"AN INVESTIGATION OF THE MAGNETIC AND OTHER RELATED PROPERTIES OF OXYANION SALTS OF SOME UNIVALENT AND BIVALENT CATIONS IN THE SOLID STATE."

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ABSTRACT

1. The magnetic mass susceptibilities have been measured in the solid state at room temperature for series of salts of uni and bivalent cations of chlorates, bromates, iodates, perchlorates, triorthophosphates, sulphates and thiosulphates. The molar volume for these salts have also been calculated by determining the density at 20°C.

2. The additivity relationships of molar susceptibilities were studied and compared with the additivity of molar volumes. The effect of co-ordination number change on the susceptibility has also been considered.

3. The theoretical susceptibility for the simple ions was calculated by Slater's method. The methods of Pascal and Pauling were used to calculate the ionic susceptibility of the XO_3' and XO_4' ions.
The experimental ionic susceptibilities were compared with the theoretical ones and a marked bond shortening effect on the susceptibility was noted.

ABSTRACT Contd.

4. Infrared spectra of the XO_3' and XO_4' ions were recorded and the characteristic vibrational frequencies were studied. An attempt was made to calculate the force constants for these ions and a comparison was made of the spectroscopic data and the magnetic susceptibilities. Some interpretation in relation to the bond length has been attempted.

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PART 1

GENERAL INTRODUCTION

Magneto-chemistry deals with the investigation of the magnetic properties of atoms, ions and molecules as applied to the study of chemical problems. In relation to inorganic chemistry magnetism has been extensively investigated during the last century. In order to make a clear interpretation of the magnetic measurements it is necessary to consider them in relation to electronic theories of atomic structure and valency. The magnetic properties of an atom or ion can be correlated with its oxidation state, valency, bond type and stereochemistry. In this way problems of molecular structure, interatomic and interionic distances, the valency state of atoms and ions have all been studied by magneto-chemical methods. The magnetic properties which are mainly investigated in this field are the magnetic susceptibility, either volume or mass susceptibility, and magnetic moments of molecules atoms or nucleii. Other magnetic properties in modern times which have become increasingly important in such studies are electron spin resonance spectroscopy and nuclear magnetic resonance spectroscopy.

According to the classical theoretical treatment of atomic magnetism every rotating or spinning electron exhibits a magnetic moment. An atom or molecule will have a permanent magnetic moment if it has an odd number of electrons or if all the electrons are not paired off. If the atom has a permanent magnetic moment, application of an external magnetic field leads to orientation of the moment and the atom is said to be paramagnetic, but if there is an even number of electrons with paired spins the resultant moment is zero, and the system exhibits only diamagnetism. Larmor showed in 1905 that if a system of electrons is rotating about an atomic nucleus, on applying a magnetic field to the system the velocities and hence the angular momenta of the electrons are altered. A "Precession effect" is imposed by the magnetic field upon the electronic orbits which tends to induce currents which give rise to a field opposite in direction to the inducing field and the substance thus exhibits diamagnetism. Langevin(1) on the basis of electronic theory put forward an explanation of diamagnetism, employing the concepts of electrons moving in closed orbits around a massive nucleus. By calculating the magnitude of the change in the magnetic moment of a moving electron induced by the external field he deduced the classical "Langevin Equation" for the underlying diamagnetism in a system of rotating electrons such as an atom. The magnitude of the diamagnetic effect for atoms which possess spherical symmetry can be expressed as the gram atomic susceptibility. This is given by the equation -

$$\chi_A = - \frac{e^2 N.}{6\ mc^2} \sum_n \bar{r}^2$$

Where e is the electronic charge (4.80288. 10^{-10} e.S.U) *C* is the velocity of light (2.99792 ± 0.8. 10^{10} cm sec^{-1}), *N* is the Avogadro number (6.0228. 10^{23} $Moles^{-1}$) and $\bar{r}^2$ is the mean square radius, summed over all the *n* orbits within the atom or ion.

Substituting the values of the various constants this becomes:-

$$\chi_A = -2.83.\ 10^{10} \sum_n r^{-2}$$

or if r is expressed in units of r_o the normal radius of the hydrogen atom ($r_o = 0.528.\ 10^{-8}$ cm.) the expression for the atomic or ionic diamagnetic susceptibility becomes:-

$$\chi_A = -0.789\ .\ 10^{6} \sum_n r^{-2} \text{ e.m.u. /g. atom.}$$

Calculation of Diamagnetic susceptibilities from the Langevin Equation

The actual calculation of atomic or ionic susceptibilities from the Langevin equation requires a knowledge of the value of the term $\sum_n r^{-2}$.

On the classical atomic model this term represented the sum of the mean square radii of the electronic orbits, projected on a plane perpendicular to the field direction. The outer electrons give a larger contribution to the susceptibility as the inner ones are more influenced by the effect of the nuclear charge. Quantum mechanical theory has been applied to calculate $\sum r^{-2}$. On the modern quantum mechanical model this term represents the spread of the electron field or electron density distribution. Owing to the complex nature of atomic systems exact calculations of this term are at present difficult to make and have not been carried out for the heavier atoms. Approximate calculations have however been made by various authors making different assumptions. In general these theoretical susceptibilities give the order of magnitude of the diamagnetic susceptibility rather than its exact value although they do account for the variation in the diamagnetism on passing from one atom to the next. Calculated susceptibilities tend to be higher than the experimental for elements in the periodic table beyond Neon (Z = 10) . This is very largely because the theoretical susceptibility refers to a free ion or atom in "empty space" rather than one surrounded by neighbouring ions in a lattice. Further discussion and use of these theoretical susceptibilities in relation to the experimental measurements found in this work is given in a later section (part IV Theoretical Discussion).

In the present work only diamagnetic substances were considered and so the theory of atomic and ionic paramagnetism is not included in spite of its great importance in interpreting properties of many inorganic substances.

Molecular Diamagnetic Pascal Constants.

Pascal(2) and his school of workers from 1908 onwards carried out systematic studies of the diamagnetism of organic molecules. Investigation of the diamagnetic susceptibilities of related series of carbon containing compounds showed that the susceptibility is determined by the nature and number of the atoms present within the molecule. If χ_M is the experimental molar susceptibility of a given compound then pascal showed that

$$\chi_M = (a\chi_A + b\chi_B + c\chi_C + \text{---}) + \Sigma\lambda$$

where χ_A, χ_B and χ_C are the atomic susceptibility constants of the various atoms, a, b and c represent respectively the numbers of these atoms and λ is a constitutive constant which is dependent on the various bonds present. Tables of values of these constitutive constants have been compiled for the various ligands present. Many other workers have used this system and the values of the atomic susceptibility constants are well established and have been summarised by Selwood(3). Some of these constants have been used in the present work to calculate a theoretical susceptibility for the oxyanions for comparison with the experimental values.

Diamagnetic Susceptibilities of Polar Salts.

The molecular diamagnetic susceptibility of a polar salt can be assumed to be the sum of the individual values for the separate ions provided that the salt is strictly polar and there is no interaction between the ions. The above expression for the diamagnetic susceptibility of a simple free atom or ion can be applied in these ideal conditions. It does not in general hold exactly under experimental conditions and hence experimental susceptibility values for salts will tend to be rather different from the ones calculated by use of the expression

$$-10^6 \chi_M = -10^6 \chi_{\text{cation}} + -10^6 \chi_{\text{anion}}.$$

Some of the earliest experimental values which show that the molar susceptibility of a salt is determined by the sum of the susceptibilities of its ions were obtained by Kido (4) working with salts in solution. He studied a linear relationship between molecular susceptibility and the number of electrons in the cations for the series of alkali salts with the same anions and also for the series of the halide ions with the same cation. However Kido did not consider the coordination number changes which cause small deviations from the linear relationships. In 1935 Brindley and Hoare (5) carried out a comprehensive study of the diamagnetic susceptibility of the alkali halides in the solid state, later including values for salts in solution. They showed that a systematic relationship exists between the susceptibilities of the salts. For example a nearly constant difference was found between the susceptibilities of sodium salts and potassium salts with the same anion. Whenever a variation was noted it could be explained as due to a difference in the coordination numbers of the ions in the salt considered. The coordination number of an ion in a crystal lattice represents the number of ions of opposite sign surrounding the ion in question. Brindley and Hoare found a small but significant difference (eg of the order of 3 - 5%) in the expected susceptibility increment on passing from potassium chloride (C.N.6) to caesium chloride (C.N.8). This was due to the effect of the change in coordination number on the ionic radius of the ion. This effect is reflected in the susceptibility as the spread of the electronic charge **is** restricted by the large number of ions surrounding a given ion. In 1936 Trew (6) showed that for a series of simple Thallium (1) compounds there was a similar additivity effect of the ionic susceptibilities. The work of Bedwell, Spencer and Trew (7) in 1949 showed that the additivity effect and the coordination number effect were found in the case of simple ammonium compounds. These authors also showed that for related series of binary salts such as the chlorides of the alkali metals and ammonium, the experimental molar susceptibility of the salt when plotted against the atomic number of the cation showed a characteristic zig-zag or periodic relationship. This was characteristic of the electron configuration of the cation when a constant anion was used. The theoretical basis of this type of curve had been earlier pointed out by Klemm(8) and further discussed by Trew(9). In 1960 Trew and Husain(10) studied the additivity relationships in polar alkali and ammonium salts. From these additivity relationships sets of diamagnetic susceptibility values for ions in crystals in various coordination states have been calculated. In general from the above work it has been shown that an increase in the coordination number of the ions surrounding a given ion brings about a lowering of the susceptibility. Ions in solution, which generally have a somewhat lower coordination number, have a higher ionic susceptibility and the field of surrounding water molecules does not restrict the spread of the electron density so much as ions in the solid state. Hydrated ions in polar salts tend to show a constant susceptibility for hydrated cations such as $\left[Mg\,6\,H_2O^{++}\right]$, the water generally giving a fixed diamagnetic contribution of 12.96 units per molecule of water. The more covalent and less polar a salt the greater is the departure from these additivity relationships. This may be illustrated by considering some mercury and cadmium compounds. Kido carried out some early work on mercury compounds, Spencer and Hollens(11) investigated cadmium compounds while Prasad Dharmatti and Ghose studied mercury (1) and (11) compounds.(12) The experimental results obtained for cadmium compounds and for mercury (1) compounds show far less definite additivity relationships. For example Spencer and Hollens give molar susceptibility values for cadmium chloride bromide and iodide of 68.74, 87.10, and 117.20 respectively. If in turn the anionic constants for the chloride bromide and iodide ions(10) are subtracted from these values the molar susceptibility of the cadmium (11) ion is 20.1, 17.5, and 16.0. This lack of constancy would seem to result from the effect of the covalent bonding in the molecules. Similar results are obtained if Prasad Dharmatti and Ghose's experimental values for mercury (1) are treated in the same way. It is obvious that the most systematic results so far obtained are for the alkali and ammonium halides. Although some results are available for other types of salts such as oxyhalides, sulphates, nitrates and chromates, little systematic work has been done. Trew has done some magnetic measurements on the chlorates bromates iodates and perchlorates of thallium (1) and potassium and calculated a constant value for the thallium (1) ion assuming that the ionic susceptibilities are additive for polar salts.(6) Prasad, Dharmatti, Kanekar and Biradar(13) studied the magnetic properties of some phosphates of bivalent cations and some chlorates and borates of univalent cations. In most other cases the authors give isolated susceptibility values and not series of results for salts of the same anion. It therefore seemed useful to undertake a much more systematic study of the following series of salts:-

1, Chlorates, bromates and iodates of sodium, potassium silver and thallium (1).

2, Perchlorates of alkali metals including Silver and thallium (1).

3. Triorthephosphates of some univalent and bivalent cations.

4. Sulphates of univalent and bivalent cations.

5. Thiosulphates of some univalent and bivalent cations.

Magnetic properties of the alkali halides (MX) have already been fully investigated and their graphical relationships with the effective atomic number of cation or anion have been worked out. The relationship of the molar susceptibility to the molar volume and to the coordination number of the cation have also been pointed out by Trew & Husain in the case of alkali halides. These series of salts therefore serve as a useful comparative one for study of similar possible relationships for the oxyhalides, peroxy-halides and other series.

Molar Susceptibilities and Molar Volumes

It can be seen from the Langevin's equation that the diamagnetic susceptibility of the ion or atom depends on the ionic or atomic radius. Molar susceptibilities of the salts under investigation have therefore been compared with the molar volumes since $V = 4/3 \pi r^3$ The molar volume is derived from the measurements of density by the relationship $V_M^{20} = \frac{M}{d_4^{20}}$ The relationships obtained between the molar susceptibility and molar volumes are discussed in part III

Some Infra Red Spectra

A search of the literature showed that the infra-red spectra of only some of the chlorates, bromates iodates and perchlorates of the present work have been previously studied. In 1952 Miller and Wilkins(14) reported an investigation of a number of the infra-red spectra and the characteristic frequencies of about 160 inorganic ions including some chlorates, bromates, iodates and perchlorates. In 1960 Dasent and Waddington(15) studied the iodates of sodium, potassium, silver and thallium (1) during a structural investigation of a number of iodine-oxygen compounds. In the same year Rocchiccioli(16) made a infra-red study of some of these iodates. It seems that many workers have investigated the spectra of the perchlorate ion in complexes but the infra-red spectra of $AgClO_3$ $AgIO_3$, $TlClO_3$, TlBrO3 and $TlClO_4$ have not been previously studied. It seemed useful to make a more systematic study of the characteristic frequencies of some of the haloxy-anions and to see whether there is any shift in frequencies on varying the cations. The infra-red spectra of the chlorate bromates, iodates and perchlorates of alkali metals including silver and thallium (1) have been recorded in the present work and given in part V .

PART II

EXPERIMENTAL A.

PURIFICATION AND ANALYSIS OF MATERIALS

The compounds studied in this investigation were obtained as pure as possible. "Analar" or "Research Reagent" salts were used whenever available. Analar substances were measured without further purification or analysis. In other cases, the salts employed were recrystallised from distilled water followed by washing with 95% ethyl alcohol. The salts which could not be obtained were prepared. The purity of the salts in both cases (recrystallised and prepared) was checked by analysis using in each case a standard method. Deliquescent salts were stored in a desiccator. All salts measured were tested for ferromagnetic and paramagnetic impurities (i.e., iron, cobalt, and nickel). Paramagnetic susceptibilities are one thousand times larger than diamagnetic susceptibilities and hence a small trace of paramagnetic impurity might appreciably affect the measured diamagnetism.

(a) IRON:- A purple colouration is given on the addition of an ammoniacal solution of thioglycollic acid to the test solution.

(b) NICKEL:- A red colouration of nickel dimethylglyoximate is given when dimethyl glyoxime is added to the ammoniacal test solution.

(c) COBALT:- An orange colouration is given on addition of the reagent a-nitroso β -napthol together with dilute caustic soda and a little ammonium chloride to the test solution.

In no case was there any positive indication of any paramagnetic or ferromagnetic impurity.

Details of the preparation of the compounds.

1. Thallium (I) Chlorate ($TlClO_3$)

Equivalent amounts of thallous sulphate and barium chlorate were separately dissolved in a minimum quantity of water and the solutions were heated to boiling. The two solutions were mixed together while stirring. The precipitated barium sulphate was filtered off and the filtrate was concentrated to crystallisation in the evaporating dish on a sand bath. When the crystallisation point was reached, the solution was cooled in ice. The crystals of thallous chlorate were filtered off and washed with alcohol and dried.

$$Ba(ClO_3)_2 + Tl_2SO_4 \longrightarrow BaSO_4 + 2TlClO_3$$

2. Thallium (I) Bromate ($TlBrO_3$)

Equivalent amounts of potassium bromate and thallous nitrate were dissolved separately in the necessary quantity of hot water. The solutions were mixed and stirred and allowed to stand for one hour in ice. The precipitated thallous bromate was filtered off, washed with cold water and then with alcohol and dried in a desiccator.

$$KBrO_3 + TlNO_3 \longrightarrow TlBrO_3 + KNO_3.$$

3. Thallium (I) Sulphate (Tl_2SO_4).

Thallous carbonate was neutralised with diluted sulphuric acid and the hot solution filtered to remove the insoluble impurity. Then the filtrate was evaporated until it was about to crystallize and then it was allowed to cool. The crystals were filtered and washed with a mixture of water and alcohol.

$$Tl_2CO_3 + H_2SO_4 \longrightarrow Tl_2SO_4 + H_2O + CO_2$$

4. <u>Thallium (I) Iodate</u> $(Tl\,IO_3)$

Thallous iodate was precipitated by mixing hot solutions of equivalent amounts of thallous sulphate and potassium iodate in water. The white crystalline precipitate of thallous iodate was filtered and washed with water and then with alcohol.

$$2\,KIO_3 + Tl_2\,SO_4 \longrightarrow K_2\,SO_4 + 2Tl\,IO_3$$

5. <u>Thallium (I) Perchlorate</u>. $(Tl\,ClO_4)$

This salt was obtained when thallous carbonate was neutral~~l~~ised by perchloric acid. The amount of perchloric acid needed to neutralise the weighed amount of thallous carbonate was calculated from the equation. The neutral~~l~~ised solution was filtered and evaporated on a water bath until the crystallisation point was reached. The crystals were filtered, washed and dried in a desiccator

$$2\,H\,ClO_4 + Tl_2CO_3 \longrightarrow 2\,TlClO_4 + H_2O + CO_2$$

6. Thallium (I) Orthophosphate (Tl_3PO_4)

A mixture of phosphoric acid and ammonia slightly more than the calculated quantity was added to a concentrated solution of thallous nitrate. The precipitated thallous orthophosphate was filtered, washed with water and then with alcohol.

7. Thallium (I) Chloride (TlCl)

Equivalent amounts of thallous nitrate and potassium chloride were weighed and dissolved separately in distilled water and heated. The hot solutions were then mixed with stirring. The precipitated thallous chloride was allowed to cool and filtered, washed with water and alcohol.

$$TlNO_3 + KCl \longrightarrow TlCl + KNO_3$$

Thallium (I) bromide and iodide were similarly prepared using potassium bromides and iodides respectively.

$$2\,KBr + Tl_2SO_4 \longrightarrow 2\,TlBr + K_2SO_4$$

$$TlNO_3 + KI \longrightarrow TlI + KNO_3$$

8. Silver Chlorate ($AgClO_3$)

Silver chlorate was prepared by dissolving separately equivalent amounts of silver nitrate and sodium chlorate in a minimum quantity of distilled water and mixing the hot solutions together. The solution was allowed to cool slowly to 0° C. and filtered by suction. The crystals were washed with small amounts of water and the compound was dried in a vacuum desiccator over concentrated $H_2 SO_4$.

$$AgNO_3 + NaClO_3 \longrightarrow AgClO_3 + Na NO_3.$$

9. <u>Silver bromate ($AgBrO_3$)</u> was prepared similarly using potassium bromate in place of potassium chlorate

$$Ag NO_3 + KBrO_3 \longrightarrow Ag BrO_3 + K NO_3.$$

10. <u>Rubidium perchlorate ($Rb ClO_4$)</u>

This salt was prepared by neutralising rubidium hydroxide with perchloric acid. The resultant solution was concentrated on a water bath to crystallisation point. The crystals were kept in a vacuum desiccator.

$$Rb OH + HClO_4 \longrightarrow RbClO_4 + H_2O.$$

<u>Ceasium perchlorate</u> ($CsClO_4$) was similarly prepared.

$$Cs OH + HClO_4 \longrightarrow CsClO_4 + H_2O.$$

TABLE I

ANALYSIS OF THE COMPOUNDS

Compound	Method of Analysis	Percentage found	Percentage calculated	Percentage difference
$T\ell C\ell O_3$	$T\ell^+$ as thallous chromate	70.8	71. 0	0.28
$T\ell BrO_3$	$T\ell^+$ " " "	61.0	61. 5	0.81
$T\ell IO_3$	$T\ell^+$ " " "	53.5	53.87	0.69
$NaIO_3 . H_2O$	IO_3' by iodimetric titration	87.8	88.3	0.57
	H_2O by dehydration	9.00	9.08	0.88
$NaC\ell O_4 . H_2O$	$C\ell O_4'$ as perchloric acid	70.81	70.83	0.028
	H_2O by dehydration	12.68	12.80	0.937
$LiC\ell O_4 . 3 H_2O$	H_2O " " (temp.130/150°)	33.4	33.65	0.743
$Mg(C\ell O_4)_2 . 3H_2O$	H_2O " "	19.3	19.48	0·924
	Mg^{++} by E.D.T.A. Titration	8.65	8.80	1·7

TABLE I (contd)

Compound	Method of Analysis	Percentage found	Percentage calculated	Percentage difference
$Ba_3(PO_4)_2$	Ba^{++} as barium sulphate	68.1	68.4	0.44
	PO_4^{3-} as magnesium ammonium phosphate	31.34	31.55	0.66
$Mg_3(PO_4)_2 \cdot 4H_2O$	Mg^{++} by E.D.T.A. titration	21.5	21.7	0.92
	PO_4^{3-} as magnesium ammonium phosphate $6H_2O$	56.2	56.7	0.88
$(NH_4)_3PO_4 \cdot 3H_2O$	PO_4^{3-} as -ditto-	47.0	46.8	0.43
	H_2O by dehydration	26.2	26.6	1.5
	NH_4^+ by distillation (method subject to large errors)	26.15	26.6	1.7

PART 11

EXPERIMENTAL B

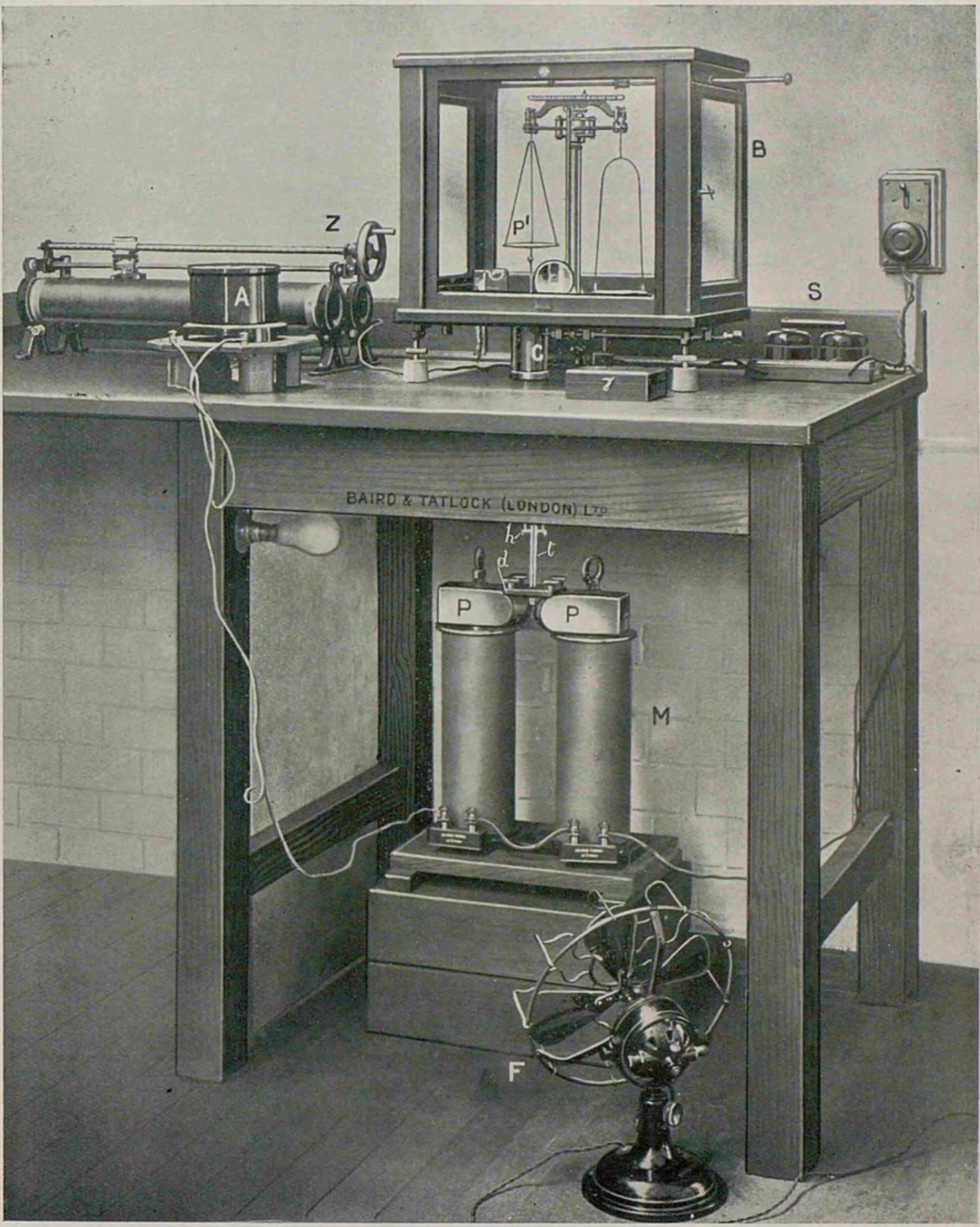
Measurements of Physical Properties of the Compounds

Measurements of Magnetic Susceptibilities of salts in the solid state.

The measurements of the magnetic susceptibility were carried out by the "Gouy Method" using a type of balance originally designed by Sugden(17) and modified by Trew and Watkins.(18) A photograph of the balance and a diagram (Diagram 1) are shown on the following page. The method is based on the principle, that when a substance is freely suspended in a non-homogeneous magnetic field, it experiences a force which induces a tendency for diamagnetic substances to move away from the region of greatest field intensity, and for para and ferromagnetic materials to move into the region of maximum field intensity. The resultant force on the specimen is measured by noting the change in weight of the sample when such a differential magnetic field is applied to it.

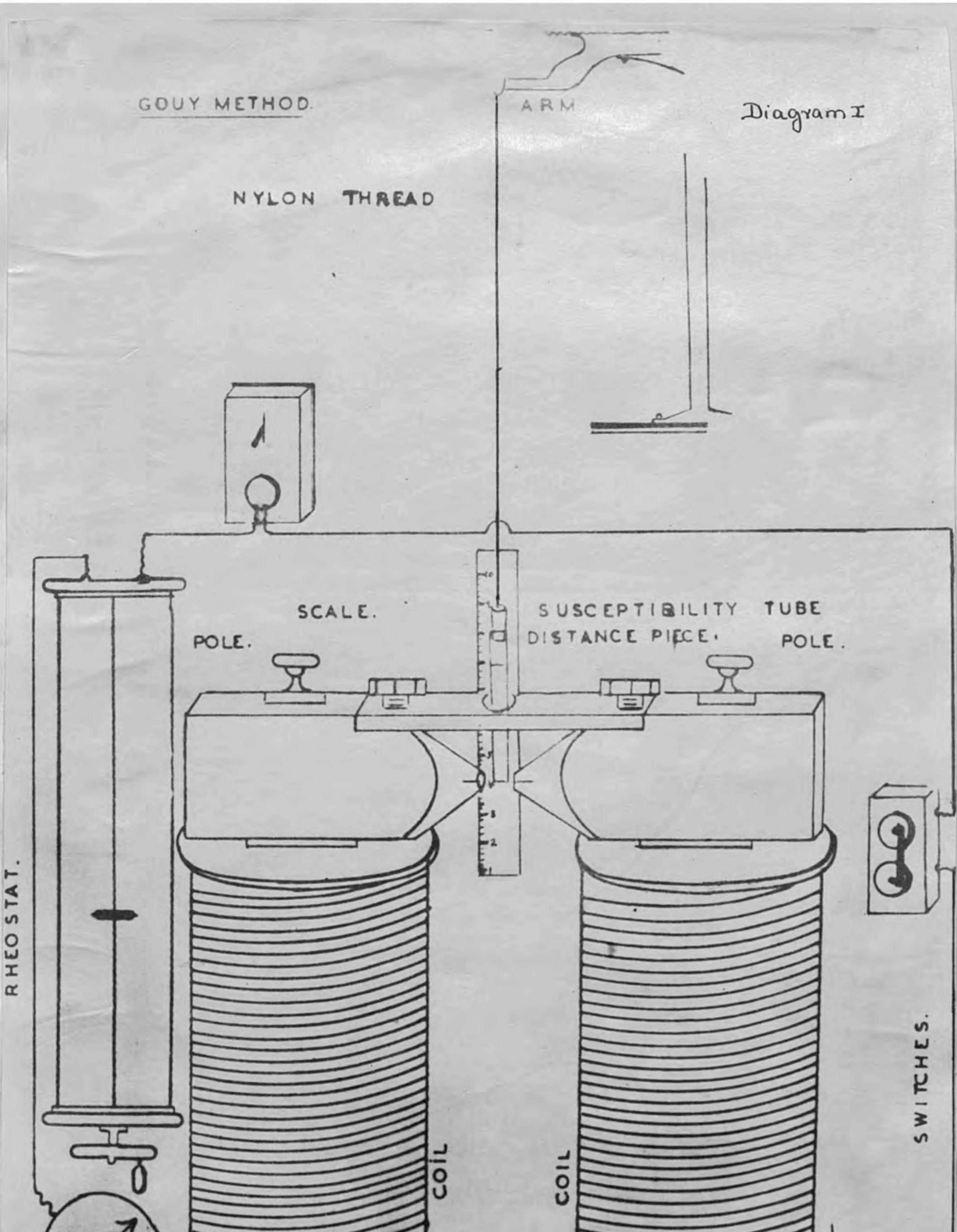
Details of magnetic balance

The magnetic field (H) was generated by means of an electromagnet (M) having coils of 20,000 turns and using


B
Z
P'
A
S
C
7
BAIRD & TATLOCK (LONDON) LTD
h
t
d
P
P
M
F

GOUY METHOD.

Diagram I



a pole gap of 1.5 cm. A current of just under 3 amperes and 220 volts was maintained which was controlled by means of a rheostat (R) and gave a field (H) of about 4,500 gauss (see Diagram 1). Overheating of the coils, which might have affected the balance oscillations by convection currents, was avoided by putting the magnet on for as brief a time as possible in taking readings. The magnetic thrust was measured by a sensitive short beam balance (sensitive to 0.00001g) placed above the electromagnet. The left hand pan of the balance was replaced by a hook to which was attached a nylon thread carrying a polythene stopper, passed through a hole in the balance beneath the left-hand arm. The susceptibility tube was suspended by the stopper and hung vertically in the centre of the gap between the pole pieces. A thrust of about 7.6 mg. was obtained for a diamagnetic liquid such as water when placed in a cylindrical tube of 0.6 cm. radius, with the bottom of the sample in the maximum field and the upper part in zero field. Nylon thread by which the tube was suspended was chosen for its cheapness and its strength.

It does not tend to kink in the same way as platinum or phosphor-bronze wire. A further advantage of its use is that it is very easy to adjust to any required length. The glass of the tube has a low magnetic susceptibility.

Care was taken to place the tube in the same position in the field each time, and in such a way that one end of it lay exactly at the centre of the pole pieces and the other end in the region of negligible field, the position of which was determined by calibration. The magnet below the bench was enclosed to prevent draughts, and the pole pieces and suspended tube were further arranged within a lagged enclosure. It was found that the temperature in the region of the suspended susceptibility tube remained remarkably constant at 20 ± 2°C on most days on which measurements were carried out.

The approximate length of the tubes used to the calibration mark was 8 cm. Each tube was separately calibrated to find its exact length and volume. The length to the calibration mark was carefully measured against a metre-ruler and the reading checked several times.

The volume was determined by filling the tube with water in a thermostat at 20°C and finding the weight of water; knowing the density at 20°C, the volume was calculated. The meniscus correction for the tube was very small and was neglected in the measurements of the susceptibility of the solids, as it was considerably less than the normal random errors of packing the tube with the sample.

The following diagram (Diagram 11) shows the experimental arrangements of the specimen relative to the field.

Calculation of Susceptibility

The substance used is in the form of a uniform cylinder of constant area of cross section

K_1 = volume susceptibility of substance

K_2 = volume susceptibility of medium (air)

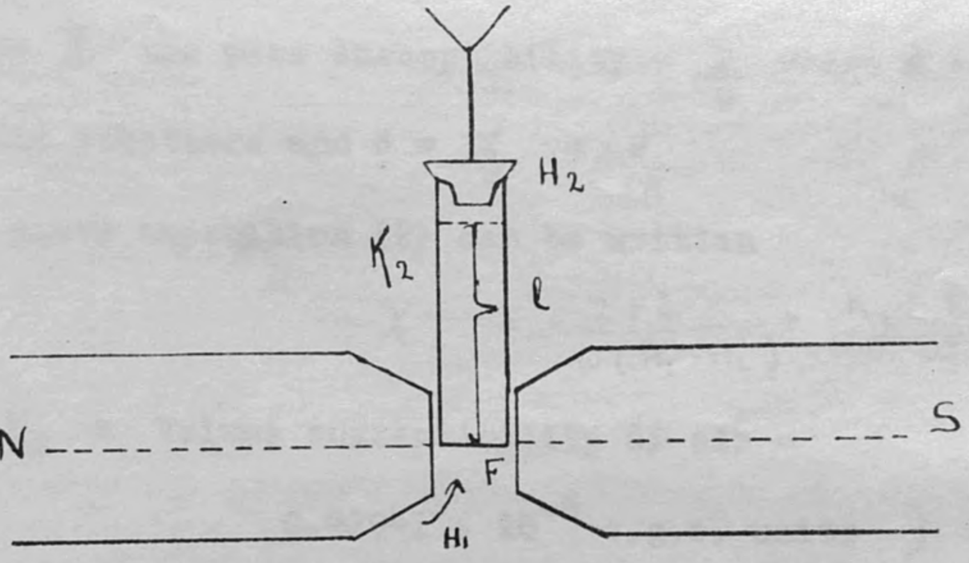
μ_1 = permeability of material

μ_2 = permeability of medium (air)

The force on a material of permeability μ_1 in a medium of permeability μ_2 is given by

$$F = \frac{(\mu_1 - \mu_2)}{8\pi} A \, (H_1^2 - H_2^2) \qquad \text{——— (1)}$$

Diagram II



H_1 = Maximum field at the Centre of the magnet. (Base of cylinder).

H_2 = Field at the top of the cylinder

l = Length of the Column of the Substance in cm.

N, S = North and South Poles of the electromagnet

F = Force (a thrust upwards for a diamagnetic material)

K_2 = Volume Susceptibility of air

substituting $\mu = 1 + 4\pi K$

$$F = 1/2 \; (K_1 - K_2) \, A \, (H_1^2 - H_2^2)$$

i.e. $$K_1 = \frac{2\,F}{A\,(H_1^2 - H_2^2)} + K_2 \qquad (2)$$

since χ, the mass susceptibility $= \frac{K}{d}$ where d = density of the substance and $d = \frac{W}{V} = \frac{W}{\ell A}$

the above expression (2) can be written

$$\chi = \frac{2F\ell}{w(H_1^2 - H_2^2)} + \frac{K_2 \cdot \ell A}{w}.$$

(K_2 = Volume susceptibility of air = $0.02941 \cdot 10^{-6}$ c.g.s. units)

In this equation $\ell A = V$ = Volume of the material

$$\therefore \chi = \frac{2F\ell}{w(H_1^2 - H_2^2)} + C_A$$

where $C_A = \frac{0.02941 \times 10^{-6} V}{W}$ is substituted for the air displacement correction.

Since diamagnetic susceptibilities are of order 10^{-6}, multiplying by 10^6 gives

$$- 10^6 \chi = \frac{2\,F\ell \,.10^6}{W\,(H_1^2 - H_2^2)} + C_A \quad \text{c.g.s.units}$$

If the material is in a differential field when this length of the cylindrical specimen (ℓ) is sufficiently long, then H_2 becomes zero. This was arranged to be the condition in the experiment.

Thus $$-10^6 \chi_g = \frac{2F\ell \cdot 10^6}{W H_1^2} + C_A \text{ c.g.s.units}$$

If the experiments are carried out using a constant field (H) and length of specimen (ℓ)

Then $$-10^6 \chi = \frac{\alpha F}{W} + C_A \text{ c.g.s. units} \quad (3)$$

(α is the balance constant for the particular field strength (H) and length (ℓ)).

i.e. $\alpha = \frac{2\ell \cdot 10^6}{H^2}$ or, if for convenience, the force (F) is measured in milligrams (ℓ) in cms and (W) in grams

$$\alpha = \frac{2\ell \cdot 10^6 \cdot 981 \cdot 10^{-3}}{H_1^2} \text{ c.g.s.units}$$

The field strength H_1 is then given by

$$H_1 = \sqrt{\frac{1.962 \times \ell \cdot 10^6}{\alpha}}$$

$$H_1 = 10^3 \sqrt{\frac{1.962 \cdot \ell}{\alpha}}$$

Thus if the length of material and the balance constant are determined, the field strength used may be calculated from measurements on substances of known susceptibility.

Calibration

The magnetic balance required to be calibrated before starting the susceptibility measurements. Various authors have employed different standards. In the investigation of paramagnetic substances, the most common standards recommended are solid copper sulphate pentahydrate and nickel ammonium sulphate hexahydrate, aqueous solutions of nickel chloride of known concentration, and solid mercury cobalt tetra-thiocyanate Hg Co $(CNS)_4$ (19) The required properties of a calibrant are (1) readily available in a pure well-crystallised form, (2) an accurately known and moderate susceptibility ($\chi_g \approx 10.10^{-6}$), (3) stability in moist air and (4) χ_g must vary in a known and simple way at least at room temperature. Figgis & Nyholm found that the complex Hg Co $(CNS)_4$ offers some advantages and its susceptibility is now well established as $10^6 \chi_g = 16.44 \pm 0.08$ c.g.s.units.

Copper sulphate pentahydrate (solid) has the disadvantage that the salt is rather hygroscopic and the dissociation pressure is somewhat low so it tends to lose water on grinding. For diamagnetic substances however it was thought more satisfactory to employ a diamagnetic standard with a susceptibility of the same order of magnitude as the substance measured. Analar benzene and conductivity water were used as magnetic standards. Benzene has an accepted room temperature specific susceptibility of $-0.7023 . 10^{-6}$ c.g.s.units and water has the susceptibility of $^{-}0.7200 . 10^{-6}$ c.g.s. units at 20°C. Being diamagnetic substances they have nearly a zero temperature coefficient. Some authors have objected to the use of water owing to small changes in the susceptibility with temperature, from changes in hydrogen bonding. Over the temperature range 15 - 25° C, this variation is negligible for the degree of accuracy of the apparatus.

The magnetic susceptibility of benzene and water have been widely studied and these are good standards. In the investigation both benzene and water were used as initial standards, later, water alone was used to check calibration during the course of work.

Precautions were taken to obtain the pure standards for reference - such as distilled water and research grade benzene. The distilled water was conductivity water from an ion-exchange column. May & Baker's "Molecular Weight Benzene" was used as a starting material in the case of benzene. This had been purified by distillation and fractional crystallisation, the middle fraction only in each case being selected, and dried over sodium. This procedure gave samples of refractive index of 1.5011 in good agreement with the accepted figure of the National Bureau of Standards(20) for pure benzene. The susceptibility tube was thoroughly cleaned with sulphuric-chromic acid mixture, rinsed several times with distilled water and steamed out for 10 minutes. It was dried and kept in a desiccator before starting the calibration process.

Calculation of the balance constant (α) and the field strength (H) used.

The balance was calibrated and the values of the balance constant (α) and the field strength (H) used were calculated by measurements on pure distilled water and benzene, using equation (2).

$$-10^6 \chi g = \frac{\alpha F}{W} + C_A$$

$$\left(\text{with } C_A = \frac{0.0294 \times V}{W}\right)$$

$$\alpha = \frac{2\,l\ .10^6}{H^2}$$

α is only constant for a particular pole gap and strength of field, and is dependent on the length of the column of the material used. As it is dependent on the field strength (H) it may be used to give a measure of (H).

Calculation of α

With water as standard ($-10^6\chi$ = 0.7200 c.g.s. units) substituting the values of the thrust (F) in milligrams and the weight of the water (W) in grams which fills the volume of the tube (V) up to the mark, α may be calculated as follows :-

eg. V = 5.852804 cc. W = 5.810898 g, F = 5.90mg.

l = 7.85 cm.

$$0.7200 = \left[\frac{\alpha(5.90)}{5.811}\right] + \left[\frac{0.02941.\ \ 5.8428}{5.811}\right]$$

$$\therefore \alpha = \left[0.7200 + 0.029.6\right]\left[\frac{5.811}{5.90}\right]$$

$$\therefore \alpha = 0.7496\ .\ 0.9849$$

$$= \underline{\underline{0.7383}}$$

Three measurements were made and the average readings were taken in the above calculation.

Calculation of H

$$H = 10^3\sqrt{1.962\ \frac{l}{\alpha}}$$

$$\alpha = \frac{2l}{H^2}.10^6\ \ .981\ \ .10^{-3}\ \ \text{c.g.s.units}$$

$$\therefore H = 10^3\sqrt{\frac{1.96\ \ 7.85}{0.7383}}$$

$$H = 10^3\sqrt{20.84} = \underline{\underline{4564}}\ \text{gauss.}$$

" α " was redetermined for each new tube used, of slightly different length ' l ' and was checked at intervals by the calibration standards.

Table A

Values of α and H for different susceptibility tubes

Tube	'ℓ' length (cm)	α (balance constant)	$\frac{\alpha}{\ell}$	H (Field strength) in gauss
1	8.00	0.7510	0.0939	4570
2	7.90	0.7553	0.0956	4528
3	8.00	0.7502	0.09374	4572
4	7.85	0.7383	0.09404	4564
5	7.90	0.7352	0.0931	4586
		mean =	0.09408	mean 4564

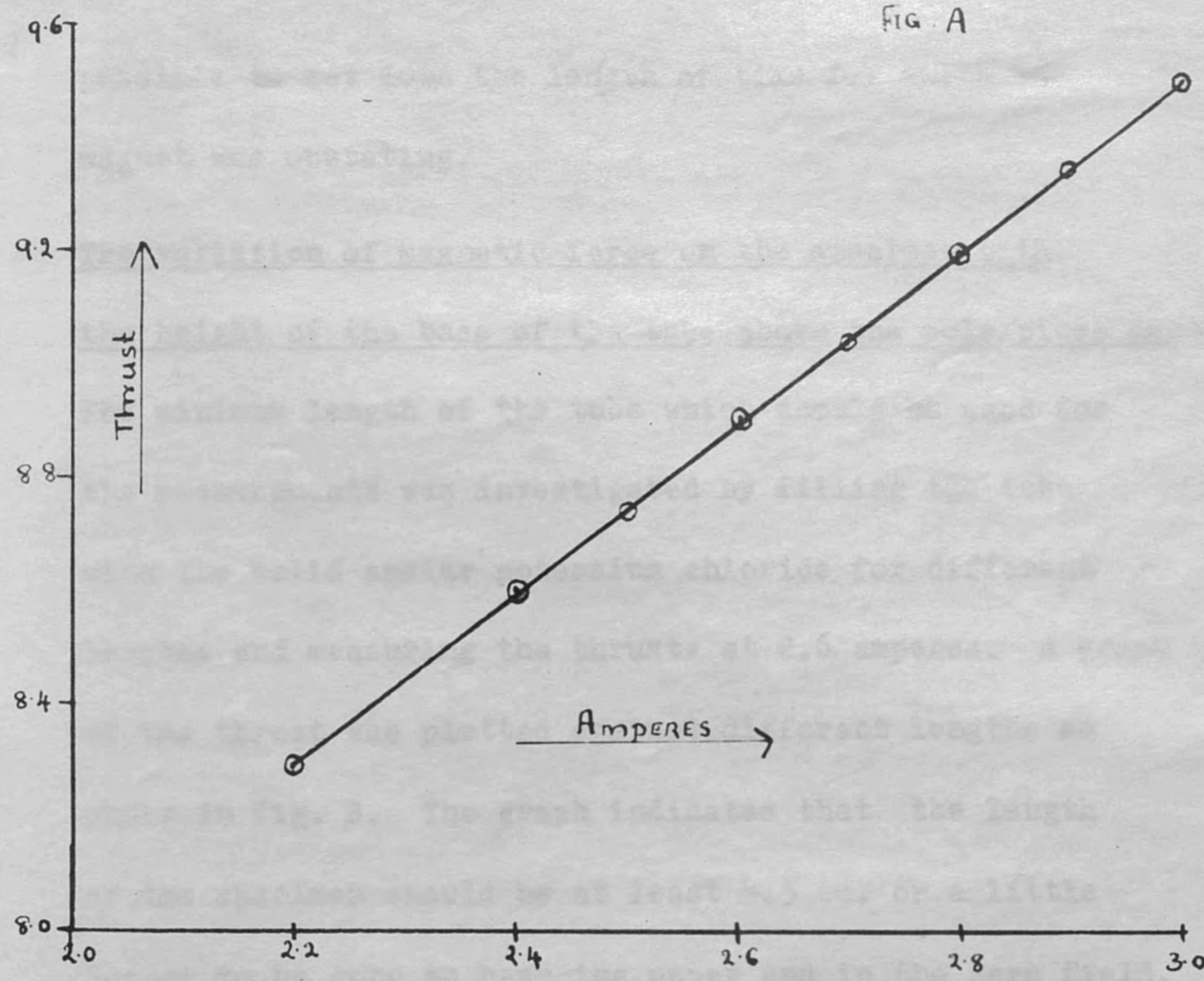
Table 'A' shows that for the different tubes, the balance constant per unit length α/ℓ is constant with a value 0.09408. This gives a mean H (4564 gauss).

The values of α were determined at intervals during the course of the work, when from time to time, new tubes were required. The figures in column 4 and 5 show a satisfactory agreement as the basis of the calibration for the magnetic measurements.

Determination of Variation of field with the current

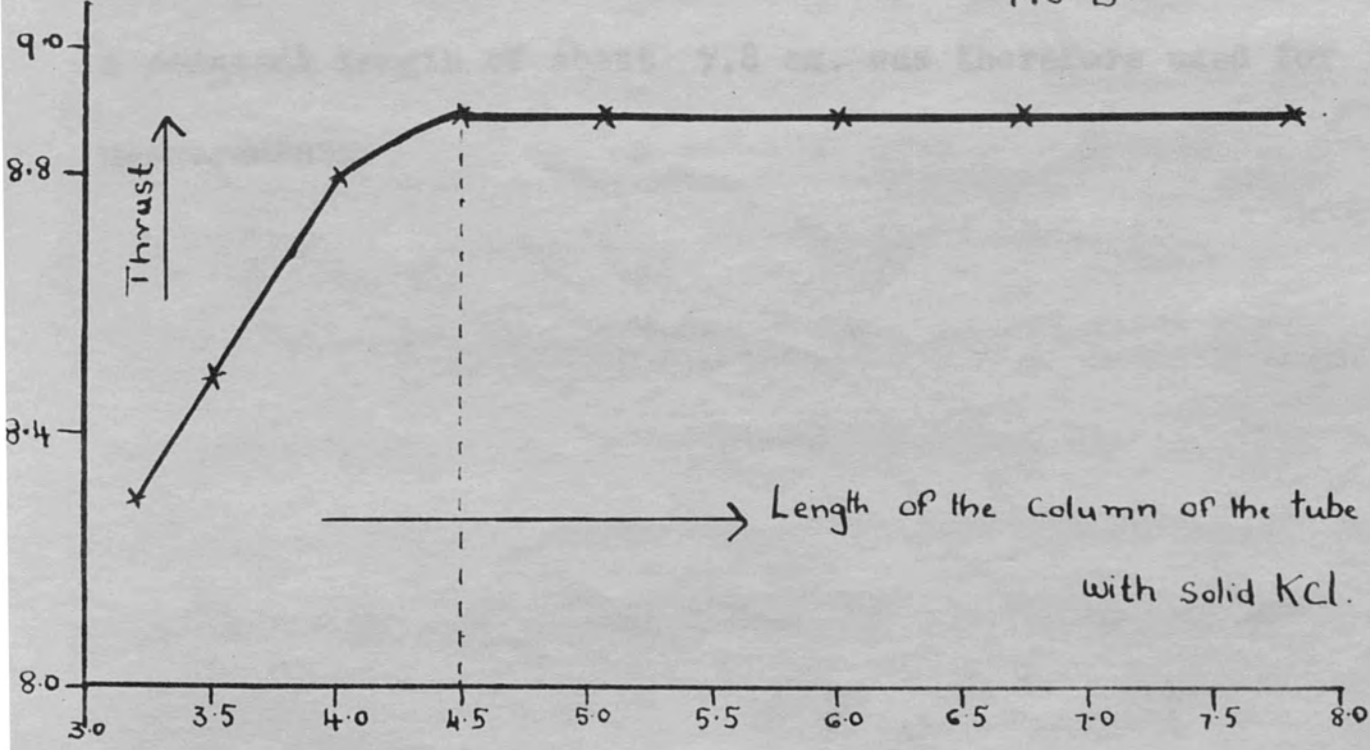
The variation of the magnetic field with the current in the coil was investigated by determining the magnetic force exerted on a tube of 7. 8 cm. length packed with solid analar potassium chloride at room temperature using different exciting currents. The pole pieces are fixed at a pole separation of 1.5 cm. The thrust on KCl and tube, plotted against exciting current is shown in fig.A. The graph is nearly a linear one. The maximum current strength was 3 amperes, a value that is obviously below the saturation current. It was thus necessary to check the ammeter reading carefully with each measurement. Since the magnet gets very hot with this current strength if left on for any length of time, a lower current of 2.6 amperes was used for the present work. This was adjusted with the help of a very sensitive rheostat R (shown in diagram 1) in series with the coils, the readings of the Crompton moving coil ammeter A being kept at exactly 2.6 amperes during the experiments. By adjusting the weights oh the balance pan when the magnet was not on, it was

FIG. A



Thrust
Amperes
9.6
9.2
8.8
8.4
8.0
2.0
2.2
2.4
2.6
2.8
3.0

FIG B.



Thrust
Length of the column of the tube with solid KCl.
9.0
8.8
8.4
8.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

possible to cut down the length of time for which the magnet was operating.

The variation of magnetic force on the specimen with the height of the base of the tube above the pole piece centre.

The minimum length of the tube which should be used for the measurements was investigated by filling the tube with the solid 'analar' potassium chloride for different lengths and measuring the thrusts at 2.6 amperes. A graph of the thrust was plotted against different lengths as shown in fig. B. The graph indicates that the length of the specimen should be at least 4.5 cm. or a little longer to be sure to have the upper end in the zero field. A constant length of about 7.8 cm. was therefore used for measurements.

Susceptibility Measurements on Compounds (In the solid State)

The cleaned and dried susceptibility tube was weighed empty and the thrust on the tube in the magnetic field found. Six readings were taken each time. The tube was then packed carefully with finely powdered salt to the calibration mark. Packing was done with great care by ramming and tapping. In the ramming technique, material to fill about 2 mm.length of the tube was added and this was rammed by use of a glass rod with a flattened base of size just less than that of the tube. Subsequent additions of the same amount were similiarly rammed until the tube was filled to the mark. In the tapping method similar amounts of material were placed in the tube, but the tube was tapped gently and regularly on a smooth surface about twenty times, turning the tube during the process. On the whole the tapping method gives more uniform packing. In the ordinary method of packing by ramming, the powder in the susceptibility tube seemed to retain variable amounts of air in the interstices of the solid particles. If this occurs, the paramagnetism of the oxygen in the air would then tend to cause discrepancies in the diamagnetic susceptibilities, which though small might affect the experimental error of the measurements. Errors in measurements will obviously be magnified in calculating the molar susceptibilities, because of the large molecular weight by which the specific susceptibility is multiplied. So great care was taken in packing the tube to get uniform packing throughout.

The weight of the salt was first determined with the magnet off (with zero field) and then the weight was found in the magnetic field (magnet on). The difference in weight gave the thrust for a diamagnetic substance from which the thrust due to the tube was subtracted. Weighings to the fifth place were made, the fifth place being found from the method of oscillations. Six readings were taken each time and the mean value was used for calculation. Three measurements were made on each compound. When there was not enough material to fill the tube up to the mark, the tube was calibrated at 5 cm. by marking the tube at this point.

The specific susceptibility of the following groups of compounds were measured :-

The chlorates, bromates, iodates, perchlorates, and borofluorides of the alkali metals together with those of univalent silver and thallium. A number of phosphates, sulphates and thiosulphates of some univalent and bivalent cations were also investigated.

<u>Example of Calculation</u> - The Specific susceptibility <u>of Thallium (I) Chlorate</u>

The specific susceptibility was calculated from the equation

$$-10^6 \chi \text{ salt} = \frac{\alpha F}{W} + C_A$$

(Where α is the balance constant, F the thrust on the salt, W, weight of the salt, 0.02941 c.g.s. units is the susceptibility of air (medium), and V the volume of the tube up to the calibrated mark)

The molecular susceptibility was calculated by multiplying the mass susceptibility by the molecular weight of the compound.

$$-10^6 \chi_M = -10^6 \chi \text{ salt} \times \text{Mol.weight}$$

Temp. 20°C.

Volume of the tube (V) = 8.179 c.c.

Weight of $TlClO_3$ (W) = 17.9318 g

Thrust on the salt (F) = 5.168 mg

Thrust on the tube = 2.615 mg

Thrust on the tube + salt = 7.783 mg

α = 0.7553

$$-10^6 \chi \text{ salt} = \frac{0.7553 \times 5.168}{17.9318} + \frac{0.02941 \times 8.179}{17.9318}$$

$$= 0.20429$$

$$-10^6 \chi_M \text{ for } TlClO_3 = 0.20429 \times 287.85 = 58.52 \text{ c.g.s.units}$$

b. <u>Determination of the Densities and Apparent Molar Volumes</u>

In the determination of the density of solids, the method to be used for a particular solid must be chosen according to the circumstances. Densities are measured by displacement of a standard liquid in a density-bottle. The liquid ~~must~~ must be chosen so that the solid does not dissolve or react with it, and the liquid should have a lower density than the solid. Carbon tetrachloride was used to determine the density of the compounds under investigation.

This is an inert solvent and its density is below that of the solids.used. It is also relatively involatile.

The experiments were made using the "Regnault density-bottle"

Experiment

The bottle with the stopper was cleaned, dried and weighed. About 5 gms. of the dried finely powdered salt were introduced and the bottle re-weighed. Then sufficient of the liquid was run in to cover the solid and all the air bubbles in between the solid particles were removed by tapping and subsequent suction on a water pump. The bottle was then filled with the standard liquid and kept in the thermostat at 20°C for 20 minutes. Using a filter paper, the level was adjusted or brought down to the mark while keeping the bottle in the thermostat. Then the bottle was quickly taken away from the thermostat, dried with a clean cloth and weighed. The experiment was repeated three times.

Calculation of Density

The density of the solid was calculated from the formula

$$D = \frac{Wd}{(W + W') - W''}$$

Where W = weight of solid

d = density of CCl_4

W' = weight of bottle + CCl_4

W'' = weight of bottle + CCl_4 + solid

The density of CCl_4 was determined experimentally and it was found to be 1.597 (Litevature figure $D_4^{20} = 1.595$)

Example of calculation of density - potassium chlorate

$$D_4^{20} = \frac{Wd}{(W + W') - W''}$$

Weight of the solid (W) = 6.66460 g

Density of CCl_4 = 1.597

Weight of bottle + liquid = 53.56350 g.

Weight of bottle + CCl_4 + solid = 55.65230 g

So, the density of $KClO_3$ $= \frac{6.66460 \times 1.597}{(6.66460 + 53.56350) - 55.65230)}$

$$= \frac{6.66460 \times 1.597}{4.5758}$$

$$= \underline{\underline{2.327\ g \cdot ml^{-1}}}$$

Determination of the Molar Volume

The molar volume of each compound was calculated from the measured density.

$$V_M^{20} = \frac{M}{D_4^{20}}$$

where M is the molecular weight of the compound, D_4^{20} is the density at 20°C.

eg. Potassium chlorate ($KClO_3$)

$$D_4^{20} = 2.325$$

$$M = 122.55$$

$$V_M^{20}\ KClO_3 = \frac{122.55}{2.325} = \underline{\underline{52.71}}$$

PART 111

Results and Discussion

1. Magnetic susceptibilities of Chlorates, Bromates, and Iodates of Sodium, Potassium, Silver & Univalent Thallium

Potassium Chloride was selected as a standard of comparison with earlier measurements, since there is more general agreement as to the experimental values of the compound as obtained by different authors. The following table shows the present values of the molar mass susceptibility using different tubes, as well as the literature values which were available.

$-10^6 \chi_M$ (KCl)	$-10^6 \chi_M$	(Literature)
39.44	38.45 (21)	37.66 (26)
38. 9	39.1 (22)	39.6 (28)
38.01	39.4 (23)(soln)	38.8 (5)
38. 6	39.6 (22)(soln)	38. 4 (27)
	35.8 (4)	36·15 (29)
	38.8 (24)	
	39.2 (25)	
	38.71 (10)	
mean 38.74	mean 38.7	

It can be seen from the table that most of the literature values are in good agreement with each other and with the present results. Kido's early value is found to be rather lower than those of any other authors.

The results in Table 1 summarise the magnetic susceptibilities which were found for the salts measured in the solid state. The results obtained for the specific susceptibilities are shown in Column 4 and for the molar susceptibilities in Column 5. These are compared with the available literature values, which are shown in Column 6. Columns 2 & 3 give the molecular weight and the co-ordination number of the cation in the salt respectively. The literature values which are available for susceptibility measurements on salts are fairly comparable with the present results. In the case of potassium bromate and potassium iodate the literature values are a few percent higher than the present ones. The measurements were repeated to check and confirmed in these cases.

In any case the variation in the susceptibility is not large in most cases and so the figures may be compared with those of other workers.

TABLE 2

Salt	Mol. wt.	C.N.	$-10^6\chi$ (salt)	$-10^6\chi_M$	$-10^6\chi_M$ Literature values
$NaClO_3$	106.45	6	0.3014 0.3008 0.3010	32.08 32.02 32.04 mean 32.05	( )
$NaBrO_3$	150,91	6	0.2942 0.2944 0.2942	44.38 44.41 44.38 mean 44.40	
$NaIO_3 \cdot H_2O$	215.92		0.2932 0.2920 0.2927	63.30 63.05 63.20 mean 63.20	
$NaIO_3$	197.92	8		50.24	
K Cl	74.55	6	0.5290 0.5218 0.5100 0.5178 mean 0.5197	39.44 38.90 38.01 38.60 mean 38.74	(see page 45)

TABLE 2 (contd)

Salt	Mol. wt.	C.N.	$-10^6 \chi$ (salt)	$-10^6 \chi_M$	$-10^6 \chi_M$ Literature values
$KClO_3$	122.55	6	0.3386 0.3408 0.3370	41.52 41.78 41.24 mean 41.51	44.3 (6) 40.81 (30)
$KBrO_3$	167.02	8	0.3256 0.3281 0.3268	54.38 54.79 54.58 mean 54.60	52.11 (31) 53.2 (4) 52.3 (32) 54.1 (6)
KIO_3	214.02	12	0.2882 0.2802 0.2810	61.7 60.00 60.3 mean 60.65	65.9 (6) 65.8 (4) 63.1 (32) ± 0.5 0.5
$AgCl$	143.34	6	0.34952	50.10	94.60 (17) 50.17 (33)
$AgClO_3$	191.34	6	0.2767 0.2743 0.2760	51.21 52.50 52.40 mean 52.5	

TABLE 2 (contd-)

Salt	Mol. wt.	C.N.	$-10^6 \chi$ (salt)	$-10^6 \chi$ M	$-10^6 \chi_M$ Literature values
Ag Br	187.8	6	0.3080	57.84	114.56(17) 61.97(33)
$AgBrO_3$	235.8	8	0.2674	63.06	
			0.2678	63.15	
			0.2673	63.04	
				mean 63.10	
$AgIO_3$	282.8	12	0.2356	66.63	
			0.2355	66.6	
			0.23515	66.5	
				mean 66.6	
Tl Cl	239.85	8	0.2439	58.4	57.8(6)
$TlClO_3$	287.85	8	0.2073	59.69	65.5(6)
			0.2043	58.52	
			0.2026	58.34	
				mean 58.96	
Tl Br	284.31	8	0.2344	66.64	63.9(6)
$TlBrO_3$	332.306	8	0.2202	73.18	75.9(6)
			0.2217	73.685	
			0.2215	73.605	
				mean 73.50	

TABLE 2(contd)

Salt	Mol. wt.	C.N.	$-10^6 \chi$ (salt)	$-10^6 \chi_M$	$-10^6 \chi_M$ Literature values
TlI	331.31	7	0.2540	84.30	82.2 (6)
$TlIO_3$	379.3	8	0.2095	79.50	86.8 (6)
			0.2095	79.50	
			0.2095	79.50	
				mean 79.50	

Where values are given in Table 1 for the anhydrous salt to compare with the literature value, these have been calculated from the experimental figure obtained from the hydrated salt by subtracting the necessary multiples of the molar susceptibility of water (-12.96×10^{-6} c.g.s units per mole of water). Prasad, Dharmatti, Kanekar and Biradar (13) have queried whether the water of hydration has precisely the same susceptibility as water in bulk. They considered that the difference in value for the susceptibility between hydrated and anhydrous salts may be affected by factors such as the strength of the bonding of the water molecules (the tighter the bonding the greater the departure), and the distribution of charge in the molecule of the hydrate. In the present investigation magnetic measurements on hydrated and anhydrous salts were only carried out with sodium perchlorate, sodium perchlorate monohydrate and anhydrous sodium perchlorate. Owing to the hygroscopic character of the hydrated salt, it is difficult to check this point from the measurements. The susceptibility for anhydrous sodium perchlorate calculated from that of the monohydrate by subtraction of $-10^6 \chi \, H_2O = -12.96$ is slightly higher than that for the anhydrous salt which was carefully packed for susceptibility measurement in a dry box. In the first case a value for the molar susceptibility of anhydrous sodium perchlorate of 40.0 was obtained and in the second case the value was 36.6. It appeared more likely that the difference was due to the hygroscopic character of the hydrated salt than a difference in the actual susceptibility for different numbers of water molecules as suggested by Prasad and co-workers. Trew, Husain & Siddiqui (34) have shown that there is a good additivity for the susceptibility on the addition of water molecules in the case of the magnesium sulphate hydrates and anhydrous magnesium sulphate. Deviations in additivity are in any case very small even if they do occur. (34) It therefore seems justifiable to make use of this additivity method which does enable a comparison to be made between present measurements and the available literature figures on anhydrous salts. A test of the additivity relationships in the salts of the alkali metals and those of silver and thallium with the oxyanions chlorate, bromate and iodate is best made by comparison with the susceptibilities of the respective halides. The addit~~i~~ivity properties of these have already been widely investigated and the effect of a change in co-ordination on the molar susceptibility of the salt has been established.(6) For the comparison with the present work, the values of the magnetic susceptibility of the alkali halides were taken from the literature.(5,6) Thallium halides were remeasured. In the case of silver halides only two sets of values were available.(17,33) Sugden's(17) work on silver halides was carried out some time ago and the obvious interest here lay in the difference between the diamagnetism of silver (1) and the paramagnetism of silver (11) rather than in obtaining accurate measurements for the diamagnetic salts. Diamagnetic measurements carried out for comparative purposes in this way are unlikely to be so accurate as systematic measurements on purely diamagnetic substances. The susceptibility of silver (1) halides were therefore reinvestigated in this current work. The measurements were made with great care using specially prepared materials. The preparations are described in Section A Part 11.

The salts were carefully tested to see if any ferromagnetic impurities were present, the most likely being iron. A few values for susceptibility measurements on silver salts given in the International Critical Tables(1) were found to be in closer agreement with the present values than those of Sugden. In addition the present values showed good systematic relationships with the salts of the alkali halides.

It can be seen from the experimental results that the values of the molar diamagnetic susceptibility increase~~s~~ with the increase in atomic number of the cations as well as of the anions.

eg. $\mathrm{Na\,ClO_3} < \mathrm{K\,ClO_3} < \mathrm{Ag\,ClO_3} < \mathrm{Tl\,ClO_3}$

$\mathrm{K\,ClO_3} < \mathrm{K\,BrO_3} < \mathrm{K\,lO_3}$

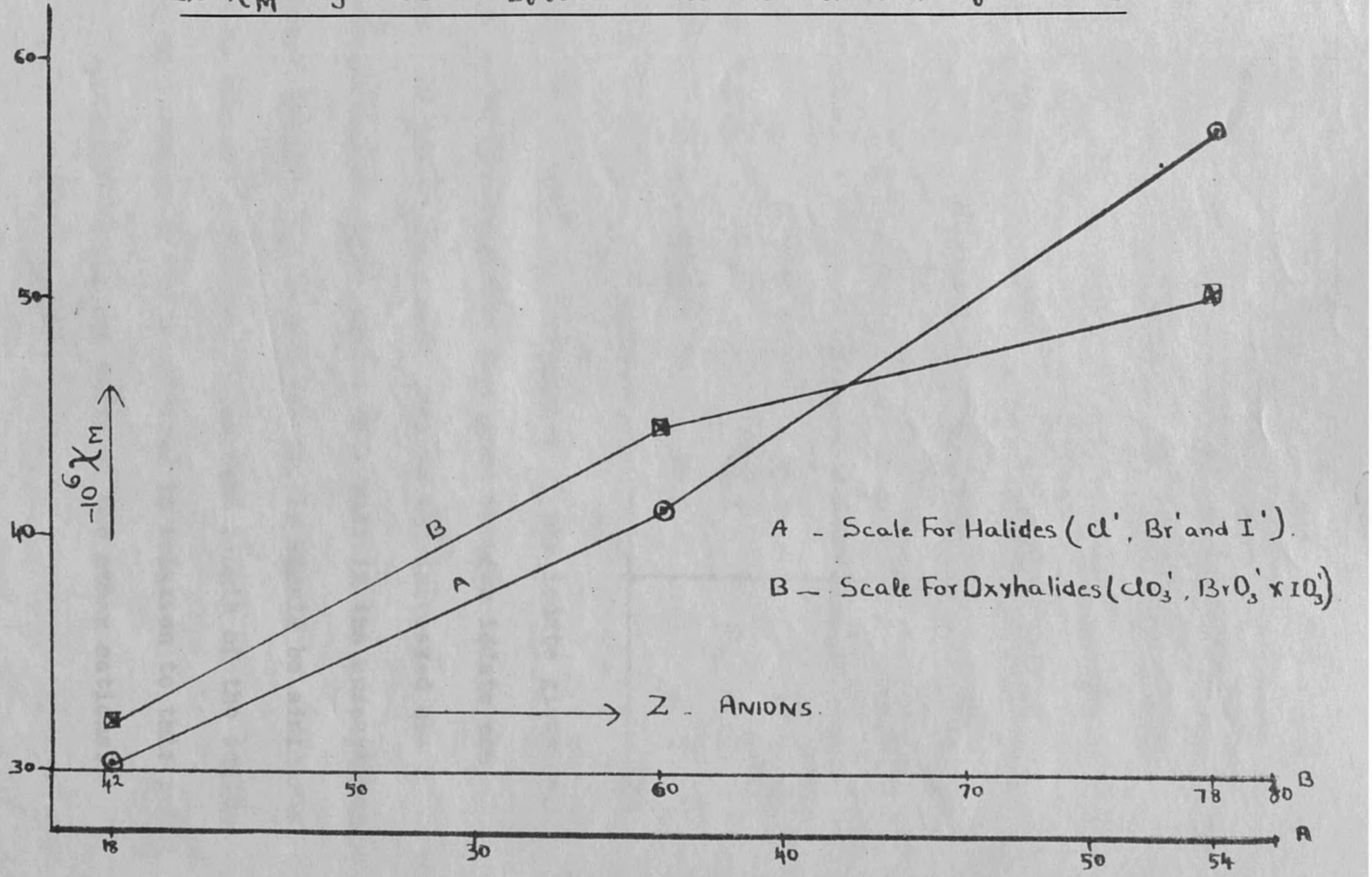
From the values in Table 1, graphs were plotted of the molar diamagnetic susceptibility of the alkali, silver and thallium oxysalts against the effective atomic number of the anion present as shown in figures 1a, 2a, 3a and 4a and the graphs are compared with the similar ones for the corresponding halides. The individual results are discussed below.

Molar susceptibility relationship of sodium salts

Fig. 1a shows the molar susceptibilities of sodium oxyhalides plotted against the effective atomic number of the anion compared with the similar graph for the sodium halides. The slope of the oxyanion graph between chlorate and bromate shows a slight increase compared with the halide graph. From the bromate to the iodate however, there is a very much smaller increase in the susceptibility, so that the graph for the oxyanions crosses that for the simple anions, The low susceptibility value of the iodate might be expected from the more dense packing of the crystal and the resultant increase in cation co-ordination number in the salt. The co-ordination number of both sodium chlorate and bromate is six and that of the iodate is eight. This increase in co-ordination number and closer packing could result in a lower susceptibility. The co-ordination number of the three halides is however the same (six), and so the magnetic-susceptibility for the halides would be expected to increase more steeply as the atomic number of the anion increases. The form of the susceptibility graph as already

SODIUM SALTS Fig. Ia.

$-10^6\chi_M$ against the effective atomic number of anions.



explained for the halides is well established and similar to that for the free halide ion. (page 53) The numerical value of the actual increments ($\Delta\chi$) between oxyhalide and halide ($-10^6 \chi$ XO_3') $-(-10^6 \chi$ X') is shown in the following table :-

Halogen	Oxyhalides Na X O_3 ($-10^6 \chi_M$)	Halides NaX ($-10^6 \chi_M$)	Susceptibilty increments (Oxyhalide-halide) $-10^6 \Delta\chi$ (XO_3-X')
Cl	32.5	30.2	+ 2.30
Br	44.4	41.1	+ 3.30
I	50.0	57.0	- 7.0

The very much lower susceptibility of the iodate gives rise in the table to a negative increment between iddate and iodide. If it is the closer packing and increased co-ordination number which causes this fall in the susceptibility increment between iodate and iodide, it should be similarly shown by the molar volumes. The bond length of the sodium oxyhalogen compounds are considered in relation to this point later, after considering the salts of the other cations.

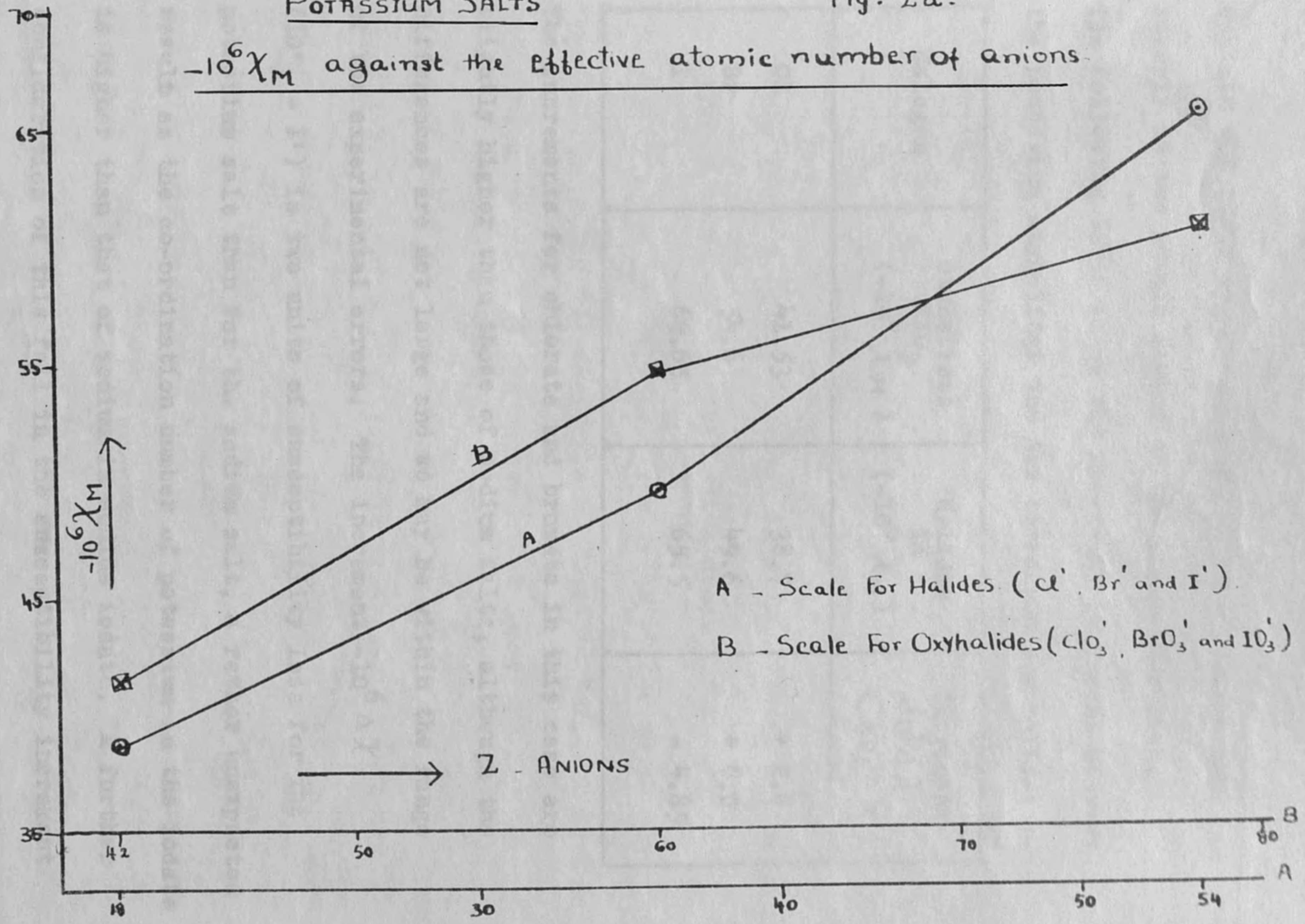
b. Potassium Salts

The molar susceptibilities of the potassium oxyhalides are shown in figure 2a, plotted against the effective atomic number of the anion, and the corresponding graph for the potassium halides is also shown. The graph is similar to that of the sodium salts. The oxyanion graph between chlorate and bromate also shows a slight increase in slope compared with the halide graph. Again from bromate to iodate however, there is a similar very much smaller increase in the susceptibility and here again, the graph for the oxyanions crosses that for the simple anions. The low susceptibility value of the iodate as in the case of sodium salts, may be expected from the increase in cation co-ordination in the iodate. The co-ordination numbers of potassium chlorate, bromate and iodate are known from crystal structure determinations. These are respectively six, eight and twelve. The cation co-ordination number of all the three potassium halides is however the same (six) and so the change in co-ordination number of the oxyhalides bromate and iodate with the increased closer packing could

POTASSIUM SALTS

Fig. 2a.

$-10^6\chi_M$ against the effective atomic number of anions



explain why their magnetic susceptibity increases less steeply as the atomic number of the anion increases. The following table shows the numerical increment between the potassium oxyhalides and the corresponding halides :-

Halogen	Oxyhalides KXO_3 $(-10^6 \chi_M)$	Halides KX $(-10^6 \chi_M)$	Increment $-10^6 \Delta\chi$ $(XO_3' - X')$
Cl	41.53	38.7	+ 2.8
Br	54.6	49.6	+ 6.0
I	60.65	65.5	- 4.85

The increments for chlorate and bromate in this case are slightly higher than those of sodium salts, although the differences are not large and so may be within the range of the experimental errors. The increment $-10^6 \Delta\chi$ $(IO'_3 - I')$ is two units of susceptibility less for the potassium salt than for the sodium salt, a rather unexpected result as the co-ordination number of potassium in the iodate is higher than that of sodium in sodium iodate. A further consideration of this fall in the susceptibility increment between iodate and iodide follows the graph for the molar volumes and bondlengths of the oxyhalogen compounds.

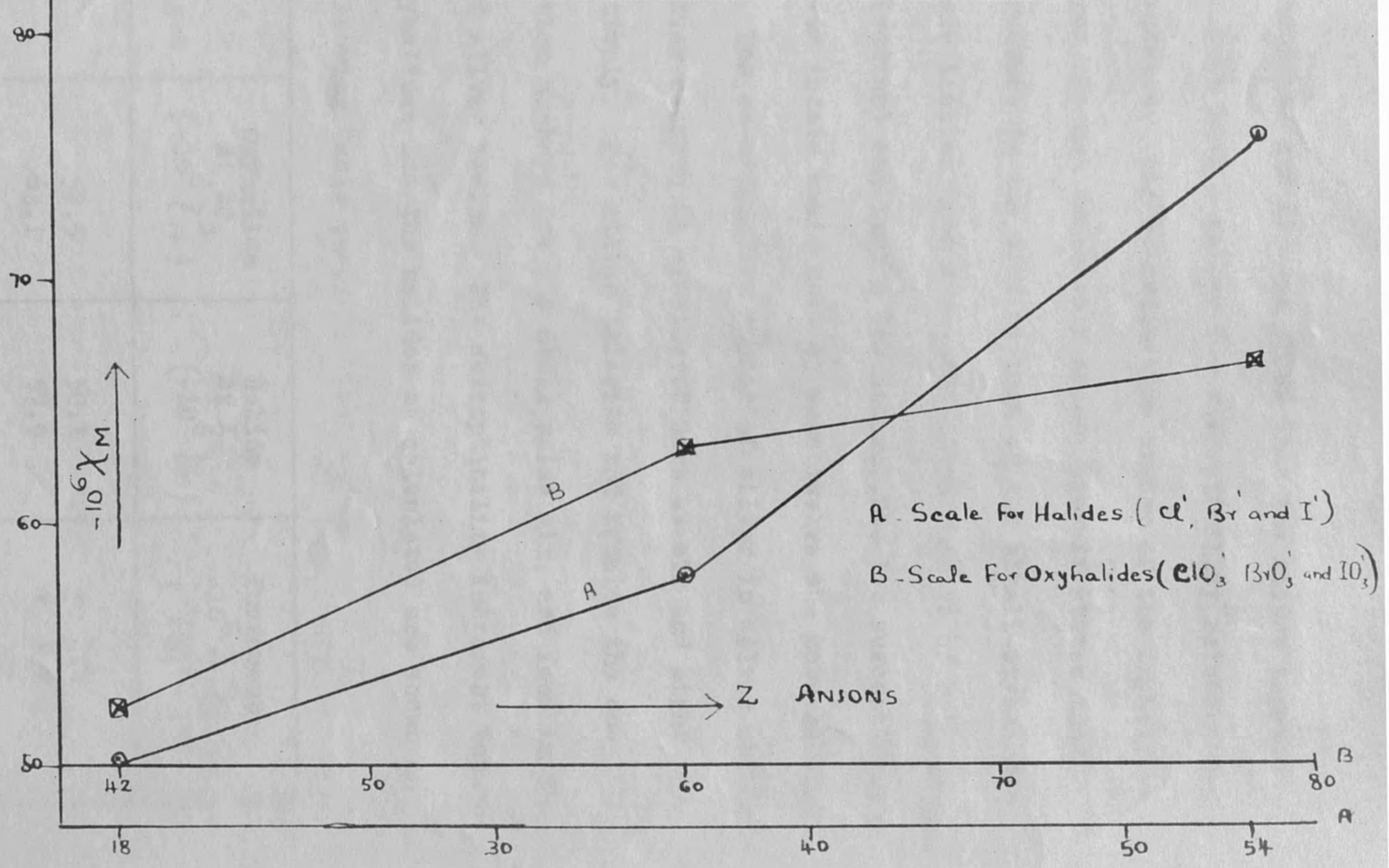
c. Silver salts.

The molar susceptibility of the silver oxyhalides and halides are plotted against the effective atomic number of the anion in figure 3a. The graph is very similar to that for the sodium and potassium salts. Once again the graph for the oxyanions shows a slight increase in slope between chlorate and bromate compared with the halide graph and once again crosses that for the halides. The value of the molar susceptibility of the silver iodate is found to be lower than might be expected. It can be seen from the graph and the following table that the increment between the iodate and the iodide in the case of silver is greater than that for sodium, potassium and thallium (1) compounds. The value for the susceptibility of silver iodide is also somewhat high and this could be expected from the low co-ordination number (4) in the salt silver iodide. The larger increment of -9.2 units of susceptibility between silver iodate and iodide may partly be due to this effect but, the slope of the graph be-

SILVER(I) SALTS

Fig. 3a.

$-10^6\chi_M$ against the effective atomic number of anions.



tween bromates and iodates shows that the silver iodate does in fact have a rather low susceptibility in relation to other iodates. The co-ordination number of the oxyhalides of silver is not definitely known. Wyckoff$^{(35)}$ states that the structure is the same as that of the alkali-oxyhalides, but these iodates have ~~a~~ co-ordination numbers of both eight (sodium) and twelve (potassium). The low susceptibility of silver iodate would seem to make twelve the more likely value. The co-ordination number of silver in silver chlorate and silver bromate is considered here as six and eight respectively. For silver chloride and bromide the co-ordination numbers are the usual value six, and four in the case of silver iodide. The susceptibility increment between the oxyhalides and the halides as calculated are shown in the following table :-

Halogen	Oxyhalide $AgXO_3$ $(-10^6\chi_M)$	Halide AgX $(-10^6\chi_M)$	Increment $-10^6\Delta\chi$ $(XO_3' - X')$
Cl	52.5	50.1	+ 2.4
Br	63.1	57.9	+ 5.2
I	66.5	75.8	- 9.2

Thallium salts

Figure 5a shows the molar susceptibilities of thallium (1) oxyhalides plotted against the effective atomic number of the anion and once again for comparison the similar graph for thallium (1) halides using the values in table 2 . The general form of the graph is similar to that of sodium potassium and silver salts. The susceptibility increments in this case are very similar to those for potassium salts except for the chlorate and chloride. The increment between thallium (1) chlorate and chloride is low compared with those of sodium, potassium and the silver (1) salts. The co-ordination number of thallium in halides is eight (CsCl structure) and in the Oxyhalides is also eight. So there is no co-ordination change in the case of thallium in passing from halides to oxyhalides, while in all other cases considered here there is a co-ordination number change. So the increments would be expected to be higher than when there is a co-ordination number change. The following table shows the numerical increments between the oxyhalides and the halides :-

THALLIUM (I) SALTS

Fig. 4a

$-10^6\chi_M$ against the effective atomic number of anions

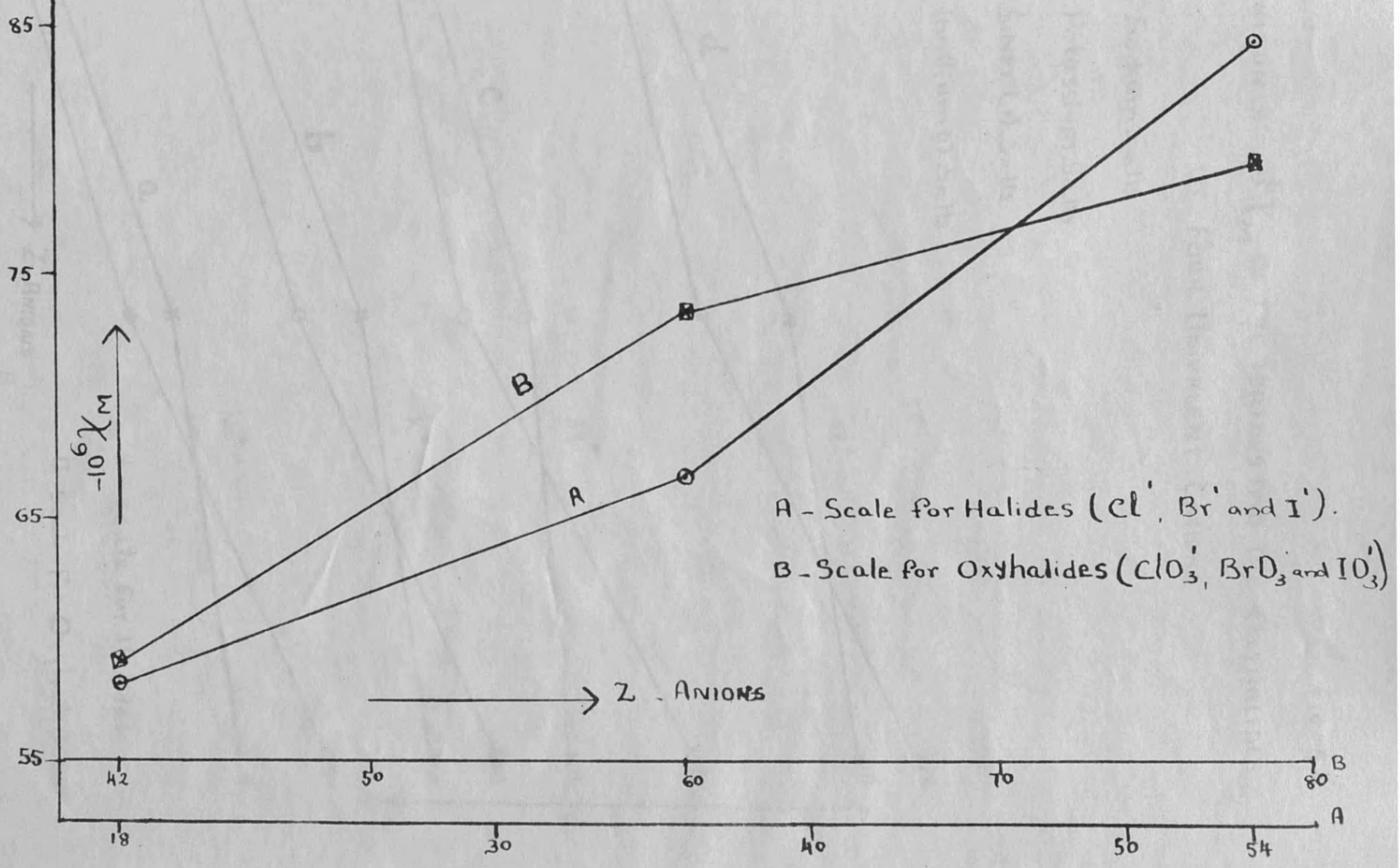
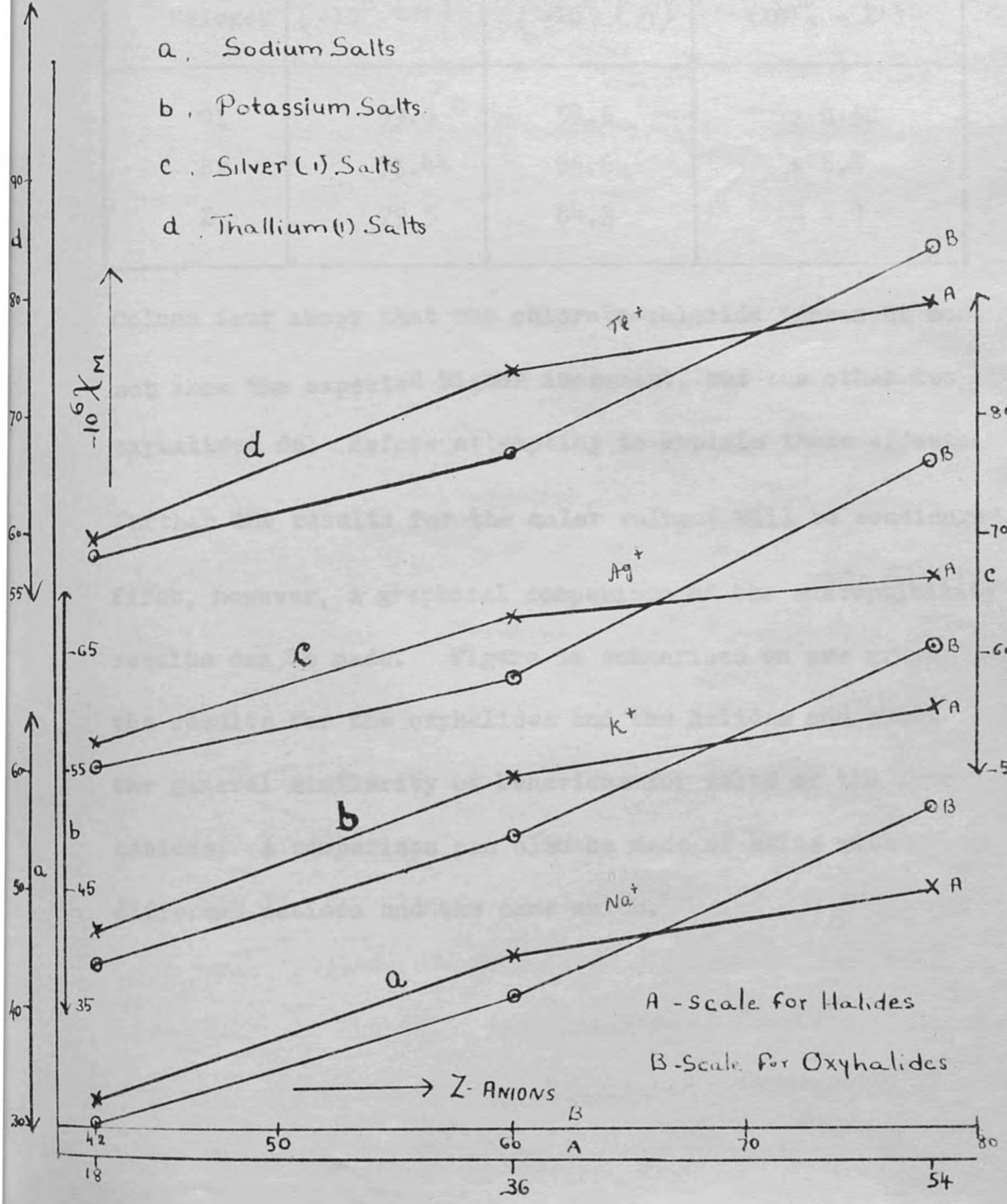


FIG. 5a

COMPARISON OF $-10^6\chi_M$ OF THE HALIDES AND THE OXYHALIDES OF FOUR UNIVALENT CATIONS



Halogen	Oxyhalide $TlXO_3$ $(-10^6 \chi_M)$	Halide TlX $(-10^6 \chi_M)$	Increment $-10^6 \Delta \chi$ $(XO'_3 - X')$
Cl	59.0	58.5	+ 0.50
Br	73.44	66.64	+ 6.8
I	79.5	84.3	- 4.8

Column four shows that the chlorate-chloride increment does not show the expected higher increment, but the other two oxyhalides do. Before attempting to explain these effects further the results for the molar volumes will be considered. First, however, a graphical comparison of the susceptibility results can be made. Figure 5a summarises on one graph the results for the oxyhalides and the halides and shows the general similarity of behavious for salts of the four cations. A comparison can also be made of salts with different cations and the same anion.

Comparison of susceptibilities of haloxy compounds $M X O_3$ with the same oxyanion and different cations.

The molar magnetic susceptibility values of the salts of the four different cations (Na^+ K^+ Ag^+ and TI^+) with the same anion can be compared. It is in this way possible to study any influence which the cation has on the susceptibility of the haloxyanion. By comparing the ionic susceptibility of the haloxyanion with the susceptibility of the corresponding halides, the susceptibility increment for the addition of three oxygens to the halides can be studied.

Chlorates

For the chlorates of different cations the magnetic susceptibilities were plotted against the effective atomic number of the cation and compared with those of chlorides, similarly plotted. On the same graph the ionic susceptibility of the cations are also shown. The values for the susceptibility of sodium and potassium cations are from Trew and Husain.(6) The values for silver and thallium cations are calculated from the present measurements of the susceptibility of the silver and thallium halides,

COMPARISON OF $-10^6\chi_M$ OF THE HALOXY COMPOUNDS WITH THAT OF HALIDES (FOR DIFFERENT CATIONS)

FIG. 6a

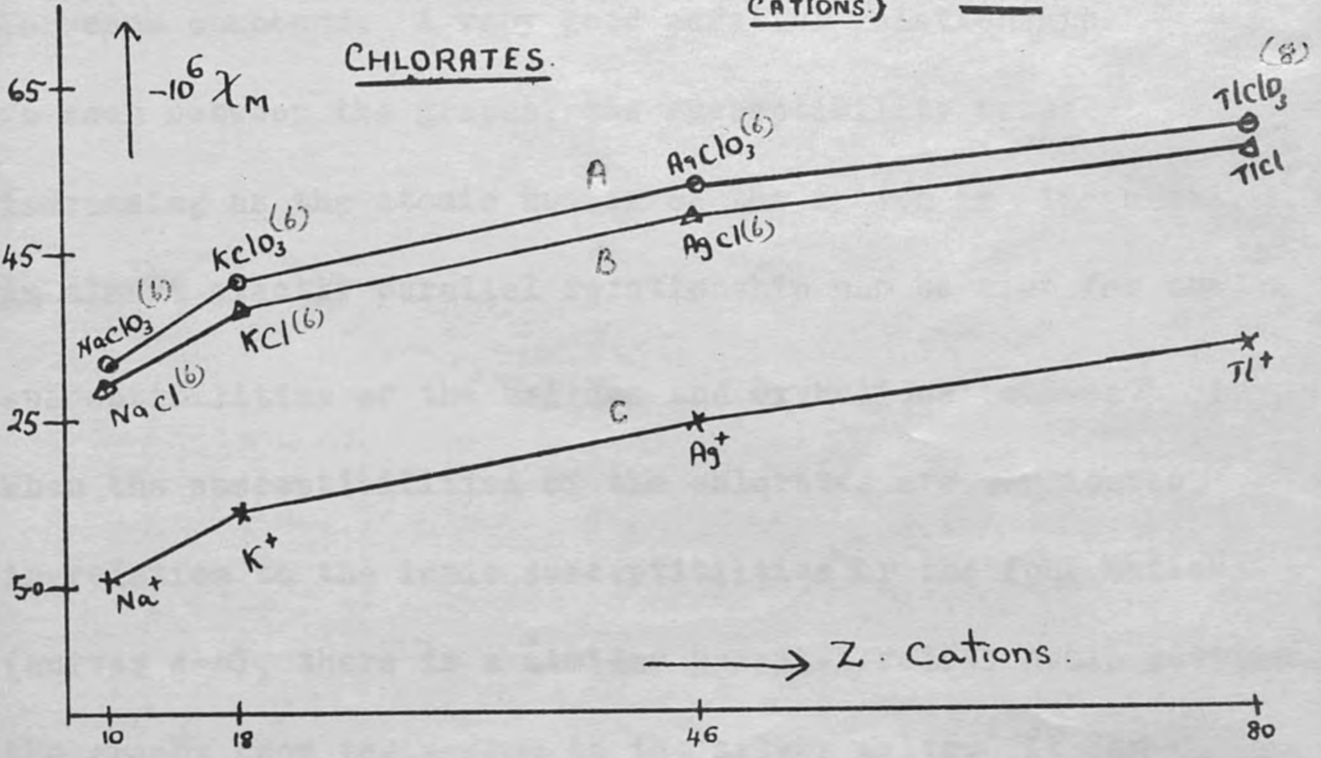
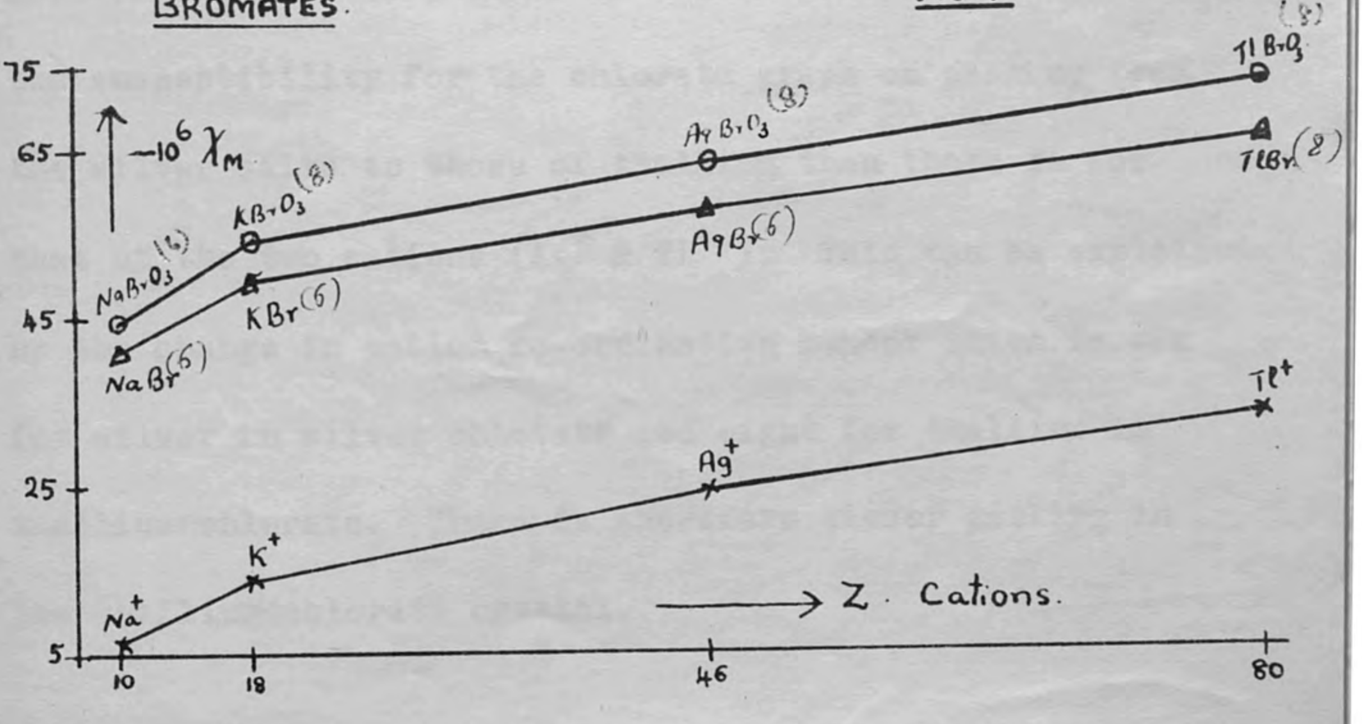


FIG. 7a



using the anion susceptibility constants of Trew and Husain. The three graphs are shown in figure 6a, the co-ordination number of the cation being indicated for each compound. A very good parallel relationship is seen between the graphs, the susceptibility value increasing as the atomic number of the cation is increased. An almost exactly parallel relationship can be seen for the susceptibilities of the halides and oxyhalides (curves B and A) When the susceptibilities of the chlorates are considered in relation to the ionic susceptibilties for the four cations (curves A and C), there is a similar parallel relationship between the graphs from the sodium to the silver salts. It can however, be seen that there is a less steep increment of the susceptibility for the chlorate graph on passing from the silver salts to those of thallium than there is for that of the two cations (Ag^+ & TI^+). This can be explained by the change in cation co-ordination number which is six for silver in silver chlorate and eight for thallium in thallium(I)chlorate. There is therefore closer packing in the thallium(I)chlorate crystal.

The actual susceptibility increment for addition of the three oxygen atoms may be calculated and is shown in the following table, together with the diamagnetic susceptibility constant for the chlorate ion which the present result would indicate :-

Cation	$-10^6 \chi_M$ chlorate	$-10^6 \chi_M$ chloride	$-10^6 \Delta\chi_M$, ($ClO_3'-Cl$)	$-10^6 \chi_M$ cation	$-10^6 \chi$ ClO_3' chlorate ion
Na^+	32.6	30.2	2.4	5.9	26.7
K^+	41.5	38.7	2.8	14.4	27.1
Ag^+	52.5	50.1	2.4	24.7	27.8
TI^+	59.0	58.4	0.6	32.9	26.1 mean 26.82

Column 4 of this table shows the increment for the three oxygen atoms and column 6 the diamagnetic susceptibility increment of the chlorate ion. The increase in susceptibility on passing from chloride to chlorate is constant at 2.6 units of susceptibility except in the case of thallium.

Bromates

Figure 7a shows similar curves for the bromates compared with those of the bromides and the ionic susceptibility of the cations. Here again we get a general parallel relationship between the curves. The slope between sodium and potassium bromates deviates from a parallel relationship with their bromides. The reason for this is not clear as correcting for the co-ordination number effect would make the curves even less parallel, i.e. the susceptibility of sodium bromate in eight fold co-ordination should be lower than in six fold co-ordination. Apart from this the slope of the curve between potassium and silver bromate is parallel to that for the corresponding bromides and the slightly lower value of the susceptibility of thallous bromide (C.N·8) can be explained in terms of its higher co-ordination number, an addition of about two susceptibility units is indicated from the graph to bring the curves parallel. This is of the same order as the susceptibility increment on changing from eight to six fold co-ordination which was found by Trew and Husain (10) for the alkali salts. With this correction for co-ordination number the curves for the bromates with co-ordination number eight are parallel to those for the bromides with co-ordination number six, with the exception of the sodium salt. The actual susceptibility increment between bromate and bromide in each case may be calculated, i.e. the susceptibility increment for addition of the three oxygen atoms. It is shown in the following table (Table a) together with the diamagnetic susceptibility constant for the bromate ion which the present results would indicate:-

Table a

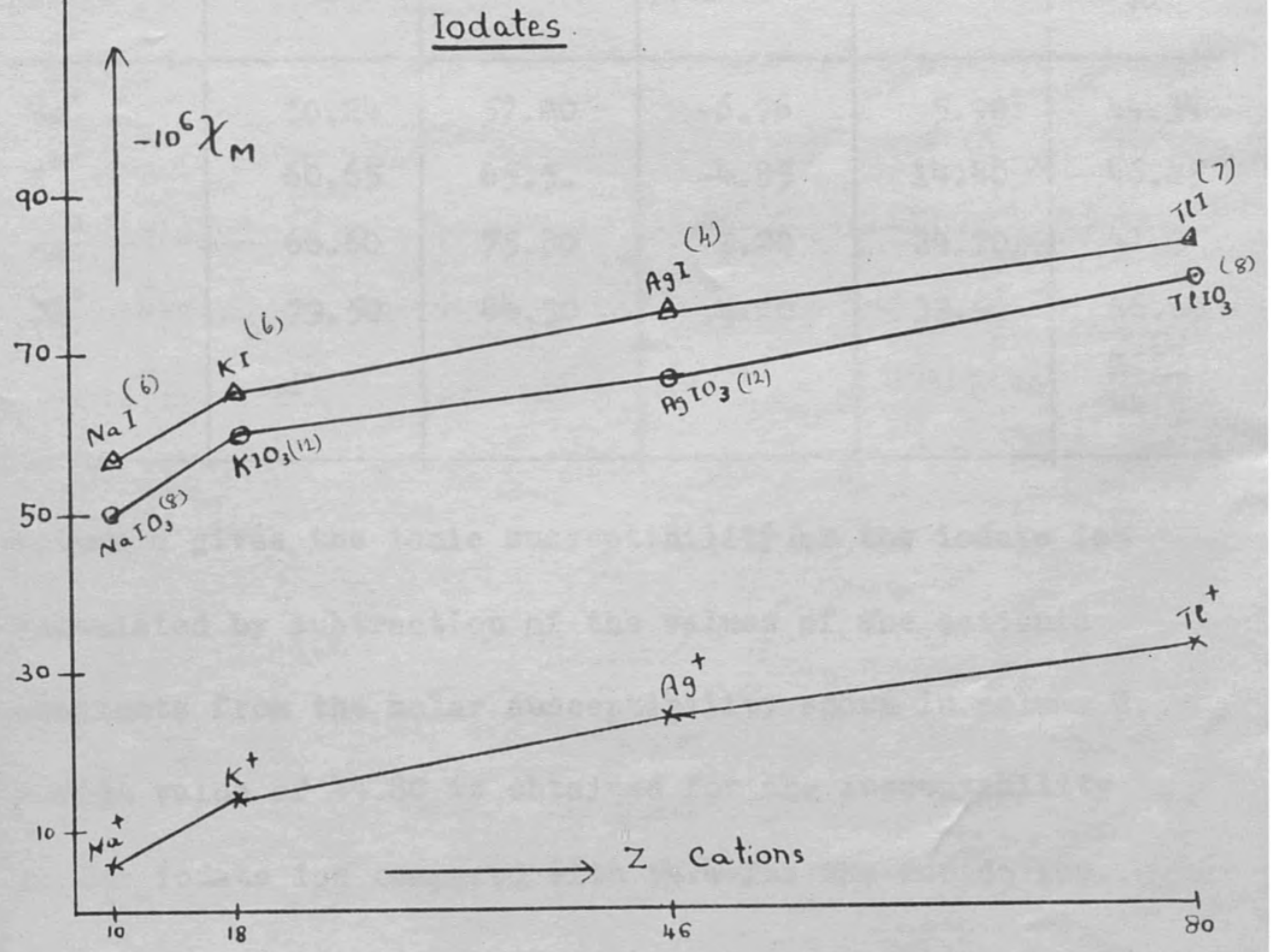
Cation	$-10^6 \chi_M$ bromate	$-10^6 \chi_M$ bromide	$-10^6 \Delta\chi$ (BrO_3'-Br')	$-10^6 \chi_M$ cation	$-10^6 \chi_{BrO_3'}$ bromate ion
Na^+	44.4	41.1	3.3.	5.9	38.5
K^+	54.6	49.6	5.0	14.4	40.2
Ag^+	63.1	57.84	5.26	24.7	38.4
TI^+	73.5	66.64	6.86	32.9	40.6
			(4.9 C.N corrected)		<u>mean</u> 39.33

Column 6 gives the ionic susceptibility for the bromate ion calculated by subtraction of the values of the cationic constants from the molar susceptibility of the salt shown in column 2. A mean value of 39,33 is obtained for the susceptibility of the bromate ion.

Iodates

For iodates of different cations the magnetic susceptibilities were plotted against the effective atomic number of the cations and compared with those of the chlorides. The curve for the iodates falls below that of the iodides, i.e. the magnetic susceptibility of the iodides is higher than that of the iodates. Though the graphs are fairly parallel, the cause for the lower susceptibility of the iodates needs to be explained and further study is needed. The negative increments for the susceptibilities between the iodates and the iodides are similar for potassium and thallium but rather larger for sodium and silver. From the graph and the table it can be seen that the magnetic susceptibility of silver iodide is high compared with other iodides and it may be due to the low co-ordination number of four. The actual experimental sus-

FIG. 8a


Iodates
$-10^6\chi_M$
90
70
50
30
10
NaI (6)
KI (6)
AgI (4)
TlI (7)
NaIO$_3$ (8)
KIO$_3$ (12)
AgIO$_3$ (12)
TlIO$_3$ (8)
Na$^+$
K$^+$
Ag$^+$
Tl$^+$
Z cations
10
18
46
80

ceptibility difference for the addition of the three oxygen atoms to the iodide ion may be calculated and is shown in the following table together with the diamagnetic susceptibility constant for the iodate ion which the present results would indicate :-

Cation	$-10^6 \chi_M$ iodate	$-10^6 \chi_M$ iodide	$-10^6 \Delta\chi$ $(IO_3' - I')$	$-10^6 \chi_M$ cation	$-10^6 \chi_{IO_3'}$ iodate ion
Na^+	50.24	57.00	-6.76	5.90	44.34
K^+	60.65	65.5.	-4.85	14.40	46.25
Ag^+	66.60	75.80	-9.20	24.70	41.9
Tl^+	79.50	84.30	-4.80	32.90	46.60
					<u>mean</u> 44.8

Column 6 gives the ionic susceptibility for the iodate ion calculated by subtraction of the values of the cationic constants from the molar susceptibility shown in column 2. A mean value of 44.80 is obtained for the susceptibility of the iodate ion compared with 54.4 for the iodide ion.

Molar Volumes of the chlorates, bromates and iodates of alkali metals and of silver and thallium

In table 2 are given the densities and molar volumes of the salts measured. The effective molar volume has been calculated from the densities of the salts, which were determined as described in part IIc. From the relationship $V_M^{20} = \frac{M}{d_4^{20}}$ the molar volumes were calculated. In some cases where the density was well established, it was not redetermined and the molar volumes were calculated from density values given in the literature. These values are indicated(a) in the table and other literature values are shown in column 6, in the case where the density was remeasured. In table 2, column 1 gives the formula of the compound. The molecular weight is given in column 2; column 3 gives the coordination number of the cation, and columns 4 and 5 give the density and the calculated molar volume. Molar volumes of the haloxy compounds of the alkali metals and those of silver (1) and thallium (1) are plotted similarly to the susceptibilities against the effective atomic number

TABLE 2

Summary of the densities and molar volumes of the oxyhalides (M XO_3)

Compound	Mol. wt.	C.N.	D_4^{20}	V_M^{20}	V_M^{20} (Literature)
Na Cl	58.45	6	2.165 (a)	27.00	
Na ClO_3	106.45	6	2.485	42.84	
Na Br	102.91	6	3.203 (a)	32.13	
Na BrO_3	150.91	6	3.30	45.73	
Na I	149.92	6	3.667 (a)	40.88	
Na IO_3	197.92	8	4.277	46.20	46.2 (36)
K Cl	74.55	6	1.988 (a)	37.5	
K ClO_3	122.55	6	2.325	52.71	52.8 (36) 52.3 (36)
K Br	119.01	6	2.75 (a)	43.27	
$KBrO_3$	167.01	8	3.22	51.87	
KI	166.02	6	3.13 (a)	53.04	
KIO_3	214.02	12	3.94	54.32	

Table 2 (contd)

Compound	Mol.wt.	C·N	D_4^{20}	V_M^{20}	V_M^{20} (Lit)
Ag Cl	143.34	6	5.56	28.8	
Ag ClO_3	191.34		4.418	43.192	43.2 (37)
Ag Br	187.8	6	6.47 (a)	29.02	
Ag BrO_3	238.80	8	5.208	45.3	45.3 (37)
Ag I	234.812	4	5.67 (a)	41.41	
Ag IO_3	282.8		5.52	51.2	51.2 (37)
Tl Cl	239.85	8	7.0 (a)	34.26	
Tl Cl O_3	287.85	8	5.01	57.455	
Tl Br	284.31	8	7.55 (a)	37.66	
Tl BrO_3	332.31	8	5.91	56.23	
Tl I	331.31	7	7.09 (a)	46.73	
Tl IO_3	379.3	8	6.045	62.75	

The literature values taken for the densities are indicated by the number in brackets given above in density values.

of the anions and these are compared with the molar volume of the corresponding halides in each case. Figures 1b, 2b, 3b and 4b show these graphs. The same scale is used throughout for comparison.

1. Sodium Salts. (Figure 1b)

In the case of sodium salts, the slope between the chlorate and the bromate is slightly less steep than for the chloride and the bromide. From the bromate to the iodate, there is very little rise in the molar volume unlike the rise in increment between the bromide and iodide. This can be seen from the graph and from the increments which are calculated by subtracting the molar volumes for the appropriate pairs.

ie;

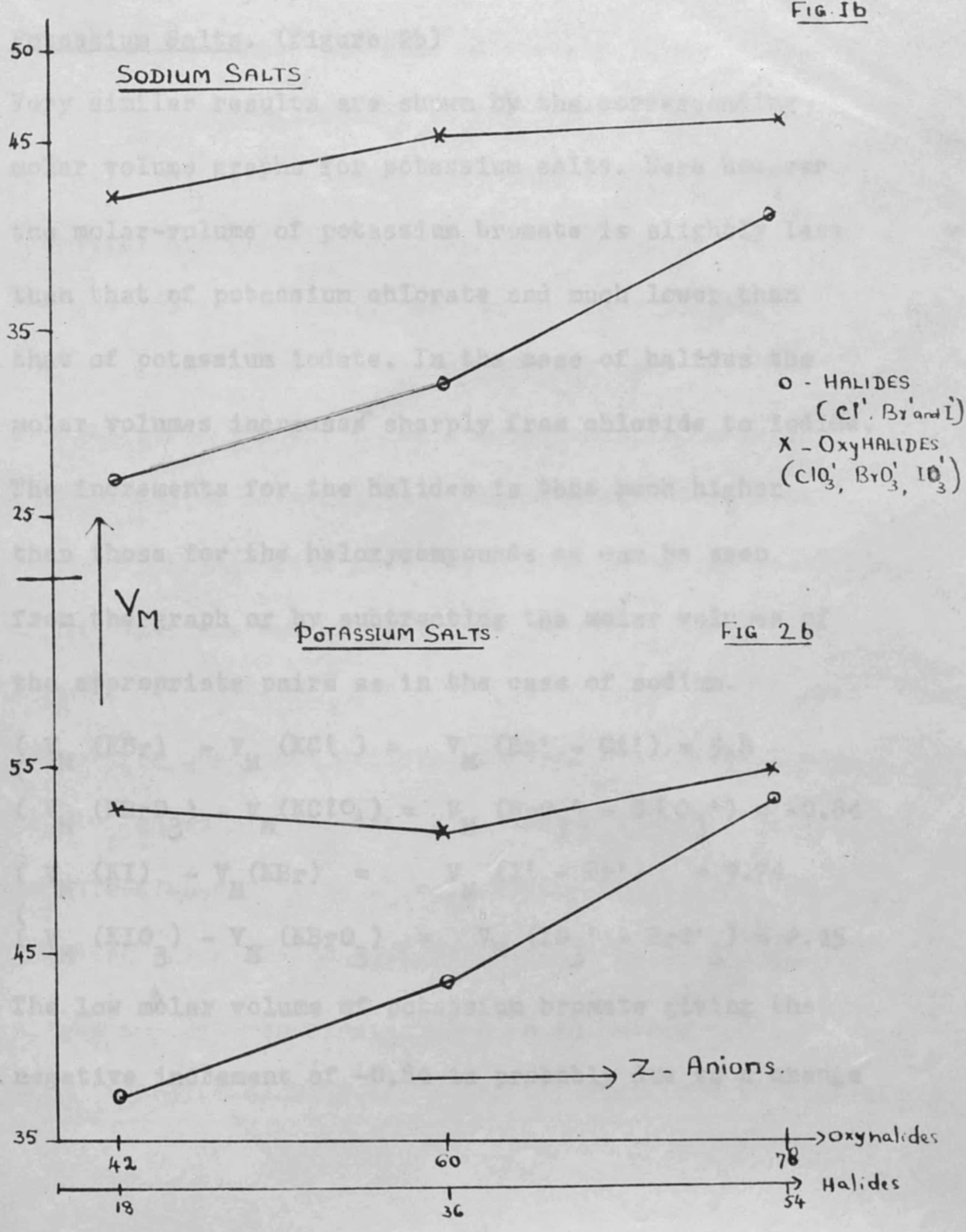
$$\begin{cases} V_M\,(NaBr) - V_M\,(NaCl) = V_M\,(Br' - Cl') = 3.85 \\ V_M\,(NaBrO_3) - V_M\,(NaClO_3) = V_M\,(BrO_3' - ClO_3) = 2.89 \end{cases}$$

$$\begin{cases} V_M\,(NaI) - V_M\,(NaBr) = V_M\,(I' - Br') = 8.75 \\ V_M\,(NaIO_3) - V_M\,(NaBrO3) = V_M\,(IO_3' - BrO_3') = 0.47 \end{cases}$$

There is therefore a much smaller increase in the total molar volume of the oxy~~x~~ anion salts for each pair than

V_M OF THE OXYHALIDES (OF Sodium and Potassium)

COMPARED WITH V_M of the Halides



for the simple halides. This is especially marked on passing from the bromate to the iodate as compared with the bromide and iodide.

Potassium Salts. (figure 2b)

Very similar results are shown by the corresponding molar volume graphs for potassium salts. Here however the molar-volume of potassium bromate is slightly less than that of potassium chlorate and much lower than that of potassium iodate. In the case of halides the molar volumes increase~~s~~ sharply from chloride to iodide. The increments for the halides is thus much higher than those for the haloxycompounds as can be seen from the graph or by subtracting the molar volumes of the appropriate pairs as in the case of sodium.

$$\left(\begin{array}{l} V_M(KBr) - V_M(KCl) = V_M(Br' - Cl') = 5.8 \\ V_M(KBrO_3) - V_M(KClO_3) = V_M(BrO_3' - ClO_3') = -0.84 \end{array}\right.$$

$$\left(\begin{array}{l} V_M(KI) - V_M(KBr) = V_M(I' - Br') = 9.74 \\ V_M(KIO_3) - V_M(KBrO_3) = V_M(IO_3' - BrO'_3) = 2.45 \end{array}\right.$$

The low molar volume of potassium bromate giving the negative increment of -0.84 is probably due to a change in coordination and hence of the packing of the potassium ion which arises from a different crystal structure. Now a systematic study of the crystal structure and coordination number for some of these haloxy compounds can be made with reference to the Landolt-Börnstein Tables,(38) Wells(39) (Structural Chemistry) and Wyckoff(35) (crystal structure). The references are indicated (a) (b) and (c) respectively. All the sodium, potassium and rubidium halides have the NaCl(O_h) type of crystal structure which has a coordination number of six.

$NaClO_3$. Sodium Chlorate is included in the G O_3 type(a). It shows similarities with the NaCl type for the position of the chlorine and sodium atoms. The ClO_3 group shows a pyramidal form arranged with the chlorine at the apex. The oxygen atoms are directed towards the Sodium,Since Na ClO_3 shows similarities with the NaCl type, the coordination of the Na atom in sodium chlorate is six. The distortion of the NaCl arrangement in $NaClO_3$ is slight so that the crystal as a whole remain cubic.

$NaBrO_3$. Sodium bromate has a similar structure to that of sodium chlorate (GO_3) and it shows similarities with the Na Cl type for the position of the bromine and the sodium atoms. The bromate group forms a rather flat pyramid with bromine at the apex. The coordination number of the sodium ion is six.

$\underline{NaIO_3}$. Sodium iodate yields an X - ray pattern very like that of $CaTiO_3$ and it was therefore originally thought to be a distorted perovskite-like pseudo cubic ( ) structure (C). The arrangement developed by a more careful analysis shows however a considerable departure from this structure. It is suggested that it has a distorted array of sodium atoms and iodate ions of the same shape as the chlorate and bromate ions. No one is certain about the structure of $NaIO_3$ so far. A coordination number of eight is suggested here since the susceptibility value for sodium iodate measured tends to support this coordination number.

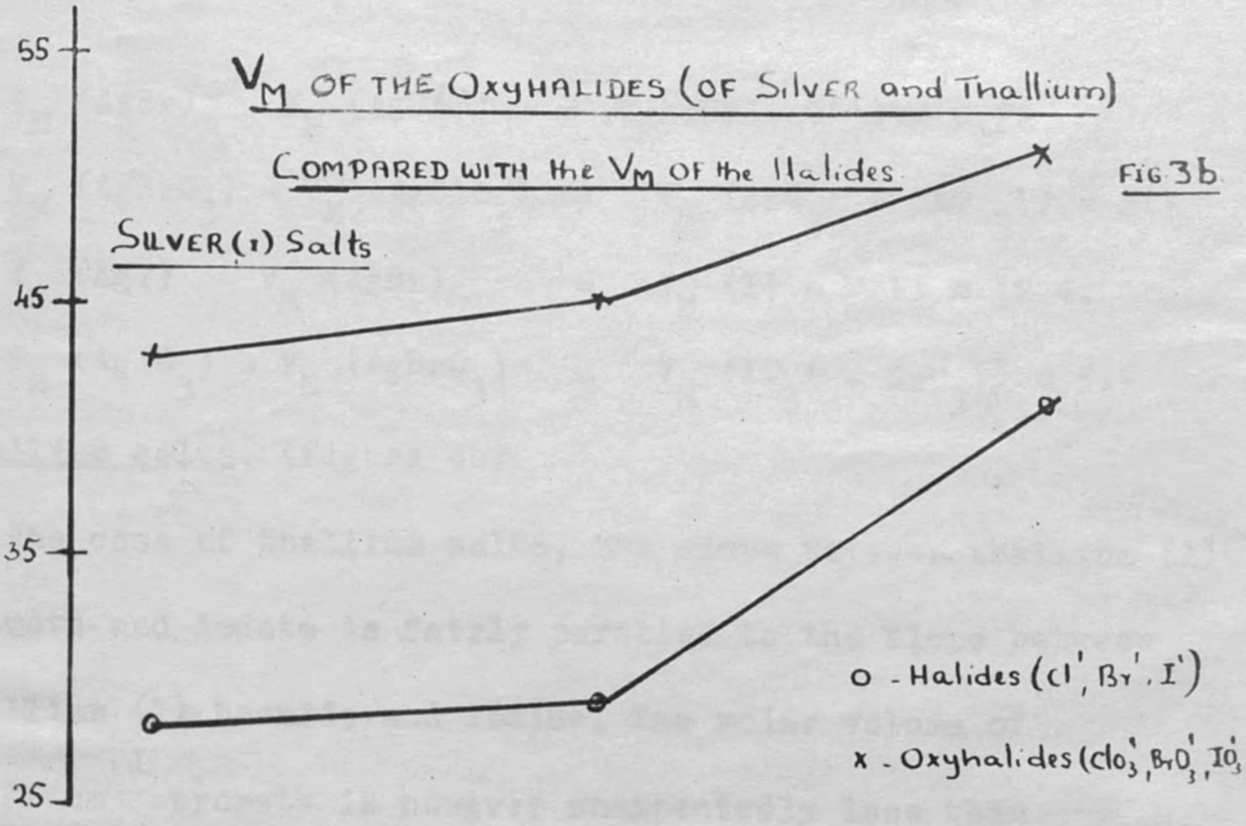
$\underline{KClO_3}$. Potassium chlorate has a structure, which in spite of its monoclinic crystal form is closely related to that of the bromate (C) and like it, is a distortion of the sodium chloride arrangement. The resulting chlorate ions are trigonal pyramids of substantially the same shape and size as those in the more definitely established sodium chlorate structure.

$\underline{KBrO_3}$. The GO_7 type of symmetry is given in the case of potassium bromate. This is of the ceasium chloride type of symmetry which has a coordination of eight.

$\underline{KIO_3}$. Potassium iodate is of the E_{2_1} symmetry type which is that of perovskite (CaTiO3). The calcium atom has the coordination number of twelve in $CaTiO_3$ and thus it is assumed that the potassium has a similar coordination number in KIO_3 (a) and (c)

G. Silver Salts. (figure 3b).

The slope of the graph from the chloride to the bromide is slightly steeper than that from chlorate to bromate, but from bromide to iodide, the slope is very much steeper than that from bromate to iodate. This can be seen from the graph and by subtracting the molar volumes of the appropriate pairs:-



V_M OF THE OXYHALIDES (OF Silver and Thallium) COMPARED WITH the V_M OF the Halides

FIG 3b.

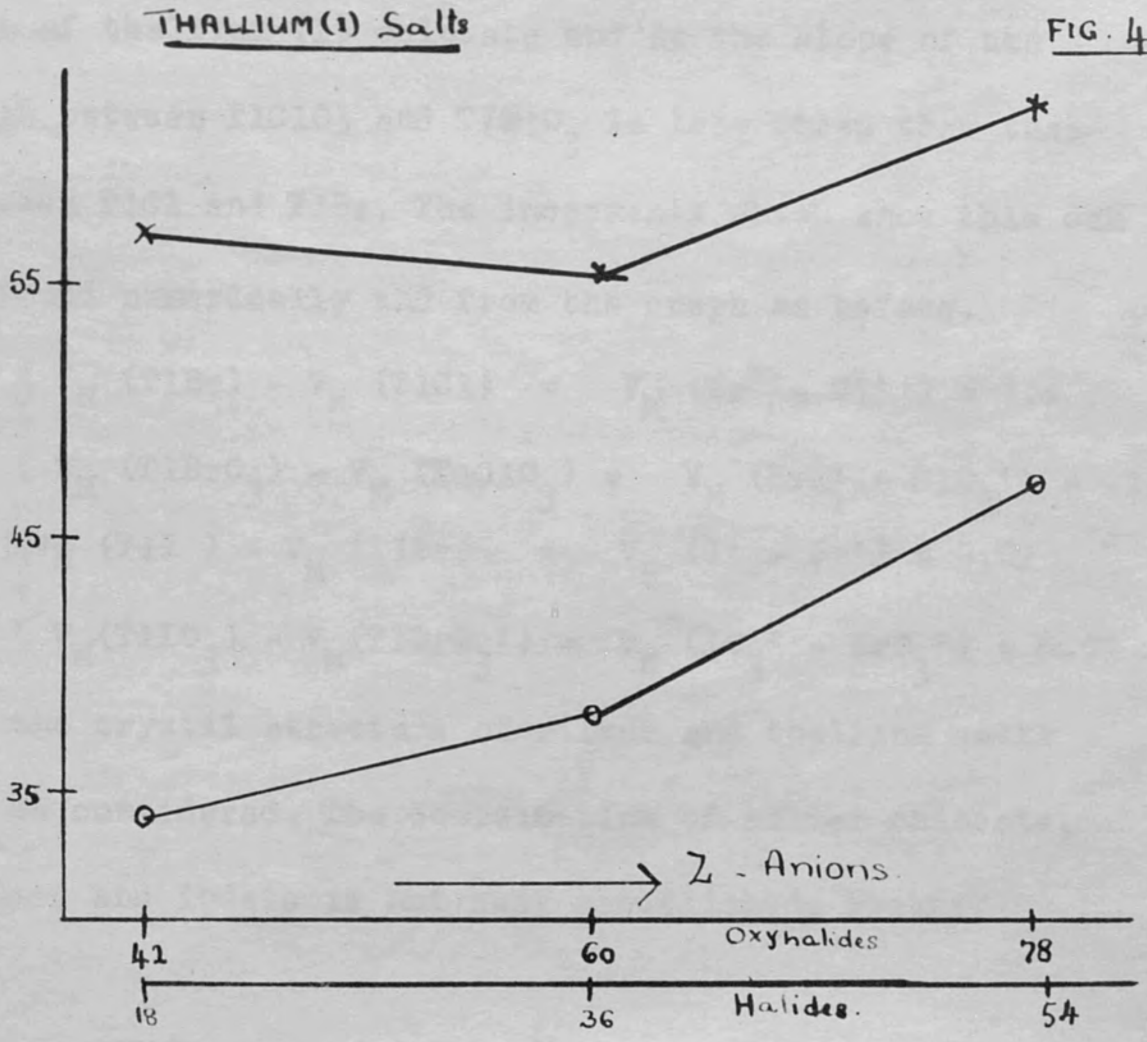


FIG. 4b.

ie-

$$\begin{cases} V_M\,(AgBr) - V_M\,(AgCl) = V_M(Br' - Cl') = 0.22 \\ V_M\,(AgBrO_3) - V_M\,(AgClO_3) = V_M\,(BrO_3' - ClO_3') = 2.1 \end{cases}$$

$$V_M\,(AgI) - V_M\,(AgBr) = V_M\,(I' - Br') = 12.4.$$

$$V_M\,(AgIO_3) - V_M\,(AgBrO_3) = V_M\,(IO_3' - BrO_3') = 5.9$$

Thallium salts. (figure 4b)

In the case of thallium salts, the slope between thallium (1) bromate and iodate is fairly parallel to the slope between thallium (1) bromide and iodide. The molar volume of thallium ^{1} bromate is however unexpectedly less than that of thallium (1) chlorate and so the slope of the graph between $TlClO_3$ and $TlBrO_3$ is less steep than that between TlCl and TlBr. The increments which show this can be found numerically and from the graph as before.

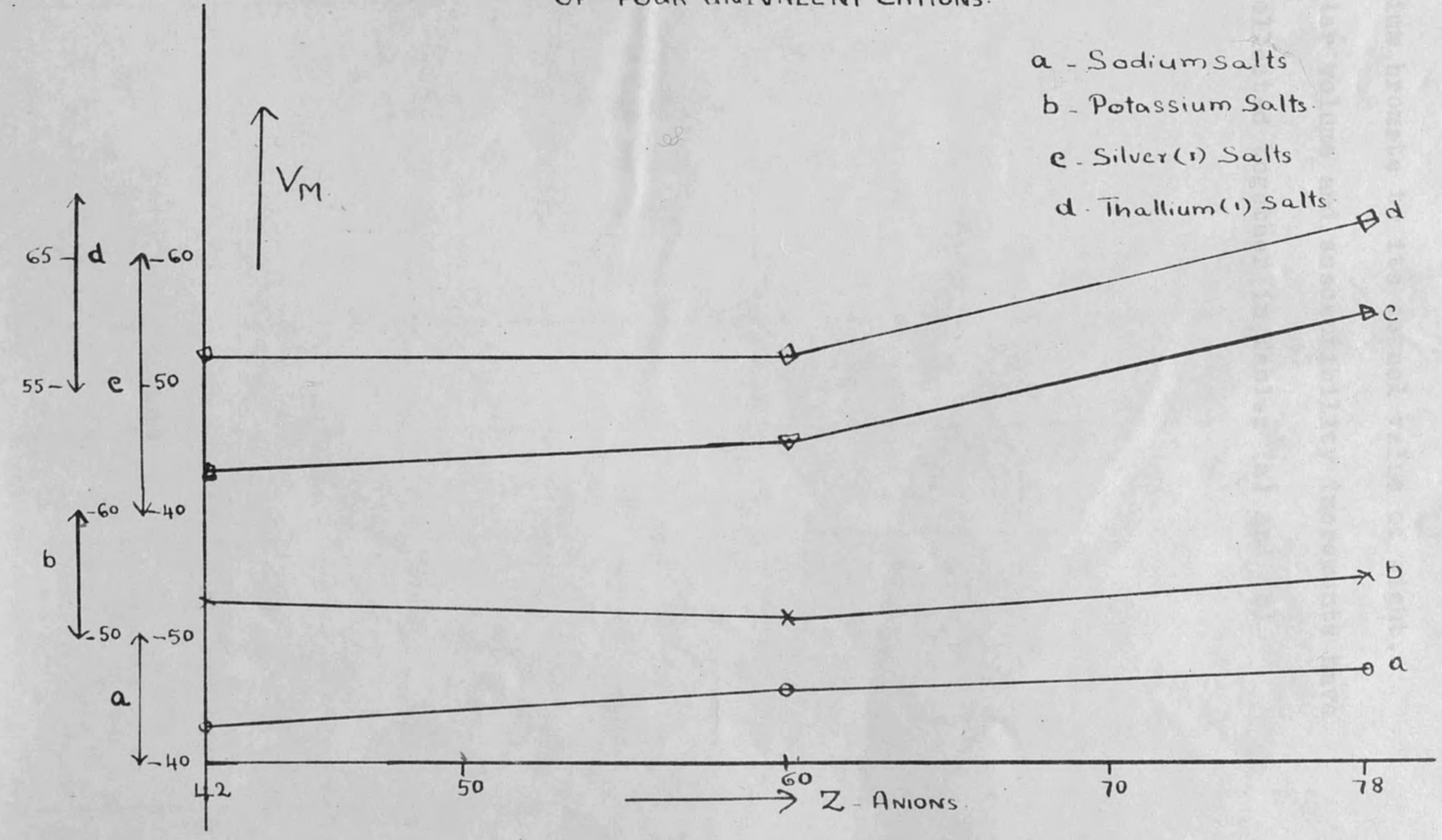
ie.
$$\begin{cases} V_M\,(TlBr) - V_M\,(TlCl) = V_M\,(Br' - Cl') = 3.4 \\ V_M\,(TlBrO_3) - V_M\,(TlClO_3) = V_M\,(BrO_3' - ClO_3') = -1.23 \end{cases}$$

$$\begin{cases} V_M\,(TlI) - V_M\,(TlBr) = V_M\,(I' - Br') = 9.07 \\ V_M(TlIO_3) - V_M(TlBrO_3') = V_M\,(IO_3' - BrO_3') = 6.52 \end{cases}$$

Now the crystal structure of silver and thallium salts can be considered. The coordination of silver chlorate, bromate and iodate is not well established. Wyckoff suggests that the chlorate ion here should have the same size and shape as in potassium chlorate and so may have the same coordination number. This is six, and the bromate and iodate, like the potassium salts, probably have a coordination number of eight and twelve.

$TlClO_3$ & $TlBrO_3$ According to Wyckoff thallous chlorate and bromate have the potassium bromate structure with a coordination number of eight. The molar volume and molar susceptibility graphs may help to support this structure. The molar volumes of all the haloxy salts are plotted on the same graph against the effective atomic number of the anions. (Figure 5b). It can be seen that all the graphs are more or less parallel to each other with the small deviations already pointed out above. The slopes between the bromates and iodates are fairly parallel while the slopes between the chlorates and the bromates are rather less parallel. This combined graph brings out very clearly the change in coordination number of potassium bromate from the six fold coordination

COMPARISON OF V_M OF THE OXYHALIDES (ClO_3' , BrO_3' and IO_3') OF FOUR UNIVALENT CATIONS. **FIG. 5b.**



of sodium bromate to its actual value of eight. The molar volume and susceptibility increments have been collected together in Tables[3](a) and (b)

TABLE 3a

Summary of molar susceptibility and molar volume increments

Salt	$-10^6 \chi$ M (chlorate)	$-10^6 \chi$ M (Bromate)	$-10^6 \chi$ M (iodate)	$-10^6 \Delta\chi$ M ($BrO_3{}' - Cl O_3'$)	$10^6 \Delta\chi$ M ($IO_3' - BrO_3{}'$)
Na^+	32.47	44.4	50.00	11.93	5.60
K^+	41.513	54.589	60.65	13.07	6.05
Ag^+	52.44	63.06	66.57	10.62	3.51
$T\ell^+$	58.96	73.5	79.5	14.54	6.00
				mean 12.54 =====	mean 5.3 ===

TABLE 3b

Salt	V_M ($Cl O_3'$)	V_M ($BrO_3{}'$)	V_M (iodate)	ΔV_M ($BrO_3' - Cl O_3'$)	ΔV_M ($IO_3' - BrO_3'$)
Na^+	42.84	45.73	46.2	2.89	0.5
K^+	52.71	51.87	54.32	0.84	2.45
Ag^+	43.192	45.3	51.2	2.10	5.1
T^+	57.45	56.23	62.75	1.22	6.52

PERCHLORATES

a. Magnetic Molecular Susceptibility

Magnetic susceptibility measurements were made of the perchlorates of the alkali metals and of silver and thallium, together with those of barium and magnesium. Lithium, rubidium, caesium and thallium perchlorates were prepared and the other perchlorates were obtained and then recrystallised. Three measurements of the magnetic susceptibility were made on each perchlorate. Each time six readings were taken and the mean value was used for calculation. The packing of the susceptibility tube was carried out in a dry box with special care as the salts are deliquescent. Table 4 summariees the results obtained for the molar susceptibility as well as the measured specific susceptibility of the perchlorates. The value of the molar susceptibility values for the perchlorates were plotted against the effective

TABLE 4

$-10^6 \chi_M$ of the Chlorides (MCl) and the perchlorates ($MClO_4$) of the univalent cations

Salt	Mol.wt.	C.N.	$-10^6 \chi$ salt	$-10^6 \chi_M$	$-10^6 \chi_M$ or $-10^6 \chi$ salt (Literature)
$LiCl$	42.4	6		23.3 (5)	
$LiClO_4.3H_2O$	160.4		0.4105	65.85	
			0.4123	66.13	
			0.4100	65.60	
				mean 65.90	
$LiClO_4$	106.4			27.02	
$NaCl$	58.45	6	0.5167	30.2 (5)	
$NaClO_4$	122.45	8	0.2960	36.25	41.0 (40)
			0.2995	36.67	
			0.3000	36.74	
				mean 36.6	

TABLE 4 (contd)

Salt	Mol.wt.	C.N.	$-10^6 \chi$ salt	$-10^6 \chi_M$	$-10^6 \chi_M$ or $-10^6 \chi$ salt (Literature)
K Cl	74.55	6	0.5191	38.7 (10)	
K Cl O_4	138.56	12	0.3305	45.75	-0.341 (41)
			0.3311	45.89	-0.328 (4)
			0.3377	46.80	$44.6^{*} \pm 0.22$ (32)
			0.3374	46.75	48.1 (6)
				mean 46.3	
RbCl	120.94	5		46.4 (5)	
Rb Cl O_4	184.94	12	0.3010	55.70	53.1 (41)
			0.3030	56.00	
			0.3007	55.61	
				mean 55.80	

TABLE 4 (contd)

Salt	Mol.wt. (M)	C.N	$-10^6 \chi$ salt	$-10^6 \chi$ M	$-10^6 \chi$ M or $-10^6 \chi$ salt (Literature)
$CsCl$	168.4	8	0.3368	56.7(5)	
$CsClO_4$	232.4	12	0.2806	65.21	70.4(41)
			0.2812	65.33	
			0.2817	65.46	
				mean 65.33	
$AgCl$	143.34	6	0.3495	50.1	
$AgClO_4$	207.34	12	0.2720	56.37	
			0.2725	56.50	
			0.2715	56.3	
				mean 56.4	
$TlCl$	239.85	8	0.2439	58.4	57.8(6)

TABLE 4 (contd)

Salt	Mol.wt. (M)	C.N.	$-10^6 \chi$ salt	$-10^6 \chi$ M	$-10^6 \chi$ M or $-10^6 \chi$ salt)Literature)
$TlClO_4$	303.85	12	0.2277	69.20	72.5(6)
			0.2274	69.10	
			0.2278	69.22	
				mean 69.2	
= = =	= = =	= = =	= = =	= = =	= = =
$MgCl_2$	95.23	6	0.5236	49.86(34)	
$Mg(ClO_4)_2$	223.23		0.3033	67.69( )	
$BaCl_2$	208.27	9	0.3501	72.92(22)	
$Ba(ClO_4)_2$	336.27		0.2679	90.1	

atomic number of the cations and compared with those of the corresponding chlorides, and with the experimental and theoretical susceptibility of the cations. As in earlier graphs the cation coordination number is shown on the graph for each salt. The theoretical ionic susceptibility calculated from Slater's atomic constants for the cations is shown on the lower part of figure 9 for comparison. There is a good general similarity for the slopes of the graphs in the case of perchlorates, chlorides, and the experimental susceptibility of the cations, although one or two significant differences are found. The graph for the theoretical susceptibility of the cations rises much more steeply for cations after rubidium than the experimental curves. This result is similar to that noted by earlier workers, especially Klemm(8) and Trew,(9) and will be considered in connection with the theoretical discussion later in section IV. Susceptibility increments between perchlorates and chlorides, and between perchlorates and cations are

FIGURE. 9

COMPARISON OF $-10^6\chi_M$ OF THE PERCHLORATES (OF Li, Na, K, Rb, Ag, Cs, and Tl) WITH THE CORRESPONDING CHLORIDES AND CATIONS

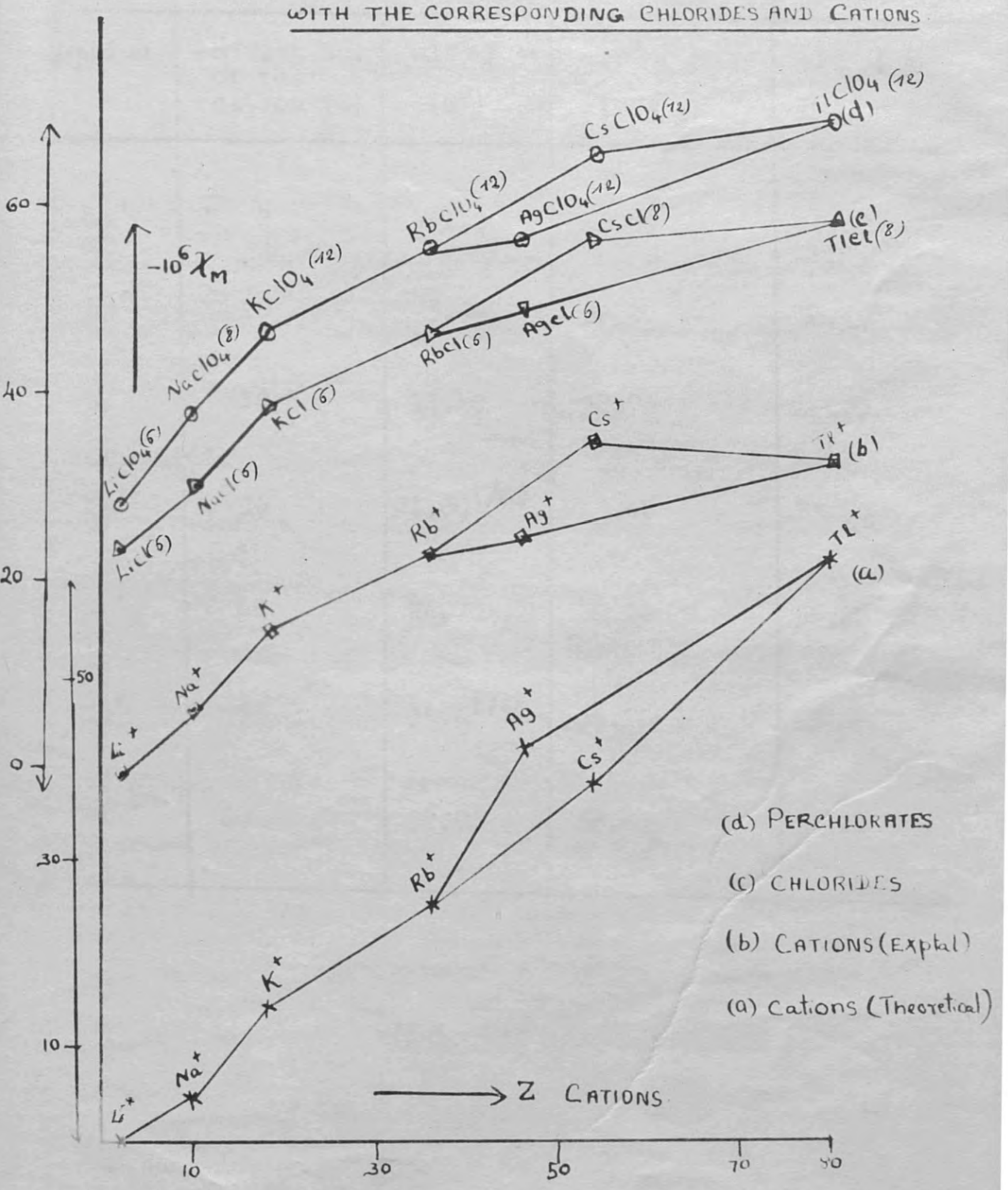


TABLE 5

Summary of the graph (figure 9) (chlorides & perchlorates)

Cation	Eff. at No. of the cation (Z)	$-10^6 \chi_M$ (M^+)	$-10^6 \chi_M$ $(MC\ell_{\cancel{2}})$	$-10^6 \chi_M$ $(MC\ell O_4)$
Li^+	2	+ 1.0	23.30	27.02
Na^+	10	5.90	30.20	36.60
K^+	18	14.40	38.70	46.30
Rb^+	36	21.80 (10)	46.40	55.80
Ag^+	46	24.70	50.10	56.40
Cs^+	54	34.4 (10)	56.70	65.40
$T\ell^+$	80	32.90	58.40	69.20

also summarised in table 5 The chief discrepancy is that of lithium perchlorate which has a susceptibility less than the expected value from the slopes of the graph. The other increments are very much as expected within the limits of experimental error, but the effect of the change in coordination is not clear in all cases. The parallel relationship is good between potassium and rubidium, and caesium and thallium, where compounds of the same coordination number are being compared for all three curves. Sodium perchlorate does not however seem to show the effect of its lower coordination number as the three curves are parallel between sodium and potassium. The silver perchlorate value seems to be a little low and the silver chloride value rather high for a good parallel relationship between rubidium and silver. From table 6 the mean molar susceptibility for the perchlorate ion from the values in column 6 is 32.5 omitting the low lithium value. A more or less constant increment would be expected corresponding to the increased volume of the

TABLE 6

Susceptibility increment between the perchlorates and the chlorides

Cation	$-10^6 \chi$ M $MClO_4$	$-10^6 \chi$ M MCl	$-10^6 \chi$ M M^+	$-10^6 \Delta \chi$ $(ClO_4' - Cl')$	$-10^6 \chi$ M (ClO_4')
Li^+	26.98	$23.3^{(a)}$	1.0 (para)	3.68	27.98
Na^+	$38.3^{(8)}$	$30.2^{(6)(a)}$	$5.9^{(b)}$	8.10	32.4
K^+	$46.3^{(12)}$	$38.7^{(6)}$	$14.4^{(b)}$	7.60	31.9
Rb^+	$55.8^{(12)}$	$46.4^{(6)(a)}$	$21.8^{(b)}$	9.4	34.0
Cs^+	$65.4^{(12)}$	$56.7^{(8)(a)}$	$34.4^{(b)}$	8.7	31.0
		$58.8^{(b)}$		6.6	
Ag^+	$56.4^{(12)}$	$50.1^{(6)}$	24.7	6.3	31.7
Tl^+	$69.2^{(12)}$	$58.4^{(8)}$	32.9	10.8	36.3

(TABLE 6 (contd)

Cation	$-10^6\chi$ M $(M(ClO_4)_2)$	$-10^6\chi$ M (MCl_2)	$+10^6\chi$ M M^{++}	$-10^6\Delta\chi$ $(ClO_4)_2' - 2Cl_2'$	$-10^6\chi$ M ClO_4'
Ba^{++}	90.1	72.92	24.3	8.6	32.9
Mg^{++}	67.69	49.86	2.6	8.92	32.55
					mean 32.5

32.5 units of susceptibility is obtained for the perchlorate ion.

<u>NOTES</u> : Co-ordination numbers are given in brackets

(a) Bringley and Hoare

(b) Trew and Husain

(Lithium salts generally show anomalous result) ion on passing from chloride to perchlorate. The increments between the perchlorates of different cations were calculated and are shown below. In each case the susceptibility of the second ion is subtracted from that of the first showing the increment for the various pairs of compounds arranged with increasing atomic number.

$(-IO^{6}\chi\,\mathrm{Na\ C104}) - (-IO^{6}\chi\,\mathrm{Li\ ClO_4}) = 9.52$

$(-IO^{6}\chi\,\mathrm{K\,C104}) - (-IO^{6}\chi\,\mathrm{Na\ ClO_{4}}) = 9.8$

$(-IO^{6}\chi\,\mathrm{Rb\ ClO_4}) - (-IO^{6}\chi\,\mathrm{KClO_4}) = 9.5$

$(-IO^{6}\chi\,\mathrm{CsClO_4}) - (-IO^{6}\chi\,\mathrm{Rb\ ClO_4}) = 9.53$

$(-IO^{6}\chi\,\mathrm{TlClO_4}) - (-IO^{6}\chi\,\mathrm{Cs\ ClO_4}) = 3.9$

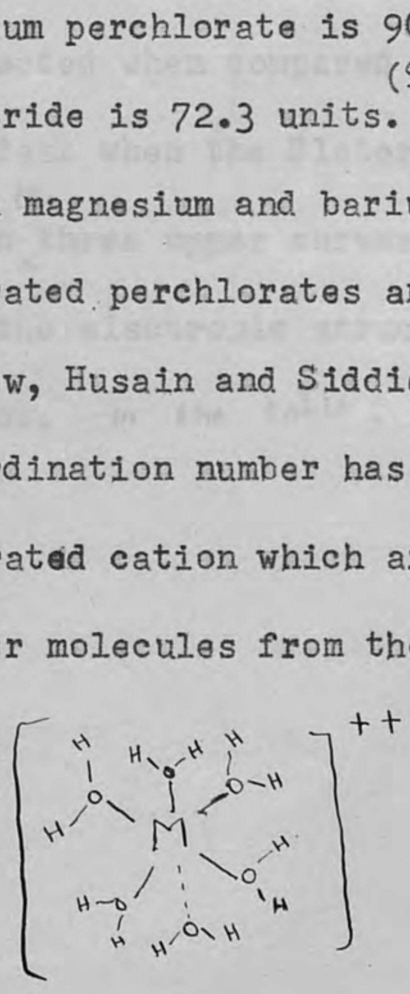
$(-IO^{6}\chi\,\mathrm{Ag\ ClO_4}) - (-IO^{6}\chi\,\mathrm{Rb\ ClO_4}) = 0.60$

The increments for the alkali compounds are almost constant showing the similarity in properties among the alkali metals. The increment between Rb^{+} & Ag^{+} and Cs^{+} & Tl^{+} are much smaller. The consideration of the magnetic susceptibility change on passing from the salts with a chloride ion to those with the perchlorate ion is of importance as it gives a measure of the effect of addition of four oxygen atoms in the anion. The experimental results may be compared with calculated values for addition of oxygen as given by Pascal's diamagnetic susceptibility constants and also with a theoretical ionic susceptibility calculated by use of Slater's(42) method. The molar susceptibility increment for addition of four oxygen atoms can also be correlated with the molar volume change and the bond length in the perchlorate ion.

Table 6 shows that it is not possible to determine with certainty (from the increments in column 5) exactly what effect the change in coordination number on passing from chloride to perchlorate has upon this $\chi \mathrm{ClO_4'} - \chi \mathrm{Cl'}$ increment. For the salts where there is a change in coordination number from six in the chloride to twelve in the perchlorate, the molar susceptibility increment varies from 6.3 (Ag compounds), 6.6 (Cs compounds with chloride corrected to six-fold coordination) 7.6 (K compounds) to 9.4 for rubidium compounds. The mean of these is 7.5 units of susceptibility.

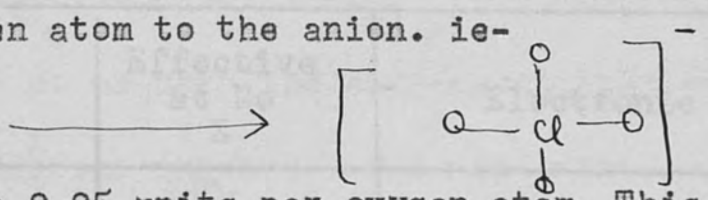
In two pairs of compounds, those of caesium and thallium there is a corresponding change in coordination number of four, ie, from a coordination number of eight in the chloride to twelve in the perchlorate. Here the perchlorate-chloride increment is 8.7 for the caesium salts (when Cs Cl is not corrected to six coordination) and 10.8 for the thallium salts. The mean of these two is 9.75 units of susceptibility. Although this is some-what higher than the mean when the change in coordination number is from six to twelve (ie, a change of six units) it is a rather uncertain figure owing to the difference of values from which it calculated. For the sodium perchlorate and chloride there is a coordination number change of two, ie, from six to eight, and here the increment between the perchlorate and chloride is 8.1. It would seem therefore as though the oxyanions are somewhat less sensitive to coordination number changes than the simple anions. The figures indicate that the perchlorate-chloride increment, when there is no change in coordination number on passing from chloride to to perchlorate, is rather greater than eight units of susceptibility and is possibly of the order of 9 units by comparison with earlier work.(10,34) Magnesium and barium salts may also be compared to find the increment and support a figure of approximately 9 units. Table 4 shows that the magnetic susceptibility of magnesium perchlorate is 67.69 calculated from the hydrated salt. The corresponding figure for magnesium chloride(34) is 49.86. The increment for two perchlorate-chloride ions is therefore 17.53 units and for one is 8.9 units. Similarly the molar susceptibility of barium perchlorate is 90.1 units while that of barium chloride is 72.3 units.(22) Here again the increment is 8.9 Both magnesium and barium values are determined on hexahydrated perchlorates and chlorides. It has been shown(34) (Trew, Husain and Siddiqi in press) That a change in coordination number has little influence on these hexahydrated cation which are well screened by the sheath of water molecules from the effect of surrounding ions.

ie.



This estimate of 9 units of susceptibility for addition of four oxygen atom to the anion. ie-

Cl'



would give 2.25 units per oxygen atom. This is very much less than the calculated susceptibility increment for oxygen, either from the Slater method or using the Pascal constants for oxygen and the reason for this is discussed in section IV

The curves show that silver and thallium (1) chlorides and perchlorates have much lower susceptibilities than expected when compared with the alkali series. This is evident when the Slater theoretical curve is compared with the three upper curves. This can be considered in terms of the electronic structure of the cations which is shown ~~below.~~ in the table .

ION	Effective at No Z	Electronic configuration
Li^+	2	$1s^2$
Na^+	10	$1s^2$; $2s^2p^6$
K^+	18	$1s^2$; $2s^2p^6$; $3s^2p^6$
Rb^+	36	$1s^2$; $2s^2p^6$; $3s^2p^6d^{10}$;$4s^2p^6$
CS^+	54	$1s^2$; $2s^2p^6$; $3s^2p^6d^{10}$; $4s^2p^6d^{10}$ $5s^2p^6$
Ag^+	46	$1s^2$; $2s^2p^6$; $3s^2p^6d^{10}$;$4s^2p^6d^{10}$
Tl^+	80	$1s^2$; $2s^2p^6$; $3s^2p^6d^{10}$; $4s^2p^6d^{10}f^{14}$ $5s^2p^6d^{10}$; $6\ s^2$

For the alkali cations, the outer shell is an inert gas configuration (S^2p^6) and the silver and thallium (1) have a d^{10} state at or near the surface of the ion. (6s is very little different in energy from 5d). These levels, as can be seen from the Hartree wave function graphs in Landolt-Bornstein, have a larger part of the d orbital energy distribution function well away from the core of the atom in the outer sphere . The part of the electronic charge in these d orbitals will be very sensitive to the surrounding ions in the environment and hence part of the susceptibility which depends upon the ionic volume is modified when the effective volume of the cation is reduced ie, the cation is very sensitive when the d^{10} shell is near the surface to crowding effects of its anionic neighbours. Both the molar volume and susceptibility graphs show this effect. The molar volume is determined by the closeness of packing of the crystal and the resultant size of the ion in its turn control the susceptibility.

The Molar Volumes of the perchlorate Series of Salts.

The densities of the perchlorates were determined and the effective molar volumes were calculated from these, from the relationship $V_M^{20} = \frac{M}{d_4^{20}}$. The results are given in table 7. Literature values used for the densities in a few cases are marked in the table.

These molar volumes were plotted against the effective atomic number of the cations as before and compared with those of the corresponding chlorides.

The slopes between lithium perchlorate and sodium perchlorate and ~~that~~ between lithium chloride and sodium chloride are parallel. The increments between the perchlorate and the chloride in these two cases are therefore constant.

ie, $\Delta V_M \; (V_M \; \mathrm{Li\,ClO_4} - V_M \; \mathrm{Li\,Cl}) = 23.3$

$\Delta V_M \; (V_M \; \mathrm{Na\,C104} - V_M \; \mathrm{Na\,Cl}) = 23.0.$

The graphs between sodium perchlorate and potassium perchlorate and that ~~of~~ between the two chlorides are less parallel, the increment being different in these cases.

$\Delta V_M \; (V_M \; \mathrm{K\,C104} - V_M \; \mathrm{K\,Cl}) = 17.7$

TABLE 7

Densities and molar volumes of the perchlorates and the chlorides

Compound	Mol, wt.	D_4^{20}	V_M^{20}
LiCl	42.4	2.068$^{(a)}$	20.53
$LiClO_4$	106.4	2.429$^{(a)}$	43.8
NaCl	88.45	2.165$^{(a)}$	27.00
$NaClO_4$	122.45	2.45	50.0
KCl	74.553	1.988$^{(a)}$	37.5
$KClO_4$	138.55	2.51	55.2
RbCl	120.94	2.76$^{(a)}$	43.8
$RbClO_4$	184.94	2.8	66.05
Cs Cl	168.37	3.97$^{(a)}$	42.40
$CsClO_4$	232.37	3.33	69.78
AgCl	143.34	5.4	26.6
$AgClO_4$	207.34	3.25	63.8
Tl Cl	239.85	7.00$^{(a)}$	34.264
$TlClO_4$	303.85	4.89	62.14

Again the molar volume increment between the perchlorates and the chlorides of rubidium and potassium are not constant and therefore the graphs are not parallel.

ΔV_M $(V_M$ $RbClO_4$ - V_M Rb Cl) = 22.25

ΔV_M $(V_M$ $KClO_4$ - V_M KCl) = 17.7

It can be seen from the graph that this is possibly because the closer packing accompanying the change from eight to twelve coordination occurs at potassium perchlorate. This change lowers the molar volume of potassium perchlorate below the figure expected for eight coordination (ie; parallel with the chloride curve.) This is shown by the dotted line in figure 10. It is obvious from the graph that the potassium-rubidium perchlorate slope is also corrected by this change becoming parallel to that for the two chlorides. A smilar explanation for the slope between rubidium and caesium chlorides is indicated. The slope between caesium and thallium is normal. But the very low molar volume of silver chloride causes a deviation in the increments in which it is concerned. It is difficult to explain the cause of this.

V_M OF THE PERCHLORATES OF UNIVALENT Cations.

Compared with the Corresponding Chlorides.

FIG. 10

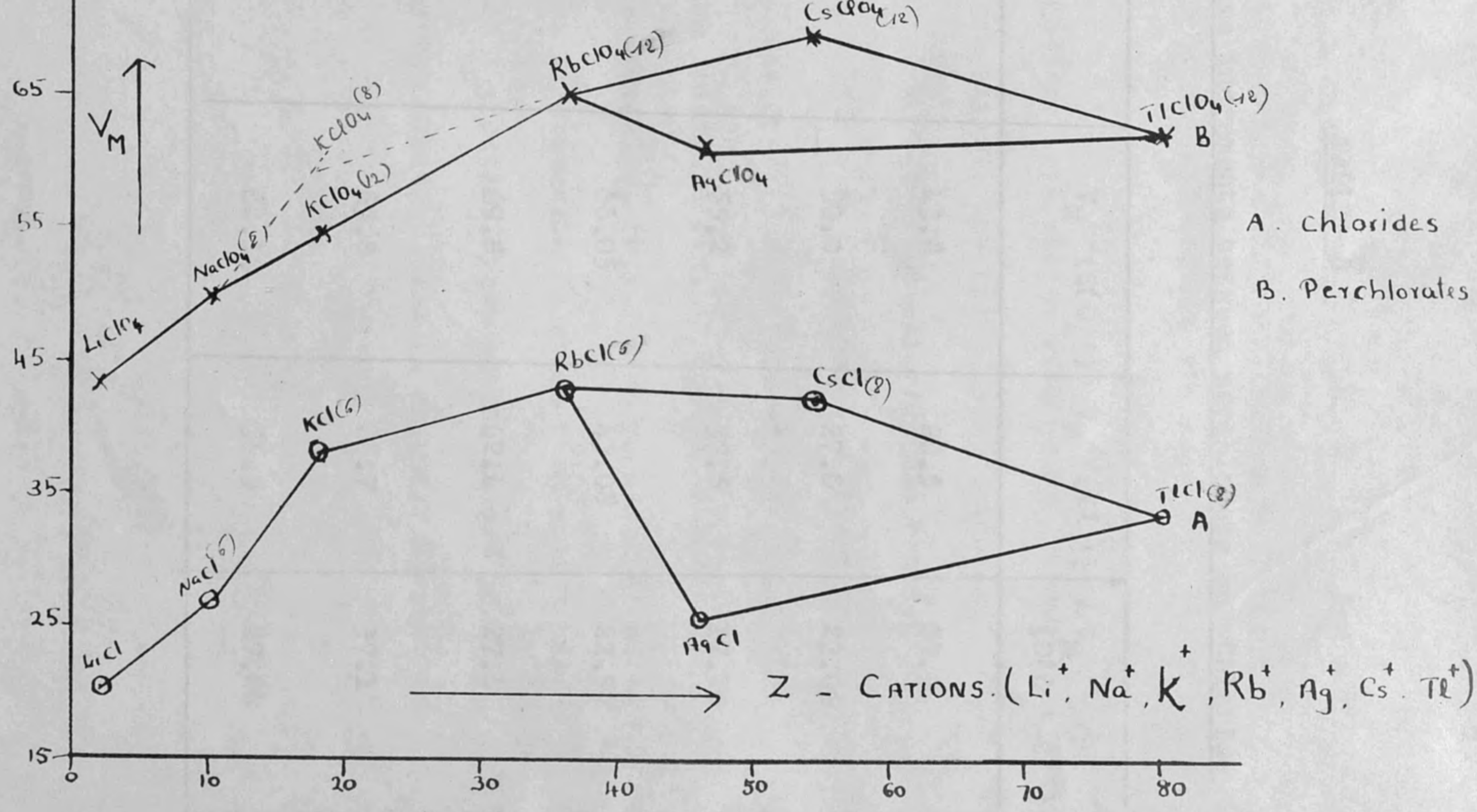


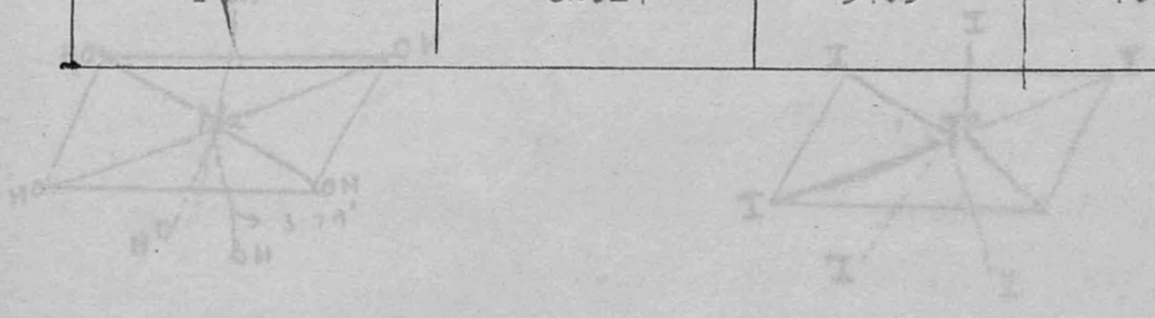
TABLE 8

Molar Volume increments between perchlorate and Chloride

Salt	$V_M^{20}(Cl O_4')$	$V_M^{20}(Cl')$	ΔV_M^{20} $(ClO_4' - Cl')$
Li^+	43.8	20.5	23.3.
Na^+	50.0	27.0	23.00
K^+	55.2	37.5	17.70
Rb^+	66.05	43.08	22.97
Cs^+	69.8	42.4	27.4
Ag^+	63.8	26.7	37.1
Tl^+	62.14	34.3	27.84

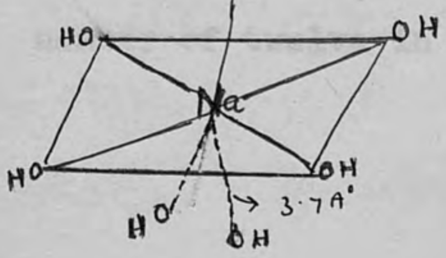
Crystal structure of the halides and the perchlorates of the cations concer[illegible]

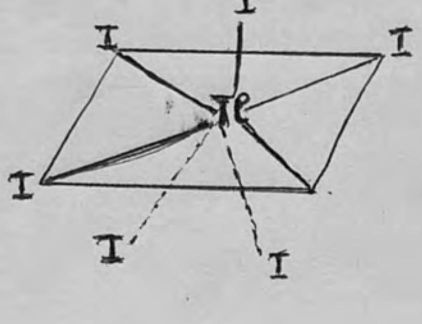
The Lithium ion has four-fold coordination in lithium chloride. At ordinary temperature and pressure, silver fluoride, silver chloride and bromide, sodium and potassium and rubidium halides crystallise with Na Cl symmetry (six-fold coordination). The chloride, bromide and iodide of caesium and [illegible] the chloride and bromide of Tl ([illegible]) crystallise with CsCl Symmetry (eight fold coordination). The crystal structure of the normal yellow thallium iodide is similar to the orthorhombic form of sodium hydroxide. This may be regarded as built of slices of Na Cl structure in which each sodium has five nearest OH' groups [illegible] five of the apices of the octahedron and the missing apex is occupied by two OH' at 3.7Å



Crystal structure of the halides and the perchlorates of the cations concerned.

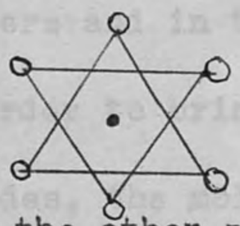
The Lithium ion has four-fold coordination in lithium chloride. At ordinary temperature and pressure, silver fluoride, silver chloride and bromide, sodium and potassium and rubidium halides crystallise with Na Cl symmetry (six-fold coordination). The chloride, bromide and iodide of caesium and [illegible] the chloride and bromide of Tl (I) crystallise with CsCl Symmetry (eight fold coordination). The crystal structure of the normal yellow thallium iodide is similar to the orthorhombic form of sodium hydroxide. This may be regarded as built of slices of Na Cl structure in which each sodium has five nearest OH ' groups at five of the apices of an octahedron and the missing apex is occupied by two OH' at 3.7Å

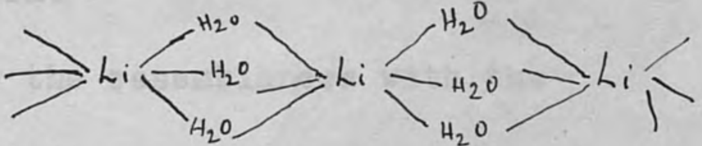




So it could be suggested that the coordination of thallium in thallium iodide is seven. The red form of thallium iodide has CsCl symmetry. Under pressure, Silver iodide can be crystallised with NaCl structure, but at ordinary temperature and pressure, silver iodide has the zinc blend structure (CN.4).

Perchlorates. Lithium has six-fold coordination in $Li\ ClO_4\ 3H_2O$. The water molecules are arranged in groups of three around planes ~~in~~ perpendicular to the plane of the paper. The lithium ions lie between the groups and are therefore surrounded octahedrally by six water mols.





All the other perchlorates concerned except Sodium perchlorate have been ~~supported~~ Shown to have twelve coordination for the cation in the salts. $BaSO_4$ type symmetry is given for all these perchlorates. Barium has a coordination number of twelve in $BaSO_4$.

Magnetic Susceptibility of the Triorthophosphates of Univalent Cations.

The results of the measurements of the susceptibilities of the triorthophosphates of univalent cations are summarised in table 9 . Columns 1 and 2 of this table give the formula and the molecular weight of the salts. The specific mass susceptibility and the molar susceptibility are given in columns 3 and 4. The molar susceptibility of the salts increases with increasing atomic number of the cations as already found for halides, nitrates, and other salts both by earlier workers and in the present work.

In order to bring out clearly the resemblances with the halides, the molar susceptibilities of the triorthophosphates (M_3PO_4) were plotted against three times the effective atomic number of the cations. Three times the molar susceptibilities of the halides of the same cations were plotted similarly on the same graph as shown in figure 11 . A very good general parallel relationship is shown in the graph. The slope between lithium

TABLE 9

Magnetic Susceptibility of the Orthophosphates of the Univalent cations

Salt	Mol.wt.	$-10^6 \chi$ (salt)	$-10^6 \chi_M$
Li_3PO_4	115.8	0.3028 0.3052 0.3028	35.10 35.34 35.10 mean 35.2
$Na_3PO_4.12H_2O$	380.16	0.5597 0.5576 0.5597_3	212,76 212.00 212.76 mean 212.8
Na_3PO_4	164.015		57.24
$K_3PO_4H_2O$	230.3	0.381 0.382 0.383	87.74 87.97 88.2 mean 87.97
K_3PO_4	212.27	0.383	75.01

TABLE 9 (contd)

Salt	Mol.wt.	$-10^6 \chi$ (salt)	$-10^6 \chi_M$
$(NH_4)_3 PO_4.3H_2O$	202.975	0.6006	122.02
		0.5911	120.1
		0.592	120.3
			mean 120.13
$(NH_4)_3 PO_4$	148.975		81.25
$(NH_4)_2 HPO_4$	132.07	0.5240	69.2
		0.5281	69.73
		0.5283	69.77
			mean 69.75
Ag_3PO_4	418.62	0.3056	127.91
		0.3051	127.72
		0.3050	127.7
			mean 127.7
$Tl_3 PO_4$	708.15	0.2087	147.8
		0.2089	148.0
		0.2084	147.6
			mean 147.8

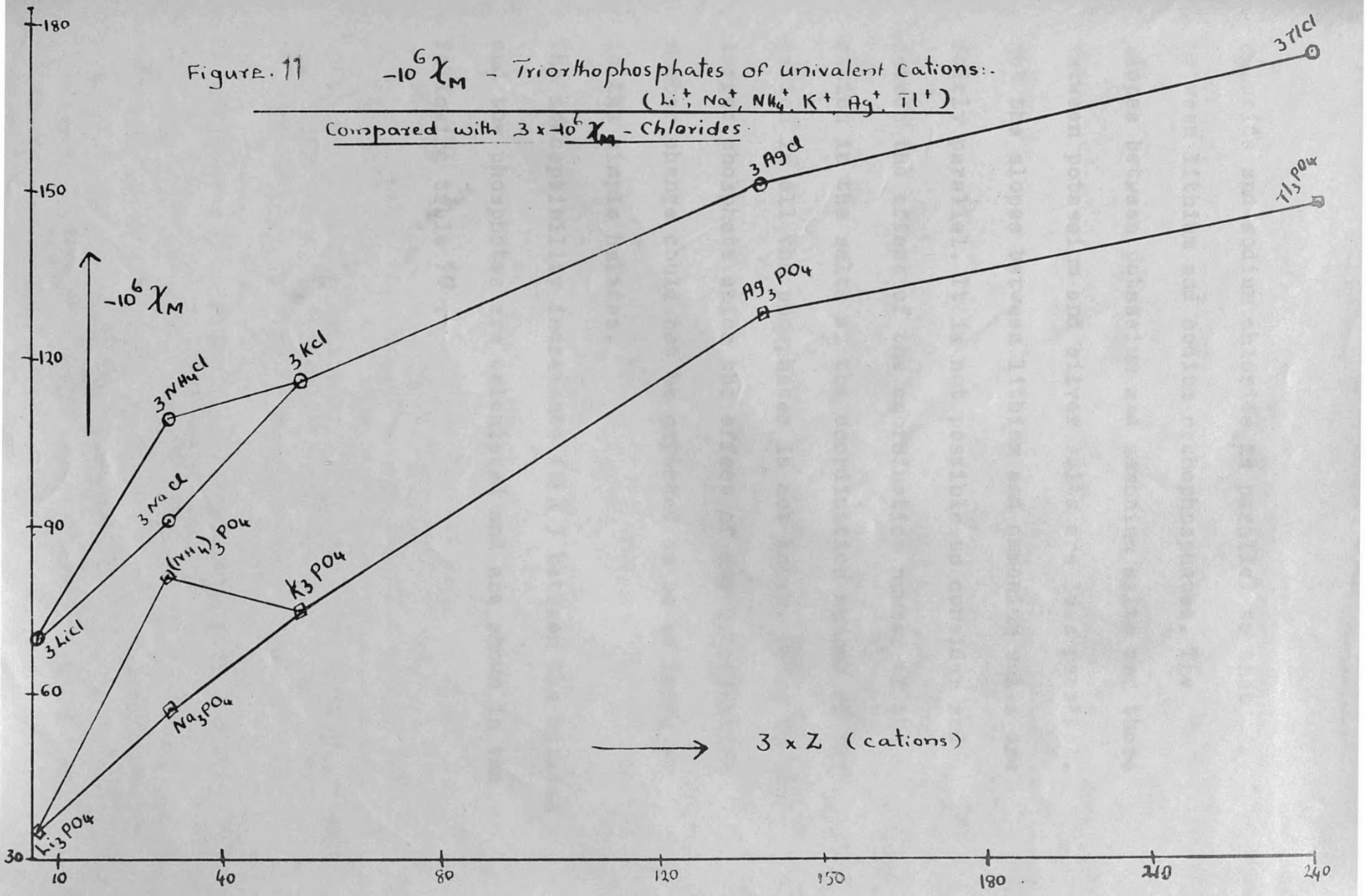


Figure. 11 $-10^{6}\chi_M$ - Triorthophosphates of univalent Cations:- (Li^+, Na^+, NH_4^+, K^+, Ag^+, Tl^+)

Compared with $3 \times -10^{6}\chi_M$ - Chlorides.

chloride and sodium chloride is parallel to that between lithium and sodium orthophosphates. The slopes between potassium and ammonium salts and those between potassium and silver salts are less parallel. But the slopes between lithium and ammonium salts are fairly parallel. It is not possible to consider and detect the effect of the coordination number of the cation in the salts as the coordination number of the cation in all the phosphates is not known. Owing to the larger phosphate anion the effect of any coordination number change could not be expected to be as large as in the simple halides.

The susceptibility increments ($\Delta \chi$) between the halides and the phosphates are calculated and are shown in the following table 10 .

In this table column 4 gives the susceptibility increment between the three chloride ions and the one phosphate ion. The increment between one chloride ion and 1/3 phosphate ion is given in column 5. If the susceptibility for the chloride ion is assumed to be 24.3 then the susceptibility of I/3 of the phosphate ion follows by subtracting the values in column 5 from 24.3. The susceptibility of the phosphate ion is given in column 6 by multiplying this figure by 3. Column 8 gives the susceptibility value for the phosphate ion by another method, ie- by subtracting 3 times the ionic susceptibility of the cations from the susceptibility of the salt. Thus columns 6 and 8 give the susceptibility for the phosphate ion calculated by two different methods. These two methods are not entirely independent as the low value for the potassium salt and the high value for the silver and thallium salts found in both cases is determined by the actual experimental value for the susceptibility of the phosphate salt.

If we take a mean value of the susceptibility for the

TABLE 10

Molar Susceptibility increments between the chlorides and the triorthophosphates

Cation	$3(-10^6\chi)$ MCl	$-10^6\chi M$ M_3PO_4	Increment $-10^6\Delta\chi$ $3Cl' - PO_4'''$	$\Delta\chi$ $(Cl' - \frac{1}{3}PO_4''')$	$-10^6\chi M$ (PO_4''')	$-10^6\chi M$ $3M^+$	$-10^6\chi M$ (PO_4''')
Li^+	69.9	35.2	34.7	11.6	38.1	+3	38.2
Na^+	90.6	57.24	33.4	11.10	39.6	17.70	39.54
NH_4^+	109.68	81.25	28.43	9.5	44.4	40.05	41.20
K^+	116.10	75.00	41.1	13.7	31.5	43.2	31.8
Ag^+	150.3	127.7	22.6	7.53	50.4	74.1	53.2
Tl^+	175.5	147.8	27.7	9.23	48.1	98.7	49.1
							mean 42.5

phosphate ion it is 42.5 units of susceptibility. This figure is somewhat uncertain since the potassium salt gives a rather lower value and silver and Thallium give a high value for the susceptibility of the phosphate ion. The low susceptibility value for the potassium salt and the high value for the silver and thallium salts may be due to a difference in coordination effect and hence of the packing of the ions in the crystals. Probably more measurements and further work are needed here in order to make a clearer study of the magnetic susceptibility relationships of orthophosphates.

Molar Volumes of the orthophosphates of the Univalent Cations.

The molar volumes of these orthophosphates were calculated from the density (37) and the results are shown in table 11. In general the molar volume increases with the increasing atomic number of the cation in the phosphates. But silver orthophosphate gives a considerably low molar volume. This is similar to the effect shown in the case of silver chloride and silver perchlorate and is due to the denser packing of the crystal.

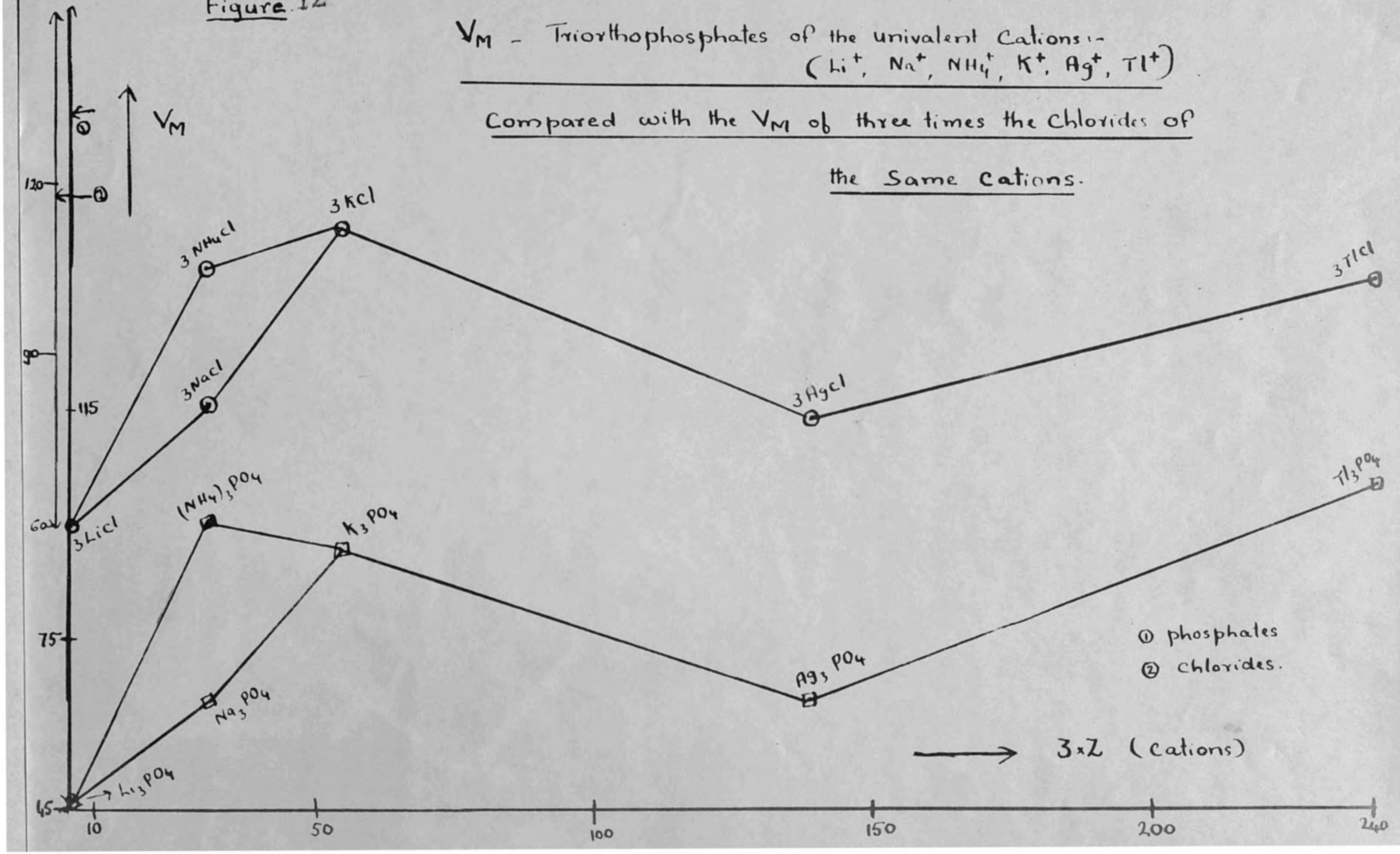
TABLE 11

Salt	Mol. Wt.	D_4^{20}	V_M^{20}
Li_3PO_4	115.8	2.48	46.70
Na_3PO_4	164.015	2.537	64.65
K_3PO_4	212.309	2.33	91.10
$(NH_4)_3 PO_4$	149.095	1.54	96.80
$(NH_4)_2 HPO_4$	132.07	1.619	81.60
$Ag_3 PO_4$	418.62	6.4	65.4
Tl_3PO_4	708.15	6.89	102.8

Figure 12

V_M - Triorthophosphates of the univalent Cations:- (Li^+, Na^+, NH_4^+, K^+, Ag^+, Tl^+)

Compared with the V_M of three times the Chlorides of the Same Cations.



Molar volumes were, similarly to the susceptibilities, plotted against three times the effective atomic number of the cations. Three times the molar volume of the corresponding chlorides were also plotted on the same graph in order to bring out clearly the resemblances with the halides. In general there is a parallel relationship between the chlorides and the phosphates in this graph and it is quite clear that these molar volume relationships are reflected in the similar parallel nature of the susceptibility relations. There is one point of difference because the molar volumes of silver chloride and phosphates are below those of potassium while the molar susceptibility values of these two salts come between those of potassium and thallium. The molar volume which is a direct property of the packing of the ions in the crystal ~~and so~~ is rather more dependent upon this, and on the coordination number, than is ~~on~~ the susceptibility. If the molar volumes and susceptibilities of the remaining members of the alkali-chloride series ie, rubidium chloride and caesium chloride are also compared with these graphs, it is clear that there is a lowering of both properties in the case of silver and thallium salts compared with the rubidium and caesium salts. ie, three times the molar susceptibility of rubidium chloride has a value of $-\mathrm{IO}^{6}\chi_{M} = 139.2$ ($\mathrm{Rb\,Cl} = 46.4$). Three times the effective atomic number of the ~~ion~~ Rb^{+} ion is IO8 and the graph (figure 11) shows this gives a point slightly above the slope between potassium and silver chlorides. In the case of caesium chloride the effect is clearer even though here the coordination number of the room temperature-form is eight. Three times the molar susceptibility of caesium chloride is 170.1 ($-\mathrm{IO}^{6}\chi\ \mathrm{CsCl} = 56.7$) and 3 Z for the cations Cs^{+} is 162 ($Z(\mathrm{Cs}^{+}) = 54$). This gives a point about 14 units of susceptibility above the slope between silver and thallium. A similar but more marked effect is found with the molar volumes. The slope of the graph for the complete halide series ~~thus~~ runs higher than the slope~~s~~ for the salts shown in ~~of the~~ figure~~s~~ 12 . The molar volumes of the room temperature forms of rubidium and caesium chlorides multiplied by three give values of 130 and 129 respectively (the caesium value being that for 8-fold coordination). These, if plotted on the molar volume graph at values of three times the effective atomic number of the cations, give ~~these~~ points which are higher than the potassium value and very much higher than the molar volumes of silver and thallium chlorides. The slope of the molar volume graph for the halide series thus comes above that for the series including silver and thallium, but the low value for caesium chloride due to the eight coordination shows clearly.

Magnetic molar susceptibility and molar volume of the orthophosphates of some bivalent cations.

The results of the measurements of the susceptibility and the calculated molar volumes are summarised in table 12. The molar susceptibilities and the molar volumes of these orthophosphates have also been compared with those of the chlorides of the same cations. The mean of the literature values was taken for the molar susceptibility of the chlorides of calcium, strontium and barium. (13) The ionic susceptibility for the cations was worked out by subtracting twice the ionic susceptibility constant for the chloride ion (2 x 24.3) from these mean values of the salts.- ~~chlorides~~. Trew, Husain & Sidiqui's (34) value was taken for magnesium chloride and for Mg^{++} cation. ie. 49.86 for $MgCl_2$ and 2.6 units for Mg^{++}. The other values are given below.

	$-10^6\chi_M$	$-10^6\chi_M$
	MCl_2	M^{++}
Ca^{++}	54.71	6.10
Sr^{++}	62.32	13.72
Ba^{++}	72.92	24.3

TABLE 12

Magnetic susceptibility of the orthophosphate of bivalent cations

Salt	Mol.wt.	$-10^6 \chi$ (salt)	$-10^6 \chi$ M
$Mg_3 (PO_4)_2 4H_2O$	334.98	0.4305	144.22
		0.4282	143.50
		0.4288	193.64
			mean 143.70
$Mg_3(PO_4)_2$	262.98		91.86
$Ca_3 (PO_4)_2$	310.2	0.3028	93.92
		0.3003	93.20
		0.3015	93.50
			mean 93.5
$Sr_3(PO_4)_2$	452.84	0.2109	95.50
		0.2113	95.70
		0.2107	95.40
			mean 95.5
$Ba_3(PO_4)_2$	602.04	0.2239	
		0.2233	134.46
		0.2238	134.73
			mean 134.6

TABLE 13

Summary of $-10^{6}\chi_M$ and V_M of the chlorides of univalent and bivalent cations (used for graphs)

Salt	Eff. at No. of the cation	$-10^{6}\chi_M$	V_M
$LiCl$ (6)	2	23.3 (5)	20.53
$NaCl$ (6)	10	30.2 (5)	27.00
NH_4Cl (8)	10	36.56 (10)	35.1
KCl (6)	18	38.7	37.5
$AgCl$ (6)	46	50.1	26.6
$TlCl$ (8)	80	58.4	34.26
$MgCl_2$ (6)	10	49.86 (34)	41.12
$CaCl_2$ (6)	18	54.71 (13)	44.20
$ZnCl_2$ (6)	28	55.3	46.9
$SrCl_2$ (8)	36	62.32 (13)	51.95
$BaCl_2$ (9)	54	72.92 (13)	53.2

TABLE 14

For Bivalent Cations

Salt	Mol.wt.	D_4^{20}	V_M^{20}
$Ca_3(PO_4)_2$	310.26	3.14	98.8
$Mg_3(PO_4)_2$	262.98	2.17	121.19
$Sr_3(PO_4)_2$	452.84	3.16	143.34
$Ba_3(PO_4)_2$	602.16	3.8	158.46

The densities at 20°C are taken from the Literature except for $Mg_3(PO_4)_2$ which is measured.

These values were used to calculate the susceptibility of the phosphate ion. The molar susceptibilities of the orthophosphates of these bivalent cations were plotted against three times the effective atomic number of the cations and three times the molar susceptibilities of the corresponding chlorides also were similarly plotted on the same graph. Similar graphs were plotted also in the case of molar volumes. (Figures 13 and 14) In considering these graphs, it should first be noted that of the orthophosphates, the magnesium orthophosphate is a hydrated salt-like substance, while the other three salts are microcrystalline amorphous anhydrous powders. There is thus a considerable difference in structure as is clearly brought out by the graph of the molar volumes (fig. 14) The sample of the magnesium orthophosphate required to measure the density and molar volume x was prepared by simple dehydration of the hydrated compound by removing the water in a vacuum over sulphuric acid. The low density and higher molar volume would appear to indicate that the lattice

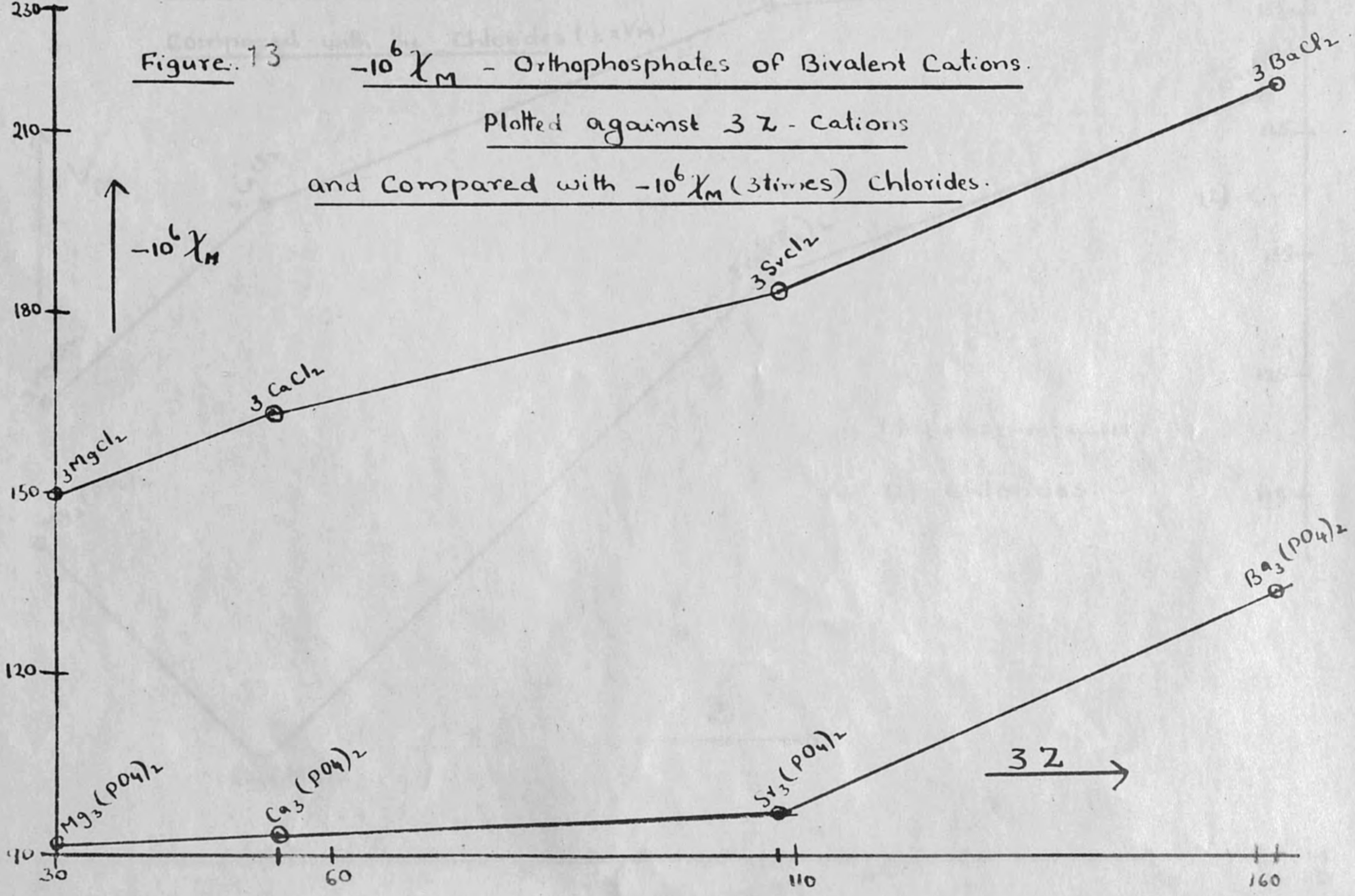
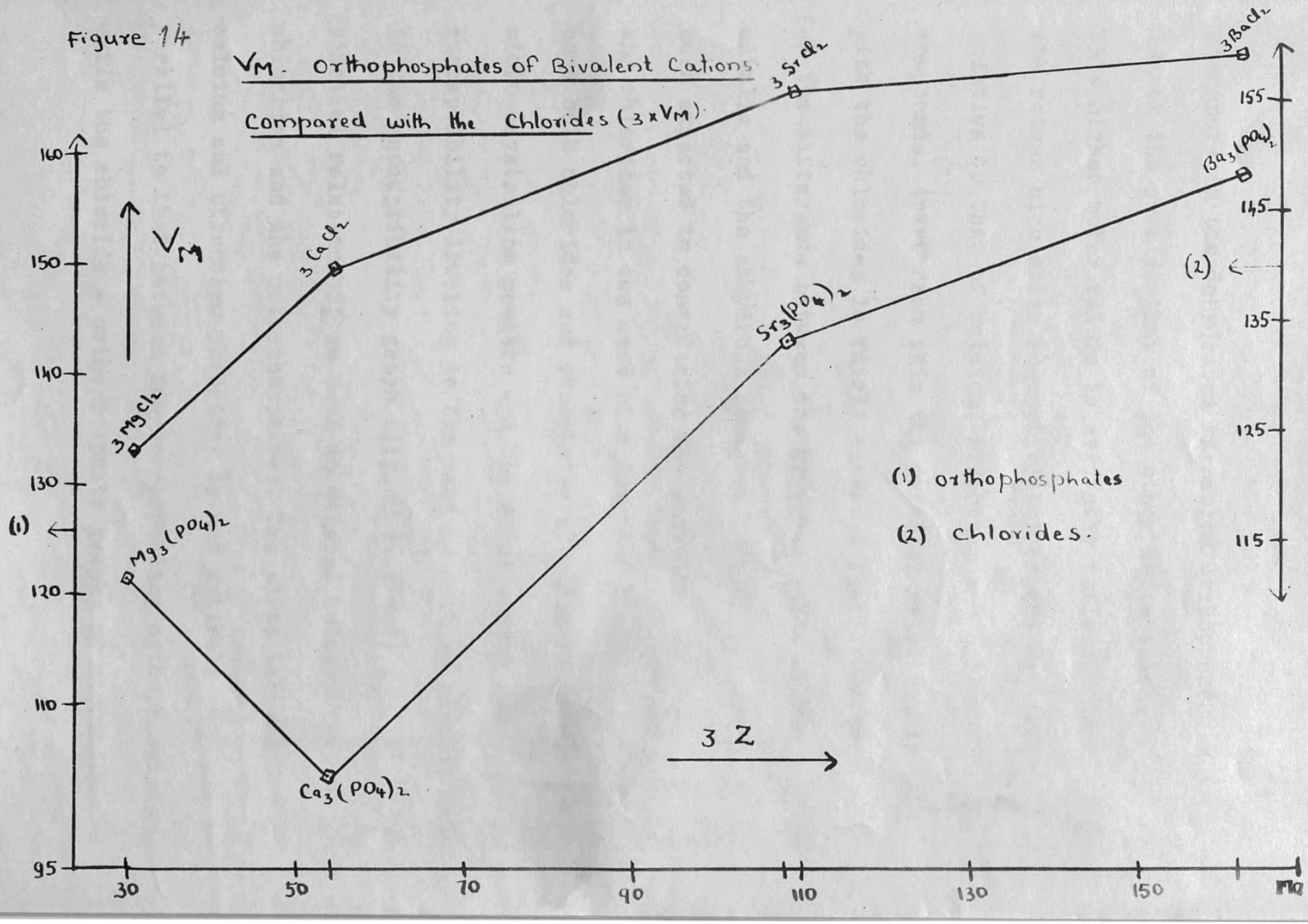


Figure. 13 $-10^6 \chi_M$ - Orthophosphates of Bivalent Cations. Plotted against 3 Z - Cations and Compared with $-10^6 \chi_M$ (3 times) Chlorides.

Figure 14



V_M. Orthophosphates of Bivalent Cations Compared with the Chlorides ($3 \times V_M$)

structure in the dehydrated magnesium orthophosphate is not the same as that of the other three salts. This higher molar volume is evidently reflected in the rather high molar susceptibility of the $Mg_3 (PO4)_2$ relative to that of calcium, strontium and barium compounds. Apart from this the parallel relationship with the chlorides is fairly close. A similar effect (of the difference between the hydrated salts of the alkalis and the anhydrous powdered salt) might have been expected in considering the univalent phosphates and chlorides in the case of silver and thallium. However here both chlorides and phosphates are similar amorphous micro-crystalline powders and the molar volume and susceptibility lowering is the same for both as already noted. In the susceptibility graph (fig. 13) a very good parallel relationship is seen in general between the chlorides and the orthophosphates. The slope between calcium and strontium chlorides is not entirely parallel to that between the corresponding orthophosphates, while the chloride - orthophosphate graphs of strontium and barium are parallel. The susceptibility increments between the chloride ion and the orthophosphate ion in each case are calculated as show in the following table. (Table 14) See next Page

Table 14

Cation M^{++}	$-10^6 \chi^M_{3 \cdot MCl_2}$	$-10^6 \chi^M_{M_3(PO_4)_2}$	$-10^6 \Delta\chi$ $(6Cl' - 2\,PO_4''')$	$-10^6 \Delta\chi$ $(Cl' - 1/3PO_4''')$	$\pm 10^6 \chi^M_{PO_4'''}$	$-10^6 \chi^M_{M^{++}}$	$-10^6 \chi^M_{PO_4'''}$
Mg^{++}	149.6	91.86	57.74	9.62	44.04	2.6	42.03
Ca^{++}	164.13	93.5	70.63	11.8	37.5	6.1	37.6
Sr^{++}	186.96	95.5	91.46	15.24	27.12	13.72	27.17
Ba^{++}	218.76	134.6	84.16	14.02	30.9	24.3	30.85

The ionic susceptibility of the phosphate ion is calculated in the above table by two methods although they are not entirely independent since both depend on the experimental susceptibility value of the orthophosphate salts. The value calculated in the case of magnesium agrees fairly well with the value obtained from the orthophosphates of univalent cations. All the other three cations give much lower susceptibility for the phosphate ion than that for the univalent cations and magnesium. This effect is especially marked for strontium. It appears that there is a lowering of the susceptibility for the phosphate ion in the case of the compounds of bivalent cations as Klemm has suggested for other anions. It is however possible that this apparently lower phosphate susceptibility occurs because the three M^{++} ions are not contributing their full susceptibility. If their susceptibility were less than three times that of the univalent cation, the ionic susceptibility of the phosphate ion would be higher.

It is not possible to decide which is the correct explanation. In the molar volume graph (fig. 14) there is a more or less general parallel relationship between the slopes of the chlorides and the orthophosphates exception for the higher molar volume of the magnesium orthophosphate. However, the molar volume of the calcium orthophosphate gives a lower value than expected which makes the slopes less parallel between the chlorides and orthophosphates of calcium and strontium. The crystal structure of all these ortho-phosphates are not well established and very little is known about the structure.

Barium and strontium orthophosphates are considered to be isostructural and rhombohedral. Zacharisen (43) has shown that the coordination number of the barium ion (or strontium ion) in the phosphate differs from that of others. ie, there are two differently arranged groups of barium and oxygen ions, and these are termed Ba_I and Ba_{II}. The barium ion Ba_I has a coordination number of twelve with six oxygen at a distance of 3.23 A° and six others at a distance of 2.80 A°. The Ba_{II} ion has a ten coordination number with six oxygens at a distance of 2.83 A° and other four oxygens at a different position.

Sr_I also has twelve coordination with six oxygens at a distance of 3.10 A° and the other six at a distance of 2.63 A°. Sr_{II} has been considered to have ten oxygen atoms around the Sr_{II} cation.

Mackay (44) in 1953 (Acta. Cryst. Vol. 6. p.743) tried to investigate the structure of - $Ca_3(PO_4)_2$ - but he was not able to ~~investigate~~ determine a definite structure.

There may be a different structure for $Ca_3(PO_4)_2$ from the other phosphates. The magnetic measurements give rather a low susceptibility and it has a much lower molar volume than expected, which would support this.

The above results show that the measurements of the susceptibilities and molar volumes of the orthophosphates of both alkali and alkaline earth elements do show very similar general trends and marked differences in molar volume relationships are in general reflected in the susceptibility graphs.

Magnetic molar susceptibilities of sulphates of the univalent and bivalent cations.

The sulphates measured were easily obtained as 'Analar' chemicals and no analysis was done on these compounds. The measurements were carried out as already shown in the case of oxyhalides. Three measurements were done on each salt and the results are summarised in table 15 . The sulphates of the univalent and bivalent cations are treated separately.

Magnetic susceptibility of the sulphates of univalent cations- Li^+, Na^+, K^+, NH_4^+, Ag^+, Tl^+.

The results for the magnetic susceptibility of the sulphates of these univalent cations are shown in table 15 . and compared with the literature values in column 6 of the table. Columns 1 and 2 give the formula and the molecular weight of the salts. The specific susceptibility and the molar susceptibility are given in columns 4 and 5. column 3 gives the coordination number of the cations in the salts. The present results agree fairly well with the available literature values.

TABLE 15

$-10^6 \chi$ M Sulphates of Univalent Cations

Salt	Mol.wt.	C.N.	$-10^6 \chi$ salt	$-10^6 \chi$ M	$-10^6 \chi$ M or $-10^6 \chi$ salt (Literature)
$Li_2SO_4 \cdot H_2O$	127.96		0.4490 0.4487 0.4487	57.46 57.42 57.42 mean 57.43	
Li_2SO_4	109.95	4		44.5	
$Na_2\ SO_4$	142.05	6	0.3665 0.3698 0.3682	52.06 52.54 52.30 mean 52.3	41.6 (4) 52.68 (45)

TABLE 15 (contd)

Salt	Mol.wt.	C.N.	$-10^6 \chi$ salt	$-10^6 \chi$ M	$-10^6 \chi$ M or $-10^6 \chi$ salt (Literature)
K_2SO_4	174.26	(9) (10)	0.3786 0.3790 0.3788	65.97 66.04 66.0 mean 66.0	67.18 (10) 65.0 (32) 67..1 (48) 65.0 (46) 66.92 (47) 67.1 (4) 70.74 (50) 76.7 (49)
$(NH_4)_2SO_4$	132.15	(9) (10)	0.5050 0.5072 0.5070	66.80 67.02 67.00	66.8 (10) 63.2 (12) 75.4 (49) 67.0 (7) 71.63 (50)
Ag_2SO_4	311.82	6	0.2980 0.2981 0.2979	92.93 92.96 92.89 mean 92.93	

TABLE 15 (contd)

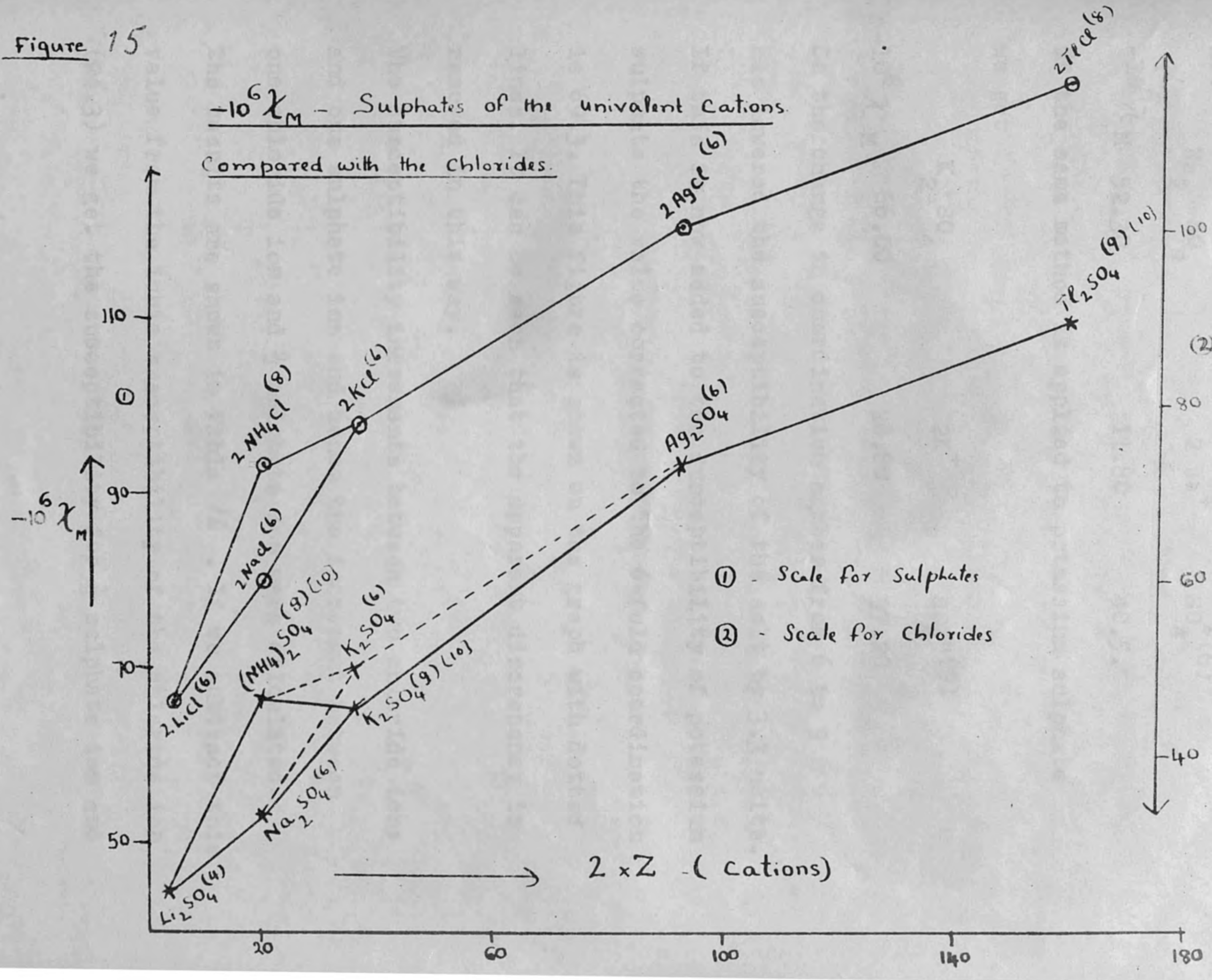
Salt	Mol.wt.	C.N.	$-10^6 \chi$ salt	$-10^6 \chi_M$	$-10^6 \chi_M$ or $-10^6 \chi$ salt (Literature)
Tl_2SO_4	504.85	(9) (10)	0.2241 0.2230 0.2234	113.15 112.60 112.80 mean 112.85	126.2(7) 112.6(6) 113.6(51)

~~$-10^6 \chi_M (SO_4{}'') = 41.76$~~

These molar susceptibilities were plotted against the effective atomic number of the cations. Twice the molar susceptibility of the corresponding chlorides was plotted similarly on the same graph for comparison as shown in figure 15 . The graph comparing the chlorides and the sulphates shows a general parallel relationship throughout. There are a few small deviations which can be seen. In particular, the graph shows a fall in susceptibility between ammonium and potassium sulphates, while there is a rise between the corresponding chlorides. This can be explained by the change in coordination number and closer packing of potassium sulphate and the effect of this change on the susceptibility can be calculated in the following way. Sodium sulphate (H_{I_7} symmetry type) has six fold coordination. An estimation of the susceptibility of the sulphate ion in this salt can be found by subtracting twice the diamagnetic correcting constant for the cation(10) from the susceptibility of the sodium sulphate.

Figure 15

$-10^6\chi_M$ – Sulphates of the univalent Cations Compared with the Chlorides.



ie.

	$Na_2\ SO_4$	$2\ Na^+$	$SO_4''^{(6)}$
$-10^6\chi_M$	52.30	11.80	40.5.

If the same method is applied to potassium sulphate we get

	$K_2\ SO_4$	$2K^+$	$SO_4''^{(9)}$
$-10^6\chi_M$	66.00	28.80	37.20

So the change in coordination number from 6 to 9 has lowered the susceptibility of the salt by 3.3 units. If this is now added to the susceptibility of potassium sulphate the value corrected to the 6-fold coordination is 69.3. This figure is shown on the graph with dotted lines. It can be seen that the apparent discrepancy is removed in this way.

The susceptibility increments between two chloride ions and one sulphate ion and hence the increment between one chloride ion and ½ sulphate ion were calculated. The results are shown in table 16 . If we subtract this value from the ionic susceptibility of the chloride ion (24.3) we get the susceptibility for ½ sulphate ion and

TABLE 16

Susceptibility increments between the chlorides and the sulphate and the calculated values for $-10^6 \chi^M$ of sulphate ion.

Cation	$-10^6 \chi^M_{2MCl}$	$-10^6 \chi^M_{M_2SO_4}$	$-10^6 \Delta\chi_{2Cl' - SO_4''}$	$-10^6 \Delta\chi_{Cl' - \frac{1}{2}SO_4''}$	$-10^6 \chi^M_{SO_4''}$	$-10^6 \chi^M_{2M^+}$	$-10^6 \chi^M_{SO_4''}$
Li^+	46.6	44.50	2.1	1.05	46.5	+2.0	46.5
Na^+	60.4	52.30	8.1	4.05	40.5	11.8	40.5
NH_4^+	73.12	67.00	6.12	3.06	42.48	26.7	40.30
K^+	77.4	(9) 66.00	11.2	5.6	37.2	28.8	37.2
		(6) (69.3)	(8.1)		(40.5)		(40.5)
Ag^+	100.2	92.93	7.07	3.53	41.54	49.4	43.53
Tl^+	116.8	112.85	3.95	1.975	44.65	65.8	47.05
							mean(Na^+, NH_4^+ K^+ corrected) 40.5 ====

hence multiplied by 2 gives the ionic susceptibility for the sulphate ion. The calculated value for the sulphate ion in the case of each salt is shown in table 16 column 6. The susceptibility of the sulphate ion is calculated by another method ie, subtracting twice the ionic susceptibility of the cation from the molar susceptibility of the salt. These values are given in column 8. The results are more or less the same in both cases. From the present measurements, a value for the ionic susceptibility constant of the sulphate ion could be obtained in the case of univalent cations which is equal to 40.5. The mean of the best three ~~agreeable~~ values are taken.

$$-10^6 \chi SO_4'' = 40.5 \text{ c.g.s. units.}$$

Molar Volumes of the sulphates of univalent cations.

Molar volumes of these sulphates were calculated from the density as already shown before. The results are given in table 17 .

To compare the molar volumes of the sulphates with the

TABLE 17

Summary of the results for the molar volumes of the sulphates of the univalent and bivalent cations

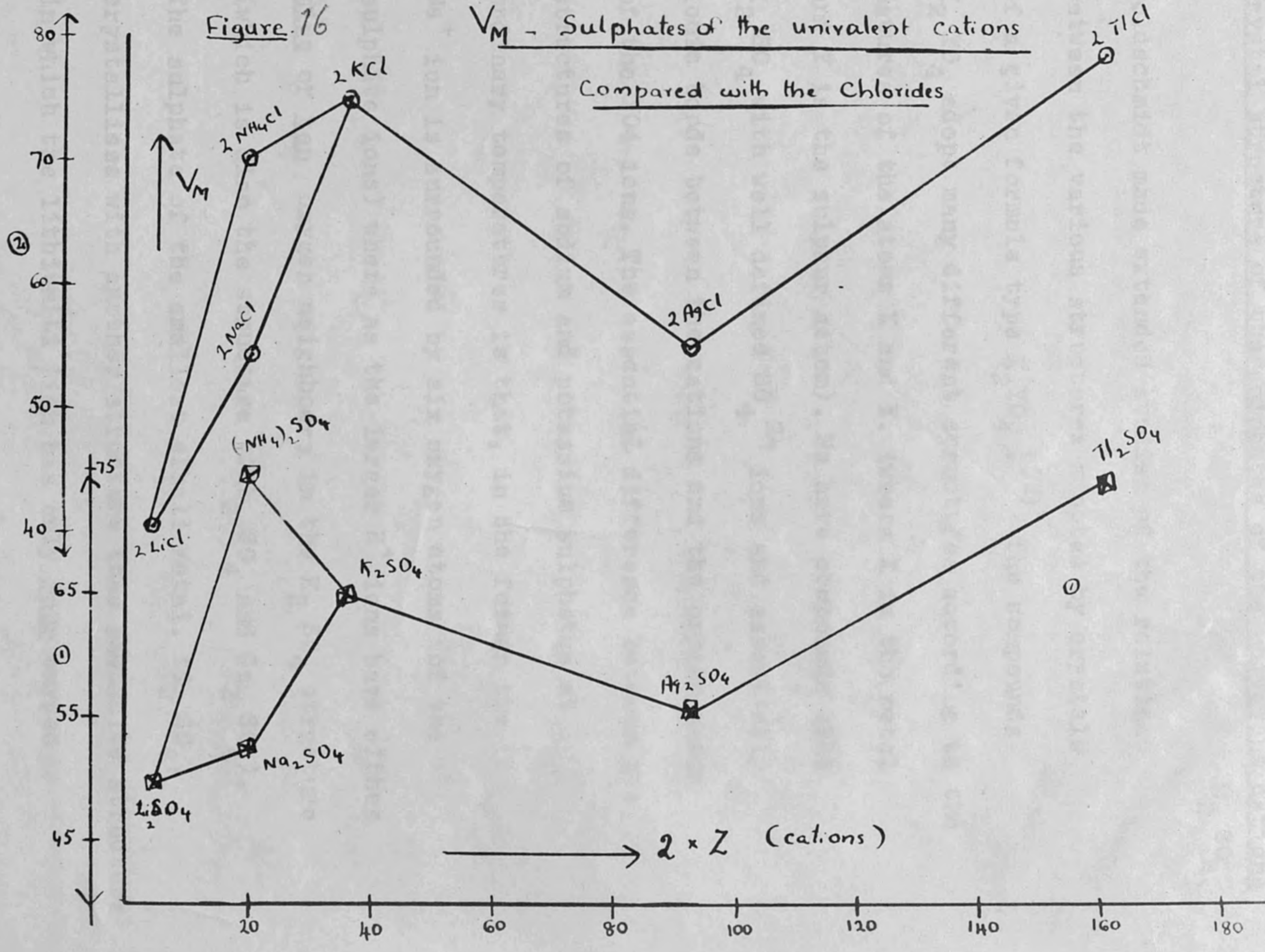
Salt	C.N	Mol.Wt.	D_4^{20}	V_M^{20}
Li_2SO_4	4	109.95	2.221	49.50
Na_2SO_4	6	142.05	2.698	52.65
K_2SO_4	(9) (10)	174.26	2.662	65.50
$(NH_4)_2SO_4$	(9) (10)	132.15	1.769	74.70
Ag_2SO_4	6	311.82	5.6	55.7
Tl_2SO_4	(9) (10)	504.85	6.77	74.6
$MgSO_4$	(6) 8	120.39	2.66	45.3
$CaSO_4$	8	136.15	2.96	45.997
$ZnSO_4$	8	161.44	3.4	47.5
$SrSO_4$	12	183.7	3.96	46.4
$BaSO_4$	12	233.43	4.2	55.6

corresponding chlorides, they were plotted against twice the effective atomic number of the cation. Twice the molar volumes were plotted similarly on the same graph as shown in figure 16 . There is once again a general parallel relationship between the sulphate-chloride molar volumes. Especially marked on the graph are the low molar volumes of silver sulphate and silver chloride. However in spite of this low molar volume the susceptibilities of Ag Cl and $Ag_2 SO_4$ are rather higher than those of potassium salts but would presumably be much higher still if the molar volumes had been normal. This effect is very similar to that discussed in detail in the case of silver and thallium triorthophosphates. Once again if the complete halide series including rubidium and caesium are considered, the molar volumes and susceptibilities give a higher slope than that for the silver and thallium salts in figures 15 and 16

Figure 16

V_M - Sulphates of the univalent cations

Compared with the Chlorides



Crystal structure of the sulphates of the univalent cations $M_2 SO_4$.

Goldschmidt made extended studies of the relations between the various structures adopted by crystals of a given formula type X_2YO_4.(52) The compounds $X_2 YO_4$ adopt many different structures according to the natures of the atoms X and Y. (where X is the metal and Y is the sulphur atom). We have compounds like $K_2 SO_4$ with well defined SO_4^{2-} ions and essentially ionic bonds between the cations and the oxygen atoms of the YO4 ions. The essential difference between the structures of sodium and potassium sulphates at ordinary temperatures is that, in the former the Na^+ ion is surrounded by six oxygen atoms (of the sulphate ions) whereas the larger K^+ ions have either *nine* or *ten* oxygen neighbours in the $K_2 SO_4$ structure (which is also the structure of $Rb_2 SO_4$ and $Cs_2 SO_4$). The sulphate of the smallest alkali metal. $Li_2 SO_4$, **crystallises** with another structure (the phenacite structure) in which the lithium(Li^+) ion has only *four* oxygen neighbours arranged tetrahedrally. Thallous Sulphate, $Tl_2 SO_4$, is isostructural with potassium sulphate, $K_2 SO_4$, i.e. the Tl^+ ions have either nine or ten oxygen neighbours around ~~it~~ them. Silver sulphate is given H_{1_7} type of symmetry (38) i.e. a sodium sulphate structure in which the cation is surrounded by six oxygen atoms of the sulphate ion.

Magnetic molar susceptibilities of the sulphates of Bivalent cations - Mg^{++}, Ca^{++}, Zn^{++}, Sr^{++} and Ba^{++}.

The results of the magnetic measurements on the sulphates of these bivalent cations are summarised in table 18. The measured susceptibilities are compared with the literature values given in column 6 of the table 18. The coordination numbers of the cation in these salts are shown in column 3. Trew Siddiqi and Husain's susceptibility value (34) is taken in the case of magnesium sulphate. The molar susceptibility values for magnesium and zinc sulphates were determined from the hydrated salts (6 C.N.) and these values were corrected for the eightfold coordination of the anhydrous salt to compare with the other anhydrous sulphates $CaSO_4$. $Sr SO_4$ and $Ba SO_4$. This correction was obtained from the experimental molar susceptibilities of calcium sulphate and heptahydrated magnesium sulphate. Calcium sulphate has eightfold coordination and by subtraction of the ionic susceptibility value for Ca^{++}, as discussed under the phosphate susceptibilities, a value for the sulphate

TABLE 18

$-10^6 \chi$ M sulphates of Bivalent Cations

Salt	Mol.wt.	C.N	$-10^6 \chi_{\text{salt}}$	$-10^6 \chi$ M	$-10^6 \chi$ M (Literature)
$MgSO_4$	120.39	6	0.363	44.24(34)	41.00(4) 42.1 (49)
		8		41.74	46.08(47) 47.2 (53)
					46.68(50) 43.34(33)
					44.54(48) 51.76(13)
$CaSO_4$	136.15	8	0.3276	44.60	48.44(54) 48.68(55)
			0.3270	44.54	48.47(56) 44.53(50)
			0.3268	44.50	43.00(57)
				mean 44.6	
$ZnSO_4 \cdot 7H_2O$	287.56	6	0.4797	137.95	54.88(13) 61.88(33)
			0.4801	138.06	52.08(59)
			0.4790	137.75	47.82(58)
				mean 137.9	

TABLE 18 (Contd)

Salt	Mol.wt	C.N.	$-10^6 \chi$ salt	$-10^6 \chi$ M	$-10^6 \chi$ M (Literature)
$ZnSO_4$	161.44	6		47.2	
		8		45.5	
$SrSO_4$	183.7	12	0.2956	54.30	52.4 (4)
			0.2957	54.32	60.3 (55)
			0.2966	54.40	57.99 (50)
				mean 54.35	
$BaSO_4$	233.43	12	0.2490	58.13	59.2 (4)
			0.2500	58.35	62.9 (4) Calc.d
			0.2496	58.26	71.44 (54)

ion in eight fold coordination is obtained (38.45 units). Subtracting the value for the susceptibility of the water and for the Mg^{++} ion in six fold coordination (34) gives an ionic susceptibility for the sulphate ion ~~of~~ with 6 coordination (41.7 units). The difference between these two values = ~~2.65~~ 3.2 enables an estimation to be made of the susceptibility difference for the SO_4'' ion in the two coordination states. This figure ~~2.65~~ 3.2 is close to that suggested by Trew, Husain and Siddiqi (34) for the similar difference between Na_2SO_4 and K_2SO_4. Both values are shown in table 18 .

In the graph (figure 17) the molar susceptibility of the sulphates of bivalent cations are compared with that of the corresponding chlorides. The molar susceptibilities of both sulphates and chlorides were plotted against the effective atomic number of the cation present in the salts. In the case of magnesium and Zinc sulphate both experimental and corrected (for eight fold coordination) susceptibilities were plotted. The experimental values

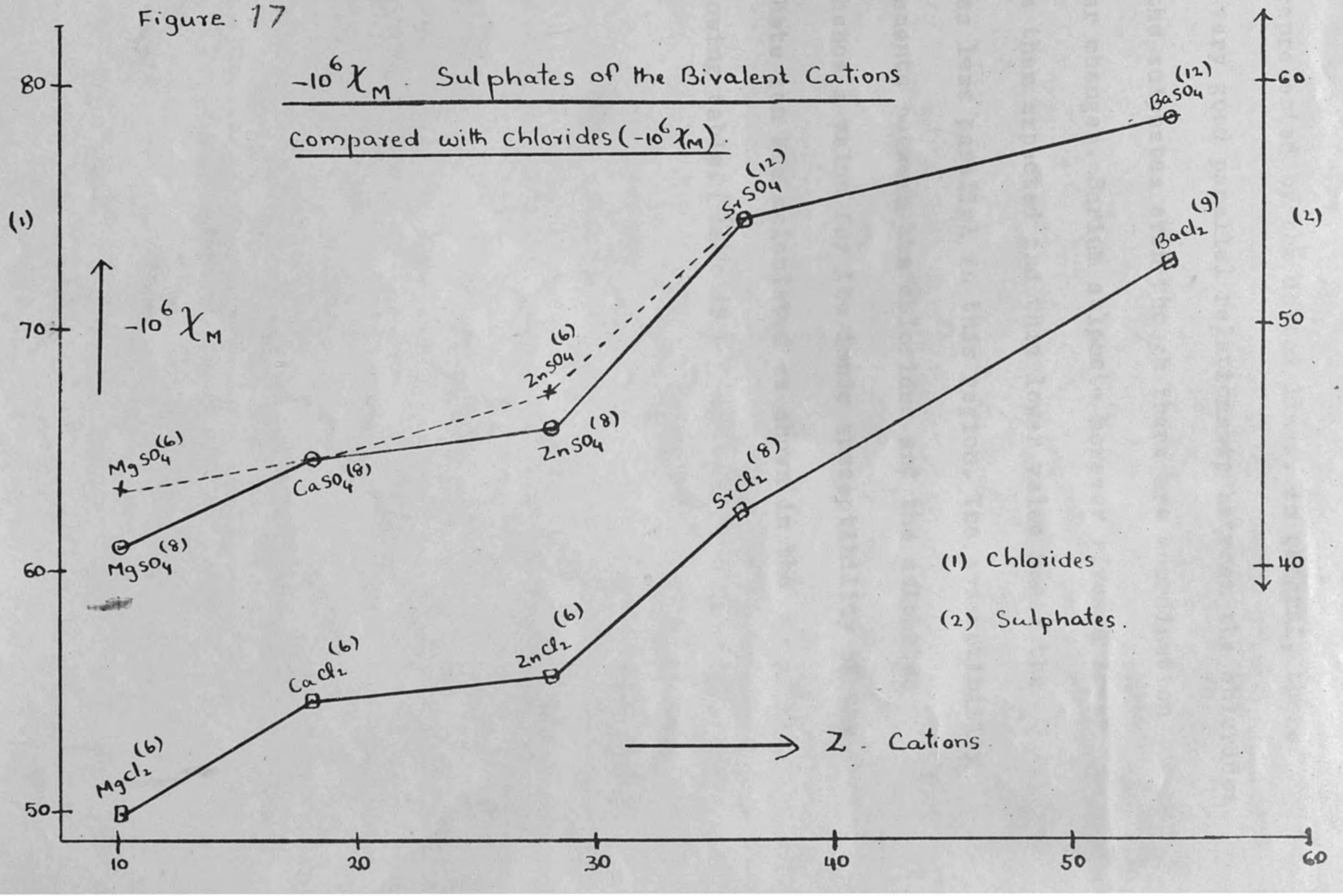


Figure 17

$-10^6\chi_M$ Sulphates of the Bivalent Cations

Compared with Chlorides ($-10^6\chi_M$).

are represented by the dotted lines. In general, there is a very good parallel relationship between the chlorides and the sulphates even though there are coordination number changes. Barium sulphate however gives a lower value than expected and this lower value makes the slopes less parallel in this region. The susceptibility increments between the chlorides and the sulphates and hence a value for the ionic susceptibility of the sulphate ion are calculated as shown in the following table. (Table 19.)

Table 19

Cation	$-10^6 \chi^M_{MCl_2}$	$-10^6 \chi^M_{MSO_4}$	$-10^6 \Delta\chi$ $(2\,Cl' - SO_4'')$	$-10^6 \chi^M_{(SO_4'')}$	$-10^6 \chi^M_{M^{++}}$	$-10^6 \chi^M_{SO_4''}$
Mg^{++}	49.86	44.24(6)	8.86	39.76	2.6	41.64
Ca^{++}	54.71	44.55(8)	10.16	38.4	6.1	39.4
Zn^{++}	55.5	47.2(6)	8.3	40.3	7.1	40.1
		45.5(8)	10.0	38.6		38.4
Sr^{++}	62.32	54.4	7.9	40.7	13.7	40.7
Ba^{++}	72.92	58.3	14.6	34.0	24.3	34.00

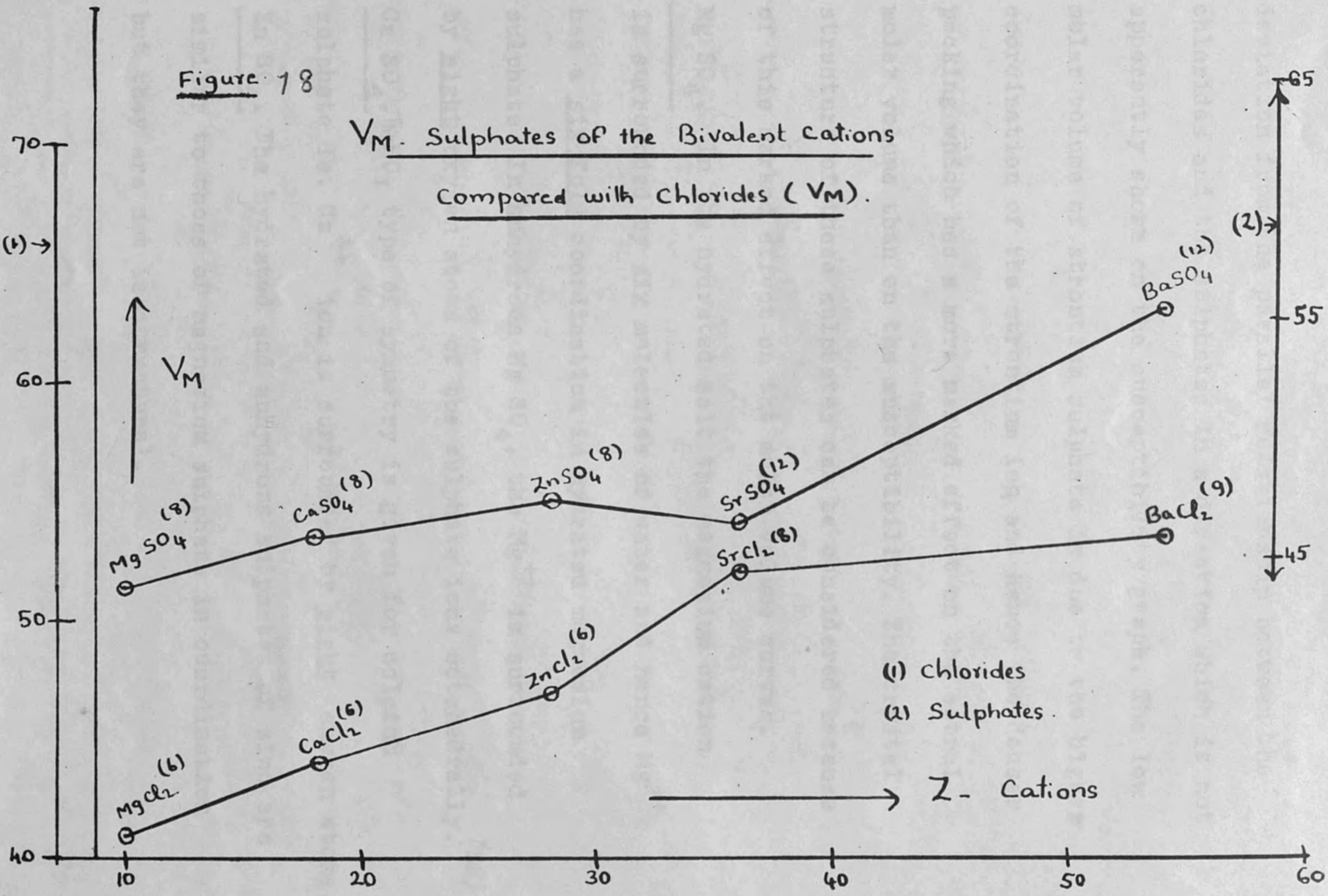
Using the increment we can calculate the ionic susceptibility of the sulphate ion by one method without knowing the cationic susceptibility. A value for the susceptibility of the sulphate ion can also be obtained by subtracting the ionic susceptibility of the cation from the salt, but these two methods are not entirely independent since both values depend on the experimental susceptibility results for the salts. The mean value of the ionic susceptibility of the sulphate ion obtained is $-10^6 \chi_{SO_4''} = 39.50$ c.g.s. units (omitting low barium value)

Molar volumes of the sulphates of Bivalent Cations.

The molar volumes calculated are shown in table 17. These were plotted similarly to the molar susceptibilities, against the effective atomic number of the cation and compared with the molar volumes of the corresponding chlorides. The graph is shown in figure 18. The slopes of the molar volume~~s~~ curves of sulphates from magnesium to zinc are fairly parallel to those for the chlorides. But the low molar volume of the strontium sulphate gives a

Figure 18

VM. Sulphates of the Bivalent cations Compared with Chlorides (VM).



deviation from the parallel relationship between the chlorides and the sulphates in a direction which is not apparently shown on the susceptibility graph. The low molar volume of strontium sulphate is due to the higher coordination of the strontium ion and hence the denser packing which has a more marked effect on the actual molar volume than on the susceptibility. The crystal structure of these sulphates can be considered because of this marked effect on the molar volume curves.

Mg SO_4. In the hydrated salt the magnesium cation is surrounded by six molecules of water and hence Mg^{++} has a six fold coordination in hydrated magnesium sulphate. In anhydrous Mg SO_4, the Mg^{++} is surrounded by eight oxygen atoms of the sulphate ions octahedrally.(39)

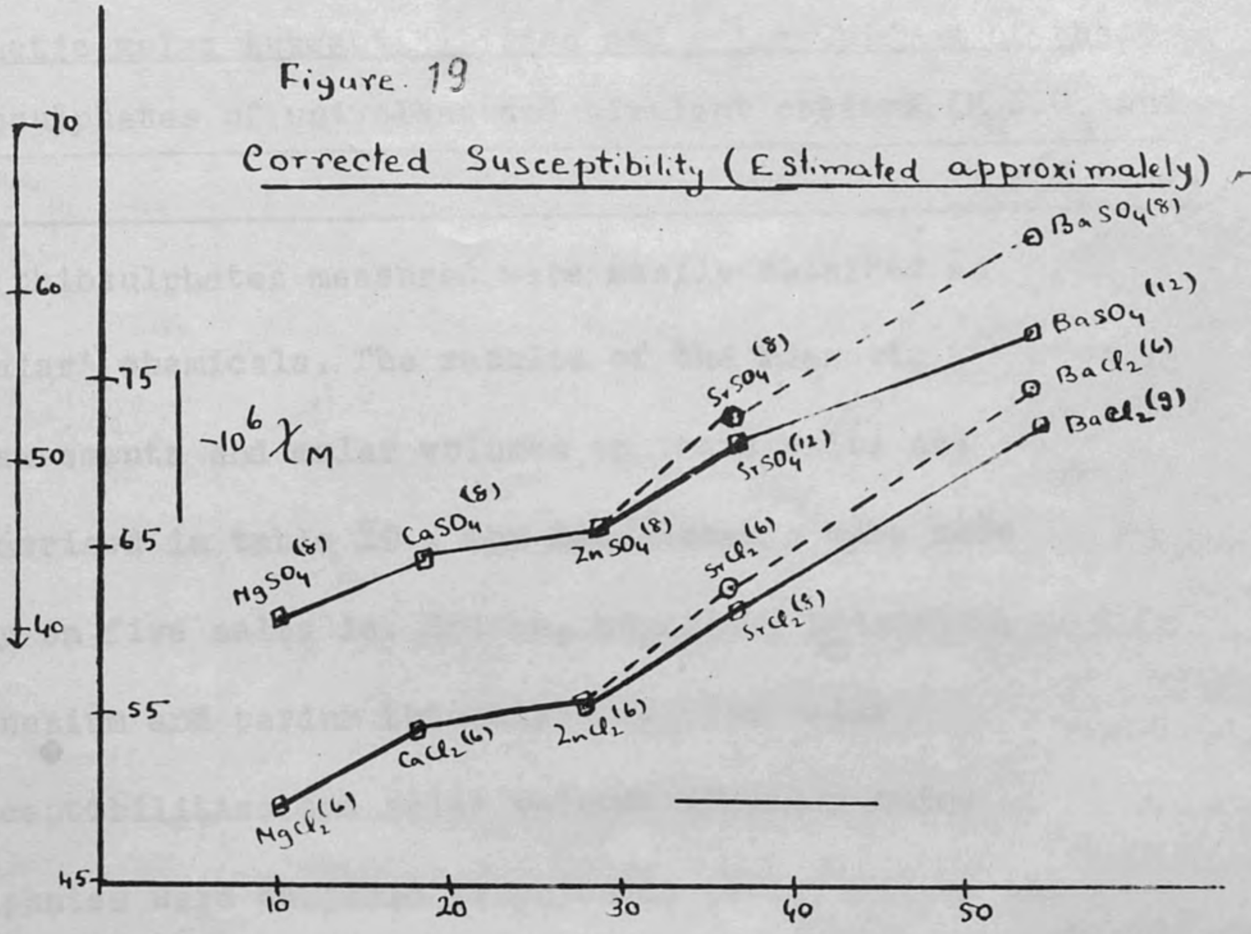
Ca SO_4. The HO_1 type of symmetry is given for calcium sulphate ie. Ca^{++} ion is surrounded by eight oxygen atoms.

Zn SO_4. The hydrated and anhydrons sulphates of zinc are similar to those of magnesium sulphate in coordination but they are not isostructural.

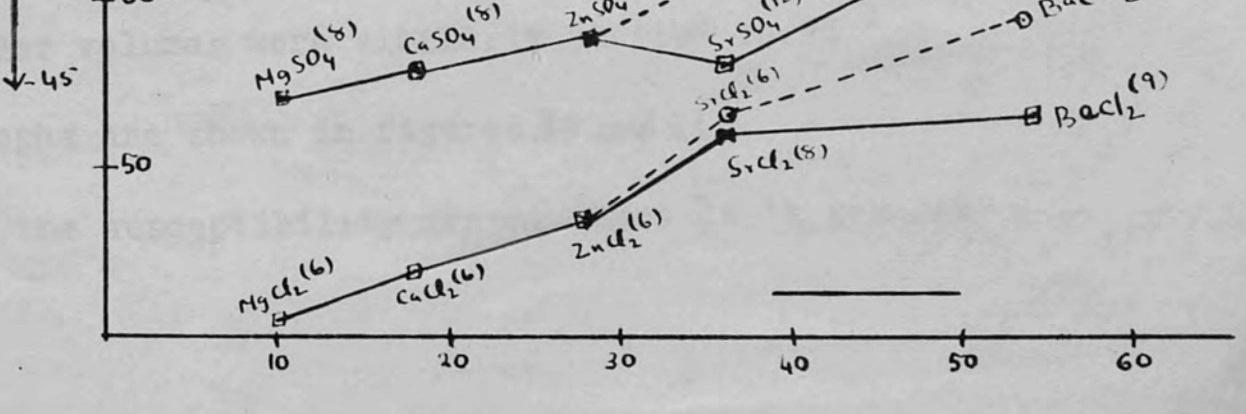
Sr SO_4" The Ba SO_4 type is given ie. 12 coordination for Sr^{++}. The deviations in the molar volume curve can be related to these differences in packing and coordination number, and this helps to explain the susceptibility deviation. From magnesium through calcium to zinc both the chloride curve and the sulphate curve refer to a constant coordination number (6 for the chlorides and 8 for the sulphates) and there is a good parallel relation over this part of the graph. Both curves show differences in coordination number between zinc and strontium and the chloride curve shows a small difference of susceptibility between strontium and barium. Strontium chloride in six fold coordination would have a **higher molar volume** and similarly that for barium chloride would be still higher than the experimental figure. This would give an even steeper slope for the chloride molar volume ~~chloride~~ graph than in the full line of fig 18 . Similarly Strontium Sulphate in 8-fold coordination would have a much higher volume than actually found for the salt in 12-fold coordination and barium sulphate would be expected to have a similar high figure. This was approximately estimated in figure 19 and these values are plotted as dotted lines. The actual direction in which deviations occur (above or below the slope) is in line with this explanation. This would explain in general the trends in the susceptibility graph as is shown by the dotted lines on this graph, although the susceptibility of barium sulphate appears somewhat low. One literature value has this somewhat higher value. The difference in methods of preparing these compounds might have a little effect on the susceptibility.

Figure 19

Corrected Susceptibility (Estimated approximately)



Corrected molar Volumes (Estimated approximately)



Magnetic molar susceptibilities and molar volumes of the thiosulphates of univalent and bivalent cations ($M_2S_2O_3$ and $M'S_2O_3$).

The thiosulphates measured were easily obtained as 'analar' chemicals. The results of the magnetic measurements and molar volumes on these salts are summarised in table 20 . The measurements were made only on five salts ie. Sodium, ammonium, potassium, magnesium and barium thiosulphates. The molar susceptibilities and molar volumes of these thiosulphates were compared graphically with those of the corresponding sulphates. In the case of the univalent cations to compare sulphates and thiosulphates, the susceptibilities were plotted against twice the effective atomic number of the cations, and in the case of bivalent cations, against Z for the cation. The molar volumes were similarly plotted these two graphs are shown in figures 20 and 21.

In the susceptibility graph, there is in general

TABLE 20

$-10^6 \chi$ M Thiosulphates of univalent and bivalent cations

Salt	Mol. wt. (M)	C.N.	$-10^6 \chi$ salt	$-10^6 \chi$ M
$Na_2S_2O_3.5H_2O$	248.21	8	0.5210	129.30
			0.5200	129.10
			0.5210	129.30
				mean
				129.30
$Na_2S_2O_3$	158.21	8		64.50
$K_2S_2O_3$	190.32		0.4033	76.77
			0.4053	77.14
			0.4014	76.40
				mean
				76.60
$(NH_4)_2\ S_2O_3$	148.21		0.5185	76.85
			0.5235	77.58
			0.5152	76.40
				mean
				76.60

TABLE 20 (contd)

Salt	Mol. wt. (M)	C.N.	$-10^6 \chi$ salt	$-10^6 \chi$ M
Mg S_2O_3 $6H_2O$	244.55	6	0.5240	128.13
			0.5234	128.00
			0.5200	127.30
				mean 127.80
Mg S_2O_3	136.55	6		50.04
BaS_2O_3 H_2O	267.6	6	0.3041	81.35
			0.3052	81.63
			0.3047	81.5
				mean 81.50
BaS_2 O_3	249.5			68.54

TABLE 21

Molar volumes and densities of the thiosulphates of univalent and bivalent cations

salt	Mol.Wt.	C.N.	D^{20}_{4}	V_M^{20}
$Na_2S_2O_3$	158.21	8	2.12	74.60
$K_2S_2O_3$	190.32	(?)	2.23	85.35
$(NH_4)_2\ S_2O_3$	148.21	(?)	1.68	88.30
MgS_2O_3	136.43	6	1.9	71.80
BaS_2O_3	249.5	6	3.5	71.30

$-10^6\chi_M$ - Thiosulphates plotted against Z - cations compared with those of sulphates.

Figure 20

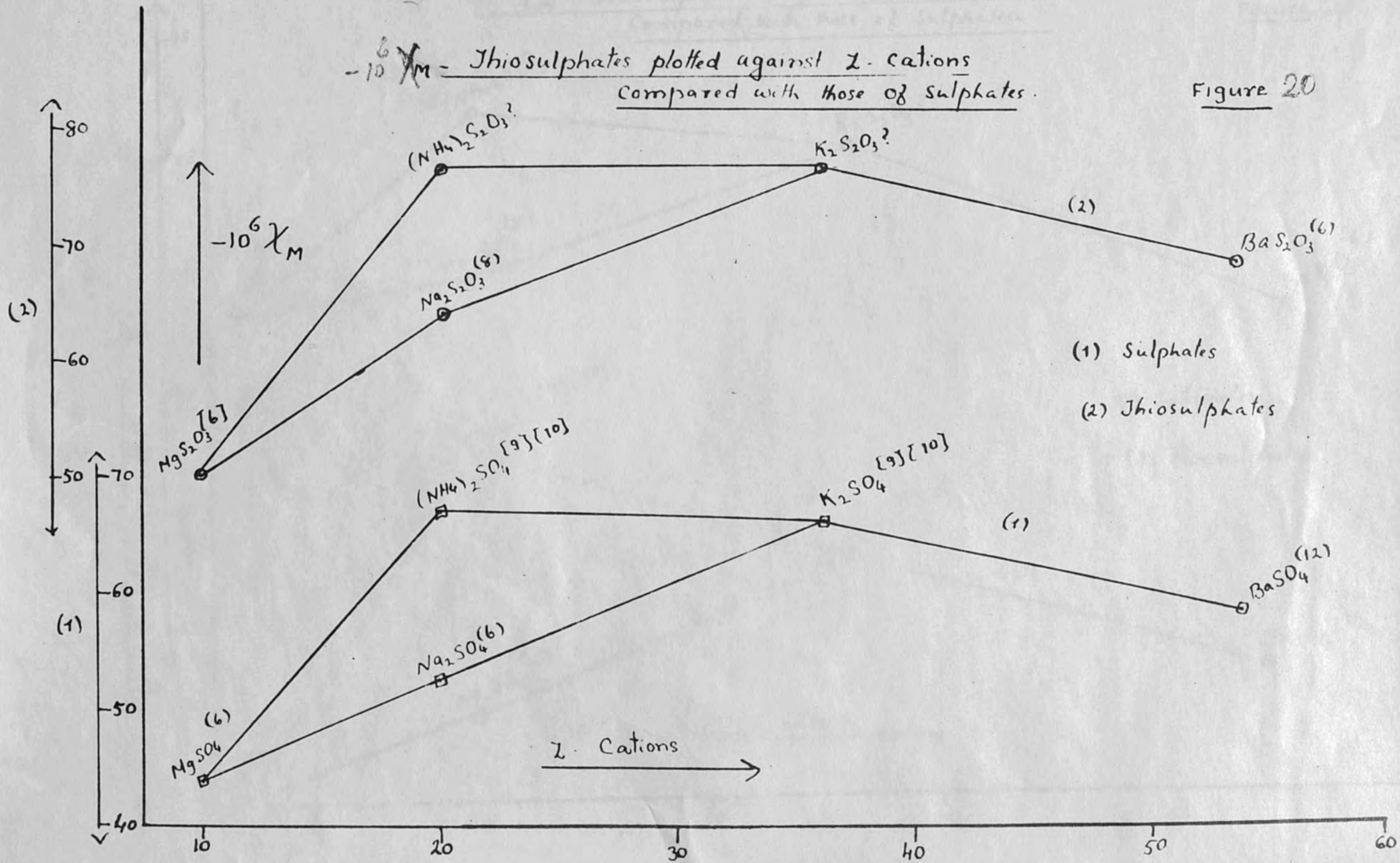
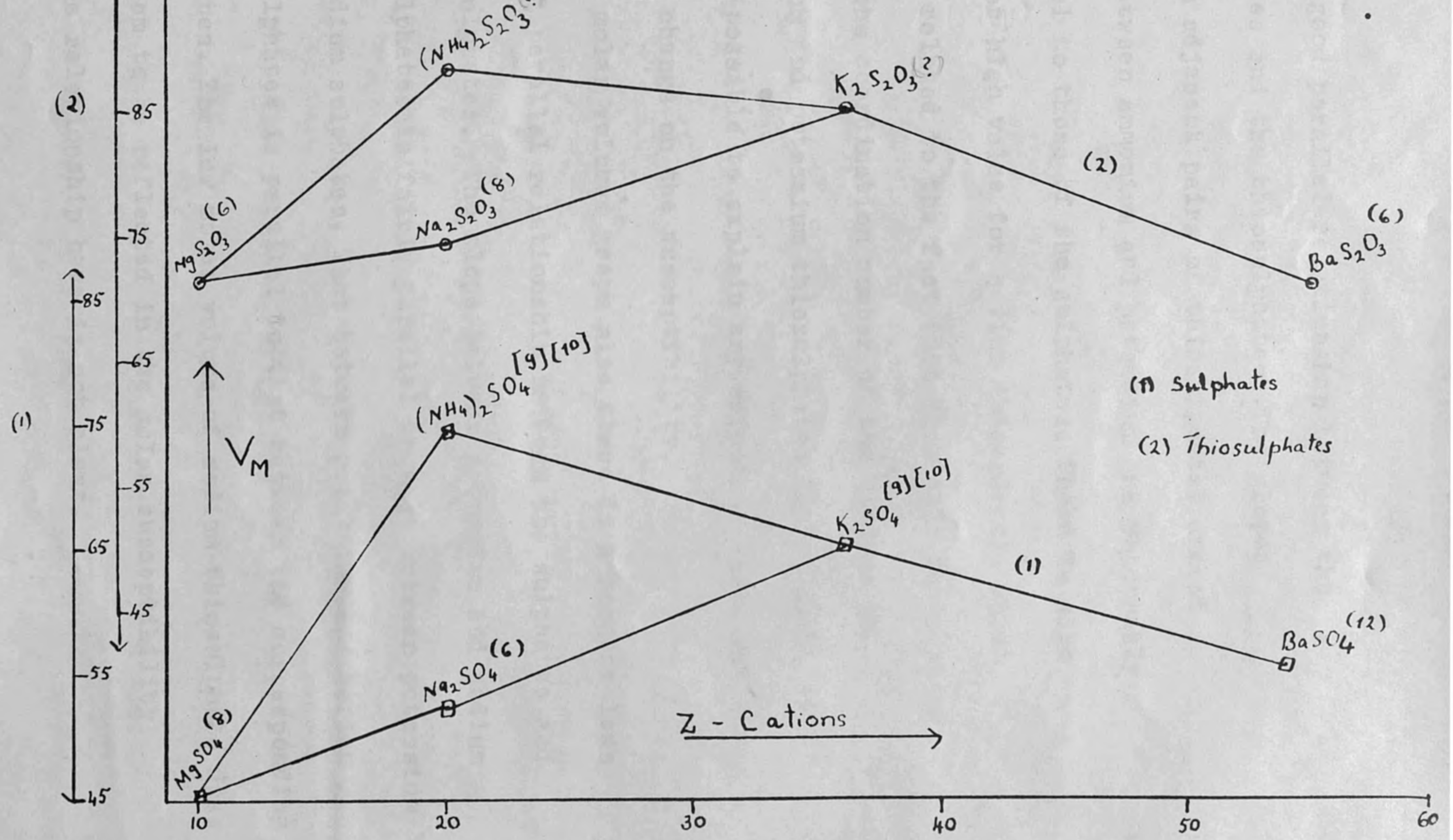


Figure 21

$-10^6 V_M$ - Thiosulphates plotted against Z - Cations.
Compared with those of Sulphates.



a very good parallel relationship between the sulphates and the thiosulphates. The slopes between adjacent pairs of thiosulphates except that between ammonium and potassium are reasonably parallel to those of the sulphates. There is also a rather high value for sodium thiosulphate which may be related to the fact that this salt is hydrated. Since the coordination number of the cations in ammonium and potassium thiosulphates is not known it is not possible to explain any effect of coordination number change on the susceptibility.

In the molar volumes graph also there is a more or less general parallel relationship between the sulphates and thiosulphates. The slope between potassium and sodium thiosulphates is fairly parallel to that between potassium and sodium sulphates. That between potassium and barium thiosulphates is parallel to that between the corresponding sulphates. The low molar volume of sodium thiosulphate does not seem to be reflected in the molar susceptibility and the relationship here is not clear.

The susceptibility increments between the thiosulphates and sulphates were worked out and a mean value of 10.7 units of susceptibility for the difference of these salts is obtained without considering the coordination effect. A value for the S_2O_3'' ion could be obtained by adding 10.7 to the mean ionic susceptibility of the SO_4'' ion. The value obtained in this manner is $50{\cdot}2 \times 10^{-6}$. An ionic susceptibility constant for the thiosulphate ion was also calculated by subtracting the ionic susceptibility of the cation from that of the salts. In the case of univalent cations, twice the ionic susceptibility was subtracted to get the ionic susceptibility for the thiosulphate ion. A mean value of <u>48.38</u> was obtained as shown in table 22. Due to the limited time which was available it was not possible for the present author to proceed any further work on the thiosulphates. Further measurements may be necessary to make a complete study on the thiosulphates and give a more accurate mean value for the ionic susceptibility constant for the thiosulphate ion.

TABLE 22

Molar susceptibility increments between the thiosulphates and sulphates and the ionic susceptibility constant of the thiosulphate ion

Cation	$-10^6 \chi_M$ (Thiosulphates)	$-10^6 \chi_M$ (Sulphates)	$-10^6 \Delta\chi$ (S_2O_3- SO_4'')	$-10^6 \chi''_M$ (S_2O_3)	$-10^6 \chi_M$ (Cation)
Na^+	64.50	52.30	12.20	52.70	5.90
NH_4^+	76.60	66.90	9.70	49.70	13.35
K^+	76.60	65.98	10.62	47.80	14.40
Mg^{++}	50.04	43.70	6.34	47.44	2.60
Ba^{++}	68.54	58.25	10.30	44.24	24.30
			mean 10.7	mean 48.38	

DIAMAGNETIC SUSCEPTIBILITY CONSTANTS

The results discussed here enable the following additional diamagnetic susceptibility constants based upon those of Trew and Husain to be suggested

Ion (Cations)	$-10^{6}\chi$ M	Ion (Anions)	$-10^{6}\chi$ M
		ClO_3^-	26.8~~7~~
		BrO_3^-	39.3~~6~~
Ag^+	24.7	IO_3^-	44.8
Tl^+	32.8	ClO_4^-	32.5
Ba^{++}	24.3	PO_4^{3-}	42.5
Sr^{++}	13.72	SO_4^{2-}	40.0
Ca^{++}	6.1	$S_2O_3^{2-}$	48.4

PART IV

Consideration of the Formula and Structure of Iodine Dioxide

During recent years the investigation of the formula of iodine dioxide has been of interest and the systematic magnetic susceptibility relationships obtained for the iodates in the current work appear to be applicable to this problem.

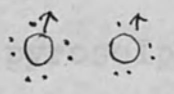
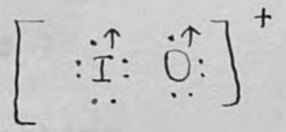
The empirical formula is IO_2, but this would be likely to exhibit paramagnetism because of the odd electron present.

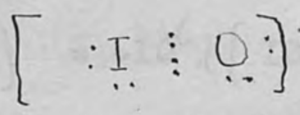
ie. $:\underset{..}{\ddot{O}}:\ \underset{..}{\ddot{I}}\cdot\ \underset{..}{\ddot{O}}:$

Cotton and Wilkinson (60) suggested that the yellow solid I_2O_4 ($(IO_2)_2$) which is obtained by partial hydrolysis of $(IO)_2SO_4$ appears to have a network built up of polymeric I - O chains which are cross linked by IO_3 groups. Kleinberg (61) pointed out that I_2O_4 and I_4O_9 although they contain only iodine and oxygen are not regarded as really being oxides. I_2O_4, commonly known as iodine textroxide, is a yellow solid obtained by the action of water on the products of reaction between iodic acid and warm concentrated sulphuric acid. These products are probably $I_2O_3 \cdot H_2SO_4$, and $I_2O_4 \cdot H_2SO_4$. The actual structure of I_2O_4 is not fully established. One formula assigned to the compound makes the presumption that it is an iodyl iodate $(IO)\,IO_3$.

Various workers have used magnetic susceptibility, and spectro-photometric methods to investigate the structure of iodine dioxide and of similar compounds. Evidence indicates that the simplest molecular formula is I_2O_4 and an attractive simple formulation is $[IO^+]\ [IO_3']$ ie. iodoxy-iodate. This formula $[IO]\,IO_3$ is supported by the existence of similar compounds such as $[IO]_2\,SO_4$ formed when iodine is dissolved in Oleum (a form of concentrated H_2SO_4). There is considerable difference of opinion about the exact structure of the iodine dioxide. Measurements of the magnetic susceptibility have been carried out by Willmarth and Dharmatti.(62) They showed that the substance is diamagnetic and suggested that the diamagnetism could be explained as due to the presence of an even number of IO_2 units. So they suggested that the compound could be $(IO^+)\ (IO_3')$. Willmarth and Dharmatti give a diamagnetic molar susceptibility value of - 76.0. IO^{-6} for this compound.

Dasent and Waddington (63) investigated the possible structure of I_2O_4 and other similar compounds. They suggested that IO^+ could not be present as such because it has the same number of valency electrons as oxygen (O_2) and so should have a $^3\Sigma$ spectroscopic state with two unpaired electron spins and be paramagnetic like the oxygen molecule. ie. oxygen is formulated:-

 and IO^+ would similarly be 

These unpaired spins could be avoided if there is a double bond , but the general indications show that these electron deficient compounds tend to have the electrons spread over the available orbitals. Dasant and Waddington pointed out that the infra red spectroscopic evidence is not in accord with a double bond structure. ie. the I - O stretching frequency does not come in the correct place in the infra-red range for a double bond. Meanwhile in 1957 Symons (64) worked on similar compounds and discussed Willmarth and Dharmatti's magnetic evidence that the iodoxy ion, $[IO^+]$ is diamagnetic since the iodoxy iodate $(IO)\ IO_3$ is diamagnetic. In 1962 Arotsky, Mischa and Symonds (65) remeasured the magnetic susceptibility of I_2O_4 and also I_4O_9, $(IO)_2\ SO_4$ and $(IO)\ HS_2O_7$), in order to calculate an ionic susceptibility value for the $[IO^+]$ ion. They also included the salt potassium acid pyrosulphate KHS_2O_7 and calculated an ionic susceptibility for the $[IO^+]$ cation by subtracting susceptibilities as follows.

$$IO^6 \chi_M \left[IO+\right] = -IO^6 \chi \left[IO^+\right] H\ S_2O_7^- - \left[-IO^6 \chi_M\ KH\ S_2O_7 - IO^6 \chi_M\ K^+\right]$$

$$= -\ 28.9 - \left[-\ 79.9 - (-13.0)\right]$$

This gives a paramagnetic susceptibility for the $[IO^+]$ ion of $IO^6 \chi_M$ = + 37.7. c.g.s units. There is however some discrepancy since Willmarth and Dharmatti, assuming that I_2O_4 was $[IO^+]\ [IO_3']$ obtained a value of

- 24.88 for the susceptibility of the cation IO^+ . This was obtained by subtracting Trew's value (6) for the diamagnetic susceptibility of the IO_3' anion from their own experimental value of - 76.0 for the I_2O_4. It therefore would appear that iodine tetroxide does not contain the cation $[IO^+]$ as a simple species contrary to Willmarth and Dharmatti's assumption. As already noted this formula should lead to a paramagnetic susceptibility. If however the susceptibility value of Arotsky, Mischa and Symons for the compound $(IO)_2 SO_4$ is considered using the present mean ionic susceptibility of the sulphate ion ($-10^6 \chi_M = 39.5$) a diamagnetic value is obtained for the cation in this compound.

ie. $$10^6 \chi_M (IO)_2 = -10^6 \chi_M (IO)_2 SO_4 - 10^6 \chi_M SO_4''$$

$$= - 80.2 -(-39.5) = -40.7$$

$$= - 40.7$$

$$-10^6 \chi \text{ For } IO^+ = = 20.35$$

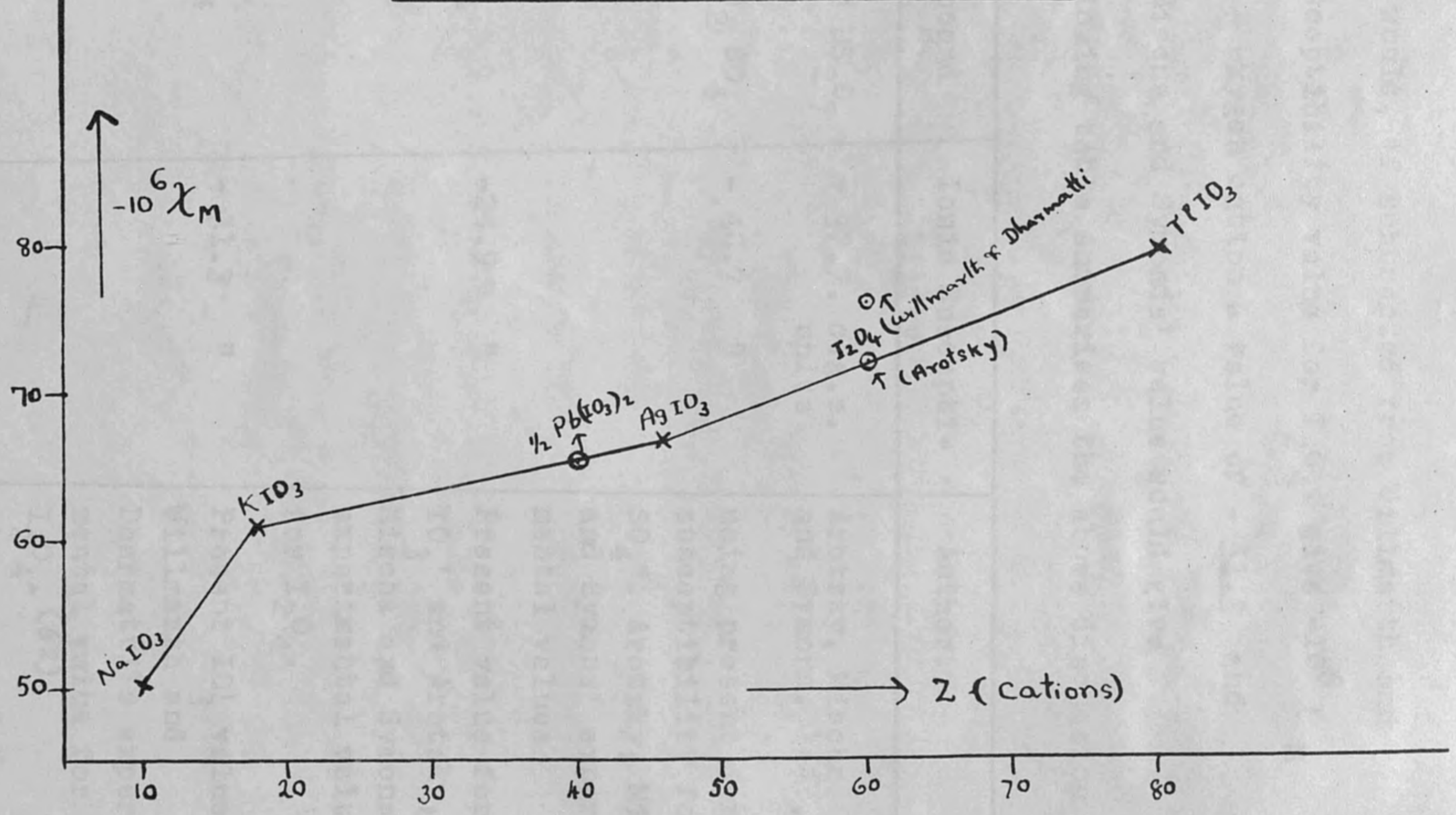
They claim that their evidence suggests that the molecule I_2O_4 consists of sheets of polymerised chains of I_2O_4 separated by IO_3' ions - and is a giant lattice type of structure.

In 1964 Grete Daehlie and Arne Kjekshus (66) reported their work on the iodine oxides and related compounds - such as $I_2O_3.SO_3$; $I_2O_3.\ 4\ SO_3H_2O$; $I_2O_3.\ SeO_3$, and I_2O_4. Their evidence showed that I_2O_4 was the stable end product of the decomposition of the other compounds at lower temperatures, itself not being decomposed until about 200°c. These authors do not give any definite indication of whether the compound contains the (IO^+) cation. It is interesting to plot the available susceptibility of I_2O_4 (Willmarth and Dharmatti and Arotsky and co-workers) on the graph of the current work for the susceptibility of the iodates. The figure shows this graph with Z (IO^+) = 60. It will be noted that the point for the molar susceptibility of I_2O_4 falls almost on the line between the molar susceptibility of silver iodate and thallium (1) iodate. It supports the idea that the compound is an iodate and that the cation must be diamagnetic. The diamagnetic constant for the iodate ion obtained in the present work is

Figure. 22

$-10^6 \chi_M$ - Iodates of Sodium, Potassium, Silver and Thallium (I)

including $-10^6 \chi_M$ of I_2O_4 and $Pb(IO_3)_2$.



-44.7. 10^6 and would, if subtracted from Willmarth and Dharmatti's Susceptibility value for I_2O_4. give $-10^6 \chi_M$ for the iodine - oxygen cation a value of - <u>31.3</u> and from Arotsky, Mischa and Symonds' value would give -24.9. The following table **summarises** the above discussion.

Cation	Compound	Ionic Susceptibility	Author.
IO^+	(IO) HS_2O_7	+ 37.7. c.g.s. units	Arotsky, Mischa and Symons. (65).
$(IO)_2$	$(IO)_2\ SO_4$	- 40.7 "	using present ionic susceptibility for SO_4". Arotsky, Mischa and Symons' experimental values
$(IO^+)_{(?n)}$	I_2O_4	-24.9 "	Present value for IO_3' and Arotsky, Mischa and Symons' experimental value for I_2O_4.
$(IO^+)_{(?n)}$	I_2O_4	- 31.3 "	Present IO_3' value, Willmarth and Dharmatti's experimental value for I_2O_4. (62)

The above evidence seems to suggest that the compound

I_2O_4 could be an iodoxy iodate, but that the simple (IO^+) cation is not present as such, but the evidence all points to a confirmation of the suggestion that there is some polymerised form present as the cation. The exact structure cannot be settled until the crystal structure determination by X-ray diffraction analysis has been made.

The use of the current values to support the idea of an iodoxy iodate is further supported by the susceptibility for $Pb(IO_3)_2$ given by Prasad Dharmatti and Kanekar(54). They found a value of $- 0.2356 .IO^6$ for the salt which with a molecular weight of 557.05 gives $-IO^6 \chi_M$ ($Pb(IO_3)_2$) of 131.24. If half of the figure is plotted against half Z for Pb^{++} (Z = 40), the point falls on the present graph between the susceptibilities of potassium and silver iodates.

PART V

Discussion of Results and Theoretical Molar Susceptibility Relationships

General Introduction

For a spherical ion the diamagnetic susceptibility may be theoretically found from the Langevin Equation -

$$-10^6\chi_A = \frac{e^2N}{6mc}\sum_n \bar{r}^2 = 2.83\cdot 10^{-10}\sum_n \bar{r}^2$$

where $\sum_n \bar{r}^2$ is the mean square radius of an orbital summed over all the n orbitals within the atom or ion. Since the equation holds only for a spherical free ion, it would not be expected to be in exact agreement with the experimental values except when these approximate to spherical symmetry in dilute solution or a dilute gas. The susceptibilty of an atom or ion is therefore proportional to $\sum \bar{r}^2$. In crystals the interionic distances depend also on the ionic radii and hence the factors which determine such distances in a crystal must influence the magnetic susceptibility. If an increase in the size of an ion tends to increase the value of $\sum_n \bar{r}^2$ for an ion in the crystal, then there should be an increase in the molar susceptibility.

This follows, because the volume of a sphere is $4/3\,\pi r^3$ and the mean square radius represents the projected part of this volume projected on a plane perpendicular to the field axis. So the charge is polarised by the field and we would expect the molar volume and molar susceptibility to be related.

There are various methods by which the value of the mean square radius $\sum \bar{r}^2$ of the atomic or ionic orbitals may be calculated. Van Vleck and Pauling (67) developed an equation for the molar susceptibility of a free gaseous ion, calculating $\sum \bar{r}^2$ by use of appropriate values of the principal quantum number n, the orbital angular momentum quantum number l, and the screening constant for a particular (n,l) orbital.

i.e. $$\chi_{n,l} = \frac{-e^2 N}{6\,mc^2} \sum_n \bar{r}^2$$

Van Vleck and Pauling have shown that -

$$\bar{r}^2 = \frac{a_0^2\, n^4}{(Z-S)^2}\left[1 + 3/2\left\{1 - \frac{l(l+1) - 1/3}{n^2}\right\}\right]$$

per gram atom

$$\chi_A = \frac{e^2 N}{6\,mc^2}\, a_0^2 \sum \frac{n^4}{(Z-S)^2}\left[1 + 3/2\left\{\frac{1 - l(l+1) - 1/3}{n^2}\right\}\right]$$

To simplify the expression Pauling multiplies by 2/5

i.e. $$2/5\left\{1+3/2\left\{1-\frac{l(l+1)-1/3}{n^2}\right\}\right\}$$

$$2/5\left[1+3/2-\frac{3l(l+1)-1}{2n^2}\right]$$

$$=\left[1-\frac{3l(l+1)-1}{5n^2}\right]$$

$$\therefore\ \chi_A = 5/2\ \frac{e^2N}{6mc^2}\ a_0^2\ \sum\frac{n^4}{(Z-S)^2}\left[1-\frac{3l(l+1)-1}{5n^2}\right]$$

In these equations N is the principal quantum number of a group of electrons with orbital angular momentum quantum number l and Z is the effective atomic number of the atom or ion. The total susceptibility is found by summing over all the sub-groups present. The screening constant s was calculated by Pauling assuming that the various sub-groups influence each other like surface spherical distributions of charge. Using the values of the universal constants e, N, m, c and a_o which were accepted in 1932, the value of $5/2\ \frac{e^2N\ .a_o^2}{6\ mc^2}$ was given by Pauling as

2. 010 .10^{-6}. This is 5/2 greater than the usual value of $\frac{e^2 N.\ a_o^2}{6\ mc^2}$ used by later workers, i.e. 0.804. 10^{-6} Using modern values of the constants a more correct figure is 0.7923 .10^{-6} which is used in this discussion (see page175). Pauling's values of theoretical susceptibilities tended to be much too high for elements in the later periods of the periodic table. Subsequently Slater introduced an improved set of screening constants and modified effective principal quantum numbers (n') for values of n greater than 3. These were a semi-theoretical set of values arranged to give a good agreement between the observed and calculated values of the energies of the various orbitals. The ionic and atomic susceptibilities obtained by Slater's method are very much closer to experimental ionic and atomic susceptibilities than the Pauling ones, although still considerably too high for elements with $n > 3$ Angus(68) has tabulated Pauling's ionic susceptibility constants for a number of ions in comparison with those obtained by the Slater method and a modified Slater method which he developed of determining $\sum_{n} \overline{r}^{2}$. The most accurate

estimations of the value of $\sum_n \bar{r}^2$ are the values calculated by Hartree(69) who developed a method for computing the distribution of electron density by a method based on quantum mechanics. This gives values of the atomic and ionic susceptibility of a free ion in good agreement with experimental values. But only a limited set of values for the ionic charge distribution is available and in the crystal, the problem of the restriction of the field has to be included.

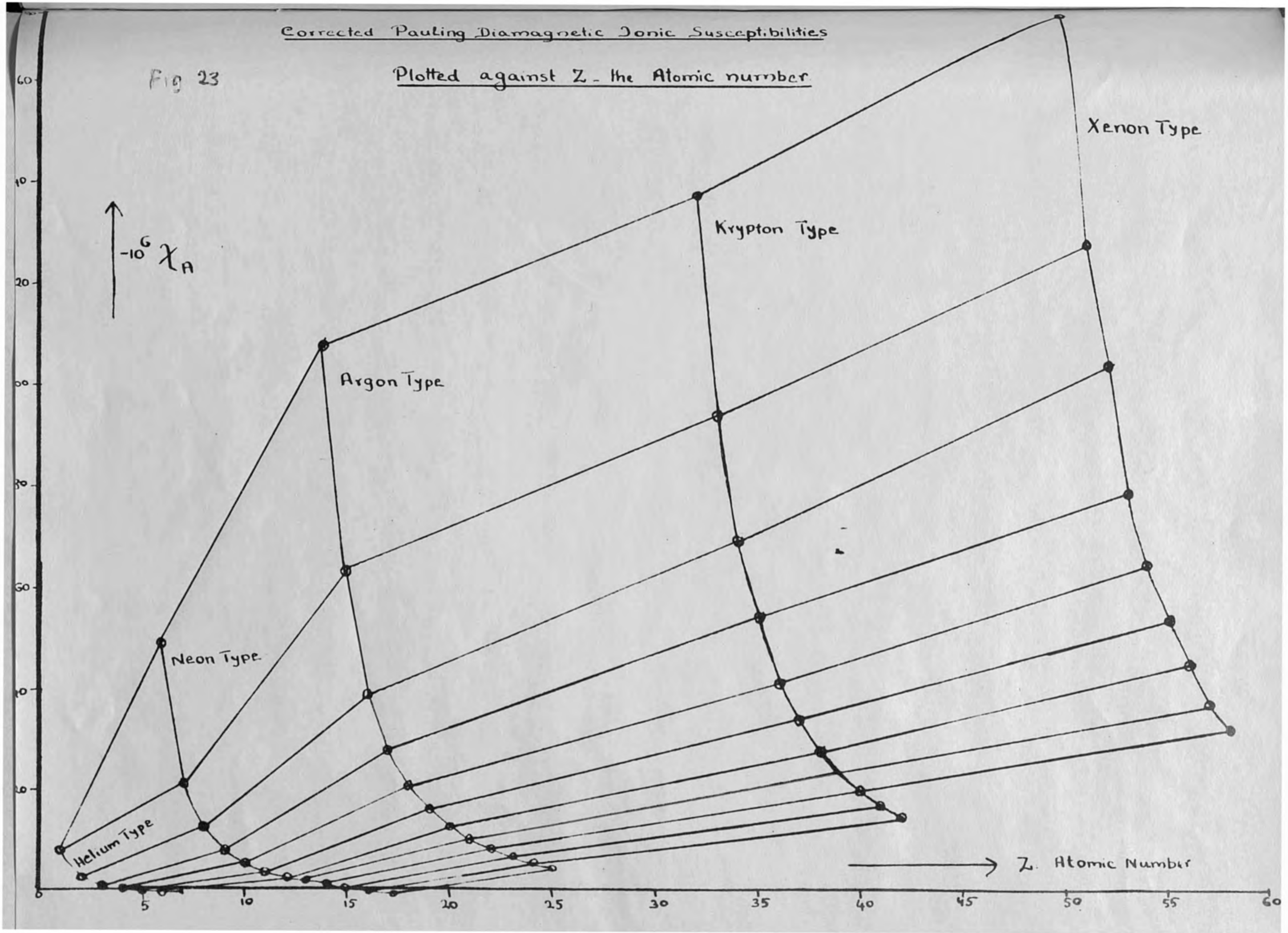
The shapes of the susceptibility-atomic number graphs and the theoretical calculations

A consideration of theoretical molar susceptibilities helps to explain the general nature of the susceptibility-atomic number curves, i.e. the zig-zag character of these curves. Certain systematic relationships exist between the susceptibilities of the salts containing ions of related series, which are best shown graphically. It has been shown that the diamagnetic susceptibility when plotted against the effective atomic number of the whole compound has a characteristic zig-zag slope (8). This effect is clear for salts of the same cation and different anions when a graph is plotted of molar susceptibility against the effective atomic number of anion (or the effective atomic number of cation for salts with the same anion). Similar types of graph are thus found in the case of isoelectronic series of salts on passing from the salts of one cation to that of the other. This effect is shown in the following figure (fig.23) and was noted by Klemm and has been further developed by Trew and co-workers.(10) In this figure there is shown the course of the graph of values for the theoretical diamagnetism of the inert gas type of ions plotted against the ordinal number, the values being taken from Angus.(68) It is obviously clear that the slope does not ascend linearly with the ordinal number although Prasad and his co-workers have tried to smooth out graphs of this type for experimental measurements of ammonium and alkaline earth salts to a straight line relationships. The figure shows that although there is a generally linear tendency, there are systematic irregularities in the graph. This type of plot is similar to that for the ionic radii, molar volumes and the molar refractivity values. There is a steeper slope from the neon to argon configuration and a rather smaller

Fig 23

Corrected Pauling Diamagnetic Ionic Susceptibilities

Plotted against Z - the Atomic number



one from argon to krypton and again a greater slope from krypton to the xenon configuration. Trew and Husain (10) also showed for simple salts of alkali metals that these parallel plots were very sensitive to changes in co-ordination number of the cation or anion. In view of the earlier work, the results for the alkali halides can be used as a useful reference for consideration of any systematic properties of the salts investigated in the present work.

A change in the slope of the susceptibility graph results when an increase in the number of the electrons occurs due to the filling in of the d and f orbitals within the ions. This will influence the size of the ionic radii. In the case of the halide ions, the increase in slope on passing from bromide to iodide is expected from the electronic configuration of the halide ions, i.e. in the chloride ion with Z = 18 the electronic configuration is IS^2, $2S^2P^6$, $3S^2P^6$ in the bromide ion with Z = 36 the arrangement is IS^2,$2S^2$,P^6, $3S^2P^63d^{10}$, $4S^2P^6$ and the iodide ion with Z = 54 has in addition the $4d^{10}$, $5S^2P^6$. There is thus a filling in of an additional d shell between bromide and iodide and this increases the charge distribution as is shown by the theoretical calculations using the Slater method. The figures below are approximated to the nearest whole number from calculations using this method as shown on page 186.

Ion	Z	$\triangle$	$\sum \bar{r}^{2}$	$\triangle$
F'	10		9	
		8		22
Cl'	18		32	
		18		19
Br'	36		50	
		18		24
I'	54		74	

A similar increase in charge distribution might have been expected on adding the 3 d^{10} electrons in the bromide ion, but the shape of the curves is explained by considering the theoretical calculations of $\sum r^{-2}$ by the Slater method (page 186). The 3 d orbital in the bromide ion contributes only about 13 percent to the total value of $\sum r^{-2}$ while in the iodide ion the contribution is about 19 percent So the increase in the slope of the susceptibility - effective atomic number graph is greater from bromide to iodide. The same effect could have been shown using the

Pauling method which is the basis of the figure 23

Theoretical calculation of the diamagnetic susceptibility of the simple ions by Slater's method

In order to compare the theoretical and experimental ionic susceptibilities of anions, the theoretical values for the simple ions like F', Cl', Br', and I', were first calculated afresh using the Slater method which is considered to be the most useful for the simple ions. In addition the ionic susceptibility of the silver ion (Ag^+) was calculated to compare with the experimental value which appears rather low.

From the Langevin Equation :-

$$-10^6 \chi_A = \frac{e^2 N \quad a_o^2}{6 \, mc^2} \sum \bar{r}^2$$

The constant term $\frac{e^2 N \quad a^2_o}{6 \, mc^2}$ was calculated using the latest values of the universal constants (70) .

$e = 4,80288 \; . \; 10^{-10}$

$e^2 = 23.06766. \; 10^{-20}$

$N = 6.02472 \; . \; 10^{23}$ atoms/mol.

$e^2 N = 13.897617.10^4$

$m = 9.1085 \; . \; 10^{-28}$ g.

$c = 2.997929. \; 10^{10}$ cms/sec.

$c^2 = 8.987578. \; 10^{20}$

$6mc^2 = 4.911801. \; 10^{-6}$

$a_o = 0.529171$ A $(10^{-8}$ cm)

$a_o^2 = 0.2800219.10^{-16}$ cm

$$\therefore \frac{e^2 N}{6mc^2} a_o^2 = 2.82943 \; . \; 10^{10} \; . \; 0.2800219.10^{-16}$$

$$= \underline{\underline{0.7923 \; . \; 10^{-6}}}$$

Where $2.82943 \; . \; 10^{10}$ is $\dfrac{e^2 N}{6mc^2}$

With the corrected value of $\frac{e^2N}{6mc^2} = 0.7923 \cdot 10^{-6}$

the figures tabulated by Angus have been corrected.

Several of these values are needed to determine calculated ionic susceptibility for the haloxy anions.

Table 23 shows these values corrected as follows :-

In Angus' paper, Table 11 column 1 needs to be multiplied by a factor $\frac{0.7923}{0.804}$ i.e. 0.985447 to correct to modern values. The values in column 2 and 3 require the factor $\frac{0.7923}{0.807}$ i.e. 0.981784. The Gray and Farquharson figures in Table 111 need to be multiplied by the factor 0.985447 since it is calculated by Pauling's method.

Proc. Roy. Soc. 1932 P. 573 TABLE 11

IONIC SUSCEPTIBILITY CONSTANTS - $10^6 \chi$ A

Ion	Linus Pauling		J. C. S.		W. R. A.	
	uncorrected	corrected	uncorrected	corrected	uncorrected	corrected
Hydrogen type						
H^o	2.42	2.39	2.42	2.38	2.42	2.38
He^{+1}	0.604	0.595	0.605	0.594	0.606	0.594
Li^{+2}	0.27	0.264	0.27	0.265	0.27	0.265
He-Type						
H^{-1}	8.00	7.90	9.87	9.69	9.87	9.69
He^o	1.54	1.52	1.68	1.65	1.68	1.65
Li^{+1}	0.63	0.621	0.665	0.653	0.665	0.653
Be^{+2}	0.34	0.335	0.35	0.344	0.35	0.344
B^{+3}	0.21	0.207	0.22	0.216	0.22	0.216
C^{+4}	0.15	0.148	0.15	0.147	0.15	0.147
N^{+5}	0.11	0.108	0.11	0.108	0.11	0.108

Table 23 (Contd)

Angus' TABLE 11 (contd)

Ion	L. P.		J. C. S.		W. R. A	
	uncorrected	corrected	uncorrected	corrected	uncorrected	corrected
Neon type						
C^{-4}	50.0	49.3	56.65	55.62	45.65	44.82
N^{-3}	22.0	21.68	23.94	23.50	19.96	19.60
O^{-2}	12.6	12.42	13.15	12.91	11.25	11.05
F^{-1}	8.1	7.98	8.30	8.15	7.25	7.12
Ne^{o}	5.7	5.62	5.72	5.62	5.07	4.98
Na^{+1}	4.2	4.14	4.17	4.09	3.74	3.67
Mg^{+2}	3.2	3.15	3.18	3.12	2.89	2.84
Al^{+3}	2.5	2.46	2.50	2.54	2.28	2.24
Si^{+4}	2.1	2.07	2.03	1.99	1.87	1.84
P^{+5}	1.7	1.67	1.66	1.63	1.54	1.51
S^{+6}	1.4	1.38	1.41	1.38	1.31	1.10
C^{+7}	1.2	1.18	1.19	1.17	1.12	1.10

Table 23 (Contd)
Angus/ TABLE 11 (contd)

Ion	L. P.		J. C. S.		W. R. A	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
Argon-type						
Si^{-4}	110.0	108.40	109.5	107.51	91.11	89.45
P^{-3}	65.0	64.05	59.40	58.31	50.78	49.85
S^{-2}	40.0	39.42	37.41	36.73	32.63	32.04
$C\ell^{-1}$	29.0	28.58	25.79	25.32	22.86	22.44
A^{0}	21.5	21.20	18.87	18.53	16.95	16.64
K^{+1}	16.7	16.46	14.4	14.14	13.06	12.82
Cn^{+2}	13.3	13.11	11.38	11.17	10.42	10.23
Sc^{+3}	10.9	10.75	9.22	9.05	8.50	8.33
Ti^{+4}	9.0	8.87	7.65	7.513	7.09	6.96
V^{+5}	7.7	7.59	6.45	6.332	6.01	5.90
Cr^{+6}	6.6.	6.50	5.50	5.27	5.15	5.06
Mn^{+7}	5.7	5.61	4.73	4.644	4.45	4.37

Table 23 (contd)

Angus' TABLE 11 (contd)

Ion	L. P.		J. C. S.		W. R. A	
	uncorrected	corrected	uncorrected	corrected	uncorrected	corrected
Nickel type						
Ca^{+}	13	12.81	19.40	18.75	19.26	18.81
Zn^{+2}	11	10.84	15.57	15.29	15.45	15.17
Ga^{+3}	9.5	9.361	12.84	12.61	12.73	12.50
Ge^{+4}	8.5	8.38	10.78	10.58	10.69	10.496
As^{+5}	7.5	7.39	9.19	9.027	9.11	8.944
Se^{+6}	6.5	6.41	7.94	7.795	7.88	7.74
Br^{+7}	6.0	5.91	6.94	6.814	6.87	6.748
Krypton type						
Ge^{-4}	140.0	137.96	107.2	105.27	93.8	92.08
As^{-3}	95.0	93.62	72.46	71.14	64.62	63.44
Se^{-2}	70.0	68.98	52.54	51.6	47.60	46.71
Br^{-1}	54.0	53.21	40.01	39.3	36.65	35.98
Kr^{o}	42.0	41.40	31.73	31.15	29.33	28.79

Table 23 (contd)

Angus' TABLE 11 (contd)

Ion	L. P.		J. C. S.		W. R. A	
	uncorrected	corrected	uncorrected	corrected	uncorrected	corrected
Krypton type contd.						
Rb^{+1}	35	34.50	25.8	25.34	24.05	23.61
Sr^{+2}	28.0	27.6	21.53	21.14	20.19	19.8
Y^{+3}	24.0	23.65	18.16	17.83	17.14	16.83
Zr^{+4}	20.0	19.70	15.63	15.35	14.79	14.52~~1~~
Nb^{+5}	17.0	16.75	13.58	13.33	12.91	12.68
MO^{+6}	15.0	14.78	11.92	11.70	11.40	11.17
Palladium type						
Ag^{+1}	44.0	43.36	42.37	41.60	42.11	41.34
Cd^{+2}	37.0	36.46	34.16	33.54	33.94	33.33~~8~~
In^{+3}	32.0	31.53~~0~~	27.26	27.745	28.08	27.57
Sn^{+4}	28.0	27.6	23.9	23.445	23.71	23.28
Sb^{+5}	24.0	23.65	20.51	20.14	20.36	19.99
Te^{+6}	20.0	19.71	17.8	17.48	17.68	17.36
I^{+7}	17.0	16.75~~1~~	15.63	15.35	15.52	15.24

Table 23 (contd)

Angus' TABLE 11 (contd)

Ion	L. P.		J. C. S.		W. R. A	
	uncorrected	corrected	uncorrected	corrected	uncorrected	corrected
Xenon type						
Sn^{-4}	180.0	177.40	152.54	149.76	134.6	132.16
Sb^{-3}	130.0	128.11	105.67	103.75	94.40	92.68
Te^{-2}	105.0	103.47	77.27	75.86	70.62	69.33
I^{-1}	80.0	78.84	59.83	58.74	55.32	54.31
Xe^{0}	66.0	65.04	48.00	47.13	44.78	43.96
Cs^{+1}	55.0	54.20	39.57	38.85	37.20	36.53
Ba^{+2}	46	45.33	33.3	32.69	31.59	21.02
La^{+3}	38	37.45	28.5	27.98	27.09	26.60
Ce^{+4}	33.0	32.52	24.71	24.26	23.60	23.16

Table 23 (Contd)

Angus' TABLE 11 (contd)

Ion	L. P.		J. C. S.		W. R. A	
	Uncorrected	corrected	uncorrected	corrected	uncorrected	corrected
Platinum type						
Au^{+1}	65.0	64.05	58.62	57.55	58.38	37.32
Hg^{+2}	55.0	54.2	47.8	46.90	47.57	46.70
Tl^{+3}	48.0	47.3	39.86	39.13~~4~~	39.68	38.96
Pb^{+4}	42.0	41.40	33.97	33.35	33.81	33.20

Table 23 (contd)

Angus' TABLE 111

Ion	G & F		Ion	G. & F.	
	uncorrected	corrected		uncorrected	corrected
C^{+4}	0.15	0.148	Br^{+1}	35.81	35.30
C^{+2}	4.83	4.76	Br^{-1}	54.00	53.21~~4~~
C^{o}	10.32	10.17	I^{+7}	17.00	16.75
C^{-2}	21.00	20.69~~4~~	I^{+5}	27.7	27.3
C^{-4}	50.0	49.272	I^{+3}	40.53	39.94
N^{+5}	0. 11	0.108	I^{+1}	57.3	56.44
N^{+3}	3.04	2.99~~8~~	I^{-1}	80.00	78.80
N^{+1}	6.2	6.10			
N^{-1}	11.46	11.29			
N^{-3}	22.0	21.68			
O^{+6}	0.08	0.079	Cl^{o}	22.85	22.51~~7~~
O^{+4}	2.09	2.06	O^{-1}	9.6	9.46
O^{+2}	4.09	4.031			
O^{o}	7.19	7.085			
O^{-2}	12.60	12.42~~7~~			
S+6	1.40	1.38			

Table 23 (contd)

Angus' TABLE 111 (contd)

Ion	G & F.	
	uncorrected	corrected
S^{-2}	40	39.42
F^{+7}	0.063	0.062
F^{+5}	1.52	1.498
F^{+3}	2.95	2.907
F^{+1}	4.98	4.908
F^{-1}	8.10	7.982
Cl^{+7}	1.20	1.183
Cl^{+5}	5.71	5.63
Cl^{+3}	10.92	10.76
Cl^{+1}	18.2	17.93
Cl^{-1}	29.0	28.58
Br^{+7}	6.00	5.913
Br^{+5}	13.74	13.54
Br^{+3}	23.09	22.75

Theoretical Calculation of the diamagnetic susceptibility of the simple ions

From the Langevin Equation :-

$$-10^6 \chi_{\text{ion}} = \frac{e^2 N}{6mc^2} \, a_0^2 \cdot \sum_n \bar{r}^2$$

Thus $$-10^6 \chi_A = 0.7923 \, . 10^{-6} \sum \frac{(n')^2 \, (n' + \frac{1}{2})(n' + 1)}{(Z - S)^2}$$

Where n' ~~is~~ the principal quantum number allows for screening of nuclear charge, Z is the actual nuclear charge.of the atom or ion and S is the screening constant giving the fraction of the nuclear charge screened by the core electrons.

For any shell $$\sum_n \bar{r}^2 = \frac{(n')^2 \, (n' + \frac{1}{2}) \, (n' + 1)}{(Z - S)^2}$$

Slater gives rules for determining n'. For any given value of n, the value of n' - the effective quantum number - is as follows :-

n = 1, 2, 3, 4, 5, 6

n' = 1, 2, 3, 3.7, 4.0, 4.2.

e.g. Potassium atom.

$1S^2$, $2S^2 p^6$, $3S^2 p^6$, $4S^1$

n = 1, 2, 3, ~~*~~ 4

n' = 1, 2, 3, 3.7

Rules for determining S - the screening constant

The electrons are divided into groups with s and p electrons of the same n taken together, but with d and f electrons taken separately. When we come to d electrons the s and p electrons of the same principal quantum number count as the groups below. For each group of electrons, the screening constants are calculated by the following method:-

The individual screening constant for all 1S electrons is 0.30

For S and p electrons for the group immediately below, it is 0.85

For all other lower groups the screening constant for each electron is 1.00.

For d and f electrons and all lower groups it is 1.00

So the total screening constant for each closed shell up to $5 s^2 p 6$ is shown as follows :-

Orbitals	Screening constant S
$1s^2$	0.30
$2s^2p^6$	(2 . 0.85) + (7. 0.35) = 4.15
$3s^2p^6$	(2 . 1.0) + (8 . 0.85) + (7 . 0.35) = 11.25
$3d^{10}$	(2 . 1.0) + (8 . 1.0) + (8 . 1.0) + (9 . 0.35) = 21.15
$4s^2p^6$	(2 . 1.0) + (8 . 1.0) + (18 . 0.85) + (7 . 0.35) = 27.75
$4d^{10}$	(2 . 1.0) + (8 . 1.0) + (8 . 1.0) + (10 . 1.0) + (9. 0.35) = 39.15
$5s^2p^6$	(2 . 1.0) + (8 . 1.0) + (18 . 1.0) + (18 . 0.85) + (7 . 0.35) = 45.75

Calculation of the ionic Susceptibility of Cl'

$Z = 17$ i.e. $1S^2;\ 2S^2\ p^6;\ 3S^2\ p^6$ (for Chloride ion)

$Z - S$ for $1S^2$ orbital $= 17 - 0.30 = 16.70$

" " " $2S^2\ p^6$ " $= 17 - 4.15 = 12.85$

" " " $3S^2\ p^6$ " $= 17 - 11.25 = 5.75$

Charge distribution (r^{-2}) for $1S^2 = 2\ \left(\frac{1^2 \cdot 1\frac{1}{2} \cdot 2}{(16.7)^2}\right) = 0.02151$

" " " " $2S^2p^6$

$$= 8 \left\{\frac{2^2 \cdot 2.5 \cdot 3}{(12.85)^2}\right\} = 1.45346$$

" " " " $3S^2p^6$

$$= 8\ \frac{3^2 \cdot 3.5 \cdot 4}{(5.75)^2} = 30.4870$$

So $\sum r^{-2}$ for Cl' $= 31.96197$

$-10^6\ \chi_A = 0.7923 \cdot \sum r^{-2}$

$\therefore\ -10^6\ \chi_{Cl'} = 0.7923\ .\ 31.96197$

$= 25.32$ c. g. s. units

$-\ 10^6 \chi_A$ for Bromide Ion

$Z = 35$ i.e. $1S^2;\ 2S^2\ p^6;\ 3S^2\ p^6;\ d^{10};\ 4S^2\ p^6$ (for Br^-)

The screening constant and $\sum r^{-2}$ are calculated as already shown in the case of chloride ion.

$$(\overline{r}^{-2}) \text{ for } 1S^2 = 2\,\frac{(1^2 \cdot 3/2 \cdot 2)}{(34.7)^2} = 0.0498$$

$$'' \quad '' \quad 2S^2\,p^6 = 8\left\{\frac{(2^2 \cdot 5/2 \cdot 3)}{(30.85)^2}\right\} = 0.2021$$

$$'' \quad '' \quad 3S^2p^6 = 8\left\{\frac{3^2 \cdot 7/2 \cdot 4}{(23.75)^2}\right\} = 1.7870$$

$$'' \quad '' \quad 3d^{10} = 10\left\{\frac{3^2 \cdot 7/2 \cdot 4}{(13.85)^2}\right\} = 6.569$$

$$'' \quad '' \quad 4S^2p^6 = 8\left\{\frac{(3.7)^2 \cdot (4.2) \cdot (4.7)}{(7.25)^2}\right\} = 41.13$$

$$\text{So} \quad \sum r^{-2} = 49.73$$

$$-10^6\,\chi\,Br^- = 0.7923 \times 49.73 = \underline{\underline{39.401}} \text{ c.g.s. units}$$

<u>$-10^6\,\chi_A$ for Iodide ion</u>

$Z = 53$, i.e. $1S^2$, $2S^2p^6$, $3S^2p^6$, d^{10}, $4S^2p^6$, d^{10}, $5S^2p^6$ (for I^-)

$$\overline{r}^{-2} \text{ for } 1S^2 = 2\,\frac{(1^2 \cdot 3/2 \cdot 2)}{(52.7)^2} = 0.000216$$

$$'' \quad '' \quad 2S^2p^6 = 8\left\{\frac{2^2 \cdot 5/2 \cdot 3}{(48.85)^2}\right\} = 0.1006$$

$$'' \quad '' \quad 3S^2p^6 = 8\left\{\frac{3^2 \cdot 7/2 \cdot 4}{(41.75)^2}\right\} = 0.5783$$

$$\overline{r}^{-2} \text{ for } 3d^{10} = 10 \left\{ \frac{3 \cdot 7/2 \cdot 4}{(31.85)^2} \right\} = 1.2421$$

$$\text{'' '' } 4d^{10} = 10 \left\{ \frac{(3.7)^2 \cdot (4.2) \cdot (4.7)}{(13.85)^2} \right\} = 14.088$$

$$\text{'' '' } 5S^2p^6 = 8 \left\{ \frac{(4.0)^2 \cdot (4.5) \cdot (5.0)}{(7.25)^2} \right\} = 54.79$$

So, total $\sum r^{-2} = \underline{74.20}$

$$-10^6 \chi A = 0.7923 \sum \overline{r}^{-2}$$

$$-10^6 \chi I' = 0.7923 \times 74.2 = \underline{\underline{58.79}} \text{ c.g.s. units.}$$

$\underline{-10^6 \chi \text{ A (Fluoride ion - } F^-)}$

$Z = 9$ i.e. $1S^2$; $2S^2p^6$ (F^-)

$Z - S$ for $1S^2 = 9.-.0.3 = 8.7$

$Z - S$ for $2S^2p^6 = 9 - 4.15 = 4.85$

<u>Charge distribution</u> $\overline{r}^{2}$

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

$$\text{'' for } 1S^2 = 2 \; \frac{(1^2 \cdot 3/2 \cdot 2)}{(8.7)^2} = 0.0792$$

$$\text{'' '' } 2S^2p^6 = 8 \left\{ \frac{(2)^2 \cdot 5/2 \cdot 3}{(4.85)^2} \right\} = 10.203$$

So, total $\sum \overline{r}^{-2} = 10.282$

$$-10^{6}\,\chi\,F^{-} = 0.7923 \times 10.282$$

$$= \underline{8.15} \text{ c.g.s units}$$

$\underline{-10^{6}\,\chi\,Ag+}$

$Z = 47$ i.e. $1S^{2}$; $2S^{2}p^{6}$; $3S^{2}p^{6}d^{10}$; $4S^{2}p^{6}d^{10}$ (Ag^{+})

$(Z - S)$ is calculated as before for each orbital

$$\overline{r}^{-2} \text{ for } 1S^{2} = 2\left(\frac{1^{2}\cdot 3/2\cdot 2}{(46.7)^{2}}\right) = 0.00275$$

$$\text{" " } 2S^{2}p^{6} = 8\left\{\frac{2^{2}\cdot 5/2\cdot 3}{(42.85)^{2}}\right\} = 0.13071$$

$$\text{" " } 3S^{2}p^{6} = 8\left\{\frac{3^{2}\cdot 7/2\cdot 4}{(28.75)^{2}}\right\} = 1.2195$$

$$\text{" " } 3d^{10} = 10\left\{\frac{3^{2}\cdot 7/2\cdot 4}{(25.85)^{2}}\right\} = 1.8856$$

$$\text{" " } 4S^{2}p^{6} = 8\left\{\frac{(3.7)^{2}\cdot(4.2)\cdot(4.7)}{(19.25)^{2}}\right\} = 5.8342$$

$$\text{" " } 4d^{10} = 10\left\{\frac{(3.7)^{2}\cdot(4.2)\cdot(4.7)}{(7.85)^{2}}\right\} = 43.8542$$

$$\text{Total} \sum \overline{r}^{-2} = 52.92693$$

$$-10^{6}\,\chi_{A} = 0.7923 \cdot \sum \overline{r}^{-2}$$

$$-10^{6}\,\chi\,Ag^{+} = 0.7923 \times 52.92693$$

$$= 42.93 \text{ c.g.s units}$$

=====

(b) Theoretical calculation of the Ionic susceptibility of oxyanions using Pascal's method.

The Bond Depression Effect. If we assume that the ionic susceptibilities of the halides (X') and that of the additional oxygens in the haloxy-anions can be treated additively, a value for the ionic susceptibility of the XO_3' and XO_4' ions based on experimental results may be calculated. Pascal has given atomic susceptibility constants for the simple elements mainly determined in diamagnetic organic compounds. His value for oxygen singly linked as in O - H and O - Cl is 4.61 c.g.s. units of susceptibility and this value can be used for the oxygen in the present calculations. The ionic susceptibility constants for the halides used were those recommended by Trew and Husain, these being based upon a number of experimental measurements. Pascal's constant for the halogen atoms was not used as it is a value for the halogen in covalent compounds being derived from organic halides and so does not allow for the additional negative charge.

For the perchlorate ion, the susceptibility of four oxygen atoms is added to that of the chloride ion and for the chlorate ion similarly the susceptibility of three oxygen atoms is required

$$Cl' + 4O \longrightarrow ClO_4'$$

$$Cl' + 3O \longrightarrow ClO_3'$$

The values obtained in this manner for the XO_3' and XO_4' ions are as follows.

X'	XO_3' or XO_4'	$-10^6 \chi$ ion
24.3	ClO_3'	38.13
34.8	BrO_3'	48.63
50.6	IO_3'	64.43
	ClO_4'	42.74

These calculated values are compared with the present experimental ionic susceptibilities and it can be seen that they are considerably higher than the experimental values. The depression of the susceptibility per bond can be calculated. If these differences are regarded as bond depressions i.e. a susceptibility lowering on formation of the X - O bond, the total depression can be divided by the number of bonds in order to find the depression per bond as shown in the following table.

Ion	Experimental ionic susceptibility	Calculated ionic susceptibility	Depression per Bond.
ClO_3'	26.82	38.13	3.77
BrO_3'	39.33	48.63	3.10
IO_3'	44. 8	64.43	6.50
ClO_4'	32.5	42.7	3.40

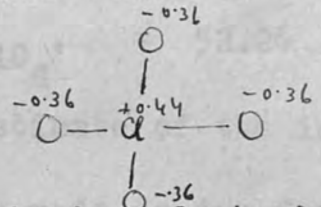
The calculated values using this method are all higher than the experimental value approximately by the same amount in the case of chlorate, bromate, and perchlorate. A much higher value for the depression **per bond** occurs in the case of the iodate. It appears that the susceptibility shows the effect of the bond shortening on formation of the XO_3' or XO_4' ion which has not been included in the theoretical ~~above~~ calculation. The ionic susceptibilities here are of course based on the experimental measurements.

(c) Theoretical Calculations of the ionic susceptibilities of the haloxy-ions by Pauling's method.

A further calculation of the theoretical susceptibility of the various haloxy-ions XO_3' and XO_4' can be made using Pauling's theoretical ionic susceptibilities and allowing for the electro-negativity difference between the atoms. This gives an ionic susceptibility which is not corrected for bond depression. It is illustrated by considering the perchlorate ion.

For the perchlorate ion ClO_4', it can be assumed according to Pauling that the negative charge (- 1) is distributed over the surface of the ion and thus each oxygen atom is assigned 0.25 of this charge in addition to the allocation from the electro-negativity difference between chlorine and oxygen. The most recent available set of electro negativity values(71) gives O = 3.5, Cl = 3.0

Therefore the electro-negativity difference is 0.5 units and from the graph given by Pauling (71) this gives rise to a percentage ionic character of 11 %. The single Cl-O bond may be represented as $\overset{+0.11}{-\mathrm{Cl}}\!-\!\overset{-0.36}{\mathrm{O}}$ adding in the quarter charge from the negative charge of the ion. Adding up for all the bonds the total charge of the perchlorate ion is as follows.



The values of the ionic and atomic susceptibility constants for the atoms and ions, Cl^{o}, O^{o}, Cl^{+1}, O^{-2} have been calculated by the Pauling$^{(67)}$ theoretical method for determining ionic susceptibilities from the Langevin Equation.

The corrected values shown on pages 177 - 185 (section (a)) were used in the present calculation.

i.e. $-10^{6}\chi_{Cl^{+1}} = 17.925$

$-10^{6}\chi_{Cl^{o}} = 22.517$

$-10^{6}\chi_{O^{o}} = 7.085$

$-10^{6}\chi_{O^{-1}} = 9.46$

Therefore allowing for the charge distribution as shown in the formula

$$-10^6 \chi_{ClO_4'} = \left[(0.44 \,.\, \chi_{Cl^{+1}}) + (0.56 \,.\, \chi_{Cl^{0}})\right] + 4\left[(0.36 \,.\, \chi_{O^{-1}}) + (0.64 \,.\, \chi_{O^{0}})\right]$$

$$= \left[(0.44 \,.\, 17.925) + (0.56 \,.\, 22.517)\right] + 4\left[(0.36 \,.\, 9.46) + (0.64 \,.\, 7.085)\right]$$

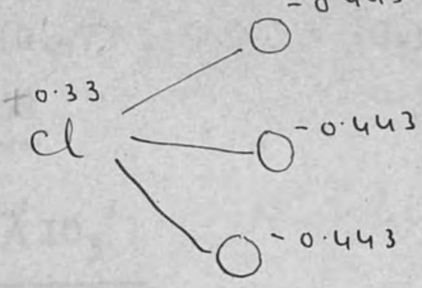
$$-10^6 \chi_{ClO_4'} = 52.26$$

This is an over estimate of the ionic susceptibility as no allowance is made so far for the change in susceptibility with formation of bonds. Similar calculations follow for the XO_3' ions. ClO_3', BrO_3' and IO_3'

<u>The chlorate ion</u> ($-10^6 \chi_{ClO_3'}$)

The electro-negativity difference between chlorine and oxygen is 0.5; and so the percentage ionic character for the ion is 11 %, The negative charge (-1) is distributed over the three oxygen atoms.

Total charge on the chlorate ion -



$$\text{Therefore, } -10^6 \chi ClO_3' = \left[(0.33\chi Cl^{+1}) + (0.67\chi Cl^{0})\right] + 3\left[(0.443\chi O^{-1}) + (0.557\chi O^{0})\right]$$

$$= \left[(0.33 \,.\, 7.925) + (0.67 \,.\, 22.517)\right] + 3\left[(0.443 \,.\, 9.46) + (0.557 \,.\, 7.085)\right]$$

$$\therefore \; -10^6 \chi ClO_3' = \underline{\underline{45.41}} \text{ (uncorrected)}$$

The bromate ion $(-10^6 \chi BrO'_3)$

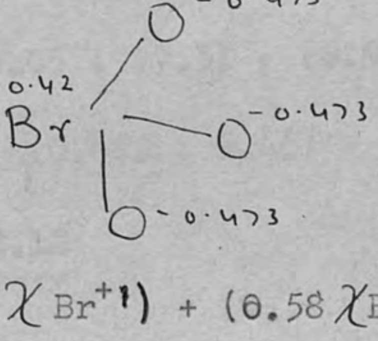
The electro-negativity difference between bromine and oxygen

is 0.70 and so the percentage ionic character for the bromate ion is 14% (read from ~~the~~ Pauling's graph).

Each Br-O has the charge distribution -

$$\overset{\delta^+ 0.14}{Br} — \overset{\delta^- 0.14}{O}$$

Total charge



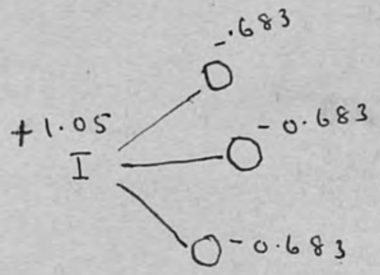
$$-10^6 \chi BrO3' = \left[(0.42\chi Br^{+1}) + (0.58\chi Br^{0})\right] + 3\left[(0.473\chi O^{-1}) + (0.527\chi O^{0})\right]$$

$$-10^6 \chi \mathrm{BrO_3}' = (0.42 \,.\, 35.29) + (0.58 \,.\, 43.5) + 3\,(0.473 \,.\, 946\,) + (0.527 \,.\, 7.085) = \underline{\underline{64.68}}$$

The iodate ion ($-10^6 \chi \mathrm{IO_3}'$)

The electronega~~t~~tivity difference between iodine and oxygen is 1.0 and so the percentage ionic character for the iodate ion read from ~~the~~ Pauling's graph is 35%. So each I - O has the charge $\mathrm{I}^{\delta^+ 0.35}$ —— $\mathrm{O}^{\delta^- 0.35}$

Total charge



$$-10^6 \chi \mathrm{IO_3}' = \left[(0.\;\;0.5\, \chi \mathrm{I}^{+2}) + (0.95\, \chi \mathrm{I}^{+1})\right] + 3\left[(0.683\, \chi \mathrm{O}^{-1}) + (0.317\, \chi \mathrm{O}^{0})\right]$$

$$-10^6 \chi \mathrm{I}^{+2} = 47.5 \;;\quad -10^6 \chi \mathrm{I}^{+1} = 56.44$$

$$\therefore\; 10^6 \chi \mathrm{IO_3}' = \left[(0.05 \,.\, 47.5) + (0.95 \,.\, 56.44)\right] + 3\left[(0.683 \,.\, 9.46) + (0.317 \,.\, 7.085)\right] = \underline{\underline{82.12}}$$

The calculated uncorrected ionic susceptibilities for the haloxy anions are summarised below :-

ION	$-10^6 \chi_A$
ClO_3'	45.41
ClO_4'	52.26
BrO_3'	64.68
IO_3'	82.12

These values represent the calculated susceptibility for the anions without any correction for the bond depression which occurs in these ions.

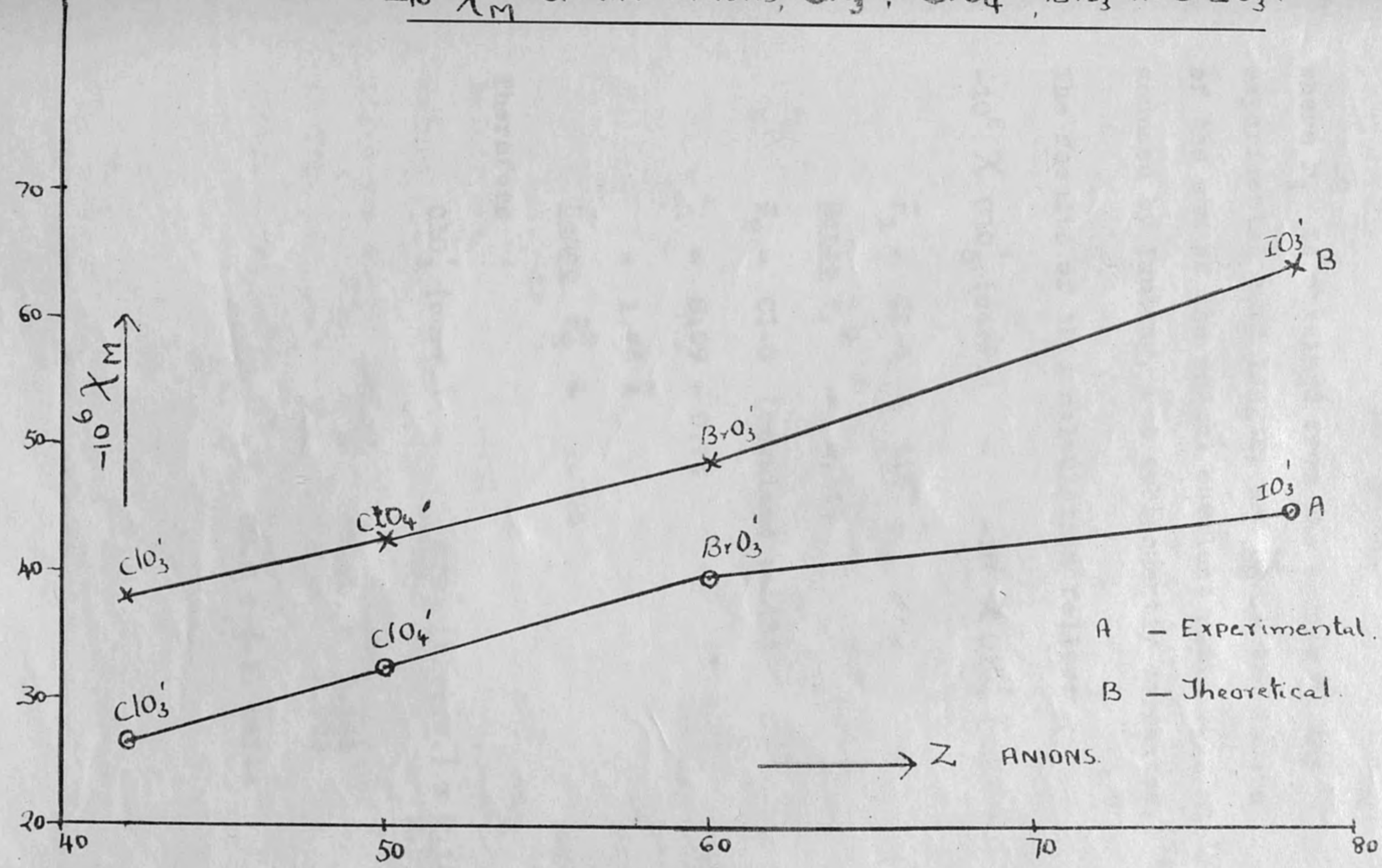
The effect on the susceptibility of diamagnetic compounds of the bond depression was originally pointed out by Gray and Cruckshank who showed that for certain simple organic compounds a bond depression effect could be calculated by reducing Pauling's theoretical atomic constants (which are corrected and used in the current paper) by a bond depression factor. This was calculated from the difference between ~~the~~ Pauling's theoretical values and Pascal's well established experimental values for some of the common light carbon containing compounds such as CH_4. Later workers found that the Gray and Cruckshank bond depression factors were not entirely satisfactory for more complex compounds. Bond depression factors are not available for the bonds used in this paper. An attempt to calculate a bond depression factor is therefore made as follows -

The Langevin Equation for the theoretical diamagnetic susceptibility of an ion is $-10^6 \chi_A = 0.7923 \sum \overline{r}^{-2}$ so the diamagnetic susceptibility is a property of the charge distribution of the ion. The expression for the theoretical susceptibility contains the mean square radius in the term $\sum \overline{r}^{-2}$. This arises from the fact that in calculating the susceptibility the charge is averaged over a plane perpendicular to the magnetic field direction since the susceptibility is a polarization induced by the external magnetic field H. Hence it seemed likely that the square of the experimental bond length for the appropriate bonds such as Cl-O, Br-O, and I-O in chlorates, perchlorates, bromates and iodates could be used to calculate a bond depression factor. The sum of the radii of the unbonded atoms is given by the covalent radius of the atoms.(71) The experimental bond lengths are available from crystal structure. It seems likely that a corrected susceptibility will follow from -

$$-10^6 \chi_{\text{corrected}} = -10^6 \chi . \overline{r}_1^{\,2} / \overline{r}_2^{\,2}$$

EXPERIMENTAL AND THEORETICAL FIGURE 24

$-10^6 \chi_M$ OF THE ANIONS, ClO_3', ClO_4', BrO_3' AND IO_3'.



where $\bar{r}_1^{2}$ is obtained from the square of the experimental bond length, and $\bar{r}_2^{2}$ is the square of the sum of the normal covalent radii originally deduced by Pauling, but subsequently corrected.(71)

The results of this calculation follow:

$$-10^6 \chi\ ClO_3' \text{ (corr.)} = -10^6 \chi\ ClO_3' \text{ (uncorr.)} \times \bar{r}_1^{2}/\bar{r}_2^{2}$$

$$\bar{r}_1 = \text{Cl-O} = 1.47 \text{ Å}$$

$$\underline{\text{Hence}}\ \bar{r}_1^{2} = 2.161$$

$$\bar{r}_2 = \text{Cl-O (covalent radii)}$$

$$= 0.99 + 0.74$$

$$= 1.73 \text{ Å}$$

$$\underline{\text{Hence}}\ \bar{r}_2^{2} = 2.993$$

Therefore

$$ClO_3' \text{ (corr.)} = ClO_3' \text{ (uncorr.)} \times \frac{2.161}{2.993}$$

$$= 45.41 \times \frac{2.161}{2.993}$$

$$= 32.8 \text{ c.g.s. units}$$

Similarly,

$$-10^6 \chi_{ClO_4'}(\text{corr.}) = 52.26 \times \frac{2.074}{2.993} \quad (\bar{r}_1 = 1.44 \text{ Å})$$

$$= 36.22 \text{ c.g.s. units}$$

$$-10^6 \chi_{BrO_3'}(\text{corr.}) = 64.68 \times \frac{2.8224}{3.5344}$$

$$= 51.65 \text{ c.g.s. units}$$

$$-10^6 \chi_{IO_3'}(\text{corr.}) = -10^6 \chi_{IO_3'}(\text{uncorr.}) \times \frac{3.312}{4.285}$$

(where $\bar{r}_1 = 1.82$ (I-O)
and $\bar{r}_2 = 2.07$)

$$= 82.12 \times \frac{3.312}{4.285}$$

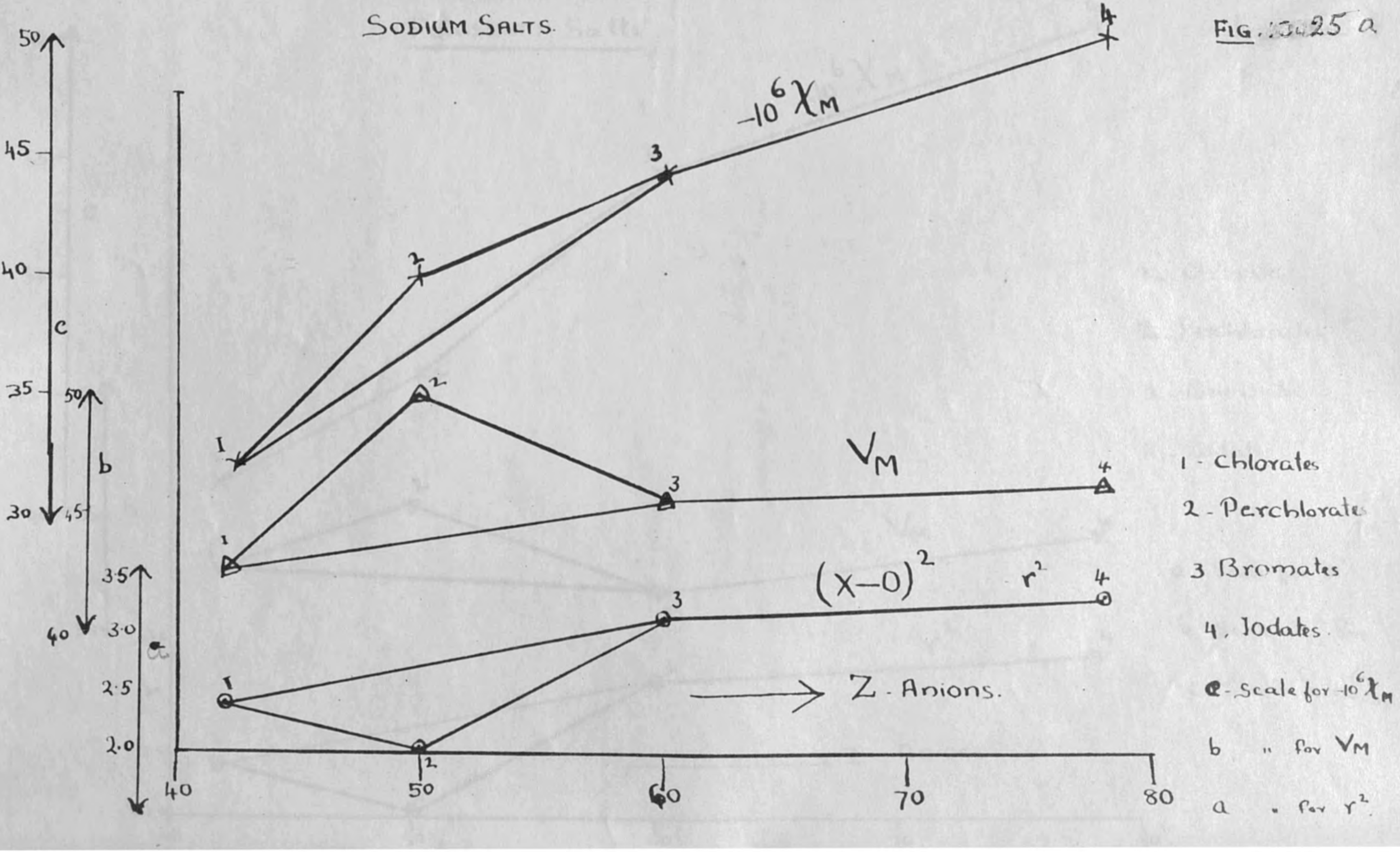
$$= 63{,}48 \text{ c.g.s. units}$$

These corrected ionic susceptibilities of the haloxy anions, together with the experimental values (p. 156), were plotted against the effective atomic number of the anions as shown in Fig. 24. In this figure, A is the experimental curve and B is the theoretical curve.

COMPARISON OF $-10^6\chi_M$ (OXYHALIDES) WITH V_M and r^2.

SODIUM SALTS.

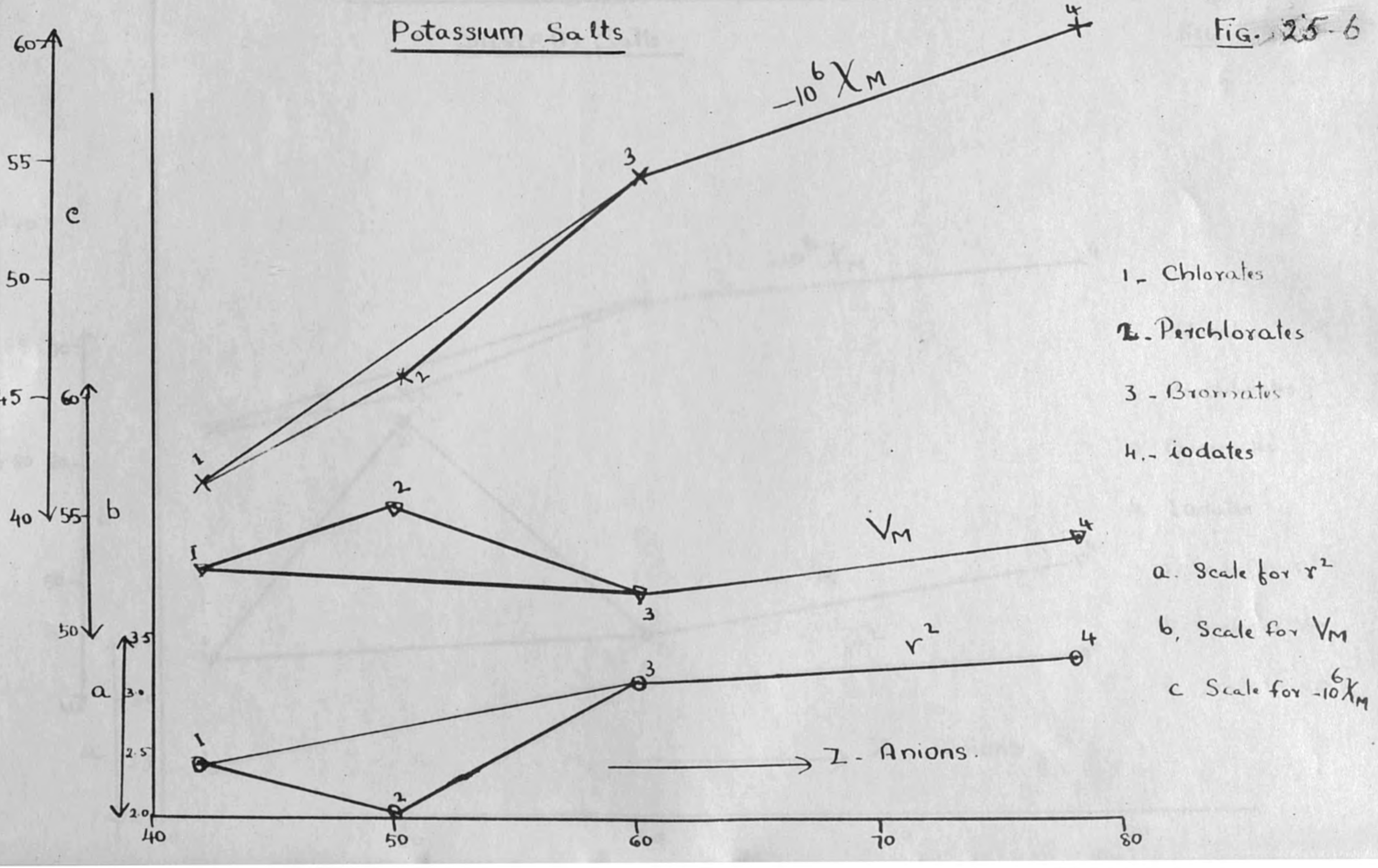
FIG. 25 a



COMPARISON OF $-10^6\chi_M$ (Oxyhalides) WITH V_M and r^2.

Potassium Salts

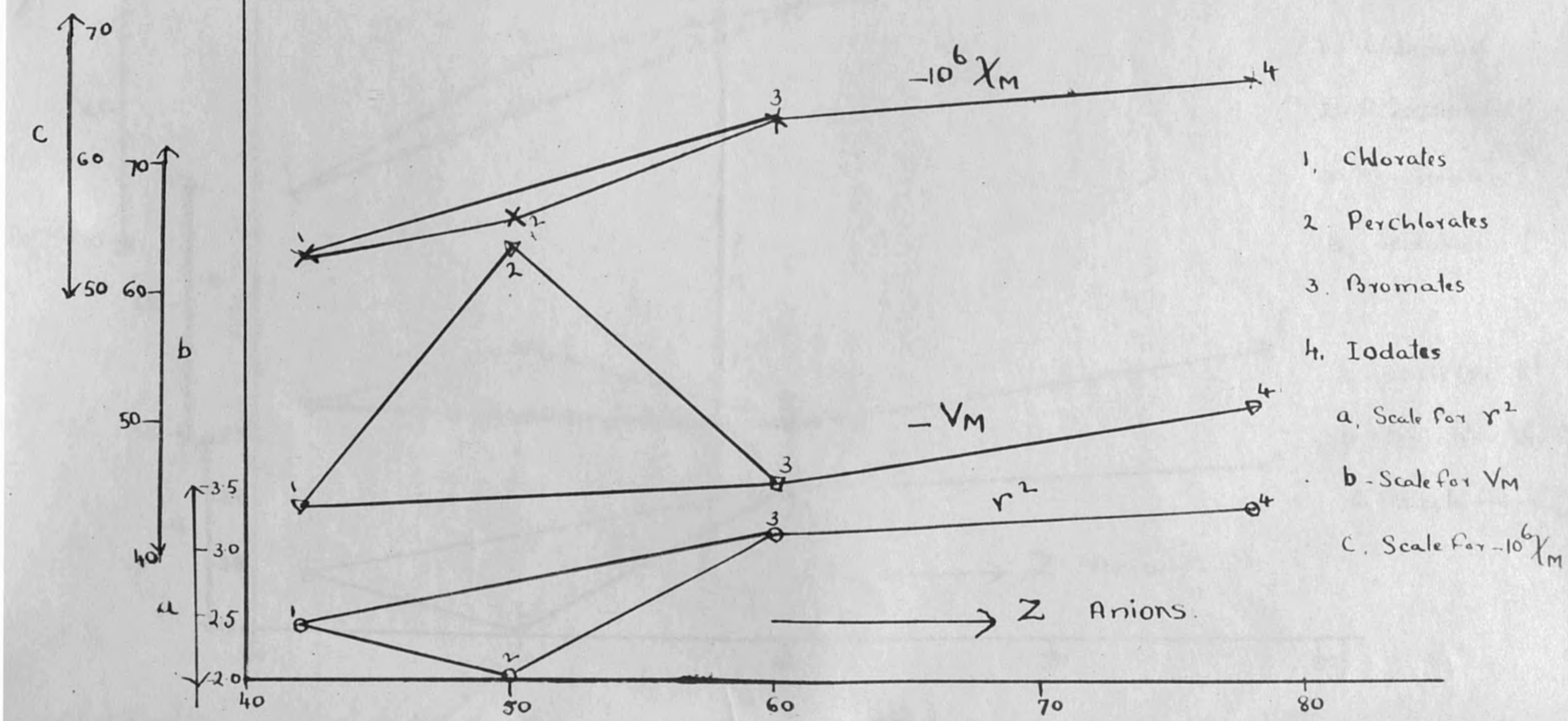
FIG. 25.6



COMPARISON OF $-10^6\chi_M$ (oxyhalides) WITH V_M and r^2

SILVER (I) Salts.

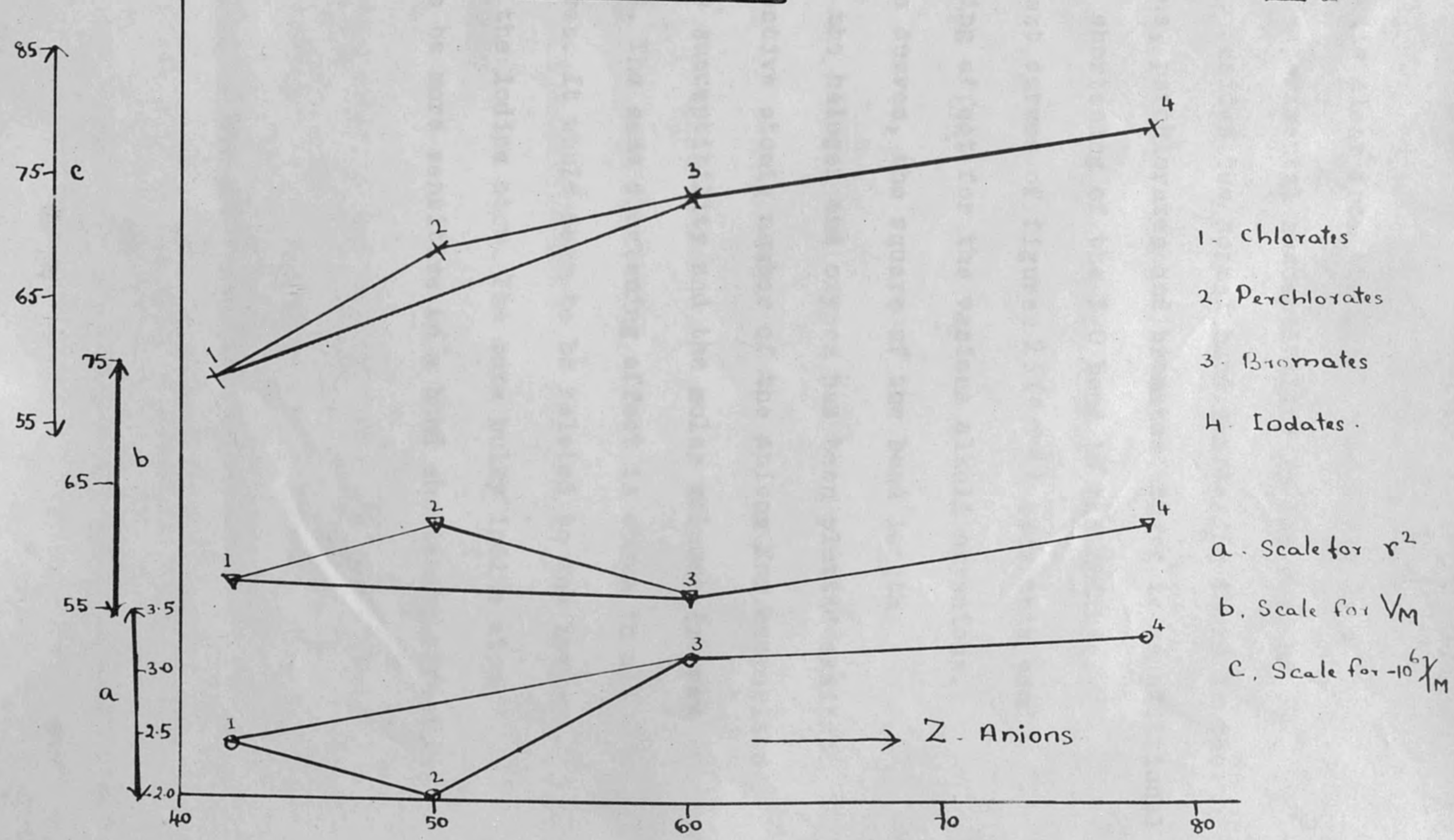
FIG. 25 C



COMPARISON OF $-10^6\chi_M$ (OXYHALIDES) WITH V_M and r^2

THALLIUM (1) Salts.

FIG. 25d



It is quite clear from the graph that there is a lowered experimental susceptibility in the case of iodates. Besides the normal bond shortening found in the chlorates, perchlorates and bromates, there is an additional further shortening of the I-O bond in the iodates. The lowest curves of figures 25(a → d) show this bond shortening effect for the various alkali oxyanions. In these curves, the square of the bond length between the halogen and oxygen has been plotted against the effective atomic number of the anions for comparison with the susceptibility and the molar volumes (upper curves). The same shortening effect is shown in all the curves. It would seem to be related to the larger size of the iodine atom. The more bulky iodine atom seems to be more sensitive to a bond shortening effect.

PART VI

Some Infra-read Spectra of the salts of the haloxy-anions

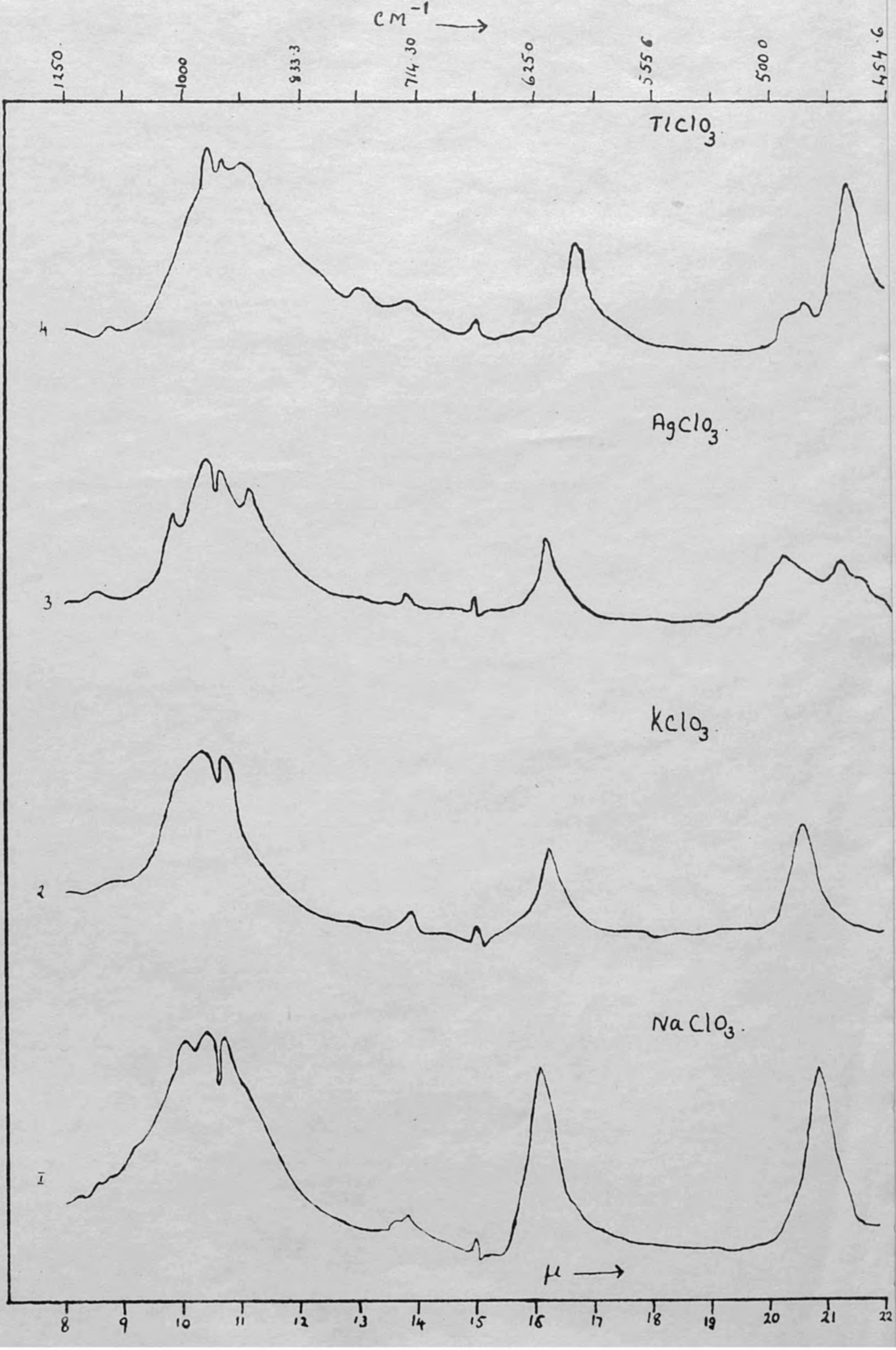
The spectra were recorded by means of a Grubb Parson's Infra-red spectrometer. The recording was made between the regions 400-2,000 cm $^{-1}$. (5-25μ). The samples were ground to a fine powder to minimize the scattering of light and were examined as nujol mulls between potassium bromide plates. A potassium bromide prism was used in this region. The experiment was repeated three times for each salt. Charts of the characteristic frequencies of the haloxy-anions are given in diagrams III, IV, V and VI Tables 24 and 25 summarise the principal maxima of the absorption bands.

Infra red spectra of the perchlorates.

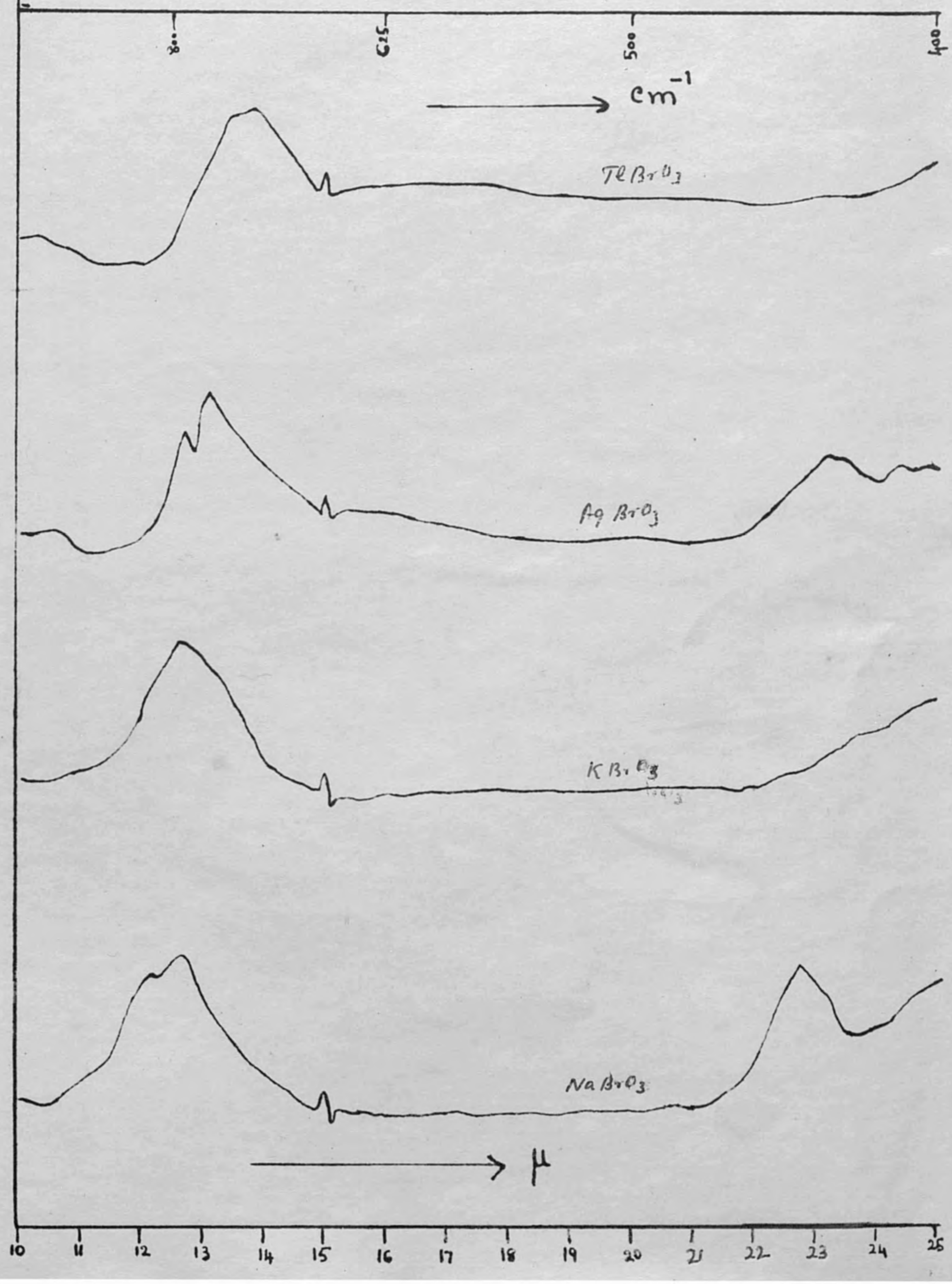
The infra red spectra of a number of ionic perchlorates are listed by Miller and Wilkins (14). The Raman spectrum of the perchlorate ion has been studied by several investigators. (72) Hathaway and Underhill (73) have investigated the infra red spectra of some transition metal perchlorates. The work of these investigators has shown that, apart from some very minor differences in the

Infrared Spectra OF The Chlorates.

Diagram III.



Infrared Spectra of the Bromates. Diagram. IV



Infrared Spectra of The Iodates

Diagram. V.

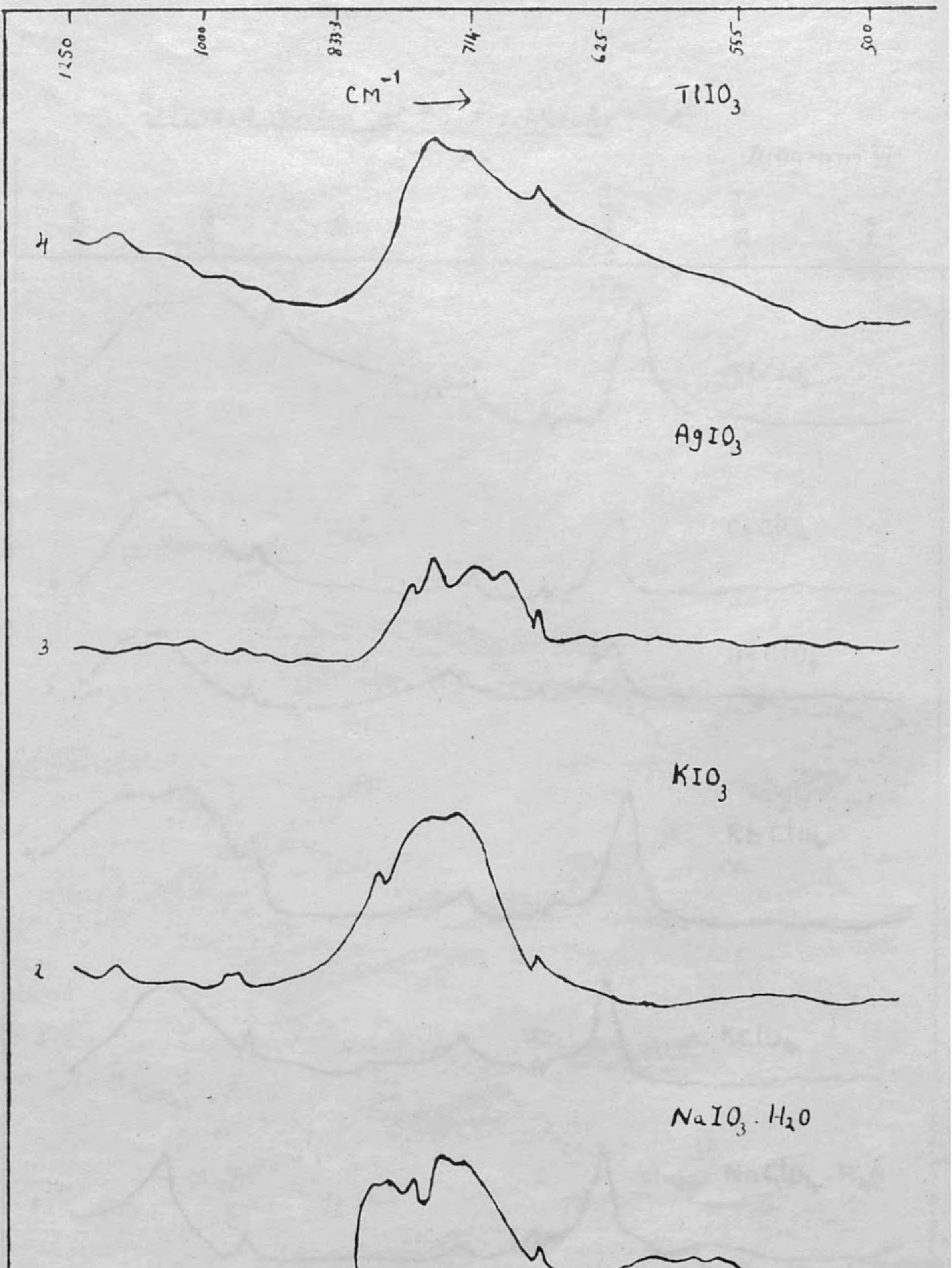


TABLE 24

The infra-red frequencies of the perchlorates

Salt	ν_1 mode symmetric stretching		ν_2 mode symmetric bending		ν_3 mode symetric stretching		ν_4 mode asymmetric bending	
	In microns	Cm^{-1}	microns	Cm^{-1}	microns	Cm^{-1}	microns	Cm^{-1}
$LiClO_4 \cdot 3H_2O$	10.65(spur)	939.0	-	-	9.3 (s+b)	1075.0	16.5 (s+b)	625.0
$NaClO_4$ H_2O	10.65 "	939.0	-	-	9.4 (s&b)	1064.0	16.0 (s+sp)	625.0
$KClO_4$	10.65 "	939.0	-	-	9.3 (s&b)	1075.0	16.03(s+sp)	624.0
$RbClO_4$	10.7 "	934.6	-	-	9.7 (s&vb)	1031.0	16.2(s)	617.3
Cs ClO_4	10.7 "	934.6	-	-	9.4 (s&b)	1064.0	16.05(s+sp)	623.2
AgCl O_4	10.65 "	939.0	-	-	8.9 - 9.3 (s&b)	1124 - 1075	16.05(s)	623.2
Tl ClO_4	10.85 "	922.0	-	-	8.7 - 10.0 (s&b)	1149 - 1000	16.4(s+sp)	609.8

S = strong b = broad v.b = very broad sp = sharp

Infrared Spectra of The perchlorates.

Diagram VI.

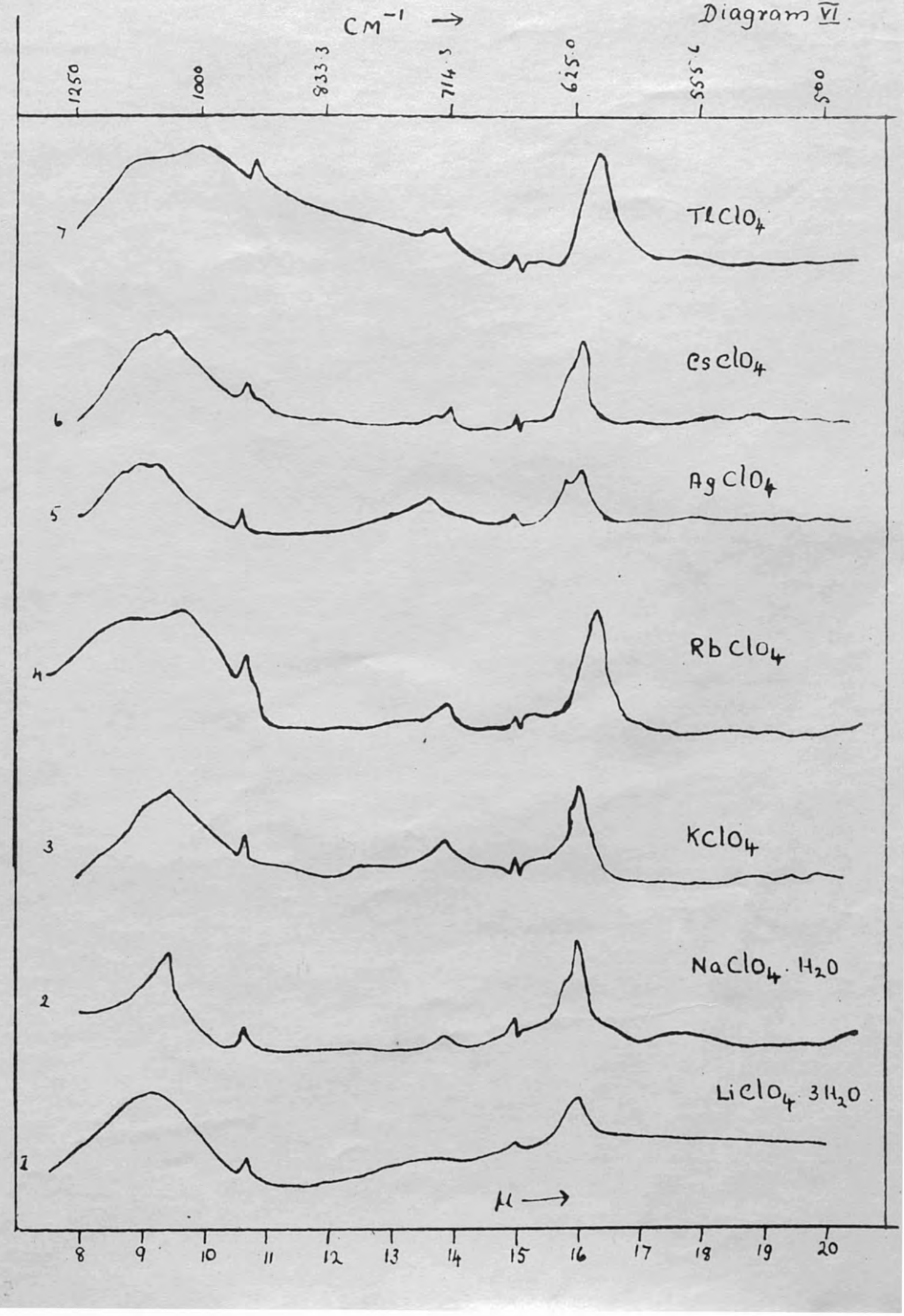


TABLE 25

The infrared frequencies of the chlorates, bromates and iodates

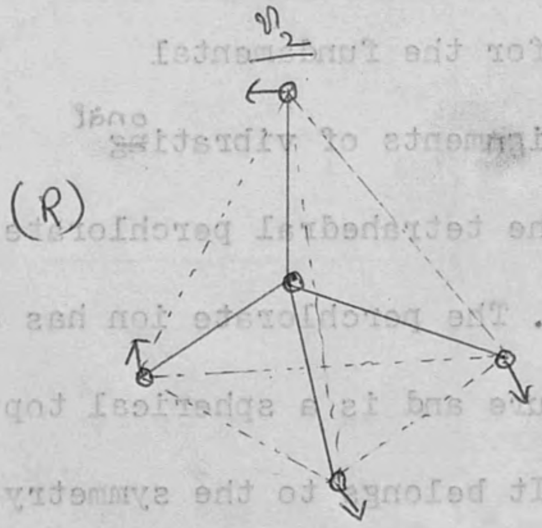
Salt	ν_1 Sym. Str. mode		ν_3 asym. Str. mode		ν_2 Sym. bend. mode		ν_4 asym. bend. mode	
	microns	Cm^{-1}	microns	Cm^{-1}	microns	Cm^{-1}	microns	Cm^{-1}
Chlorates								
(a) $NaClO_3$	-	-	10.4 (s & b)	961.5	16.1 (s)	621	20.8 (s)	480
							10.1 (sh)	990($2\nu_4$)
$KClO_3$	-	-	10.4 (s & b)	961.5	16.1 (s)	621	20.55 (s)	485
$AgClO_3$	11.15 (m & b)	893	10.4 (s & b)	961.5	16.2 (s)	617.3	20.2 (m)	495
$TlClO_3$	11.0 (s & b)	909	10.4 (s & b)	961.5	16.7 (m)	599	20.6 (m)	485

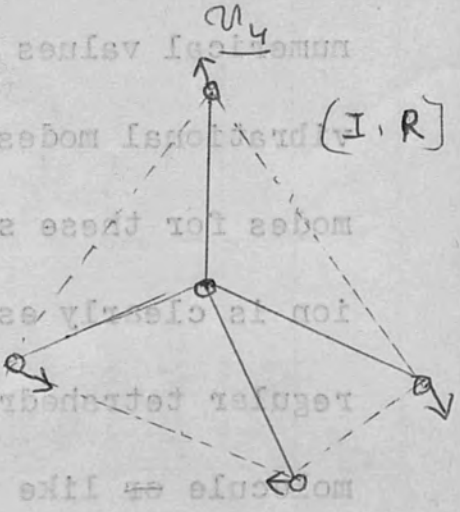
s = strong, sh = shoulder, m = medium, b = broad

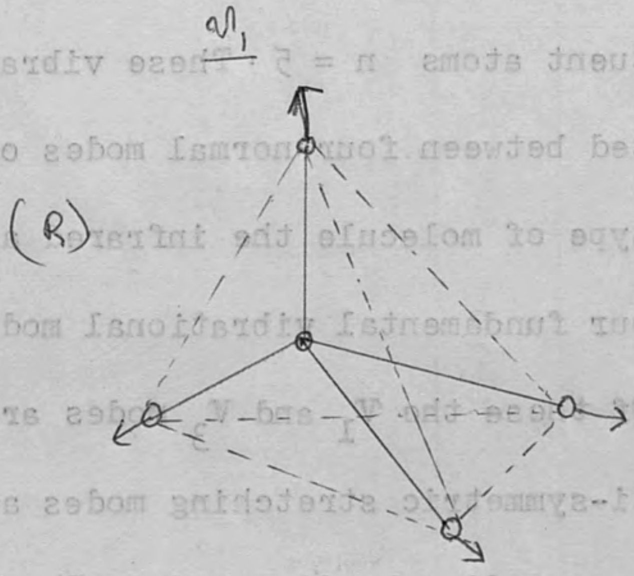
TABLE 25 Contd

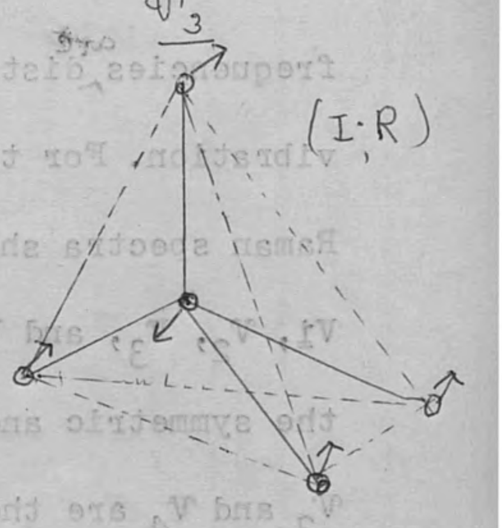
	Bromates	ν_1 and ν_3		ν_2		ν_4
		microns	Cm^{-1}	microns	Cm^{-1}	
	$NaBrO_3$	12.7 - 12.24 (s & b)	787 - 816	22.7(s)	440.5	-
	$KBrO_3$	13.00- 12.5 (s & b)		22.7(s)	440.5	-
(b)	$AgBrO_3$	12.7 (s)	787	13.1(s)	760	-
	Tl BrO_3	13.9 - 13.5(s & b)	719 - 740	-	-	-
	Iodates	ν_1 and 2 ν_2		ν_3		ν_4
	$NaIO_3.H_2O$	13.1 - 12.77(s & b)	763 - 781	12.55(s)	797	-
(c)	KIO_3	13.3	752	12.55(s)	747	-
	$AgIO_3$	1 4 - 14.5 (m & b)	714 - 690	13.1 (m) 13.4	763 746.3	
	Tl IO_3			13.5(s & b)	741	

s = strong, sh = shoulder, m = medium, b = broad numerical values obtained for the fundamental vibrational modes, the assignments of vibrati~~ng~~onal modes for these salts in the tetrahedral perchlorate ion is clearly established. The perchlorate ion has a regular tetrahedral structure and is a spherical top molecule ~~or~~ like methane. It belongs to the symmetry point group Td. For this type of molecule the theoretical number of fundamental vibrational modes given by the general equation (3n - 6) is nine since the number of constituent atoms n = 5 · These vibrational frequencies are distributed between four normal modes of vibration. For this type of molecule the infrared and Raman spectra show four fundamental vibrational modes ν_1, ν_2, ν_3, and ν_4. Of these the ν_1 and ν_3 modes are the symmetric and anti-symmetric stretching modes and ν_2 and ν_4 are the corresponding bending modes. The ν_2 mode is doubly degenerate and the ν_3 and ν_4 modes are triply degenerate making nine in all. The following diagram shows these four fundamental modes.









R: Raman active (I.R) = Infrared active

Theoretically the triply degenerate modes ν_3 and ν_4 are infra red active and these can be observed in the infrared spectra of inorganic perchlorates. The ν_1, and ν_2 modes are theoretically only Raman active, but owing to distortion of ions in a crystal field of lower symmetry than that of the ion itself, the nondegenerate ν_1 mode may appear in the infrared spectra of crystalline salts. The ν_3 band appears as a very broad strong band with a poorly defined maximum which is sometimes split.

Cohn (74) and Hathaway & Underhill (73) have given the following assignments for the four fundamental modes.

	ν_1 (R)	ν_2 (R)	ν_3 (Iand R)
cm^{-1}.	932 (H & U) (crystal)	460 (H & U and C)	cryst. solid { 1110 (H & U.) 1090-1140 (C)
	935 (C) (Raman soln.)		

ν_4 (I and R)
crystal { 626 (H & U) 624 (C) .

In the present work the infra red spectra of the perchlorates of alkali metals and of silver and thallium (I) have been examined. Lithium, rubidium, caesium and thallium (I) perchlorates do not appear to have been investigated previously and there is no single systematic study of the infra red spectra of all the salts studied here.

Lithium perchlorate trihydrate. Li $ClO_4 \cdot 3 H_2O$.

Since the present work is mainly concentrated on the perchlorate anion the absorption frequencies of the water molecule at 1631 cm^{-1} is not further discussed here. In the spectra of solid lithium perchlorate a strong and broad band appears at 1143 - 1075 cm^{-1} ($9 \cdot 3 \mu$) which can be ascribed to the ν_3 asymmetric stretching vibration. A strong band appears at 625 cm^{-1} which can be assigned to the F2 or ν_4 asymmetric bending frequency. The ν_1 symmetric stretching frequency appears in the spectrum of this salt as a spur of moderate intensity at 939 cm^{-1} on the low frequency side of the broad ν_3 band. There is no indication of the ν_2 symmetric bending frequency in the spectrum at 460 cm^{-1}. The above assignments appear to be correct by comparison with Cohn's measurement on $KClO_4$.

Sodium perchlorate monohydrate $NaClO_4 . H_2O$.

In the infra red spectra of this salt a strong broad band with a defined maximum appears at 1075 cm^{-1} (9.3 μ) and a weak band appears as a spur at 939 cm^{-1} (10.65 μ). These are assigned to the same frequencies as in lithium perchlorate. The strong band at 624 cm^{-1} (16.03) is similarly ascribed to the asymmetric bending frequency of the tetrahedral ClO_4' ion. There is also a shoulder at 633 cm^{-1} (15.8 μ). Miller and Wilkins give only one strong broad band at 1100 cm^{-1} (9.1 μ) for the perchlorate ion in $NaClO_4$ H_2O.

Potassium perchlorate $KClO_4$. Both Cohn and Miller & Wilkins have examined the infra red spectra of this salt. In the present investigation there are three bands appearing in the spectrum. The band at 624 cm^{-1} (16.03 μ) (ν_4 mode) is in the position found by Cohn. This band has also a shoulder at 633 cm^{-1} (15.8 μ) which is not found in Cohn's spectra for this salt. Miller and Wilkins give a weak band in this region at 637 cm^{-1} (15.7 μ) but their spectrogram shows that the band is very broad and has no clearly defined maximum. The broad band which has a maximum at 1075 cm^{-1}(9.3 μ) has also a subsidiary maximum at 1145 cm^{-1} (8.75 μ) These correspond reasonably with Cohn's observations of bands at 1090 and 1140 cm^{-1} (ν_3 mode). Miller and Wilkins record a band at 1075 cm^{-1} with a shoulder at 1140 cm^{-1}. Agreement is satisfactory with these earlier observations. A medium sharp band again occurs at 939 cm^{-1}.

<u>Rubidium perchlorate $RbClO_4$.</u> The spectrum is very similar but there is a slight shift in position. A very broad and strong band with a poorly defined maximum appears at 1031 cm^{-1} (9.7 μ) (ν_3). The strong band due to the ν_4 bending frequency occurs at

619 cm^{-1} (16.18 μ). The forbidden frequency appears here as a stronger and sharper spur at 936 cm^{-1} (10.68 μ), than in the earlier salts. There is no shoulder for the band at 619 cm^{-1} in the case of rubidium perchlorate.

Caesium perchlorate $CsClO_4$. The strong and broad band appears here with a poorly defined maximum at 1064 cm^{-1} (9.4 μ). The theoretically forbidden frequency again appears here at 934.6 cm^{-1} (10.7 μ) and the band at 623.2 cm^{-1} (16.05 μ) is very strong and sharp.

Silver perchlorate $Ag ClO_4$. In the spectrum of this salt the ν_3 mode appears as a broad and strong band with two shoulders and a poorly defined maximum at 1075 cm^{-1} (9.3 μ). The shoulders appear at 1124 cm^{-1} and at 1093 cm^{-1} (8.9 μ and 9.15 μ) These correspond with the strong and broad band at 1160 - 1030 cm^{-1} given by Hathaway and Underhill for the monohydrate of silver perchlorate (${AgClO_4}\cdot{H_2O}$). The ν_4 mode appears as a strong and broad band at 623 cm^{-1} (16.05 μ).

Thallium (I) perchlorate $TlClO_4$. The ν_3 band appears between 1149 cm^{-1} and 1000 cm^{-1} (8.7μ - 10.0μ) and is very strong and very broad. At 922 cm^{-1} (10.85 μ) the forbidden band in the infra red region appears to be strong and sharp. The V_4 bending mode gives a very strong band at 610 cm^{-1} (16.4 μ).

In considering these perchlorates as a group certain comparisons can be made.

The asymmetric stretching mode V_3. The broad band arising for the degenerate asymmetric stretching V_3 mode is of a very similar form for $LiClO_4$ $3 H_2O$, $KClO_4$, and $CSClO_4$ with comparable width and maximum at 1075 - 1064 cm^{-1}. In sodium perchlorate the band is much sharper, although the maximum is still at 1075 cm^{-1}. Rubidium perchlorate shows considerable differences as the band is very broad and flat with a maximum shifted to 1031 cm^{-1}. This band for silver perchlorate is very similar to that for potassium perchlorate in its width and the exact position of the maximum. In thallium (I) perchlorate this band is very flat and broad and the spectrum here is similar to that of rubidium.

There is a definite shift in the maximum to 1000 cm^{-1} (10.0 μ).

There seems no systematic trend which can be noted here except that in the case of two of the heavier atoms, rubidium and thallium, there is a shift in the maximum to shorter frequencies. Although a similar shift was expected in the case of caesium it was not observed.

The symmetric stretching mode (ν_1)

This appears in all the spectra studied, as a spur on the longer wave length side of the above broad band. In the series lithium, sodium, potassium rubidium and caesium there is a slight shift in the position of the maximum. For lithium, sodium and potassium this appears at 939 cm^{-1} (10.65 μ) while for rubidium and caesium it occurs at 934 cm^{-1} (10.7 μ) which represents a slight displacement to longer wave length with increasing weight of the cation. The spectrum of the silver salt in this region is comparable with those of sodium and potassium, but thallium shows a marked shift from

939 cm^{-1} (10.65 μ) to 922 cm^{-1} (10.85 μ) indicating the effect of the heavy cation.

Hathaway and Underhill have pointed out that there will be a shift in the frequencies of the perchlorate ion if the perchlorate group becomes involved in partial covalent bonding between one of its oxygen atoms and a cation. This changes the symmetry from Td to the C_{3v} type and would involve a considerable shift of the band due to the ν_1 vibrational mode at 932 cm^{-1}. They consider this should be shifted to 739 cm^{-1} as found in the ν_1 vibrational mode of perchloric acid. There is no indication in the spectra of any of the present salts, including lithium perchlorate, for any similar covalent bonding. The clear spur occuring throughout for the ν_1 mode at 939 cm^{-1} shows that the salts are purely ionic.

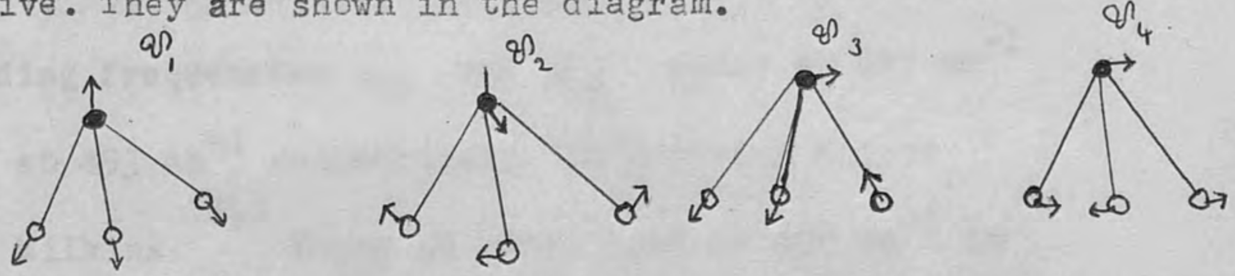
The asymmetric bending mode (ν_4).

This strong band appears in a similar position in the case of lithium, sodium, potassium, caesium and silver.

There is a slight shift in the case of rubidium (617 cm^{-1} (16.2. μ)). There is a more marked shift in the case of thallium (609 cm^{-1} (16.4 μ)) Although there is no regular shift there is again evidence for a shift to longer wavelength in the case of salts of largest atom.

Infra-red spectra of the chlorates, bromates and iodates.

X-ray spectroscopy has shown that the chlorate, bromate and iodate ions are pyramidal with C_{3v} symmetry. There are four normal modes of vibration as in the case of perchlorates but these are all both infra-red and Raman active. They are shown in the diagram.



The ν_1 and ν_3 modes, the symmetric and antisymmetric stretching frequencies, are near each other in their frequencies for all these ions. The stretching vibrations are therefore usually observed as one strong broad band. The two bending modes ν_2 and ν_4 appear as distinct strong sharp bands.

The infrared spectra of a number of crystalline alkali metal chlorates, bromates and iodates have already been examined[1]. Of the compounds studied in the present work the infrared spectra of silver chlorate, thallium (I) chlorate and bromate do not appear to have been examined before.

The Chlorates.

It has been well established by earlier work (75) that a broad band at 960 cm^{-1} represents the ν_3 asymmetric stretching frequency with a subsidiary spur or small peak on the low frequency side at 910 cm^{-1} which is due to the ν_1 symmetric stretching frequency. The bending frequencies ν_2 and ν_4 occur at 617 cm^{-1} and at 493 cm^{-1} respectively. In addition Miller and Wilkins (14) found an extra band at 990 cm^{-1} in the case of sodium chlorate and a band at 935 - 938 cm^{-1} in the case of sodium and potassium chlorates, but they gave no assignment of the bands observed in their work to any particular vibrational mode. The infrared spectra of potassium and sodium chlorates were remeasured in the present case as a standard and in addition, the spectra of silver and thallium (I) chlorates are recorded here for the first time. Diagram III and Table 25 indicate that the spectra of sodium and potassium chlorates showed bands which are identical with those obtained earlier and reproduced by

Nakamoto, ie; the band at 962 cm^{-1} is evidently the ν_3 stretching frequency while those at about 621 cm^{-1} and 480-495 cm^{-1} are the ν_2 and ν_4 bending frequencies. The ν_1 stretching frequency was only observed for silver and thallium (I) chlorates and occurs at 909 cm^{-1}. An additional peak observed both in the present work and by Miller and Wilkins in the case of sodium chlorate at 990 cm^{-1} could be the first overtone band of the ν_4 frequency (mean - 490 cm^{-1}). This also appears as a flat addition to the maximum at 980 cm^{-1} for potassium chlorate and slightly shifted in the case of silver and thallium (I) chlorates. Twice the frequency of the ν_4 band in the case of silver chlorate (2 x 495 cm^{-1}) would occur at 990 cm^{-1}, where there is a slight indication of a broadening of the band. In the case of thallium (I) chlorate the ν_4 bending frequency occurs at 485 cm^{-1} and double this would give an overtone which would reinforce the ν_3 frequency. It appears to be this effect which has strengthened the ν_3 band which is more pronounced in intensity in the case of this salt.

The well defined band at 938 cm^{-1}, also observed by earlier workers (75) is difficult to assign, but it could be an overtone of the additional band observed at 471 cm^{-1} in the case of thallium and silver chlorates.

Silver Chlorate.

This showed a very broad band at 1015-897 cm^{-1} which was split into four components. The maxima occured at 1015, 962, 938 and 897 cm^{-1}. The strongest peak at 962 cm^{-1} appears to be due to the ν_3 mode and that at 897 cm^{-1} the ν_1 mode with a slight shift. The other two peaks cannot be absolutely interpreted at present, but the peak at 1015 cm^{-1} may be due to the first overtone band of the ν_4 bending mode at 495 cm^{-1}. Dasent and Waddington (15) suggested a similar explanation for a band observed in the solid state spectra of the iodates which complicated the ν_1 and ν_3 frequencies here. The maxima at 617 cm^{-1} and 495 cm^{-1} are in the correct place for the ν_2 and ν_4 vibrational modes but in addition a further weak peak occurs at 471 cm^{-1}. The fact that this band also appears as a very strong band in the thallium (I) chlorate spectrum would indicate that it is an actual band and is not due to impurity. At present the assignment of this band is not clear, but it might be the metal-oxygen band observed as an extra band.

Thallium (I) Chlorate.

Here again the four frequencies appear but with some of the maxima shifted. The ν_3, ν_1 and ν_4 bands appear at 961, 910, and 486 cm^{-1} in the normal positions but the ν_2 band is shifted to a lower frequency and occurs at 599 cm^{-1}. There is a very strong band at 471 cm^{-1} as found in the case of silver chlorates.

Bromates.

Miller and Wilkins have reported investigations of the infrared spectra of sodium, potassium and silver bromates. In the case of sodium and potassium bromates only one strong and rather broad band was observed at 807 cm^{-1} and 790 cm^{-1} respectively. For silver bromate they found that this band split into two with maxima at 797 cm^{-1} and 765 cm^{-1} and a further band at 1280 cm^{-1} which reinforces the nujol band giving a stronger peak than usual to the low frequency nujol band. In Raman spectra the four fundamental modes have been assigned as follows (76) :-

	ν_1	ν_2	ν_3	ν_4
cm^{-1}	806	421	836	356 .

The infra red bands of crystalline bromates, where they occur are likely to be shifted slightly. For example in the chlorates, the stretching frequencies occur at lower frequencies in the crystalline solid while the two bending frequencies are shifted to higher frequencies. It is likely therefore that the bands observed by Miller and Wilkins in the region 810-730 cm^{-1} for sodium and potassium bromates are the double ν_1 and ν_3 bands shifted somewhat in the solid. This explanation is confirmed by the fact that the band is resolved into two peaks at 765 and 797 cm^{-1} in silver bromate. This interpretation is also confirmed by the fact that the interval between these peaks for silver bromate is the same as the difference between the ν_1 and ν_3 frequencies of the Raman solution measurements.

In the present investigation Diagram IV shows that for <u>sodium bromate</u> a broad and strong band appears with a maximum at 787.4 cm^{-1} and with a shoulder at 816 cm^{-1}. Another broad strong band is found with a maximum at 440 cm^{-1}. Although the spectrometer used did not record for frequencies less than 400 cm^{-1} the spectrum shows a tendency to be rising to another maximum below this point. From a comparison with the frequencies of the Raman spectra in solution the following assignments are suggested.

Bromates	ν_1	ν_2	ν_3	ν_4	
present I-R	787	440	816	400	cm^{-1}
Raman Spectra	806	421	836	356	cm^{-1}

This assignment is supported by a comparison of the solid infrared and Raman spectra of the chlorates.

Chlorates	ν_1	ν_2	ν_3	ν_4	
Present I-R	909	621	962	490	cm^{-1}
Raman	930	610	982	479	cm^{-1}

The shifts here are similar to those for the bromates, which supports the suggested assignment for the bromates. This may be checked by considering the Infra red spectra of the other bromates.

Potassium bromate. The spectra shows one strong broad band with a maximum at 794 cm^{-1} which must be due to the combined ν_1 and ν_3 bands which are not resolved in the solid spectra. There is no indication for the ν_2 band. The trace is rising steadily until the limit of the instrument at 400 cm^{-1} and so in this region there appears to be evidence for a very broad band representing the unresolved ν_2 and ν_4 bands.

Silver bromate. The broad band between 790-750 cm^{-1} is resolved into two clear peaks at 787 and 760 cm^{-1}. The peak at 787 cm^{-1} represents the ν_3 asymmetric stretching frequency. The band at 760 cm^{-1} is probably at too low a frequency to be the ν_3 frequency (816 cm^{-1}) shifted by the heavier cation. It could be an overtone of the ν_4 band which by comparison with the Raman measurements on solution should occur at about 376 cm^{-1} This estimate is obtained by assuming that there is a similar difference between the position of the bands in the solid I-R spectra and those in Raman solution spectra for the ν_2 and ν_4 bands. The difference for the ν_2 band is an increase in frequency of about 20 cm^{-1} and so if this is added to the Raman value of ν_4 (356 cm^{-1}) it would give 376 cm^{-1} for this frequency in the solid spectra. Double this figure would give 752 cm^{-1} for the first overtone band which is approximately in the correct region for the observed band (760 cm^{-1}). The ν_2 band occurs clearly as a mediumly strong band at about 430 - 440 cm^{-1}.

Thallium (I) bromate. A strong broad band was found and its maximum is between 740 and 719 cm^{-1} which represents the ν_1 and ν_3 stretching frequencies which are shifted to a lower frequency. This shift seems consistent for all the thallium (I) compounds studied.

Iodates. More studies have been carried out on iodates than on the chlorates and bromates. In the present investigation the infrared spectra of sodium, potassium silver and thallium (I) iodates were recorded. Shen, Yao and Wu (77) examined the Raman spectra of solutions of iodates and the following assignments were made.

ν_1	ν_2	ν_3	ν_4
779	390	826	330 cm^{-1}.

They are all infrared and Raman active. Dasent and Waddington (15) have studied the infrared spectra of a number of crystalline iodates between 4000 and 400 cm^{-1}. They observed ν_1 and ν_3 and in a few cases ν_2 frequencies. The frequency ν_4 in most cases lay beyond the spectral region accessible with sodium chloride and potassium bromide plates. Both the ν_1 and ν_3 frequencies lay between 800 - 700 cm^{-1}. They found it was difficult to assign these with certainty because the overtone frequency 2 ν_2, with amplified intensity, occurs near the ν_1 frequency (ie. $2 \times 390 = 780$ cm^{-1}).

In the present investigation the spectra of the iodates of the alkali metals including those of silver and thallium were recorded.

Sodium iodate monohydrate ($Na\,IO_3 \cdot H_2O$). There is a strong broad band between 795 and 738 cm^{-1} with four maxima at 794, 783, 763 and 738 cm^{-1}. The peak at 794 cm^{-1} can be assigned, following Dasent and Waddington suggestion, to the ν_3 frequency and the 763 cm^{-1} probably to the ν_1 mode. The maximum at 783 cm^{-1} occurs in a reasonably correct position for the 2 ν_2 bending frequency since the ν_2 frequencies occurs in the Raman solution spectra at 390 cm^{-1}. The band at 739 cm^{-1} found here is not observed by Dasent and Waddington in the anhydrous sodium iodate, but was noted by them as occuring in the case of rubidium and caesium iodates. In a subsequent paper (78) they ascribed this to the I = 0 asymmetric stretching frequency (ν_3) occuring over the range 743 - 796 cm-1. As however the I ═ 0 symmetric stretching frequency (ν_1) also occurs over the range 695 - 780 cm^{-1} there is an overlapping of the bands in this region which makes it difficult to assign them with certainty.

The complex character of the metallic iodate spectrum has thus been assigned by Dasent and Waddington to the double band character of the iodine oxygen bond and this appears to be reflected in the lowered magnetic susceptibility.

Potassium iodate (KIO_3). Here again a broad strong band with three maxima is found at 787, 752, and 725 cm^{-1}. The maxima at 787 cm^{-1} may be assigned to the ν_3 frequency and it is difficult to say which is ν_1 and $2\nu_2$ of the other two maxima.

Silver iodate ($Ag I O_3$). The broad band appears with four maxima at 764, 746, 714, and 694 cm^{-1} and these are definitely shifted to lower frequencies. These bands are almost in the same position as those given by Dasent and Waddington who assigned the strong bands at 766 and 742 cm^{-1} to the ν_3 stretching frequency and the bands at 705 and 695 cm^{-1} to the ν_1 and $2\nu_2$ modes.

Thallium (I) iodate ($Tl IO_3$). The spectrum found was much simpler and one very broad and strong band with a poorly defined maximum at 741 cm^{-1} was obtained.

This is probably due to the ν_3 frequency which agrees well with the value for this frequency found by Dasent and Waddington in the case of $Tl\ IO_3$. There was no indication of a band at 705 cm^{-1} in the present spectra where one was obtained by Dasent & Waddington and assigned to the ν_1 and $2\ \nu_2$ modes. There was a definite decrease of intensity found in this region in the present spectra.

PART VII

Comparison of magnetic susceptibilities and Spectroscopic Data

It is possible to make a comparison between the magnetic susceptibility and the spectroscopic date. As has been shown in part IV the diamagnetic susceptibility of polar compounds is determined by the charge distribution in the ions.

The shift in the maxima of the various fundamental frequencies of the infrared spectra on passing from a compound containing one halogen ion to the next can be deduced from the present infrared measurements. For example in the series ClO_3', $Br\ O_3'$ and IO_3' the following table shows the four fundamental modes for the chlorate, bromate, and iodate ions.

	ν_1	ν_2	ν_3	ν_4
Cl - O	909 cm^{-1}	621	962	490
Br - O	787	440	816	$< 400 \sim 376$
I - O	763	391	794	—

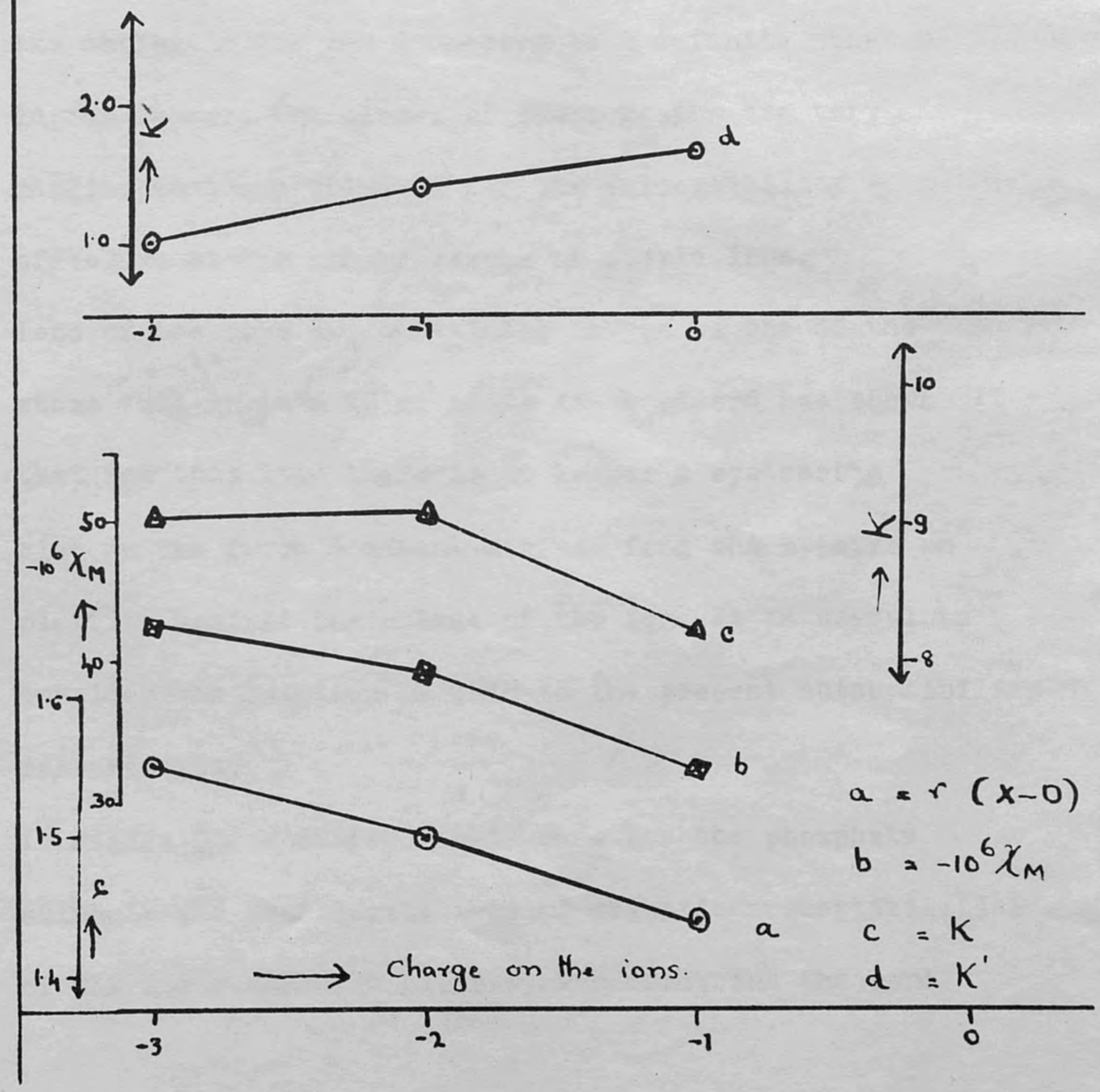
The shift in the maxima has been established for Raman spectra and is related to the nature of the atoms forming the bonds, there being a change towards lower frequencies on passing from chlorates to the iodates. This group is however not the most symmetrical type of molecule studied in the present investigation.

XY_4 Type of Ions. Of the anions investigated here, the phosphate, sulphate and perchlorate ions form an isoelectronic series of the XY_4 type. These are symmetrical tetrahedral ions and being isoelectronic have the same effective nuclear charge ($Z = 50$). The interpretation of the infrared spectra of this type of molecule is fairly simple.

For a regular tetrahedral molecule of the type XY_4 the symmetrical stretching frequency ν_1 can be considered as related to a single force constant. The value is given by $K_1 = 4 \pi^2 \nu_1^2 M_Y$, where M_Y is the mass of the atom Y. The position of the atom X is unchanged in this symmetrical type of vibration where all four bonds are stretching evenly. Woodward (79) has considered the systematic relationships of force constants derived in this way for simple regular tetrahedral molecules of the XY_4 type. He has shown that for a number of series of isoelectronic molecules, the series fall into various classes depending on the way in which the force constant changes with the charge on the ion. He has also brought out the relationships between these changes in the force constant and the radial distance between the atoms forming the bond. Since the magnetic susceptibility and the force constant derived from the spectra of these symmetric molecules are both related to this radial distance it seems useful to investigate the relationship of the two properties. Woodward's class I type of isoelectronic molecules represents

Figure 26

Comparison of $-10^6\chi_M$ with Force Constant K and r - the bond length (X–O) of the Tetrahedral ions - PO_4''', SO_4'' and ClO_4'.



the XH_4 type such as BH_4^- CH_4 , NH_4^+ , his class II type are the ions containing a halogen atom where the other atom is not a member of the first short period of the periodic table such as $\left[\mathrm{Al\,Cl_4}\right]^-$, $\left[\mathrm{P\,Cl_4}\right]^+$

In both these two classes he has shown for a number of examples that the force constant when plotted against the charge on the ion increases in a definite non-linear manner. The slopes of these graphs are very similar to those obtained for the susceptibility - effective atomic number graphs of simple ions.

Ions of the type XO_4 containing oxygen as one of the atoms fall into a third class and Woodward has shown that for this type there is no longer a systematic rise in the force constant derived from the spectra on plotting against the charge of the ion. It is useful to consider the relation of this to the present susceptibility measurements.

In figure 26 a comparison is made for the phosphate sulphate and perchlorate ions of magnetic susceptibilities, of the force constant given by Woodward, and the bond length in the ions. These properties are plotted against the charge on the ions. The lowest graph represents the literature values of the bond lengths which have been observed from X-ray crystallographic measurements (39). These are not very different from those calculated by Pauling (71) except the perchlorate where the calculated value is a little high. The next graph (b) represents the ionic susceptibility of the phosphate, sulphate and perchlorate ions calculated from the present measurements. Graph (c) Figure 26 represents the force constants for these three ions calculated by Woodward from the Raman spectra using the relationship $K_1 = 4 \pi \nu^2 \mu M_y$. Graph (d) Shows for comparison one of his class II groups of ions $[Cd\, I_4]^{2-}$, $[InI_4]^{-}$. and SnI_4 plotted similarly.

The close resemblance of the curves b and B shows that the same effect which is causing a lowering of the force constant is acting in the case of the susceptibility.

The lowering of the force constant has been shown to be related to the formation of π bonds (79) (80). In the case of a simple σ bond between the atoms an increase in the charge Z_x of a central atom of an isoelectronic triad will result in a shortening of the bond length and a corresponding increase in force constant due to the tightening of the bond by electrostatic attraction exerted by the nucleus of the central atom on the electrons of the surrounding ions. When there is π bonding, either involving p orbitals or $p\pi$ - $d\pi$ bonds an increase of the nuclear charge of this central atom may produce another effect (80). The shortening of the bond may alter the relative distribution of the electronic charges in the donor orbitals and the acceptor orbitals so that they no no longer overlap so well. This will tend to reduce the double bond character of the bond and so lower the force constant. This opposition of effects which strengthen the σ bond character and weaken~~ing~~ the π bond character has been used by Woodward to explain the anomalous behaviour of class III isoelectronic ions. The shortening of the bond affects the magnetic susceptibility directly. In this way it can be seen for these isoelectronic molecules that both the spectroscopic and magnetic propreties are related in their dependence on the bond lengths.

Calculation of the Force Constants for the XO_3^- Ions.

These ions are pyramidal structures with a lone pair of electrons at the apex of the pyramid. Herzberg(81) has applied a valence force - field approximation to deduce the force constants of XY_3 pyramidal structures. This approximation assumes that the only forces operating are those which resist bond extensions and bond deformations, ie. deformation of the interbond angles. There is in this symmetrical type of molecule only one type of bond and one type of inter bond angle. Thus only one bond stretching and one bond bending constant are required to calculate the potential energy of the system. Putting these into suitable co-ordinates, equations for the normal frequencies have been deduced (Herzberg, Infra red and Raman Spectra p. 176);

The bond stretching constant and bond bending constants, the so called force constants can be calculated from these equations. No one set of equations will give an exact result because of the initial force field approximations but, using a consistent treatment force constants for all three ions, chlorate, bromate and iodate may be calculated which are sufficiently accurate for comparative purposes.

Herzberg's equations II 204 and 205 for the normal frequencies are the best to apply with a few simplyfying assumptions. By assuming that the ions are of an approximately tetrahedral form, the angle β in the equation is $70^\circ\ 32'$, $\cos^2\beta = \frac{1}{9}$ and $\sin^2\beta = \frac{8}{9}$ and the factor $\frac{12 \cos^2\beta}{1 + 3 \cos^2\beta} = 1$

Then expressing the equations in frequencies we have:-

$$4\pi^2 \nu_1^2 + 4\pi^2 \nu_2^2 = \left(1 + 3\frac{M_y}{M_x}\cos^2\beta\right)\frac{K_1}{M_y} + \left(1 + 3\frac{M_y}{M_x}\sin^2\beta\right)\frac{K_2}{M_y} \qquad \text{——— (I)}$$

and $$16\pi^4 \nu_1^2 \nu_2^2 = \left(3\frac{M_y}{M_x} + 1\right)\frac{K_1 K_2}{M_y^2} \qquad \text{——— (2)}$$

Where Mx and My are the masses of the atoms X and Y and K_1 is the bond stretching constant in force/unit length and K_2 has been written as an abbreviation for $\frac{K\sigma}{l^2}$ Thus K_2 is also a force/unit length since $K\delta$ is an angle constant (force - radius) and for small angle deformations the chord equals the arc. Thus by dividing by the (radius of rotation) ^{2}, or (bond length) ^{2}, this constant is converted into the same units as K_1 such as dynes/cm. To apply the equation to the experimental data from the Infrared spectra the wave number frequencies must be converted to absolute frequencies ($\sec^{-1}$). The wave number frequencies must be multiplied by $2.998.10^{10}$, the value of C, the velocity of light.

The masses must be converted from gram atomic weights to grams per atom to keep the equation dimensionally correct. To simplify the calculations, wave numbers and gram atomic weights may be **employed** if the terms in which $4\pi^2$ appears are **used** with a correction factor $0.05889 = \frac{4\pi^2C^2}{N}$ to correct for the above dimensional factors.

Example of calculation for the Bromate ion.

The symmetric stretching ~~frequency~~ frequency	The symetric ~~The symmetric~~ bending frequency.
$\nu_1 = 787\ cm^{-1}$	$\nu_2 = 440\ cm^{-1}$
$\nu_1^2 = 6.19.10^5\ cm^{-2}$	$\nu_2^2 = 1.94\ .\ 10^5\ cm^{-2}$

Eqn. I.

$$0.05889\ (\nu_1^2 + \nu_2^2) = \left(1 + 3\,\frac{My}{Mx}\,\cos^2\beta\right)\frac{K_1}{My} + \left(1 + 3\,\frac{My}{Mx}\,\sin^2\beta\right)\frac{K_2}{My}$$

Eqn. II

$$0.5889^2\,(\nu_1 \cdot \nu_2)^2 = \left(3\,\frac{My}{Mx} + 1\right)\frac{K_1K_2}{My^2}$$

$$0.5889\ .\ 8.13\ .\ 10^5 = \left(1 + 3\ .\ \frac{16}{80}\ .\ \frac{1}{9}\right)\frac{K_1}{16} + \left(1 + \frac{3 \times 16}{80}\ .\ \frac{8}{9}\right)\frac{K_2}{16} \quad \text{from (I)}$$

$$\text{and } 0.5889^2\ .\ 6.19\ .\ 1.94\ .\ 10^{10} = \left(1 + \frac{3\ .\ 16}{80}\right)\frac{K_1K_2}{256} \quad \text{from (II)}$$

$$\text{But from (II)} \quad 1.6\,\frac{K_1K_2}{256} = 4.16\ .\ 10^8$$

$$K_2 = 6.66\ .\ \frac{10^{10}}{K_1}$$

Substitute in (I) for K_2 :-

$$4.79 \,.\, 10^4 K_1 = 0.0667 K_1^2 + 6.39 \,.\, 10^9$$

$$K_1 = \frac{4.79 \,.\, 10^4 \pm \sqrt{2.294 \,.\, 10^9 - 1.704 \,.\, 10^9}}{0.1333.}$$

Taking the positive sign $K_1 = 5 \,.\, 42. \, 10^5$ dynes/cm.

The positive sign gives the only acceptable solution as taking the negative sign gives an impossible value for K_2. Therefore the force constant for the bond stretching mode

$K_1 = 5 .42 \,.\, 10^5$ dynes/cm[+] for the bromate ion.

Similar calculations give for the chlorate ion

$K_1 = 6.24 \,.\, 10^5$ dynes/cm.

and for the iodate ion.

$K_2 = 5.24 \,.\, 10^5$ dynes/cm.

Comparison of Molar susceptibility and spectroscopic Data for XO_3' ions

It is possible to make a comparison of the molar susceptibilities with the force constants calculated from the fundamental vibration modes of the infrared spectra and also to compare them with the bond lengths. In order to explain the lowering of the molar susceptibility of the iodate ion it is useful to consider the three properties of the oxyhalides with those of the simple halide ions. The molar susceptibility and covalent radii of the halide ions are known and one half of the force constant for the simple halogen molecule may be used for comparison(82).

Table 26 gives the values of the bond lengths, force constants and the molar susceptibilities of these two groups of ions and figure 27 shows comparative graphs for these properties plotted against the effective atomic number of the ions. The curves (a) show the bond lengths of the haloxy-ions and the crystal radii of the halide ions. Curves (b) represent the reciprocal of the force constants for the haloxy-ions and the reciprocal of one half of the force constant for the halogens to obtain a comparable quantity. Curves (c) represent the molar susceptibilities similarly plotted. Figure 27 clearly shows the effect of the shortening of the bond length in the haloxy-ions. The actual bond length curve for these ions is below that for the halide ions and becomes increasingly low on passing to the iodate ion. The force constant curve plotted as a reciprocal function for comparison shows how the actual force constants for the haloxy-ions are greater than those for the simple halogen molecules and that there is an effect tending to enhance the force constant in the case of the iodate ion. The molar susceptibility shows the same anomaly for the iodate, the value for the iodate ion falling below that for the iodide ion. These effects can be explained by the influence of π bonding in a somewhat similar manner to that discussed for the perchlorate ion. The possibility of forming a π-bond between the orbitals of the halogen and those of the oxygen atoms can explain the trend of the curves in figure 27. The π bond character between the halogen and the oxygen increases from chlorate to iodate, the larger halogens giving a better orbital overlap(80) The present results show that this effect can be clearly detected in the lower diamagnetic susceptibility of the iodate ion.

The present work provides experimental data for the systematic comparison of the diamagnetism of the various oxyanions studied with other properties such as the molar volumes, coordination number and the spectroscopic data. It also shows how the magnetic properties are related to the fundamental bond length of the atoms in the ions.

Figure 27

Comparison of molar susceptibility, Force Constants, and Bond length of the oxyhalides and halides XO_3' and X'.

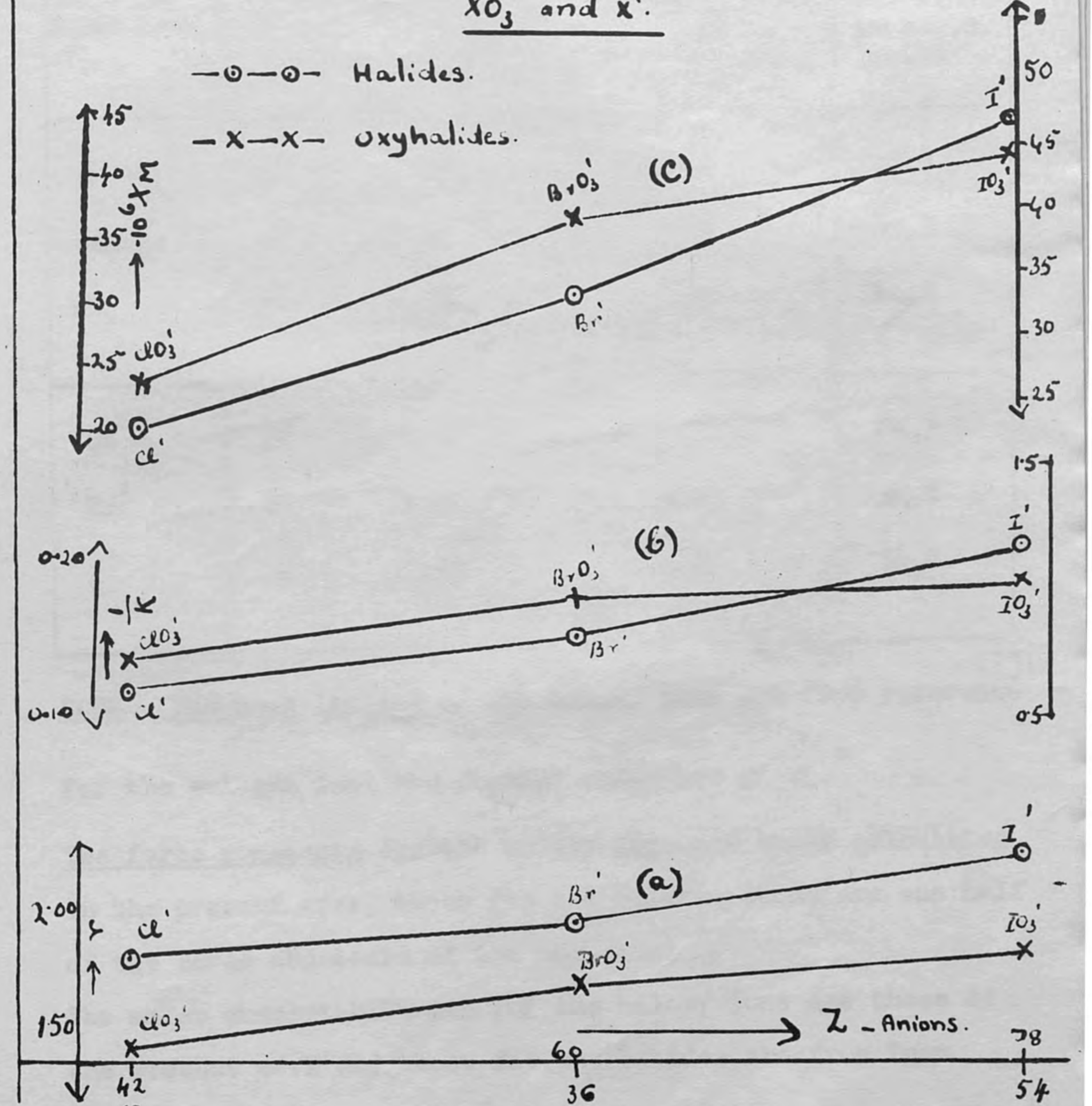


TABLE 26

Molar susceptibilities, Bond lengths and Force constants of the haloxy ions and halide ions

Substance	Z	Bond lengths r in Å	Force constant $K \cdot 10^5$ dynes/cm.	$-10^6 \chi_M$ in c.g.s. units
CO_3'	42	1.46	6.24	26.8
BrO_3'	60	1.68	5.42	39.3
IO_3'	78	1.82	5.24	44.8
Cl'	18	1.81	3.19	24.3
Br'	36	1.96	2.42	34.8
I'	54	2.20	1.70	50.6

NOTE The bond lengths of the haloxy ions are from reference (39)

For the halogen ions the crystal radii are given. (71)

The force constants for the haloxy-ions are those calculated in the present work, those for the halogen atoms are one half of the force constants of the molecules (82)

The molar susceptibilities for the haloxy-ions are those of the present work and those for the halides are from Trew and Husain.

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