1 cc. of glacial acetic acid in 100 cc. of water) dropwise and with constant stirring. When a slight excess of precipitant had been added, the milky solution cleared appreciably. The mixture was boiled for a few minutes with stirring, allowed to settle, and complete precipitation tested for by the addition of a few drops of reagent. It was necessary to avoid a large excess of reagent. The mixture was digested on the steam bath for 15-30 minutes, and the clear solution decanted through a sintered crucible; the precipitate was washed by decantation three or four times with 75 cc. portions of hot 2-3% ammonium nitrate solution. The precipitate was transferred to the filter and washed until all soluble salts were removed. It was dried at 130° to constant weight.

Results

Weight of $PbMoO_4$ = 0.3120 gm. (A), 0.3414 gm. (B)

Weight of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ = $\begin{cases} 0.1448 \text{ gm. (A)} \\ 0.1597 \text{ gm. (B)} \end{cases}$

Weight of MoO_4 (found) = 93.87%. (A). 93.13%. (B)

Weight of MoO_4 (calculated on the above formula) = 94.75%

∴ Mean % Purity of $(NH_4)_6Mo_6O_{24}\cdot 4H_2O$ = <u>98.48%</u>

(8) Hydroxylamine Hydrochloride. $NH_2OH.HCl$

(Pure)

Qualitative Analysis. Impurities: no trace of inorganic impurity
No Fe, Co, Ni, detectable.

Recrystallised once from hot alcohol in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Volumetric) About 0.1 gm. of hydroxylamine hydrochloride were placed in a 500 cc. flask and dissolved in a little water. 30 cc. of a cold saturated solution of ferric ammonium alum were added and 10 cc. of dilute sulphuric acid (1:4). The contents of the flask were heated to boiling and kept at this temperature for five minutes, after which the solution was diluted with distilled water to a volume of approximately 300 cc. and immediately titrated with potassium permanganate solution which was first standardised with ferrous ammonium sulphate solution.

Results

Normality of $FeSO_4.(NH_4)_2SO_4.6H_2O$ = 0.10053 N.

Titration value of $KMnO_4$ with " = 22.97 cc.

∴ Normality of $KMnO_4$ = 0.10937 N.

Titration value of $KMnO_4$ with $NH_2OH.HCl$ = 31.70 cc. (A)
29.15 cc. (B)

∴ No. of gms. of NH_2OH in solution = 0.64625 gm. (A) 0.60532 gm. (B)

No. of gms. of $NH_2OH.HCl$ weighed out = 0.1111 gm. (A)
0.1208 gm. (B)

.˙. Weight of NH_2OH (found) = 47·42% (A). 47·42% (B)

Weight of NH_2OH (calculated) = 47.50%

.˙. Mean % Purity of $NH_2OH.HCl$ = 99.84%

(9) Hydroxylamine Sulphate. $2NH_2OH.H_2SO_4$

Qualitative Analysis. Impurities

No Fe, Co, Ni, detectable.

Recrystallised once from hot water in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Volumetric) The hydroxylamine was estimated in exactly the same manner as was employed in the case of hydroxylamine hydrochloride.

Results

Normality of $FeSO_4.(NH_4)_2SO_4.6H_2O$ = 0.10009 N
Titration value of $KMnO_4$ with " = 29.60 cc.
$\therefore$ Normality of $KMnO_4$ = 0.084528 N.
Titration value of $KMnO_4$ with $2NH_2OH.H_2SO_4$ = 26.35 cc. (A)
31.50 cc. (B)

$\therefore$ No. of gms. of NH_2OH in solution = 0.36782 gm. (A)
0.43984 gm. (B)

No. of gms. of $2NH_2OH.H_2SO_4$ weighed out = 0.0925 gm. (A)
0.1120 gm. (B)

$\therefore$ Weight of NH_2OH (found) = 39.74% (A)
39.28% (B)

Weight of NH_2OH (calculated) = 40.25%

$\therefore$ Mean % Purity of $2NH_2OH.H_2SO_4$ = 98.18%

(The volumetric method employed in the estimation of hydroxylamine salts was that due to Raschig.[58]).

The ionic equation for the reaction is:-

$$2NH_2OH + 4Fe^{+++} \rightarrow 4Fe^{++} + N_2O + 4H^+ + H_2O$$

(10) Hydrazine Hydrochloride. $N_2H_4.HCl$

(Pure Cryst)

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable.

Recrystallised from hot alcohol in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Volumetric) About 0.05 gm. of hydrozine hydrochloride was weighed into a 250 cc. conical flask and a mixture of 30 cc. of concentrated hydrochloric acid, 20 cc. of water and 5 cc. of chloroform added. The mixture was titrated against 0.1 N potassium iodate which was run in slowly from a burette, with shaking between the additions, until the organic layer was just decolorised:-

$$IO_3^- + N_2H_4 + 2H^+ = I^+ + N_2 + 3H_2O$$

Results

Normality of KIO_3 = 0.09983 N

Titration value of KIO_3 with $N_2H_4.HCl$ = 30.62 cc. (A)
= 28.72 cc. (B)

.˙. No. of gms. of N_2H_4 in solution = 0.0245 gm. (A)
0.0230 gm. (B)

No. of gms. of $N_2H_4.HCl$ weighed out = 0.0533 gm. (A)
0.0500 gm. (B)

.˙. Weight of N_2H_4 (found) = 45.98% (A)
= 46.10% (N)

Weight of N_2H_4 (calculated) = 46.74%

.˙. Mean % Purity of $N_2H_4.HCl$ = 98.53%

(11) Phenylhydrazine Hydrochloride. $C_6H_5NHNH_2.HCl$
(Pure)

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable

Recrystallised from hot water in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Gravimetric) Estimation of the chloride as silver chloride in aqueous solution gave results too high owing to the reducing properties of the phenylhydrazine, so that it was necessary to employ Carius's method. About 1 gm. of finely powdered pure silver nitrate was placed at the bottom of the unsealed Carius tube, and 1·5 - 2·0 cc. of fuming nitric acid added. About 0.3 gm. of phenylhydrazine hydrochloride was weighed into a small tube which was then allowed to slide gently into the inclined Carius tube so that it rested with the mouth above the liquid. The Carius tube was sealed and heated in an outer iron tube in a furnace, the temperature being allowed to rise to 260-270° in two hours, and maintained there for another four hours. After allowing to cool overnight the tube was carefully unsealed, and the silver chloride particles rinsed into a beaker and boiled for half an hour to ensure coagulation. The precipitate was then filtered and treated by a method exactly similar to that employed in the estimation of ammonium bromide.

Results

Weight of AgCl (A) = 0.3026 gm. (B) = 0.3088 gm.

Weight of $C_6H_5NHNH_2.HCl$ (A) = 0.3107 gm. (B) = 0.3187 gm.

Weight of Cl (found) (A) = 24.10% (B) = 23.98%

Weight of Cl (calculated) = 24.52%

∴ Mean % Purity of $C_6H_5NHNH_2.HCl$ = 98.03%

(12) Ammonium Formate. $HCOONH_4$

(Pure Cryst)

Qualitative Analysis. Impurities

No Fe, Co, Ni, detectable

Recrystallisation was not attempted owing to the instability of the salt, the decomposition rate being high at the boiling-point of alcohol, but it was dried in a desiccator since it was very deliquescent.

Quantitative Analysis. (volumetric) The method employed was that due to Lieben (59). About 0.50 gm. of ammonium formate were weighed out accurately into a 500 cc. conical flask, an excess of sodium carbonate was added to render the solution alkaline, and the solution was heated, since manganous acid does not settle well from a cold solution. Standard potassium permanganate was then run into the solution until the clear liquid above the precipitate appeared reddish. The equation for the reaction was:-

$$2KMnO_4 + 3HCOONH_4 = K_2CO_3 + (NH_4)_2CO_3 + 2MnO_2 + H_2O + NH_4HCO_3$$

Results

Normality of $FeSO_4.(NH_4)_2SO_4.6H_2O$ = 0.10009 N.

Titration value of $KMnO_4$ with " = 25.08 cc.

.˙. Normality of $KMnO_4$ = 0.09977 N.

Titration value of KMnO with $HCOONH_4$ } = 24.85 cc. (A)
24.70 cc. (B)

∴ No. of gms. of $HCOOH$ in solution = 0.39794 gm. (A)
0.34577 gm. (B)

∴ Weight of $HCOOH$ (found) = 72.96% (A)
72.96% (B)

Weight of $HCOOH$ (calc.) = 72.98%

∴ Mean % Purity = <u>99.95%</u>

(13) Monomethylamine Hydrochloride. $NH_2CH_3.HCl$

(14) Dimethylamine Hydrochloride. $NH(CH_3)_2.HCl$

(15) Trimethylamine Hydrochloride. $N(CH_3)_3.HCl$ (Laboratory Reagent)

Qualitative Analysis. Impurities

No Fe, Co, Ni, detectable.

Recrystallised once from hot water in a platinum dish, dried at the pump, and then in a desiccator.

Quantitative Analysis. (Gravimetric) The chloride in these three salts was estimated as silver chloride in a manner exactly similar to that employed in the estimation of ammonium bromide.

Results: (I) Monomethylamine Hydrochloride

Weight of AgCl(A) = 0.2376 gm. (B) = 0.3148 gm.

Weight of $NH_2CH_3.HCl$ (A) = 0.1127 gm. (B) = 0.1488 gm.

Weight of Cl (found) (A) = 52.16% (B) = 52.34%

Weight of Cl (calculated) = 52.44%

$\therefore$ Mean % Purity of $NH_2CH_3.HCl$ = 99.82%

(II) Dimethylamine Hydrochloride

Weight of AgCl (A) = 0.2818 gm. (B) = 0.2807 gm.

Weight of $NH(CH_3)_2.HCl$ (A) = 0.1695 gm. (B) = 0.1691 gm.

Weight of Cl (found) (A) = 43.07% (B) = 43.01%

Weight of Cl (calculated) = 43.48%

$\therefore$ Mean % Purity of $NH(CH_3)_2.HCl$ = 98.99%

(III) Trimethylamine Hydrochloride

Weight of AgCl (A) = 0.2996 gm. (B) = 0.3234 gm.

Weight of $N(CH_3)_3$.HCl (A) = 0.2010 gm. (B) = 0.2157 gm.

Weight of Cl (found) = 36.81% (A). (B) = 37.09%

Weight of Cl (calculated) = 37.10%

$\therefore$ Mean % Purity of $N(CH_3)_3$.HCl = 99.61%

(16) Diethylamine Hydrochloride. $NH(C_2H_5)_2.HCl$

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable

Recrystallised from hot water in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Gravimetric) The chloride was estimated as silver chloride in a manner exactly similar to that employed in the estimation of ammonium bromide.

Results

Weight of AgCl (A) = 0.2862 gm. (B) = 0.2987 gm.

Weight of $NH(C_2H_5)_2.HCl$ (A) = 0.2322 gm. (B) = 0.2433 gm.

Weight of Cl (found) (A) = 31.94% (B) = 31.79%

Weight of Cl (calculated) = 32.35%

∴ Mean % Purity of $NH(C_2H_5)_2.HCl$ = 98.52%

(17) Tetraethylammonium Chloride. $N(C_2H_5)_4Cl$

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable.

Recrystallised from hot alcohol in a platinum dish dried at the pump and then in a desiccator.

Quantitative Analysis. (Gravimetric) The chloride was estimated as silver chloride in a manner exactly similar to that employed in the estimation of ammonium bromide.

Results

Weight of AgCl (A) = 0.2824 gm. (B) = 0.2807 gm.

Weight of $N(C_2H_5)_4Cl$ (A) = 0.3312 gm. (B) = 0.3302 gm.

Weight of Cl (found) (A) = 21.08% (B) = 21.00%

Weight of Cl (calculated) = 21.40%

∴ Mean % Purity of $N(C_2H_5)_4Cl$ = 98.45%

(18) Tetramethylammonium Bromide. $H(CH_3)_4Br$

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable.

Recrystallised from hot water in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Gravimetric) The bromide was estimated as silver bromide in a manner exactly similar to that employed in the estimation of ammonium bromide.

Results

Weight of AgBr (A) = 0.2783 gm. (B) = 0.2895 gm.

Weight of $N(CH_3)_4Br$ (A) = 0.2334 gm. (B) = 0.2421 gm.

Weight of Br (found) (A) = 50.75% (B) = 50.89%

Weight of Br (calculated) = 51.89%

∴ Mean % Purity of $N(CH_3)_4Br$ = 98.22%

(19) Tetramethylammonium Iodide. $N(CH_3)_4I$

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable.

Recrystallised from hot water in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Gravimetric). The iodide was estimated as silver iodide in a manner exactly similar to that employed in the estimation of ammonium bromide.

Results

Weight of AgI. (A) = 0.3066 gm. (B) = 0.2902 gm.

Weight of $N(CH_3)_4I$ (A) = 0.2635 gm. (B) = 0.2502 gm.

Weight of I (found) (A) = 62.89%. (B) = 62.69%

Weight of I (calculated) = 63.10%

$\therefore$ Mean % Purity of $N(CH_3)_4I$ = 99.91%

(20) Tetraethylammonium Bromide. $N(C_2H_5)_4Br$

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable.

Recrystallised from hot water in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Gravimetric) The bromide was estimated as silver bromide in a manner exactly similar to that employed in the estimation of ammonium bromide.

Results

Weight of AgBr. (A) = 0.3201 gm. (B) = 0.2907 gm.

Weight of $N(C_2H_5)_4Br$ (A) = 0.3313 gm. (B) = 0.3277 gm.

Weight of Br (found) (A) = 37.50%. (B) = 37.74%

Weight of Br (calculated) = 38.02%

$\therefore$ Mean % Purity of $N(C_2H_5)_4Br$ = 98.95%

(21) Tetraethylammonium Iodide. $N(C_2H_5)_4I$

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable

Recrystallised from hot aqueous alcohol in a platinum dish, dried rapidly at the pump and then in an evacuated desiccator to prevent atmospheric oxidation.

Quantitative Analysis. (Gravimetric) The iodide was estimated as silver iodide in a manner exactly similar to that employed in the estimation of ammonium bromide.

Results

Weight of AgI (A) = 0.3398 gm. (B) = 0.3253 gm.

Weight of $N(C_2H_5)_4I$ (A) = 0.3727 gm. (B) = 0.3568 gm.

Weight of I (found) (A) = 49.27% (B) = 49.28%

Weight of I (calculated) = 49.34%

$\therefore$ Mean % Purity of $N(C_2H_5)_4I$ = 99.88%

(22) <u>Sodium Formate</u>. $HCOONa.H_2O$

(Pure Cryst)

<u>Qualitative Analysis</u>. Impurities:

No Fe, Co, Ni, detectable.

<u>Recrystallised</u> from hot water in a platinum dish, dried at the pump, and then in a desiccator (being careful not to cause dehydration of the crystals by prolonged drying.)

<u>Quantitative Analysis</u>. (Volumetric). The formate was estimated by a method exactly similar to that employed in the estimation of ammonium formate.

<u>Results</u>

Normality of $FeSO_4.(NH_4)_2SO_4.6H_2O$ = 0.10533 N

Titration value of $KMnO_4$ with " = 27.40 cc.

∴ Normality of $KMnO_4$ = 0.096161 N

Titration value of $KMnO_4$ with $\left.\begin{matrix} HCOONa. \\ H_2O \end{matrix}\right\} = \begin{cases} 26.50 \text{ cc. (A)} \\ 26.35 \text{ cc. (B)} \end{cases}$

∴ No. of gms. of HCOOH in solution $= \begin{cases} 0.3522 \text{ gm. (A)} \\ 0.3520 \text{ gm. (B)} \end{cases}$

∴ Weight of HCOOH (found) = $\begin{cases} 52.99\% \text{ (A)} \\ 52.80\% \text{ (B)} \end{cases}$

Weight of HCOOH (calculated) = 53.51%

∴ Mean % Purity of $HCOONa.H_2O$ = <u>98.86%</u>

(23) Potassium Formate. HCOOK

(Pure Cryst.)

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable.

Recrystallised from hot water in a platinum dish, dried rapidly at the pump (since the salt was very deliquescent), and then in a desiccator.

Quantitative Analysis (Volumetric). The formate was estimated by a method exactly similar to that employed in the estimation of ammonium formate.

Results:

Normality of $FeSO_4.(NH_4)_2SO_4.6H_2O$ = 0·10533 N

Titration value of $KMnO_4$ with " = 27·40cc.

∴ Normality of $KMnO_4$ = 0·096161 N.

$$\text{Titration value of } KMnO_4 \text{ with } HCOOK = \begin{cases} 25{\cdot}95 \text{ cc. (A)} \\ 26{\cdot}15 \text{ cc. (B)} \end{cases}$$

$$\therefore \text{No. of gms. of } HCOOH \text{ in solution} = \begin{cases} 0{\cdot}3445 \text{ gm. (A)} \\ 0{\cdot}3470 \text{ gm. (B)} \end{cases}$$

$$\therefore \text{Weight of } HCOOH \text{ (found)} = \begin{cases} 53{\cdot}70\% \text{ (A)} \\ 53{\cdot}86\% \text{ (B)} \end{cases}$$

Weight of KCOOH (calculated) = 54·71%

∴ Mean % Purity of HCOOK = 98·28%

(24) Sodium Propionate. C_2H_5COONa

(25) Potassium Propionate. C_2H_5COOK

Qualitative Analysis. Impurities:

No Fe, Co, Ni, detectable.

Recrystallised from hot water in a platinum dish, dried at the pump and then in a desiccator.

Quantitative Analysis. (Gravimetric). About 0·4 gm. of the sodium or potassium propionate was weighed into a platinum crucible, and a few ccs. of concentrated sulphuric acid added. The solution was evaporated gently to dryness in the fume cupboard, with the crucible lid slightly tilted to allow of the escape of gas, until fuming ceased. This operation was repeated twice. After allowing to cool, a few small pieces of solid ammonium carbonate were added to decompose any pyrosulphate present, and the mixture heated to dull redness for a few minutes, the heating being repeated to constant weight.

Results; Sodium Propionate.

Weight of Na_2SO_4(a) = 0·3194 gm. (B) = 0·3202 gm.
Weight of C_2H_5COONa (A) = 0·4395 gm. (B) = 0·4435 gm.
Weight of Na(found)(A) = 23·53%. (B) = 23·36%
Weight of Na (calculated) = 23·93%
∴ Mean % of Purity of C_2H_5COONa = 97·98%

Potassium Propionate.

Weight of K_2SO_4(A) = 0·3086 gm. (B) = 0·3003 gm.

Weight of C_2H_5COOK(A) = 0·4015 gm. (B) = 0·3930 gm.

Weight of K (found)(A) = 34·48% (B) = 34·36%.

Weight of K (calculated) = 35·10%

∴ Mean % purity of C_2H_5COOK = 98·09%

Organic Liquids which were Purified by Distillation in an All-Glass Apparatus

Name of Compound	Formula of Cpd.	No. of times distilled.	Boiling Pt. observed. °C.	Boiling Pt. (pure) °C.
m-Toluidine	$C_6H_4.CH_3NH_2$	2	201	201-5
Monomethylaniline	$C_6H_5NH(CH_3)$	2	193	193
Monoethylaniline	$C_6H_5NH(C_2H_5)$	1	203	204
Dimethylaniline	$C_6H_5N(CH_3)_2$	2	192	193
Diethylaniline	$C_6H_5N(C_2H_5)_2$	2	214	214

Summary

(1) The magnetic mass susceptibilities of a number of compounds of ammonium and the substituted ammoniums have been measured, and also, for purposes of comparison, certain corresponding salts of sodium, potassium, rubidium and caesium. The experimental results were compared with those previously published, and were found to form a fairly consistent series.

(2) The gram-ionic susceptibility of the ammonium ion in four uni-univalent salts measured, was found to have a value of $-13{\cdot}56.10^{-6}$, when the correcting constants of Trew were employed. Deviations from this value were found in many other cases, since the Langevin equation was not strictly applicable to many of the compounds considered. The gram-ionic susceptibilities of the substituted ammonium ions were calculated, but here again, the method was approximate.

(3) The present values of the molecular susceptibility of the halides and nitrate of ammonium, measured in both the solid state and solution, showed a decrease of susceptibility with increasing coordination number, as Brindley and Hoare have found for certain halides of rubidium and caesium. In the present case a linear relationship was found to exist between molar susceptibility

and coordination number for any one compound, in the halide series.

(4) The measurements on the salts of sodium, potassium, and ammonium with the lower fatty acids, were used to calculate values of the gram-ionic susceptibilities of the corresponding carboxyl ions, and slight variations were observed, according to the cation of the salt. The measurements on the sulphates of ammonium, sodium, rubidium and caesium, gave, with Pascal's value for potassium sulphate, a mean value of the gram-ionic susceptibility of the sulphate ion which agreed closely with the tentative value of Trew.

(5) Using the present values of the gram-ionic susceptibility of the ammonium ion in various states of combination, the values of gram-ionic susceptibility of the inorganic anions in certain salts measured, were calculated, assuming the validity of the additivity law. Of these, the values for the vanadate and dichromate ions had not previously been determined.

(6) The susceptibilities of the ions and compounds considered were calculated theoretically, and the experimental curves on the susceptibility/atomic number graphs confirmed the shape of curve found theoretically. This also applied to the corresponding curves for the group CH_2, in the substituted aniline series and chlorides of the substituted

ammoniums. The mean experimental value of $-11{\cdot}25.10^{-6}$ agreed closely with Pascal's value of $-11{\cdot}86.10^{-6}$ for the susceptibility of the CH_2 group.

(7) The bond depression concept of Gray and Cruikshank has been used to determine the nature and proportions of the possible resonating structures in the series of salts of ammonium with some fatty acids and the corresponding anions. The values of bond depressions were found inapplicable in the series of substituted anilines, owing to the uncertainty of which of several resonant forms is the most satisfactory.

(8) From susceptibility measurements on certain salts of ammonium with sulphur- and chromium - oxyacids, a maximum value of the increase in molecular susceptibility up the sulphur series due to the addition of one atom of oxygen was found to be $-9{\cdot}62.10^{-6}$, which is closer to Sone's value of $-9{\cdot}8.10^{-6}$ than is Kido's value of $-9{\cdot}2.10^{-6}$. The "oxygen difference" was larger in the chromium series $(-11{\cdot}22 \times 10^{-6}$(, and the increase found above Pascal's value for homopolar atomic oxygen $(-4{\cdot}61.10^{-6})$ was attributed to the effect of bond depressions on the homopolar bond.

(9) The present results for position isomers have confirmed the observations and deductions of Bhatnagar and his co-workers, in the benzene series of compounds, and the present work on α- and β- naphthylamine showed that their deductions apply also to the naphthalene series. The theoretical interpretation of the differing susceptibilities of isomers

was also discussed. The present results for electronic isomers were found to conform approximately with their empirical equation.

Finally, the author desires to express her thanks to Professor J. F. Spencer for his advice during the course of this research.

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