The MAGNETIC PROPERTIES of ZINC and ITS COMPOUNDS.

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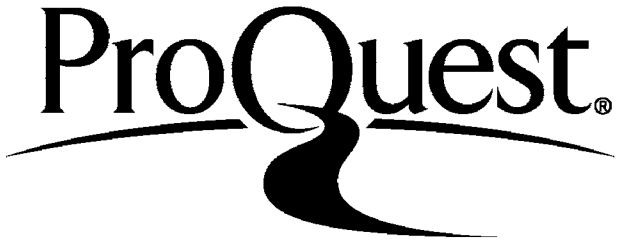

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Abstract of Thesis:

The object of this research is an investigation of the magnetic properties of Zinc and its commoner compounds. The magnetic susceptibilites of twenty-eight highly purified zinc compounds have been determined , and from a consideration of the values obtained a mean experimental value of the susceptibility of the Zinc ion has been found. A comparison between the experimental value and the theoretical value, calculated from considerations of atomic structure, has been made.

From a consideration of the molecular susceptibilities of the compounds measured, it was found that there is a probable relationship between magnetic susceptibility and co-ordination number.

The susceptibilities of the Zinc halides were found and, from a graph showing the relationship between molar susceptibility and the total number of electrons, it was found that Ikenmeyer's flattening of the curve is without justification.

From the susceptibilities of the organic salts measured, the value of the group $>CH_2$ has been calculated; and also, the effect of substituting a Chlorine atom for a Hydrogen atom in the side-chain of a fatty acid, has been estimated.

The zinc salts of the oxy-acids of Phosphorous were found to behave in an anomalous manner. There was found to be some regularity in these compounds showing that the anomaly is similar throughout the series.

THE MAGNETIC PROPERTIES OF ZINC AND ITS COMPOUNDS.

The object of this research is an investigation of the magnetic properties of Zinc and its commoner compounds. The history of Magneto-Chemistry is short, and the elements which have been completely investigated are few. Ikenmeyer[1] made a systematic investigation of a series of similar compounds, the alkali halides; Sugden[2] has investigated the Copper and Silver compounds; Spencer and Hollens[3] the Cadmium compounds; and Trew[4] the Thallous compounds.

The magnetic susceptibilities of only five zinc compounds are recorded in the literature.

Zinc[5]	$X = -0.157 \times 10^{-6}$
Zinc Sulphate $7M_2O$[6]	$X = -0.480 \times 10^{-6}$
Zinc Oxide[7]	$X = -0.362 \times 10^{-6}$
Zinc Hydroxide[8]	$X = -0.487 \times 10^{-6}$
Zinc Bromide[9]	$X = -0.40 \times 10^{-6}$
Zinc Chloride (Aq)[10]	$X = -0.47 \times 10^{-6}$

These values are sufficient to show that the normal compounds of Zinc are diamagnetic, but they are insufficient to show whether the laws of diamagnetism are obeyed, nor can it be found from these values whether there is any regularity amongst compounds containing a common ion.

The magnetic susceptibilities of twenty-eight highly purified zinc compounds have been determined including the five already mentioned. The modified Gouy[11] method was used

for the determination of the values; this method has an experimental error of rather less than 1%. From a consideration of these values the extent to which these compounds conform to the additivity law has been found, and the existence of a relationship between compounds of a similar type demonstrated.

Presuming the electovalence of Zinc salts and the relevance of the additivity law, then, by use of the known experimental values of the magnetic susceptibilities of the anions, the mean experimental value of X for the zinc ion can be obtained. A theoretical value of the susceptibility of the Zinc ion can be calculated from considerations of atomic structure, and a comparison made between the experimental and theoretical values.

Zinc has an atomic number 30; that is the extranuclear electrons are (2.8.18.2) and in the Zinc ion (2.8.18). The inner quantum levels are complete, consequently a paramagnetic effect is not to be expected, and the metal and its ion should be diamagnetic. The formula for calculating the susceptibility of a mononuclear spherically symmetrical atom or ion is, according to the Langevin[12] ~~is~~

$$X_A = \frac{-Ne^2 \Sigma \bar{r}^2}{6mc^2}$$

where N = the number of atoms per gram atom.
e = the charge per electron
r = the radius of the orbit
m = the electronic mass
c = velocity of light
X_A is the gram atomic susceptibility.

The above formula can only be applied to strictly polar compounds and anomalous results would be expected when a covalent link is present. The Zinc compounds are considered to have a strong tendency towards covalency. This would cause imperfect additivity which a consideration of the results will confirm.

THE METHODS OF PREPARATION OF THE COMPOUNDS.

The difficulties of preparation of zinc compounds are mainly technical due to their deliquescence and to the tendency to hydrolyse and form basic compounds.

ZINC

Sticks of pure Zinc were obtained cast to the size of the tube in which they were to be measured. They were "Analar" reagents their analysis being given as:-

Acid insoluble matter	passed test
Iron	0.002%
Oxidisable impurity	0.0008%
As_2O_3	0.00001%
Total impurity	0.00281%

Small pieces of the metal were sawn from each end and carefully cleaned with emery paper and acid to remove any iron which had been left by the saw. The pieces were then weighed and dissolved in dilute hydrochloric acid and the solution made up to 500 c.c.s. The amount of zinc present was estimated by the pyrophosphate method, which was used for all estimations unless the contrary is stated.

Weight of zinc dissolved in acid = 1.4586 gms.

∴ Theoretical amount of zinc in 100 ccs. of solution = 0.2917 "

Weight of zinc pryophosphate obtained = 0.6799 "

∴ Weight of zinc in 100ccs of solution = 0.2916 "

∴ The metal used is therefore pure.

ZINC OXIDE.

Zinc oxide was prepared from A.R. Zinc oxide. The A.R. oxide was dissolved in concentrated nitric acid, and the solution of nitrate, thus obtained, was evaporated on a sand bath to crystallising point. The crystals of zinc nitrate were difficult to obtain due to their tendency to form a basic compound which is precipitated as an opaque mass. A slight excess of acid was found to be necessary for the normal crystals to come out. These were filtered and recrystallised from water.

The zinc nitrate was dried over calcium chloride and partially dehydrated, and then heated in a silica crucible in a blowpipe flame for ten days. It was found to be impossible to remove a slight permanent yellow colouration due to a small quantity of basic nitrate.

Analysis:-

(1)	Weight of zinc oxide taken	= 0.3156 gms.
	Weight of Pyrophosphate obtained	= 0.5882 ,,
	Percentage ZnO in material taken	= 99.54%
(2)	Weight of zinc oxide taken	= 0.3192 gms.
	Weight of zinc pyrophosphate obtained	= 0.5974 gms.
	Percentage zinc oxide in material	= 99.95%

ZINC HYDROXIDE.

Zinc Hydroxide was prepared many times from different solutions and reagents but it was not possible to obtain a pure specimen. The best results were obtained from caustic soda and zinc nitrate. The zinc nitrate solution was prepared from A.R. zinc oxide and nitric acid. The nitrate solution was precipitated by a filtered solution of 99% caustic soda. The precipitate of zinc hydroxide was washed

and redissolved in nitric acid, and again precipitated. This process was repeated. The maximum purity obtainable was 96%. The impurity was zinc carbonate, this was allowed for in the susceptibility determination of the hydroxide.

Analysis:-

Weight of hydroxide taken	0.4486 gms.
Weight of pyrophosphate obtained	0.6397 ,,
% $Zn(OH)_2$ in material taken	93.01%
Weight of hydroxide taken	0.3258 gms.
Weight of pyrophosphate obtained	0.4818 ,,
% $Zn(OH)_2$ in material taken	96.23%
Weight of hydroxide taken	0.6221 gms.
Weight of pyrophosphate obtained	0.8828 ,,
% $Zn(OH)_2$ in material taken	92.55%

ZINC FLUORIDE.

Zinc fluoride was prepared by precipitation. A solution of zinc chloride was made from sticks of the pure compound and a little hydrochloric acid added to prevent hydrolysis. The zinc fluoride was precipitated by the addition of potassium fluoride solution. The white powder obtained was washed several times and heated to 200°C in an air oven to give the anhydrous salt.

The analysis of zinc fluoride proved difficult. The ordinary pyrophosphate method could not be used as it was found that the zinc fluoride was partially precipitated as fluorophosphate.

A weighed quantity of the fluoride was fused with sodium carbonate and the product washed with water. The residue was filtered off and dissolved in diluted hydrochloric

acid. This solution should contain all the zinc as zinc chloride. The gravimetric estimation was carried out in the usual way. The experimental error of the method was large.

Weight of Zinc fluoride taken	0.4480 gms.
Weight of Zinc pyrophosphate obtained	0.6438 ,,
% ZnF_2 in material taken	97.50%
Weight of Zinc fluoride taken	0.3268 ,,
Weight of Zinc pyrophosphate obtained	0.4801 ,,
% ZnF_2 in material taken	99.68%

ZINC CHLORIDE

Zinc chloride was prepared by dissolving pure zinc (Kahlbaum product) in dilute hydrochloric acid. The solution was taken down to dryness in an evaporating basin on a sand bath. A deliquescent white amorphous powder of zinc chloride was obtained. This was dissolved in water and again taken down to dryness. The chloride was kept in a desiccater over phosphorus pentoxide. Analysis:-

Weight of Zinc chloride taken	1.4808 gms.
Weight of Zinc pyrophosphate obtained	1.6372 ,,
% $ZnCl_2$ in material taken	98.88%
Weight of Zinc chloride taken	0.4618 ,,
Weight of Zinc pyrophosphate obtained	0.5066 ,,
% $ZnCl_2$ in material taken	97.92%

ZINC BROMIDE

Zinc bromide was bought as a very deliquescent yellowish-white powder. It was kept in a desiccator over phosphorous pentoxide. It was analysed by precipitation as silver bromide.

Weight of Zinc bromide taken	0.7700 gms.
Weight of silver bromide obtained	1.2759 "
% $ZnBr_2$ in material taken	99.36%
Weight of zinc bromide taken	1.0013 "
Weight of silver bromide obtained	1.6612 "
% $ZnBr_2$ in material taken	99.49%

ZINC IODIDE

Zinc iodide was prepared by the direct union of its elements. An excess of zinc dust was placed in a round-bottomed flask together with sublimed iodine. The flask was fitted with a dropping funnel containing distilled water. The water was dropped on to the mixture in the flask, which was shaken after each addition. A vigorous reaction occurred and zinc iodide solution was formed with evolution of heat. The solution was filtered to remove the excess zinc and then evaporated to dryness. A white deliquescent powder was obtained which was kept in a dessicator over phosphorus pentoxide. Zinc iodide was estimated by precipitation as silver iodide.

Weight of zinc iodide taken	0.7585 gms.
Weight of silver iodide obtained	1.1134 "
% ZnI_2 in material taken	99.74%
Weight of Zinc iodide taken	0.5407 "
Weight of silver iodide obtained	0.7955 "
% ZnI_2 in material taken	100%

ZINC IODATE

Zinc iodate was prepared by precipitation. A boiling solution of potassium iodate was added to a boiling solution of zinc sulphate in equivalent quantity. The zinc iodate was precepitated together with a little potassium iodate. The precipttate

was filtered and suspended in boiling water. The mixture was filtered whilst hot. This process was repeated.

Analysis:-

Weight of Zinc iodate taken = 1.6863 gms
Weight of Zinc pyrophosphate obtained = 0.6087 "
% $Zn(IO_3)_2$ in material taken = 98.58% "
Weight zinc iodate taken = 0.7424"
Weight of zinc pryophospate obtained = 0.2678"
% Zn $(IO_3)_2$ in material taken = 98.28%

ZINC AMMONIUM CHLORIDE

Zinc ammonium chloride was bought in crystalline form. This was recrystallised twice and its purity estimated. The analysis was found to agree with the formula $ZnCl_2$ $4NH_4Cl$ although the compound was expected to be $ZnCl_2$ $3NH_4Cl$. Several estimations were made.

Analysis:-

Weight of Zinc ammonium chloride taken = 1.3144 gms.
Weight of Zinc pyrophospate obtained = 0.5523 "
% $ZnCl_2$ $4NH_4Cl$ in material taken = 93.87%
Weight of Zinc ammonium chloride taken = 0.6811 gms
Weight of zinc pyrophosphate obtained = 0.3011 gms
% $ZnCl_2$ $4NH_4Cl$ in material taken = 98.74%
Weight of zinc ammonium chloride taken = 0.8352 gms
Weight of zinc pyrophosphate obtained = 0.3588 gms
% $ZnCl_2$ $4NH_4Cl$ in material taken = 95.96%

ZINC SULPHATE HEPTAHYDRATE

Crystals of zinc sulphate heptahydrate were bought as an A.R. material and twice recrystallised from water.

Analysis:-

Weight of Zinc sulphate taken = 0.9514 gms
Weight of pyrophosphate obtained = 0.5076 "
% $ZnSO_4$ $7H_2O$ in material taken = 100.6%

Weight of Zinc sulphate taken = 0.9533 gms
Weight of Zinc pyrophosphate obtained = 0.5059 "
% $ZnSO_4$ $7H_2O$ in material taken = 100.2%

ANHYDROUS ZINC SULPHATE

Pure, hydrated zinc sulphate was heated in an air oven at 200°C for six days, when the anhydrous salt was formed.

Analysis:-

Weight of Zinc sulphate taken = 0.3530 gms
Weight of Zinc pyrophosphate obtained = 0.3353 "
% $ZnSO_4$ in material taken = 100.6%
Weight of Zinc sulphate taken = 0.5409 "
Weight of Zinc pyrophosphate obtained = 0.5154 "
% $ZnSO_4$ in material taken = 100.9%

ZINC AMMONIUM SULPHATE HEXAHYDRATE

Crystals of zinc ammonium sulphate hexahydrate were bought and twice recrystallised from water.

Analysis:-

Weight of Zinc ammonium sulphate taken = 1.1071 gms
Weight of Zinc pyrophosphate obtained = 0.4228 "
% $ZnSO_4(NH_4)_2SO_4 6H_2O$ in material taken 100.7%
Weight of Zinc ammonium sulphate taken = 0.8631 "
Weight of Zinc pyrophosphate obtained = 0.3288 "
% $ZnSO_4(NH_4)_2SO_4 6H_2O$ in material taken 100.4%

ZINC SULPHITE HEMIPENTAHYDRATE

Zinc sulphite was prepared by passing a stream of sulphur dioxide through a suspension of zinc carbonate in water. A clear solution of zinc bisulphite was obtained. This solution was heated until crystals of the normal sulphite began to come out. The solution was allowed to stand until crystallisation was complete. It was then filtered and the crystals dried on a porous

plate.

Analysis:-

Weight of zinc sulphite taken	=	0.3337 gms.
Weight of zinc pyrophosphate obtained	=	0.2653 ,,
% $ZnSO_3$ $2\frac{1}{2}$ H_2O in material taken	=	99.40%
Weight of zinc sulphite taken	=	0.4755 ,,
Weight of zinc pyrophosphate obtained	=	0.3786 ,,
% $ZnSO_3$ $2\frac{1}{2}$ H_2O in material taken	=	99.54%

ZINC CARBONATE

Zinc carbonate, when prepared by the ordinary method of precipitation, was found to contain basic carbonate as an impurity.

Commercial ammonium carbonate was digested with alcohol. The ammonium carbonate dissolved leaving a residue of ammonium bicarbonate. This residue was dissolved in water and the solution added to a solution of zinc carbonate. A precipitate of amorphous zinc carbonate was obtained, which was filtered and digested with excess of a cold solution of the precipitant, ammonium bicarbonate. After five days a crystalline form was produced. The crystals were filtered and dried. This compound was zinc carbonate hemihydrate, but on keeping it was found to lose water and agree with the formula $ZnCO_3\frac{1}{4}H_2O$.

Analysis:-

Weight of Zinc carbonate taken	=	0.9851 gms
Weight of Zinc pyrophosphate obtained	=	1.1586 "
% $ZnCO_3\frac{1}{4}H_2O$ in material taken	=	100.3%
Weight of Zinc carbonate taken	=	0.5723 "
Weight of Zinc pyrophosphate obtained	=	0.6700 "
% $ZnCO_3\frac{1}{4}H_2O$ in material taken	=	99.82%

ZINC MERCURITHIOCYANATE

Zinc mercurithiocyanate was prepared by adding solutions of mercuric chloride and potassium thiocyanate in equivalent quantities to a slightly acid solution of zinc chloride. The mercurithiocyanate was precipitated and dried at 100°. It was a pale pink, soft powder.

Analysis:-

Weight of zinc mercurithiocyanate taken	=	0.6315 gms.
Weight of zinc pyrophosphate obtained	=	0.2011 ,,
% $ZnHg(CNS)_4$ in material taken	=	104%
Weight of zinc mercurithiocyanate taken	=	0.9509 gms.
Weight of zinc pyrophosphate obtained	=	0.3011 gms.
% $ZnHg(CNS)_4$ in material taken	=	103.5%

ZINC NITRATE TETRAHYDRATE

Zinc nitrate was prepared by crystallising the solution obtained by dissolving A.R. zinc oxide in concentrated nitric acid. The filtered solution was evaporated down to the point of crystallisation. It was found that a slight excess of acid was necessary to prevent the formation of basic compounds. Too great an excess acid prevents crystallisation. The crystals are extremely deliquescent but ~~are~~ over strong drying agents, such as concentrated sulphuric acid or phosphorous pentoxide, they decompose giving zinc oxide and oxides of nitrogen. The crystals were dried in a desiccator containing calcium chloride. Dehydration occurred but a definite compound was obtained; this was zinc nitrate quadrihydrate, two molecules of water having been lost.

Analysis:-

Weight of zinc nitrate taken	=	0.6461 gms.
Weight of zinc pyrophosphate obtained	=	0.3775 ,,
% $Zn(NO_3)_2 4H_2O$ in material taken	=	100.2%

Weight of zinc nitrate taken = 0.6944 gms.
Weight of zinc pyrophosphate obtained = 0.4054 ,,
% $Zn(NO_3)_2 4H_2O$ in material taken =100.2%

BASIC ZINC CHROMATE

Basic zinc chromate was prepared by precipitating a solution of zinc chloride with a solution of pure potassium chromate. The precipitate was filtered, washed and dried as a beautiful red-gold powder.

The analysis agreed with the formula $ZnO2CrO_3 2H_2O$.
Weight of zinc chromate taken = 1.1884 gms.
Weight of zinc pyrophosphate obtained = 0.5646 ,,
% $ZnO2CrO_3 2H_2O$ in material taken = 99.04%
Weight of zinc chromate taken = 1.0764 ,,
Weight of zinc pyrophosphate obtained = 0.5032 ,,
% $ZnO2CrO_3 2H_2O$ in material taken = 97.45%

ZINC ORTHOPHOSPHATE TETRAHYDRATE

Hydrated zinc orthophosphate was obtained by precipitating a boiling solution of zinc sulphate with a hot solution of disodium hydrogen phosphate. The zinc orthophosphate came down in the form of shining orthorhombic plates.

Analysis:-
Weight of zinc phosphate taken = 0.3130 gms.
Weight of zinc pyrophosphate obtained = 0.3077 ,,
% $Zn_3(PO_4)_2 4H_2O$ in material taken 98.58%
Weight of zinc phosphate taken = 0.5734 ,,
Weight of zinc pyrophosphate obtained = 0.5700 ,,
% $Zn_3(PO_4)_2 4H_2O$ in material taken = 99.68%

ANHYDROUS ZINC ORTHOPHOSPHATE

Anhydrous zinc orthophosphate was prepared by heating the hydrated salt in a porcelain crucible over a bunsen flame. The anhydrous salt was a white infusible powder, only soluble in concentrated nitric acid.

Analysis:-

Weight of zinc phosphate taken	=	0.9664 gms.
Weight of zinc pyrophosphate obtained	=	1.1514 ,,
% $Zn_3(PO_4)_2$ in material taken	=	100.6%
Weight of zinc phosphate taken	=	0.5470 ,,
Weight of zinc pyrophosphate obtained	=	0.6488 ,,
% $Zn_3(PO_4)_2$ in material taken	=	99.97%

ZINC AMMONIUM ORTHOPHOSPHATE

Zinc ammonium phosphate was prepared by the addition of a solution of ammonium phosphate to a solution of zinc sulphate, which was slightly acid to phenol phthalein. The precipitate was allowed to stand until it became crystalline. It was then filtered and dried. It was analysed by heating a weighed quantity and weighing the zinc pyrophosphate obtained.

Weight of zinc ammonium phosphate taken	=	0.5619 gms.
Weight of zinc pyrophosphate obtained	=	0.4729 ,,
% $ZnNH_4PO_4$ in material taken	=	100.9%
Weight of zinc ammonium phosphate taken	=	1.0032 ,,
Weight of zinc pyrophosphate obtained	=	0.8454 ,,
% $ZnNH_4PO_4$ in material taken	=	98.74%

ZINC PYROPHOSPHATE

The pyrophosphate was prepared by heating zinc ammonium phosphate until a constant weight was obtained. No analysis was performed as zinc pyrophosphate is the end product of the pyrophosphate method of estimation.

ZINC PHOSPHITE HEMIPENTAHYDRATE

Zinc phosphite was prepared from a solution of phosphorous trichloride in water, which had been neutralised by a solution of sodium carbonate. This solution of sodium phosphite was added to a boiling solution of zinc sulphate. Crystals of zinc phosphite were precipitated, filtered and dried on a porous plate.

Analysis:-

Weight of zinc phosphite taken	=	0.7248 gms.
Weight of zinc pyrophosphate obtained	=	0.5806 ,,
% $ZnHPO_3 2\frac{1}{2}H_2O$ in material taken	=	100.1%
Weight of zinc phosphite taken	=	0.6026 ,,
Weight of zinc pyrophosphate obtained	=	0.4947 ,,
% $ZnHPO_3 2\frac{1}{2}H_2O$ in material taken	=	102.7%

ZINC METAPHOSPHATE

Zinc metaphosphate was prepared by fusing zinc oxide with excess glacial phosphoric acid. The metaphosphate formed a glass, from which the crucible had to be broken away. It was then boiled with water and filtered whilst hot to remove the excess phosphoric acid. The results were not sufficiently good to justify measurement.

Weight of zinc metaphosphate taken	=	0.2107 gms.
Weight of zinc pyrophosphate obtained	=	0.1348 ,,
% $Zn(PO_3)_2$ in material taken	=	93.87%

ZINC FERROCYANIDE

Zinc ferrocyanide was bought from Kahlbaum. The analysis of the compound proved difficult due to its insolubility in any reagent except potassium cyanide, which solution would not give a phosphate precipitate.

A weighed quantity of zinc ferrocyanide was fused with sodium carbonate and the product dissolved in water. The residue was extracted with dilute hydrochloric acid. To this solution a little concentrated nitric acid was added, followed by ammonium chloride solution and ammonia. The precipitate of ferric hydroxide was filtered off and the filtrate was acidified. The solution was then used for the gravimetric estimation which was carried out in the usual way. A large experimental error was introduced by the number of filtrations and the large volumes which were obtained at the end of the experiment. The analysis is not completely reliable.

Weight of zinc ferrocyanide taken	=	1.3642 gms.
Weight of zinc pyrophosphate obtained	=	1.1900 gms.
% $Zn_2Fe(CN)_6$ in material taken	=	98.09%
Weight of zinc ferrocyanide taken	=	1.0928 ,,
Weight of zinc pyrophosphate obtained	=	0.9062 ,,
% $Zn_2Fe(CN)_6$ in material taken	=	93.22%

ZINC FERRICYANIDE

Zinc ferricyanide was prepared by precipitating an acid solution of pure zinc chloride with a solution of pure potassium ferricyanide. Zinc ferricyanide was precipitated as a brown powder which was filtered and dried.

The analysis of zinc ferricyanide was carried out in a similar manner to that af zinc ferrocyanide. It was not satisfactory.

ZINC ACETATE DIHYDRATE.

Crystals of zinc acetate were bought and twice recrystallised from water and dried.

Analysis:

Weight of zinc acetate taken	=	0.7447 gms.

Weight of zinc pyrophosphate obtained = 0.5238 gms.

% Zn $(CH_3COO)_2$ $2H_2O$ in material taken =101.4%

Weight of zinc acetate taken = 0.5775 "

Weight of zinc pyrophospate obtained = 0.4026"

% Zn $(CH_3COO)_2$ $2H_2O$ in material taken 100.4%

ZINC TRICHLORACETATE DIHYDRATE

Zinc trichloracetate was obtained from Kahlbaum.

Analysis:-

Weight of zinc trichloracetate taken = 0.7131 gms.

Weight of zinc pyrophosphate obtained = 0.2527 "

% Zn $(CCl_3COO)_2$ $2H_2O$ in material taken= 99.10%

Weight of zinc trichloracetate taken = 0.4861 "

Weight of zinc pyrophosphate obtained = 0.1716 "

% Zn $(CCl_3COO)_2$ $2H_2O$ in material taken = 98.74%

ZINC BUTYRATE

Zinc butyrate was obtained from Kahlbaum.

Analysis:-

Weight of zinc butyrate taken = 0.3051 gms.

Weight of zinc pyrophosphate obtained = 0.1986 "

% Zn $(CH_3CH_2CH_2COO)_2$ in material taken 102.3%

Weight of zinc butyrate taken = 0.8861 gms

Weight of zinc pyrophosphate obtained = 0.5918 "

% Zn$(CH_3CH_2CH_2COO)_2$ in material taken 105%

ZINC OXALATE DIHYDRATE

Zinc oxalate was prepared by adding a boiling solution of ammonium oxalate to a boiling solution of zinc sulphate. The zinc oxalate was precipitated as a fine, white powder. It was filtered and dried.

Analysis:

Weight of zinc oxalate taken = 0.5282 gms

Weight of zinc pyrophosphate obtained = 0.4114 "

% Zn $(COO)_2$ $2H_2O$ in material taken = 96.81%

Weight of zinc oxalate taken = 0.4544 gms.
Weight of zinc pyrophosphate obtained = 0.3538 "
% $Zn(COO)_2\ 2H_2O$ in material taken = 96.79%

ZINC SUCCINATE

Zinc succinate was prepared by adding a solution of sodium succinate to a solution of zinc sulphate. The zinc succinate was precipitated, filtered and dried.

Analysis:-

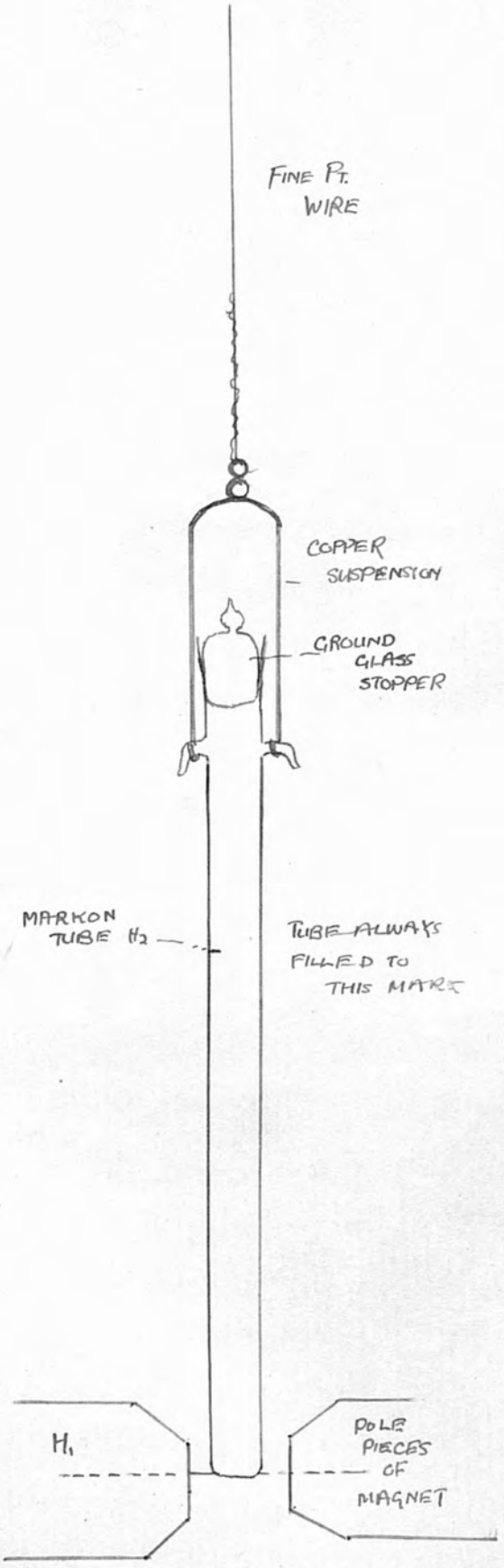
Weight of zinc succinate taken = 0.3598 gms.
Weight of zinc pyrophosphate obtained = 0.2972 "
% Zn $(CH_2COO)_2$ in material taken = 98.33%
Weight of zinc succinate taken = 0.4002 gms.
Weight of zinc pyrophosphate obtained = 0.3310 "
% Zn $(CH_2COO)_2$ in material taken = 98.45%

THE METHOD OF MEASURING THE SUSCEPTIBILITIES OF THE COMPOUNDS.

The instrument used for measuring the susceptibilites of the compounds was a modification of the Gouy balance.[11] The basis of the method is the suspension of a uniform cylinder of the material in a non-homogeneous field. See Fig. 1 P. 17A.

The maximum field is at the centre of the pole-pieces, let it equal H_1 gauss. The field at the top of the cylinder above the pole-pieces is equal to H_2 gauss where $H_1 > H_2$. The direction of the force exerted will depend upon whether the material is diamagnetic or paramagnetic. If it is diamagnetic the tube will tend to move upwards, away from the point of maximum intensity. That is an upward force will be exerted and the weight will be apparently diminished.

FIG. I.


FINE Pt. WIRE
COPPER SUSPENSION
GROUND GLASS STOPPER
MARKON TUBE H2
TUBE ALWAYS FILLED TO THIS MARK
H1
POLE PIECES OF MAGNET

Let a be the area of cross-section of the cylinder in sq. cms.

μ_1 " " permeability of the material

μ_2 " " " " " medium (air)

K_1 " " volume susceptibility of the material

K_2 " " " " " " medium

$$\text{Force } F = \frac{(\mu_1 - \mu_2)\, a\, (H_1^2 - H_2^2)}{8\pi}$$

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

$$\therefore F = \tfrac{1}{2}(K_1 - K_2)\, a\, (H_1^2 - H_2^2)$$

$$\text{or } K_1 = \frac{2F}{a(H_1^2 - H_2^2)} + K_2$$

If X is the mass susceptibility

then $X = \frac{K}{d} = \frac{K}{\ell a} \cdot W$ where W = weight, ℓ = length of tube.

K_2 for air = 0.03×10^{-6} $(\ell a) = V$ = volume

$$\therefore X = \frac{2F\ell}{W(H_1^2 - H_2^2)} + \frac{0.03V}{W}$$

If ℓ is sufficiently large then H_2 is zero. ℓ & H_1 are constant for a given tube and a fixed distance between the polepieces

$\therefore 2\ell/H_1^2 = \alpha$, a constant

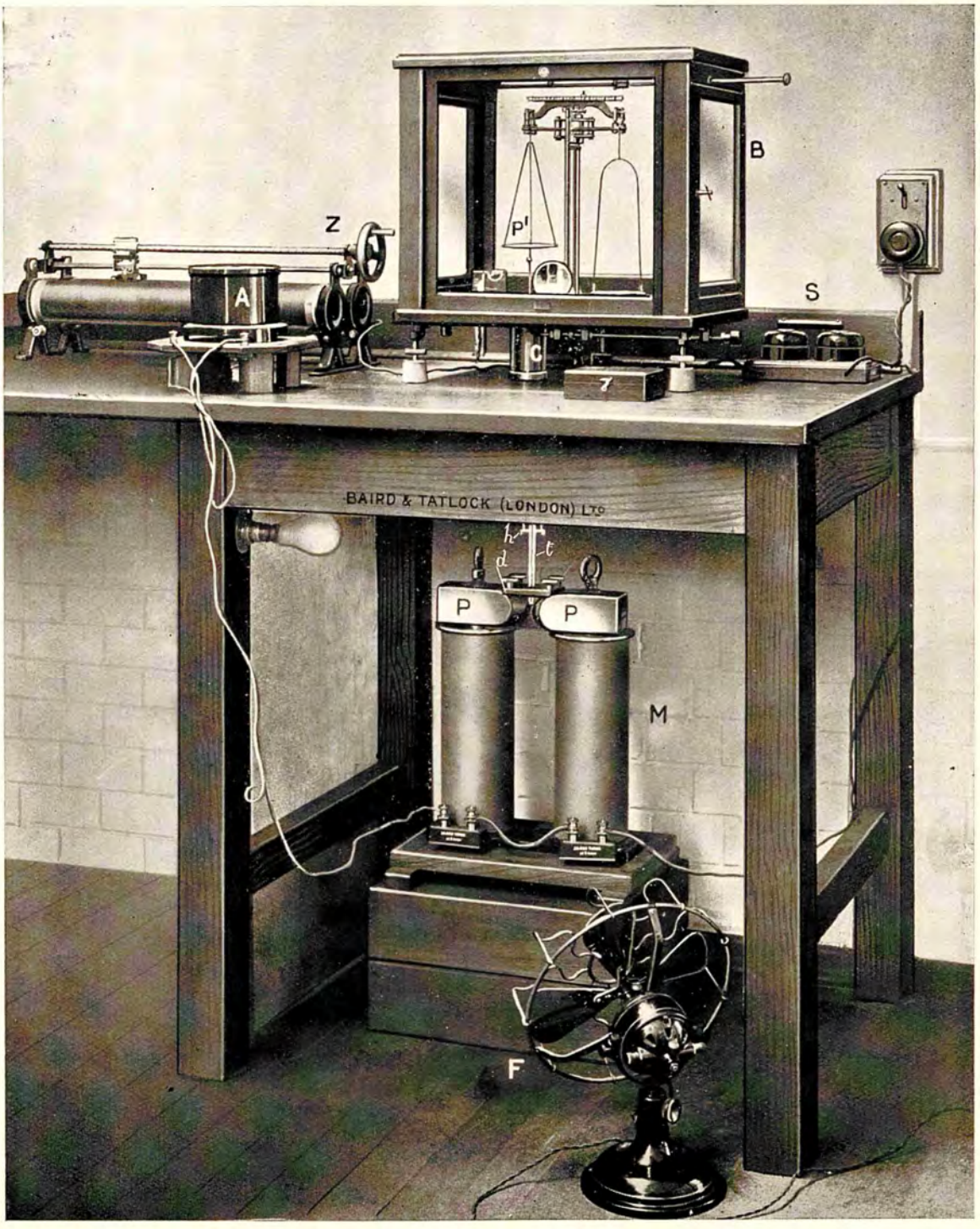
$$\therefore X \times 10^6 = \frac{\alpha F}{W} + \frac{0.03V}{W}$$

DETAILS OF ACTUAL APPARATUS

See Fig.2 Photograph of Apparatus P.18A

An electromagnet of 20,000 turns was used, capable of taking a current of 5 amps. The current used was 3 amps.

There was a distance piece adjustment fixed to the polepieces to maintain a constant distance of 1.2cms between the polepieces. The voltage was 240 and the current was kept at 3 amps by a variable rheastat and registered by an ammeter in the circuit. The current was controlled by a twopole switch.


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

PHOTOGRAPH. FIG. 2.

B. BALANCE
P' = DISC WITH HOOK
S . TWO-POLE SWITCH
Z . RHEOSTAT
A . AMMETER
C . TUBE ENCASING SUSPENSION
P . POLE-PIECES OF MAGNET
M . MAGNET
F . FAN (FOR COOLING MAGNET)
d . DISTANCE-PIECE ADJUSTMENT
t . GLASS TUBE
h = HOOKS OF SUSPENSION ON SIDEARMS OF TUBE

The field obtained was 5000 gauss.

To measure F, the force, a sensitive balance of the Burge type with a short beam was used. This balance was capable of weighing 0.01 mgm. The left hand scale was replaced by a light support and disc, fitted with a hook. The tube was suspended from the hook by a fine platinum wire and copper suspension, so that the bottom of the tube was exactly level with the centre of the polepieces and lay in the maximum field.

The tube was made of glass and fitted with a ground glass stopper. About 1.5cms from the top of the tube were two glass sidearms for suspension. The tube was about 11 cms long and 0.6 cms in diameter; about 7 cms from the bottom of the tube a small mark was made. The tube was always ~~fitted~~ filled to this mark, at which the field was H_2 gauss.

The weight of the tube was found by weighing, by the method of oscillations, and the force due to its magnetic nature was found by the difference in its weight when the magnet was switched on.

Great care had to be takento prevent draughts. The magnet was under a bench and encased in a large wooden box. Round the polepieces and tube a second box was fitted and the suspension was encased in a tube that led directly to the inside of the balance case. The balance case was protected from draughts by curtaining. The magnet had to be kept ~~to~~ cool to prevent convection ~~eddys~~ currents. The apparatus was accurate to 1%

TO FIND THE CONSTANTS OF THE BALANCE.

The value of a α for a given tube was found by measuring the susceptibility of a substance of known susceptibility.

Benzene was used for this determination. The tube was weighed empty and its pull found, and then filled to the mark with pure, distilled, dry benzene. The tube was again weighed and the pull found. To find the pull of a substance, generally,

three sets of readings were taken and the mean found. The mean value of three of these 'means' was used to give the final value of the pull. Three or more packing were done in this way for each compound.

The length of the column was measured and its volume found. Taking the value of χ, the mass susceptibility, for benzene to be -0.716×10^{-6}, a value for α was found.

Tube 1.

Weight = 7.9584 gms. Length of coloumn = 7.25cms.

Pull of Tube Empty:

WEIGHT WITHOUT MAGNET	WEIGHT WITH MAGNET	PULL
8.494 mgms.	7.954 mgms	-0.54 mgms
8.545 "	7.997 "	-0.55 "
8.532 "	7.985 "	-0.55 "
8.478 "	7.930 "	-0.55 "
8.171 "	7.631 "	-0.54 "

Pull of Tube = -0.54 mgs.

Weight of Tube empty = 7.9040 gms

Weight of Tube + water = 11.5757 "

Weight of water = 3.6717 "

Volume of column = 3.6717 ccs

$3.672 \times 0.03 = 0.1102$

Weight of Benzene: = (11.1504 - 7.9584) gms

= 3.1920 gms.

WEIGHT WITHOUT MAGNET	WEIGHT WITH MAGNET	PULL
5.531 gmgs	1.144 mgms	-4.39 mgms
5.496 "	1.104 "	-4.39 "
5.520 "	1.146 "	-4.37 "
5.556 "	1.176 "	-4.38 "
5.398 "	0.986 "	-4.41 "
5.539 "	1.134 "	-4.41 "

Mean value. — 4.39 mgms.

Pull of Tube + Benzene - 4.39 mgms.

Pull of Benzene = - (4.39 - 0.54) mgms = - 3.85 mgms

$$-0.716 = \frac{-(\alpha \times 3.85) + 0.1102}{3.192}$$

$$\alpha = \frac{(0.716 \times 3.192) + 0.1102}{3.85}$$

$\alpha = 0.6223$ $\alpha = 0.6223$

Constant of Balance for Tube 1. = 0.622

TUBE 2

Weight = 8.0553 gms.

Lenght of column = 7.42 cms

Pull of Tube Empty

WEIGHT WITHOUT MAGNET	WEIGHT WITH MAGNET	PULL
5.381 mgms	4.736 mgms	-0.65 mgms
5.309 "	4.634 "	-0.68 "
5.216 "	4.559 "	-0.66 "
5.321 "	4.657 "	-0.66 "
5.298 "	4.640"	-0.66 "

Pull of Tube = -0.66 mgms

Volume of column = 3.6344 ccs

3.634 x 0.03 = 0.1090

Pull of Tube + Benzene

WEIGHT WITHOUT MAGNET	WEIGHT WITH MAGNET	PULL
6.320 mgms	1.915 mgms	-4.41 mgms
6.492 "	2.063 "	-4.43 "
6.245 "	1.863 "	-4.38 "
6.085 "	1.689 "	-4.40 "
5.928 "	1.510 "	-4.41 "

Pull of Tube + Benzene = -4.40 mgms

Weight of Benzene = (11.2143 - 8.0553) gms = 3.1590 gms

Pull of Benzene = - (4.40 - 0.66) mgms = - 3.74 mgms

$$-0.716 = \frac{-(\alpha \times 3.74) + 0.109}{3.159}$$

$$\alpha = \frac{(0.716 \times 3.159) + 0.109}{3.74} = 0.6336$$

CONSTANT OF THE BALANCE FOR TUBE 2 = 0.634

The values of the constants were checked by plotting a graph of the variation between length of column and value of α The values were obtained by different workers using different tubes and liquids. The same field was used in all cases and the relation was found to be ~~l mea~~ linear. Graph 1 P. 22A

The strength of the field can be calculated from these values of α

(I) $0.622 = \frac{14.5 \times 10^3 \times 981}{H_1^2}$ c.g.s.

$$H_1^2 = \frac{14.5 \times 10^3 \times 981}{0.622}$$

$$H_1 = 4782 \text{ gauss}$$

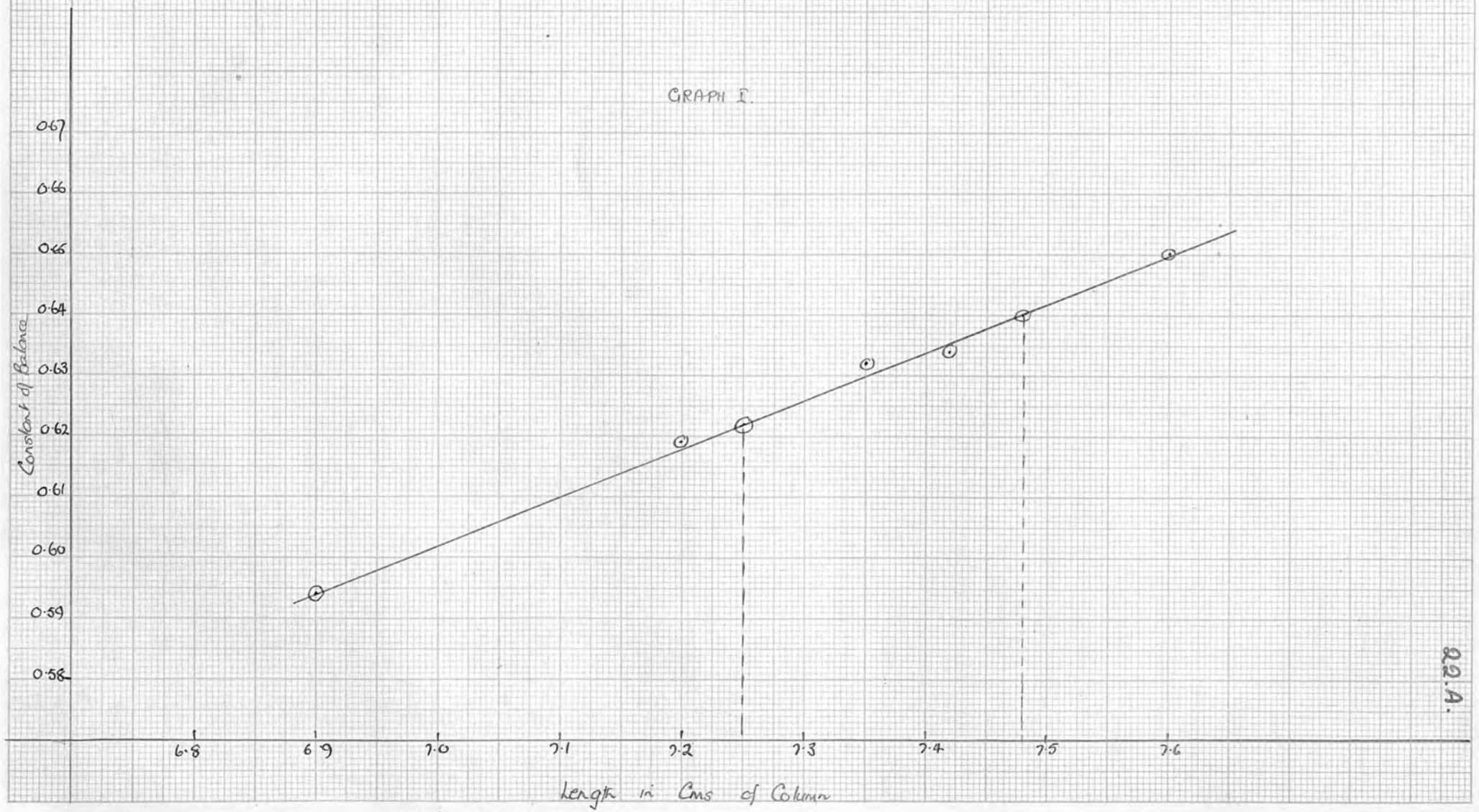
(II) $0.634 = \frac{14.84 \times 10^3 \times 981}{H_1^2}$

$$H_1 = 4792 \text{ gauss}$$

THE METHOD OF MEASUREMENT OF THE COMPOUNDS

To measure a compound, it was ground up into a very fine powder and then packed into the tube by hammering with a flattened glass rod until it was so closely packed that the amount of air-space was negligible. The tube was always filled to the mark, so that the lenght of coloumn was always the same.

GRAPH I.



Q2.A.

The tube was suspended from the balance by means of a very fine platinum wire and copper suspension so that the bottom of the tube was level with the mid-point of the pole-pieces. Care was taken to ensure that the tube was hanging vertically between the polepieces, it was then allowed to become steady. Nine measurements were taken on each packing of the compound and the mean pull for each packing used in calculating the value of X. A mean value of X was then taken. The value of Xm, the gram mass susceptibility was obtained by multiplying the mean value of X by the molecular weight of the compound.

The sticks of zinc were not exactly the same length as the column used in the tube. The value of α for each stick was obtained from graph 1.

Stick A Length = 7.58 cms. α = 0.648

Stick B Length = 7.53 ,, α = 0.644

The volumes of the sticks were found by taking a mean value of their diameters at several places along their lengths.

Stick A Volume = 2.289 ccs.

Stick B Volume = 2.215 ccs.

MATERIAL	WEIGHT IN GMS.	PULL + TUBE IN MGMS.	CORRECTED PULL IN MGM.	MEAN OF NINE MEASUREMENTS X x 10^6	Xm x 10^6
Zinc Metal Stick A	16.7014	-3.87 -3.95 -3.94	-3.66	-0.138	
Reversed	16.7014	-4.04 -4.05 -4.04	-3.78	-0.143	-8.96
Stick B	16.6942	-3.83 -3.92 -3.70	-3.56	-0.134	
Reversed	16.6942	-3.83 -3.92 -3.88	-3.62	-0.36	

COMPOUND	WEIGHT IN GMS.	PULL + TUBE IN MGMS.	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS $X \times 10^6$	$Xm \times 10^6$
Zinc Oxide ZnO	10.3903	- 6.39 - 6.38 - 6.45	- 5.85	- 0.340	
	10.4808	- 6.46 - 6.48 - 6.51	- 5.94	- 0.342	- 27.91
	10.6791	- 6.68 - 6.65 - 6.75	- 6.15	- 0.348	
Zinc Hydroxide $Zn(OH)_2$ (4% Zinc Carbonate)	4.7477	- 2.86 - 2.87 - 2.89	- 2.21	- 0.272	
	4.7044	- 2.83 - 2.80	- 2.15	- 0.267	- 26.54
	4.7507	- 2.80 - 2.73 - 2.83	- 2.18	- 0.261	
	4.8473	- 2.90 - 2.89 - 2.84	- 2.22	- 0.268	
Zinc Fluoride ZnF_2	4.9378	- 3.52 - 3.49 - 3.50	- 2.84	- 0.843	

COMPOUND	WEIGHT IN GMS.	PULL + TUBE IN MGMS.	CORRECTED MEAN PULL. Y - 10	mEAN OF NINE MEASUREMENTS X x 10^6	Xm x 10
	5.1238	- 3.58 - 3.55 - 3.59	- 2.91	- 0.339	- 35.91
	5.2369	- 3.73 - 3.72 - 3.71	- 3.06	- 0.350	
Zinc Chloride $ZnCl_2$	6.4206	- 4.98 - 4.98	- 4.32	- 0.410	
	7.4731	- 5.62 - 5.54 - 5.57	- 4.92	- 0.403	- 55.34
	7.4725	- 5.66 - 5.62 - 5.57	- 4.96	- 0.406	
Zinc Bromide $ZnBr_2$	8.7542	- 5.56 - 5.60 - 5.64	- 5.06	- 0.347	
	8.2515	- 5.51 - 5.41 - 5.37	- 4.89	- 0.355	
	8.4293	- 5.35 - 5.32 - 5.33	- 4.79	- 0.341	- 78.38

COMPOUND	WEIGHT IN GMS.	PULL + TUBE IN MGMS.	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS X x 10^6	Xm x 10^6
Zinc Iodide	9.6390	- 6.07 - 6.05 - 6.00	- 5.50	- 0.344	
	9.4084	- 5.85 - 5.85 - 5.88	- 5.32	- 0.340	- 108.5
	9.6189	- 5.95 - 5.85 - 6.03	- 5.40	- 0.337	
Zinc Iodate $Zn(IO_3)_2$	8.7607	- 4.31 - 4.29 - 4.31	- 3.64	- 0.251	
	8.6644	- 4.18 - 4.17 - 4.19	- 3.52	- 0.245	- 103.8
	8.8302	- 4.37 - 4.30 - 4.40	- 3.70	- 0.253	
Zinc Ammonium Chloride. $ZnCl_2$ $4NH_4Cl$	4.0196	- 4.39 - 4.34 - 4.36	- 3.82	- 0.564	

COMPOUND	WEIGHT IN GMS	PULL + TUBE IN MGMS	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS $\chi \times 10^6$	Xm x 10^6
	4.0411	- 4.38 - 4.37 - 4.36	- 3.83	- 0.562	- 197.2
	4.0485	- 4.36 - 4.34 - 4.35	- 3.81	-0.558	
Zinc Sulphate heptahydrate Tube 1. $Zn\ SO_4\ 7H_2O$	4.7269	- 4.22 - 4.27 - 4.25	- 3.71	- 0.465	
	4.8664	- 4.36 - 4.35 - 4.27	- 3.79	- 0.462	+ 134.7
Tube 2.	4.1585	- 3.94 - 3.90 - 3.89	- 3.25	- 0.469	
	4.1404	~~- 3.97~~ -3.97 - 3.90	- 3.29	- 0.478	
Anhydrous Zinc Sulphate $Zn\ SO_4$.	6.0511	- 3.43 - 3.45 - 3.43	- 2.90	- 0.280	
	5.9975	- 3.60 - 3.60 - 3.60	-3.06	- 0.299	- 47.94
	6.0859 -	- 3.61 - 3.62 - 3.64	- 3.08	- 0.297	

COMPOUNDS	WEIGHT IN GMS	PULL + TUBE IN MGMS	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS X x 10^6	Xm x 10^6
	6.1689	- 3.78 - 3.74 - 3.76	- 3.27	- 0.312	
Zinc Ammonium Sulphate $Zn\ SO_4 . (NH_4)_2\ SO_4 . 6H_2O$	4.3594	- 4.08 - 4.01 - 3.93	- 3.54	- 0.481	
	4.3915	- 4.21 - 4.18 - 3.98	- 3.58	- 0.482	- 194.0
	4.4691	- 4.18 - 4.24 - 4.32	- 3.70	- 0.490	
Zinc Sulphite $ZnSO_3\ 2\frac{1}{2}H_2O$	4.2167	- 2.75 - 2.72 - 2.72	- 2.07	- 0.285	
	4.2637	- 2.91 - 2.80 - 2.84	- 2.19	- 0.300	
	4.5404	- 3.06 - 3.07 - 3.04	- 2.39	- 0.316	- 57.82
	4.4209	- 2.93 - 2.92 - 2.92	- 2.26	- 0.300	
	4.2369	- 2.96 - 2.92 - 2.95	- 2.28	-0.316	

COMPOUND	WEIGHT IN GMS.	PULL + TUBE IN MGMS	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS X x 10^6	Xm x 10^6
Zinc Carbonate $ZnCO_3 \frac{1}{4}H_2O$	4.6946	- 2.83 - 2.83 - 2.87	- 2.19	- 0.273	-35.34
	4.8685	- 2.85 - 2.92 - 2.96	- 2.25	- 0.271	
	4.9845	- 2.96 -2.95 -3.00	- 2.31	- 0.272	
Zinc Nitrate tetrahydrate $Zn(NO_3)_2\ 4H_2O$	4.1042	-3.42 -3.39 -3.41	-2 .75	- 0.399	-103.0
	4.1126	-3.33 -3.42 -3.36	- 2.71	- 0.391	
	4.0707	-3.26 -3.34 -3.41	- 2.68	- 0.391	
Zinc Mercurithiocyanate $Zn\ Hg\ (CNS)_4$	5.3549	-4.16 -4.10 -4.13	-3.47	- 0.391	-197.7
	5.3824	-4.17 -4.21 -4.23	-3.54	- 0.397	
	5.2587	-4.16 -4.18 -4.19	-3.51	-0.402	

COMPOUND	WEIGHT IN GMS	PULL + TUBE IN MGMS	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS $X \times 10^6$	$X_m \times 10^6$
Basic Zinc Chromate $ZnO\ 2CrO_3\ 2H_2O$	5.2176	-1.24 -1.30 -1.29	-0.64	-0.057	
	5.2061	-1.35 -1.23 -1.35	-0.67	-0.061	-19.05
	5.2866	-1.36 -1.37 -1.36	-0.70	-0.063	
Zinc Orthophosphate tetrahydrate $Zn_3(PO_4)_2\ 4H_2O$	4.0972	-0.30 -0.40 -0.37	+0.18	+0.054	
	4.0788	-0.27 -0.28 -0.27	+0.27	+0.068	+28.87
	4.4309	-0.34 -0.30 -0.29	+0.23	+0.057	
	4.2016	-0.22 -0.29	+0.28	+0.068	
	4.0852	-0.22 -0.21 -0.25	+0.31	+0.069	
Anhydrous Zinc orthophosphate $Zn_3(PO_4)_2$	6.1278	-1.75 -1.80 -1.70	-1.21	-0.105	

COMPOUND	WEIGHT IN GMS	PULL + TUBE IN MGMS	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS X x 10^6	Xm x 10^6
$Zn_3(PO_4)_2$	6.3452	-1.77 -1.82 -1.70	-1.24	-0.104	-40.55
	6.2798	-1.79 -1.80 -1.79	-1.26	-0.107	
Zinc Ammonium orthophosphate $Zn\ NH_4\ PO_4$	3.8266	-1.63 -1.66 -1.56	-1.08	-0.147	
	3.9002	-1.28 ? -1.63 -1.66	-1.11	-0.149	-26.56
	3.5105	-1.59 -1.58 -1.59	-1.03	-0.151	
Zinc pyrophosphate. $Zn_2P_2O_7$	6.1792	+1.22 +1.23 +1.22	+1.76	+0.179	
	6.1053	+1.18 +1.15 +1.16	+1.70	+0.191	
	6.0904	+1.22 +1.18 +1.16	+1.69	+0.191	+58.37
	5.8107	+1.07 +1.01 +1.08	+1.71	+0.205	

COMPOUNDs	WEIGHT IN GMS.	PULL + TUBE IN MGMS	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS X x 10^6	Xm x10
Zinc Phosphite $ZnHPO_3 2\frac{1}{2} H_2O$	5.3463	-4.29 -4.29 -4.27	-3.74	-0.415	
	5.4518	-4.34 -4.32 -4.33	-3.79	-0.412	-78.86
	5.4733	-4.360 -4.375 -4.387	-3.83	-0.415	
Zinc ferrocyanide $Zn_2\ Fe\ (CN)_6$	2.4015	-2.10 -2.10 -2.13	-1.57	-0.361	
	2.5015	-2.17 -2.14 -2.19	-1.63	-0.361	-124.8
	2.3734	-2.15 -2.15 -2.15	-1.61	-0.375	
Zinc Ferricyanide $Zn_3\{Fe(CN)_6\}_2$	3.0799	+25.31 +25.41 +25.21	+25.85	+5.27	
	3.0214	+24.89 +24.64 +24.58	+25.25	+5.24	+3273
	3.0275	+25.29 +25.21 +25.45	+25.38	+5.33	

COMPOUNDS	WEIGHT IN GMS	PULL + TUBE IN MGMS	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS $X \times 10^6$	$Xm \times 10^6$
5. Zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$	4.2515	-4.15 -4.07 -4.04	-3.54	-0.494	
	4.3203	-4.13 -4.16 -4.16	-3.61	-0.489	-107.5
	4.3915	-4.16 -4.15 -4.17	-3.62	-0.491	
6. Zinc trichloracetate dihydrate $Zn(CCl_3COO)_2 \cdot 2H_2O$	4.2328	-3.67 -3.62 -3.67	-3.11	-0.431	
	4.1410	-3.52 -3.59 3.64	-3.04	-0.430	-184.5
	4.3733	-3.78 -3.82 -3.78	-3.25	-0.437	
7. Zinc Butyrate $Zn(CH_3CH_2CH_2COO)_2$	3.1891	-2.69 -2.72 -2.72	-2.17	-0.389	
	3.2937	-2.79 -2.78 -2.83	-2.26	-0.394	-94.21
	3.0863	-2.79 -2.75 -2.74	-2.10	-0.396	

COMPOUND	WEIGHT IN GMS	PULL + TUBE IN MGMS	CORRECTED MEAN PULL	MEAN OF NINE MEASUREMENTS X x 10^6	Xm x 10^6
Zinc Oxalate dihydrate $Zn(COO)_2 2H_2O$	3.9256	-3.16 -3.12 -3.10	-2.59	-0.382	
	3.9606	-3.17 -3.14 -3.14	-2.61	-0.382	-72.36
	3.8990	-3.10 -3.11 -3.12	-2.57	-0.382	
Zinc Succinate $Zn(CH_2COO)_2$	3.5273	-2.85 -2.82 -2.84	-2.18	-0.361	
	3.5261	-2.86 -2.85 -2.84	-2.19	-0.363	-66.21
	3.6529	-3.01 -2.96 -2.94	-2.31	-0.371	

A CONSIDERATION OF THE VALUE OF THE ZINC ION.

From the experimental value of the susceptibility of a compound, the susceptibility of one ion can be found, provided the value for the other ion is known, and it is assumed that the additivity law holds.

$$\text{i.e.} \quad X_m = X_c + X_A$$

where X_m is the gram mass susceptibility of the compound and X_A and X_c are respectively the susceptibilities of the anion and cation.

ZINC FLUORIDE

ZnF_2 $X_m = -35.91 \times 10^{-6}$

Stoner's[13] value for the fluorine ion, combined with a divalent metal is -10×10^{-6}

From this the value of the Zinc ion is $-(35.91-20) \times 10^{-6}$

Value of Zinc ion from Zinc Fluoride is

$$-15.91 \times 10^{-6}$$

ZINC CHLORIDE

Stoner's value for the chlorine ion, when in combination with a divalent metal is -22.3×10^{-6}

$ZnCl_2$ $X_m = -55.34 \times 10^{-6}$

$\therefore$ X_m for Zinc ion is $-(55.34-44.6) \times 10^{-6}$

Value of Zinc ion is -10.74×10^{-6}

ZINC BROMIDE $ZnBr_2$

Stoner's value for the bromide ion when in combination with a divalent metal is -34×10^{-6}

$ZnBr_2$ $X_m = -78.38 \times 10^{-6}$

Value for Zinc ion $= -(78.38-68) \times 10^{-6}$

Value of Zinc ion $= -10.38 \times 10^{-6}$

ZINC IODIDE ZnI_2

Stoner's value for the iodide ion, when in combination with a divalent metal is -50×10^{-6}

ZnI_2 $X_m = -108.5 \times 10^{-6}$

X_m for Zinc ion $= -(108.5 - 100) \times 10^{-6}$

Value of X_m for zinc ion $= -8.5 \times 10^{-6}$

ZINC AMMONIUM CHLORIDE $ZnCl_2 4NH_4Cl$

Stoner's value of the susceptibility of ammonium chloride is -34.3×10^{-6}

X_m for $4NH_4Cl = -137.2 \times 10^{-6}$

Value of X_m for $ZnCl_2 4NH_4Cl = -197.2 \times 10^{-6}$

$\therefore$ Value of X_m For $ZnCl_2 = -60 \times 10^{-6}$

Value of X_m for Zinc ion $= -(60 - 44.6) \times 10^{-6}$

Value of X_m for Zinc ion $= -15.4 \times 10^{-6}$

ZINC IODATE $Zn(IO_3)_2$

The value of the Iodate ion was found by Hollens[3], from measurements on iodic acid, to be -45×10^{-6}.

$Zn(IO_3)_2$ $X_m = -103.8 \times 10^{-6}$

$\therefore$ Value of X_m for Zinc ion is $-(103.8 - 90) \times 10^{-6}$

Value of X_m for Zinc ion is -13.8×10^{-6}

ANHYDROUS ZINC SULPHATE $ZnSO_4$

Pascal's value for the sulphate ion is -33.6×10^{-6}.

$ZnSO_4$ $X_m = -47.82 \times 10^{-6}$

Value of X_m for Zinc ion is $-(47.82 - 33.6) \times 10^{-6}$

Value of X for Zinc ion is -14.22×10^{-6}

ZINC SULPHATE HEPTAHYDRATE $ZnSO_4 7H_2O$

Value of X_m for water is -13×10^{-6}

$\therefore$ Value of X_m for seven molecules of water is -91×10^{-6}

X_m for $ZnSO_4 7H_2O$ is -134.7×10^{-6}

Value of X_m for $ZnSO_4$ is $-(134.7 - 91) \times 10^{-6}$

$= -43.7 \times 10^{-6}$

Value of X for Zinc ion is $-(43.7 - 33.6) \times 10^{-6}$

Value of X for Zinc ion is $\underline{-10.1 \times 10^{-6}}$

ZINC AMMONIUM SULPHATE $ZnSO_4(NH_4)_2SO_4 6H_2O$

The value of the molecular susceptibility of Ammonium sulphate was found by Spencer and Sister Mary Cecilia, from a private communication, to be -71.57×10^{-6}.

Value of X_m for six molecules of water is -78×10^{-6}

Value of X_m for $ZnSO_4(NH_4)_2SO_4 6H_2O$ was found to be -194.0×10^{-6}

Value of X_m for $ZnSO_4 = -(194.0 - 78 - 71.57) \times 10^{-6}$

$= -44.43 \times 10^{-6}$

Value of X for Zinc ion is $-(44.43 - 33.6) \times 10^{-6}$

Value of X for Zinc ion is $\underline{-10.83 \times 10^{-6}}$

ZINC CARBONATE $ZnCO_3 \frac{1}{4}H_2O$

The value of X_m for the Carbonate ion can be calculated by Pascal's method.

The structure of the carbonate ion is $\left[O = C \begin{matrix} O \\ O \end{matrix} \right]''$

Value for carbon atom $= -6.2 \times 10^{-6}$

Value for $\begin{matrix} C \\ \diagdown \\ C{=}O \end{matrix}$ $= -8.3 \times 10^{-6}$

$\therefore$ Susceptibility of ion $= -(6.2 + 2 \times 8.3) \times 10^{-6}$

$= -22.8 \times 10^{-6}$

$ZnCO_3 \frac{1}{4}H_2O$ X_m $= -35.34 \times 10^{-6}$

Value of X_m for $\frac{1}{4}H_2O$ $= -3.25 \times 10^{-6}$

Value of X for Zinc ion $= -(35.34 - 22.8 - 3.25) \times 10^{-6}$

Value of X for Zinc ion $= \underline{-9.29 \times 10^{-6}}$

ZINC NITRATE QUADRIHYDRATE $Zn(NO_3)_2 4H_2O$

The value for the susceptibility of the nitrate ion obtained by Sugden[2] is -18.0×10^{-6}

X_m for $Zn(NO_3)_2 4H_2O$ was found to be -103.0×10^{-6}

Value of X_m for Zinc ion is $-\{103.0 - (4 \times 13) - (2 \times 18)\} \times 10^{-6}$

$= -\{103.0 - 52 - 36\} \times 10^{-6}$

Value of X for Zinc ion is $\underline{-15.0 \times 10^{-6}}$

ZINC SULPHITE $ZnSO_3 2\frac{1}{2}H_2O$

The value of X for $Na_2SO_3 7H_2O$ which is given in the International Critical Tables is -0.462×10^{-6}. This gives a value of X_m for the sulphite ion $= -15.02 \times 10^{-6}$.

The value of X_m for zinc sulphite was found to be -57.82×10^{-6}

$\therefore X_m$ for $ZnSO_3 = -(57.82 - 32.5) \times 10^{-6}$

$= -25.32 \times 10^{-6}$

Value of X for zinc ion is $-(25.32 - 15.02) \times 10^{-6}$

Value of X for zinc ion is $\underline{-10.3 \times 10^{-6}}$

ZINC FERROCYANIDE

The value of X for potassium ferrocyanide trihydrate which is given in the International Critical Tables is -0.420×10^{-6}

This gives a value of X_m for the ferrocyanide ion

$X_m = -84.8 \times 10^{-6}$

$Zn_2Fe(CN)_6$ $X_m = -124.8 \times 10^{-6}$

Value of X_m for zinc ion is $-\frac{1}{2}(124.8 - 84.8) \times 10^{-6}$

X for zinc ion is $\underline{-20 \times 10^{-6}}$

ZINC ACETATE DIHYDRATE

The value for the molar susceptibility of the acetate ion was calculated by Pascal's method. The structure of the acetate ion is $\left[CH_3 - C\begin{matrix}O\\ \\O\end{matrix}\right]'$.

Value of X_m for acetate ion is:

$-\{(2 \times 6.2) + 8.3 + (3 \times 3.0)\} \times 10^{-6}$

Value of acetate ion : $X_m = -29.7 \times 10^{-6}$

The value of X_m for $Zn(CH_3.COO)_2.2H_2O$ was -107.5×10^{-6}

Value of X_m for $Zn(CH_3.COO)_2 = -81.5 \times 10^{-6}$

Value of X for zinc ion $= -(81.5 - 59.4) \times 10^{-6}$

Value of X for Zinc ion $= \underline{-22.1 \times 10^{-6}}$

ZINC OXALATE DIHYDRATE

The value of X_m for the oxalate ion was also calculated by Pascal's method.

The structure of the oxalate ion is $\left[\begin{matrix} O & & \\ & \diagdown & C - O \\ O = & C & - O \end{matrix}\right]''$

$\therefore$ Value of $X_m = -\{(2 \times 6.2) + (2 \times 8.3)\} \times 10^{-6}$

$= -29.0 \times 10^{-6}$

The molar susceptibility of $Zn(COO)_2.2H_2O$ was found to be -72.36×10^{-6}

Value of the susceptibility of the zinc ion =

$-(72.36 - 26 - 29) \times 10^{-6}$

X_m for zinc ion = $\underline{-17.36 \times 10^{-6}}$

ZINC SUCCINATE

The value for the susceptibility of the succinate ion was also calculated.

The structure of the ion is $\left[\begin{matrix} CH_2 - C & O & \\ & & - O \\ CH_2 - C & & - O \\ & O & \end{matrix}\right]''$

The value of the molar susceptibility of the succinate ion is $-\{(4 \times 6.2) + (4 \times 3.0) + (2 \times 8.3)\} \times 10^{-6}$

Value of X for succinate ion is -53.4×10^{-6}

The molar susceptibility of zinc succinate is -66.21×10^{-6}

$\therefore$ Value of X for zinc ion = $-(66.21 - 53.4) \times 10^{-6}$

Value of X for zinc ion = $\underline{-12.81 \times 10^{-6}}$

In the following table δ represents the ionic susceptibility of the anion:-

SUBSTANCE	N	$-10^6 X$	$-10^6 X_m$	$-\delta \times 10^6$	$-10^6 X$ Zinc Ion
ZnF_2	48	0.344	35.91	10	15.91
$ZnCl_2$	64	0.406	55.34	222.3	10.74
$ZnBr_2$	100	0.348	78.38	34	10.38
ZnI_2	136	0.340	108.5	50	8.5
$Zn(IO_3)_2$	184	0.250	103.8	45	13.8
$ZnCl_2.4NH_4Cl$	176	0.563	197.2	22.3	15.2
$ZnSO_4 7H_2O$	148	0.468	134.7	33.6	10.58
$ZnSO_4(NH_4)_2SO_4 6H_2O$	208	0.484	194.0	33.6	11.27
$ZnSO_4$	78	0.297	47.82	33.6	14.42
$ZnSO_3 2½H_2O$	95	0.302	57.82	15.0	10.3
$ZnCO_3 ¼H_2O$	62.5	0.272	35.34	22.8	9.30
$Zn(NO_3)_2 4H_2O$	132	0.394	103.0	18.0	9.16
$Zn_2Fe(CN)_6$	134	0.365	124.8	84.8	20.0
$Zn(CH_3COO)_2 2H_2O$	112	0.491	107.5	29.7	22.1
$Zn(COO)_2 2H_2O$	94	0.382	72.36	29.0	17.36
$Zn(CH_2.COO)_2$	90	0.365	66.21	53.4	12.81

The values of the trichloracetate and butyrate ions were not known. The calculated value of the butyrate ion was found to be -54.1×10^{-6}. This gives a value of the zinc ion of $+13.9 \times 10^{6}$. As the butyrate was not pure the value cannot be relied upon.

The hydroxide contained 4.01% of zinc carbonate. From the measurements made upon $ZnCO_3 ¼H_2O$, it is found that the difference in pull due to this impurity is + 0.002 mgms. This difference is not appreciable and is not outside the limits of experimental error. The value of the molar susceptibility of zinc hydroxide is -26.54×10^{-6}.

A value of the susceptibility of aqueous potassium hydroxide is given in I.C.T. $X = -0.33 \times 10^{-6}$. This gives

the value of X for the hydroxyl ion to be -5.1×10^{-6}. Using this value the susceptibility of the zinc ion is found to be -16.34×10^{-6}.

The behaviour of the zinc phosphates was found to be anomalous and a value for the zinc ion could not be obtained from them.

The values obtained for the susceptibility of the zinc ion are approximately constant . The values are sufficiently close for a mean value to be taken. The salts of the mineral acids agree most closely, this is to be expected as they would be the most highly ionised. The organic salts and the ferrocyanide give a value which is too high. This discrepancy of organic salts has already been noted by Spencer and Hollens[3] in the work on the Cadmium compounds and by Trew[4] in the work on the Thallium compounds.

The imperfect agreement shows that the compounds of zinc do not obey completely the additivity law. This was expected as the compounds of zinc have strong covalent tendencies.

In finding the mean experimental value of the zinc ion, the values obtained from zinc ferrocyanide and zinc acetate were omitted, as they were too high.

Mean Experimental value of the susceptibility of the Zinc Ion is -12.40×10^{-6}.

THE THEORETICAL VALUE OF THE ZINC ION.

According to the Langevin[12] equation

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

where the symbols have the significance delined on page 2. Before a value of X can be calculated, the value of $\Sigma\bar{r}^2$ the mean square radius must be found.

a) Slater[14] has formulated a set of rules by means of which the value of $\Sigma\bar{r}^2$ can be calculated.

Slater extended the work done by Zener[15] on shielding constants. The radial part of a wave function of a single electron is given by

$$\psi \chi = r^{n'-1} e^{-\{(z-s)/n'r\}}$$

where Z is the nuclear charge; r is the radius in atomic units ($a_o = 0.532 \times 10^{-8}$); s is the screening constant; and n' is the effective quantum number. Therefore $(Z-s)$ is the effective nuclear charge.

Slater has derived a set of semi-empirical rules which give good agreement between the experimental and calculated energy values. The total negative energy of an atom in Rydberg units is the sum of the values of $\{(Z-s)/n'\}^2$ for all electrons.

For the calculation of the value of the susceptibility of an atom or an ion the value of the mean square radius, $\bar{r}^2$ for all electrons is required.

The electron density per unit radial thickness is given by $4\pi r^2 \chi^2$

$$\therefore \bar{r}^2 = \frac{\int_0^\infty r^2 (4\pi r^2 \chi^2)\, dr}{\int_0^\infty (4\pi r^2 \chi^2)\, dr}$$

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

The susceptibility equation however involves $\Sigma_M \bar{r}^2$ which is the value of $\bar{r}^2$ summed over all the electrons in the atom or ion.

$$X_A \times 10^6 = -2.83 \times 10^{10} (0.528 \times 10^{-8})^2 \frac{\Sigma (n')^2 (n'+\frac{1}{2})(n'+1)}{(Z-s)^2}$$

2.83×10^{10} is the value of $e^2N/6mc^2$

and $\bar{r}$ was in atomic units

$$X_A \times 10^6 = -0.790 \frac{\Sigma (n')^2 (n'+\frac{1}{2})(n'+1)}{(Z-s)^2}$$

X_A is now in susceptibility units.

Slater assigned values of n', the effective quantum number, and (Z-s) the effective atomic number, to the electrons in each shell of the atom or ion and so a complete set of wave functions is obtained.

The semi-empirical rules which Slater put forward are:-

(i) The effective quantum number is assigned in terms of the principal quantum number n.

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

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

(ii) For determining the value of (Z-s) the electrons are divided into groups each having a different screening constant. The groups are:-

1s; 2s,p; 3s,p; 3d; 4s,p; 4d; 4f; .....

Thus the s and p groups for a given principal quantum level are grouped together. The shells are considered as arranged from inside out, i.e., in the order given.

(iii) The value of the screening constant for any group is formed from the following contributions:-

a) Nothing from any shell outside the one considered.

B) Amount 0.35 from each electron in group considered (except in 1s shell when 0.30 is used).

c) If shell is an sp shell then it is affected by an amount 0.85 from each electron with total quantum number less by one than group considered, and an amount 1.00 from each group still nearer the nucleus.

If the shell is a d or an f shell then the amount an electron is shielded by each electron in its own shell is 1.00.

By means of these rules (Z-s) is evaluated for a given ion and hence the value of $\tilde{r}^2$ for each shell. By computation the value of the mean ionic radius is found and thus the value of X for the ion.

CALCULATION OF THE VALUE OF X FOR THE ZINC ION BY SLATER'S METHOD.

Atomic number of zinc is 30, i.e., Z = 30.
The Zinc ion has lost two electrons, Zn^{++}, so that its electron states are 2: 8: 18., i.e., $1s^2$; $2s^2 2p^6$; $3s^2 3p^6$; $3d^{10}$.

Values of s

$1s^2$: 1 x 0.30 = 0.30
$2s^2p^6$: (7 x 0.35) + 2(0.85) = 4.15
$3s^2p^6$: (7 x 0.35) + 8 x 0.85 + 2 x 1.00 = 11.25
$3d^{10}$: 9 x 0.35 + 18 x 1.00 = 21.15

Values of (Z-s)

$1s^2$: 30 - 0.30 = 29.70
$2s^2p^6$: 30 - 4.15 = 25.85
$3s^2p^6$: 30 - 11.25 = 18.75
$3d^{10}$: 30 - 21.15 = 8.85

Values of $\tilde{r}^2$

$$\tilde{r}_1^2 = \frac{2 \cdot 1^2 \times \frac{3}{2} \times 2}{(29.70)^2} = 0.0068$$

$$\bar{r}_2^{-2} = \frac{8 \cdot 2^2 \times 5/2 \times 3}{(25.85)^2} = 0.2882$$

$$\bar{r}_3^{-2} = \frac{9 \cdot 3^2 \times 7/2 \times 4}{(18.75)^2} = 2.869$$

$$\bar{r}_{3d}^{-2} = \frac{10 \cdot 3^2 \times 7/2 \times 4}{(8.85)^2} = 16.09$$

$$\sum_N \bar{r}^{-2} = 16.09 + 2.869 + 0.2882 + 0.0068$$
$$= 19.254 \text{ atomic units}$$

$$-X_A \times 10^6 = 0.790 \times 19.254$$

$$X_{Zn} = -15.21 \times 10^{-6}$$

THE BRINDLEY - SLATER METHOD

Brindley modified Slater's method of calculation by using the proportional distribution of the electrons. This method was the first used by Ikenmeyer[16] in his work on the alkali halides. He assumed the ionic susceptibilities were inversely proportional to the nuclear charges. He found the gram molecula susceptibility of CsI was -95×10^{-6}
Both Cs^+ and I' have 54 electrons but nuclear charge for Cs^+ is 55 and for I' is 53.
This gives $X_{Cs^+} = -45.75 \times 10^{-6}$

$$X_{I'} = -49.25 \times 10^{-6}$$

The inverse ratio used by Ikenmeyer is not exact. Brindley[17] suggested it would be more accurate to use the effective atomic number i.e. (Z -s)

He first calculated the value of $X_A \times 10^{-6}$ for each ion using the Slater method.

This gave for CsI $X_{Cs} = -39.4 \times 10^{-6}$

$X_{I} = -59.8 \times 10^{-6}$

Total value is -99.2×10^{-6}

He then took the experimental value of CsI in this ratio and obtained the value of XA for the ions. Experimental value -92.5×10^{-6}

i.e. $-\frac{39.4}{99.2} \times 92.5 = -36.8$

and $-\frac{59.8}{99.2} \times 92.5 = -55.7$

$X_{Cs^+} = -36.8 \times 10^{-6}$

$X_{I'} = -55.7 \times 10^{-6}$

VALUE OF ZINC ION BY THE BRINDLEY SLATER METHOD.

(I) Zinc Bromide

Zinc ion by Slater method gives value

$X_{Zn^{"}} = -15.21 \times 10^{-6}$

Bromide ion by Slater method gives value

$X_{Br'} = -39.29 \times 10^{-6}$

$\therefore$ Xm Zn $Br_2 = -(15.21 + 78.58) \times 10^{-6}$

-93.79×10^{-6}

Experimental value $= -78.38 \times 10^{-6}$

Value for Zinc ion: $-\left\{\frac{15.21}{93.79} \times 78.38\right\} \times 10^{-6}$

$= \underline{-12.72 \times 10^{-6}}$

(II) Zinc Chloride

Slater's method gives value for $X_{Cl'} = -25.24 \times 10^{-6}$

$\therefore$ Xm for Zn $Cl_2 = -(15.21 + 50.48) \times 10^{-6}$

$= -65.69 \times 10^{-6}$

the Experimental value for Zinc Chloride

$= -55.34 \times 10^{-6}$

$$\text{Value for zinc ion} = -\left\{\frac{15.21}{65.69} \times 55.34\right\} \times 10^{-6}$$

$$\underline{X_{Zn^{++}} = -12.81 \times 10^{-6}}$$

ANGUS' MODIFICATION OF SLATER'S METHOD.

Angus[18] used Slater's formula

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

and applied Slater's rules but considered the s & p electrons separately and thus obtaining a different value of the ionic susceptibility, which will agree better with the experimental value.

VALUES OF SCREENING CONSTANTS

$1s^2$	$= 1 \times 0.30$	$= 0.30$
$2s^2$	$= (1 \times 0.35) + (2 \times 0.85)$	$= 2.05$
$2p^6$	$= (7 \times 0.35) + (2 \times 0.85)$	$= 4.15$
$3s^2$	$= (1 \times 0.35) + (8 \times 0.85) + (2 \times 1.00)$	$= 9.15$
$3p^6$	$= (7 \times 0.35) + (8 \times 0.85) + (2 \times 1.00)$	$= 11.25$
$3d^{10}$	$= (9 \times 0.35) + 18(1.00)$	$= 21.15$

VALUES OF EFFECTIVE NUCLEAR CHARGE

$1s^2$	$= 30 - 0.30$	$= 29.70$
$2s^2$	$= 30 - 2.05$	$= 27.95$
$2p^6$	$= 30 - 4.15$	$= 25.85$
$3s^2$	$= 30 - 9.15$	$= 20.85$
$3p^6$	$= 30 - 11.25$	$= 18.75$
$3d^{10}$	$= 30 - 21.15$	$= 8.85$

$$\bar{r}^2_{1s} = \frac{2 \times 1 \times \frac{3}{2} \times 2}{(29.70)^2} = 0.0068$$

$$\bar{r}^2_{2s} = \frac{2 \times 4 \times \frac{5}{2} \times 3}{(27.95)^2} = 0.0768$$

$$\bar{r}^2_{2p} = \frac{2 \times 4 \times \frac{5}{2} \times 3}{(25.85)^2} = 0.2882$$

$$\bar{r}^2_{3s} = \frac{2 \times 9 \times \frac{7}{2} \times 4}{(20.85)^2} = 0.5929$$

$$\bar{r}^2_{3p} = \frac{8 \times 9 \times \frac{7}{2} \times 4}{(18.75)^2} = 2.869$$

$$\bar{r}_{3d} = \frac{10 \times 9 \times \frac{7}{2} \times 4}{(8.85)^2} = 16.09$$

$$\sum \bar{r}^2 = 19.92$$

$$-X_A \times 10^6 = 0.79 \times 19.92 = -15.73$$

$$X_{Zn}.. = -15.73 \times 10^{-6}$$

This modification has no theoretical basis.

The screening effect of the s level electrons is considered twice; first separately and then again, together with the p level electrons.

Thus for example the two s electrons when considered alone would exert a screening effect.

$$2s^2 = \{(1 \times 0.35) + (2 \times 0.85)\}$$

If the screening effect of the six P electrons is now to be considered the value should be

$$2p^6 = \{(5 \times 0.35) + (2 \times 0.85)\}$$

but Angus groups the s electrons he has already considered with the six p electrons obtaining a value given by

$$2p^6 = \{(7 \times 0.35) + 2(0.85)\}$$

By this method each s electron exerts a double screening effect, i.e., 0.70 on electrons in its own level instead of 0.35.

COMPARISON OF RESULTS

Method of obtaining Value	$-X_{Zn}$ " x 10^6
Slater	15.21
Slater-Brindley	12.72 ; 12.81
(Angus)	15.73
Experimental Mean Value	12.40

There is good agreement between the experimental value and the theoretical value obtained by the Brindley-Slater method. It has been found that, provided the ion has a small atomic number, the agreement is generally good.

THE RELATIONS BETWEEN SUSCEPTIBILITY AND TOTAL NUMBER OF ELECTRONS

To find whether there was any regularity displayed amongst a series of compounds containing a common ion, a graph was drawn with value of - Xm x 10^6 as ordinates and the total number of electrons in the compound, i.e N as abscissae (Graph II) P.50A

The points were found to fall approximately on to three parallel straight lines. Since the lines were straight their equations could be found in terms of Tan θ and C, where Tan θ is a measure of the slope of the line and C is the value of Xm when the atomic number is zero.

$$- Xm \times 10^6 = \text{Tan } \theta N + C$$

Since the lines are parallel, Tan D is the same for them all

$$\text{Tan } \theta = -0.822$$

The value of C however is different for each line

Line (I) C = +13.8

Line (II) C = -4.0

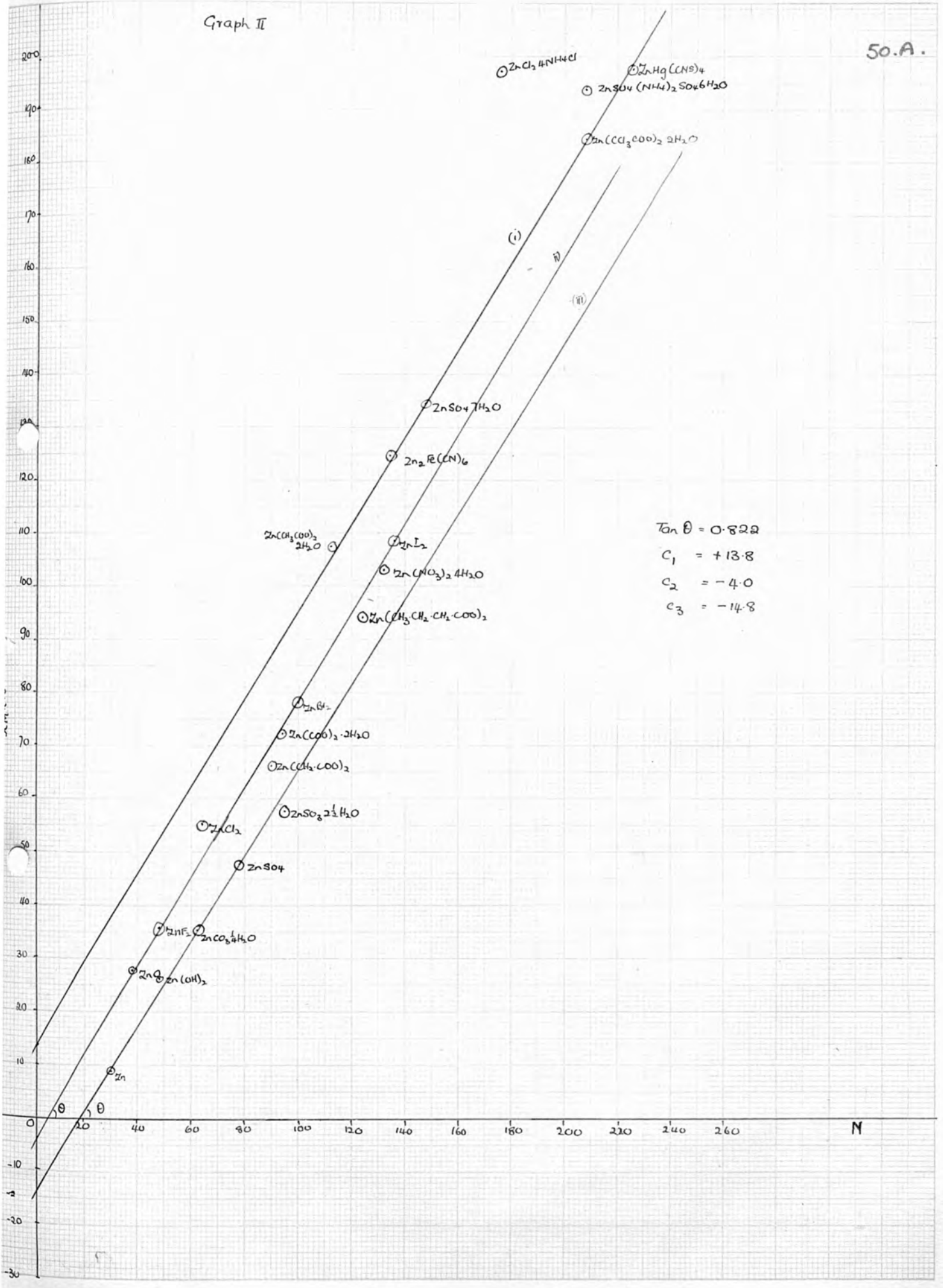
Line (III) C = -14.8

Equation of line (I) $-Xm \times 10^6 = + 0.822N + 13.8$

Equation of line (II) $-Xm \times 10^6 = + 0.822N - 4.0$

Equation of line (III) $-Xm \times 10^6 = + 0.822N - 14.8$

Graph II



$\tan \theta = 0.822$

$C_1 = +13.8$

$C_2 = -4.0$

$C_3 = -14.8$

Since the value of tan θ is constant, the mean square radius of the common ion is constant, since tan θ is a measure of the variation of susceptibility with electron number, and since susceptibility is a function of the mean square radius.
Tan $\theta = -0.822 \times 10^{-6}$; this means that the gram mass susceptibility per electron is -0.822×10^{-6}

From the Largevin[12] equation it follows, by substituting numerical values that

$$\chi_m = -2.85 \times 10^{10} \sum_N \bar{r}^2$$

Since the value of χ_m per electron is -0.822×10^{-6} a value of the mean square radius can be calculated

$$-0.822 \times 10^{-6} = -2.85 \times 10^{10} \sum_N \bar{r}^2$$

$$\sum \bar{r}^2 = \frac{0.822 \times 10^{-6}}{2.85 \times 10^{10}} = 0.2885 \times 10^{-16}$$

$$\bar{r}^2 = (0.537 \times 10^{-8})^2$$

This radius value can be compared with the radius of the innermost hydrogen orbit, which, calculated on the Bohr theory, has a radius of 0.532×10^{-8} cm

This value of 0.532×10^{-8} does not alter much with the size of ion, and as the zinc ion is small it would be expected that values of the radii would be comparable.

A similar type of compound occupies each line. Line II runs through the points of zinc fluoride, bromide, iodide and oxide. These are all binary compounds and three of them are halides.

The zinc salts of the oxyacids such as anhydrous zinc sulphate, zinc sulphite and zinc carbonate all lie approximately on line III.

The compounds of line I are complex compounds such as zinc ferrocyanide and zinc mercurithiocyanate,

This regularity suggests that there may be some relationship between susceptibility and molecular structure, since compounds of the same type have the same values of tan θ and C.

Goldschmidt[19] put forward the theory that there is a relationship between atomic radius and co-ordination number. The theory was developed from a classification of crystals with regard to

their types of co-ordination number, i.e. to the arrangement of the atoms with regard to each other. It was found that a change in structure in a series of similar compounds occurred at a certain limiting point. This limit depended upon interatomic distances, i.e the sum of the radii of the two atoms in the molecule. The limits were determined in terms of the quotient $R_A : R_X$ where R_A & R_X are the radii of the atoms A and X in the compound AX. At a certain value of $R_A : R_X$ a change in structure occurred, i,e a change in co-ordination number.

If two atoms are considered in a series of comparable states, such as the magnesium and fluorine atoms joined by a single bond (- Mg-F) as in magnesium fluoride MgF_2 and in magnesium potassium fluoride $KMgF_3$, it is found that the interatomic distance is constant to a first approximation. There are however, beyond this, regular and measurable departures from additivity which are partly correlated to the type of co-ordination. That is the ionic radius is modified by the co-ordination number, which is the number of ions of opposite sign surrounding the ion in question, as also by the nature and size of such ions. The influence of co-ordination number upon interatomic distances was found to be :-

For a transition of co-ordination No.8 to 6 there was a decrease of radius 3%

For a transition 6 to 4 there was a decrease of ~~5.8%~~ 5% - 8%

And for transitions of 8 to 4 and 6 to 3 there was a decrease of 3%.

Similar variations in atomic diamagnetic susceptibility would be expected to follow

$$X = \frac{-Ne^2}{6Mc^2} \sum_{1N} \bar{r}^2$$

which gives $X = -0.790 \sum \bar{r}^2$

There atomic susceptibility is proportional to the mean square radius. Hence if the radius of the atom is altered by co-ordination number, the susceptibility will be similarly effected.

If there had been no variation in the susceptibility of the common ion the values plotted in Graph II would all approximate to one line. The variation of the value of C however indicates that there is a regular and definite modification of the susceptibility. The compounds on a particular line are of similar type and have probably the same co-ordination number. The halides of zinc are all similar and would be expected to have the same co-ordination. These are colinear.

THE COMPLEX COMPOUNDS OF THE FERROCYANIDE LINE

This line has an equation

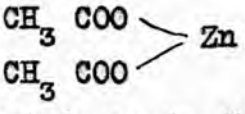
$$-Xm \times 10^6 = 0.822N + 13.8$$

and has on it the compounds; zinc acetate dihydrate; zinc ferrocyanide zinc sulphate heptahydrate; zinc ammonium sulphate; zinc mecuri-thiocynate.

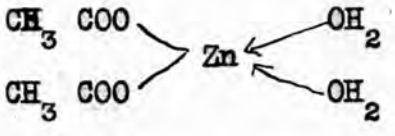
Superficially there seems to be little justification for the colinear nature of these compounds. If there is a connection between co-ordination number and susceptibility, then these compounds should have a similar structure with respect to their common atom, Zinc.

ZINC ACETATE DIHYDRATE $Zn(CH_3.COO)_2\ 2H_2O$

In the anhydrous state, the zinc in this compound will have only four electrons in its outer shell, unless it is ionised, which is unlikely

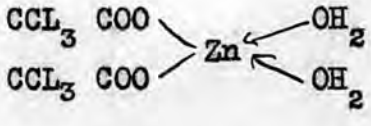


If two molecules of water are co-ordinated on to the zinc ~~action~~ atom, its ~~outer~~ octet will be complete and all the atoms satisfied.



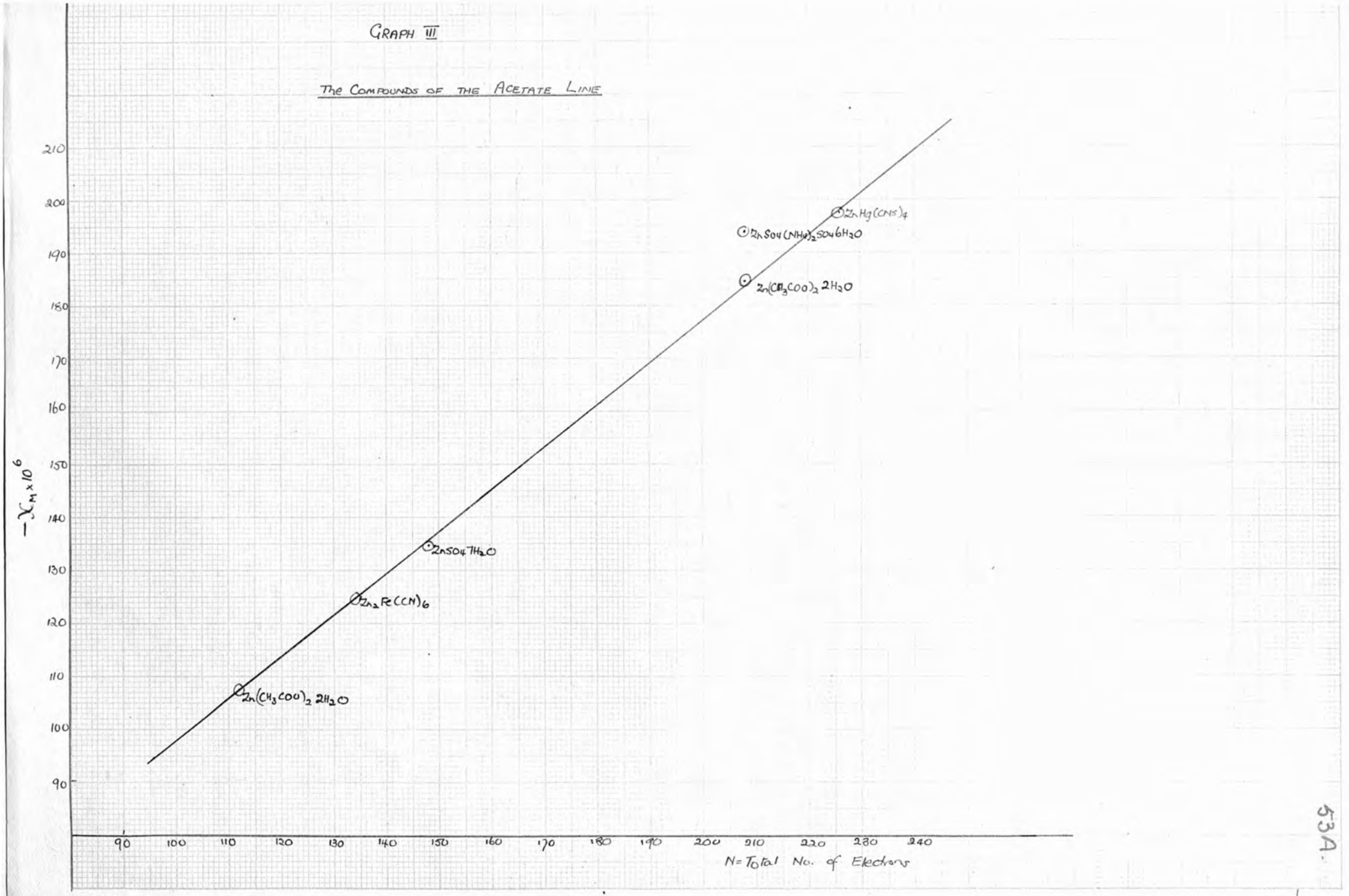
ZINC TRICHLORACETATE DIHYDRATE

The structure of this compound will be similar to that of the acetate since it is only in the chain of the anion that it is altered



GRAPH III

The Compounds of the Acetate Line



53A.

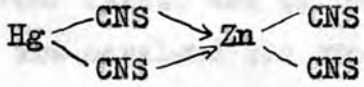
ZINC MECURITHIOCYANATE $Zn\ Hg\ (CNS)_4$

This is a compound formed between zinc thiocyanate and mecuric thiocyanate.

The structures of the two individual compounds are similar

The most likely method for the formation of the double compound is the co-ordination of one molecule on to the metallic part of the other. Mecuric thiocyanate in its higher state of valency so it is unlikely that it will undergo further co-ordination.

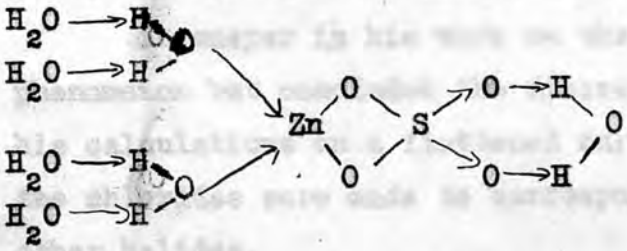
The structure of the compound if $Hg\ (CNS)_2$ is co-ordinated on to the zinc atom would be



ZINC SULPHATE HEPTAHYDRATE

Sidgwick[20] in "The Electronic Theory of Valency" gives the structure of the group of compounds of general formula $M''SO_4\ 7H_2O$ as, $(M''(H_2O)_6)\ SO_4H_2O$; the structure of zinc sulphate heptahydrate is therefore $(Zn\ (H_2O)_6)\ SO_4\ H_2O$

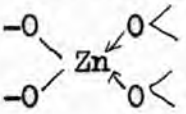
If the six molecules of water were all co-ordinated directly on to the zinc atom it would mean there being twelve electrons in its outer shell. A more likely structure would be



ZINC AMMONIUM SULPHATE $ZnSO_4\ (NH_4)_2\ SO_4\ 6H_2O$

Sidgwick[20] has stated that the vitriols are remarkable for giving a series of double salts with alkali sulphates of general form $M_2'\ SO_4\ M''\ SO_4\ 6H_2O$ in which one molecule of water appeared to be replaced by a molecule of alkali sulphate.

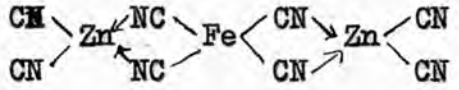
If this theory is correct the co-ordination number of the zinc atom, in zinc ammonium sulphate, would be unaltered by the replacement, that is zinc would still occupy a similar position, with respect to its surrounding atoms,



to that in zinc sulphate heptahydrate

ZINC FERROCYANIDE $Zn_2 Fe(CN)_6$

A possible structure of zinc ferrocyanide is



If the structures of these compounds are correct, the zinc atom, which is common to all of them, is in the same state of co-ordination in each compound. It is surrounded by four oxygen atoms in four cases, and by four sulphur atoms in one case. Two of the links are covalent and two are co-ordinate bonds.

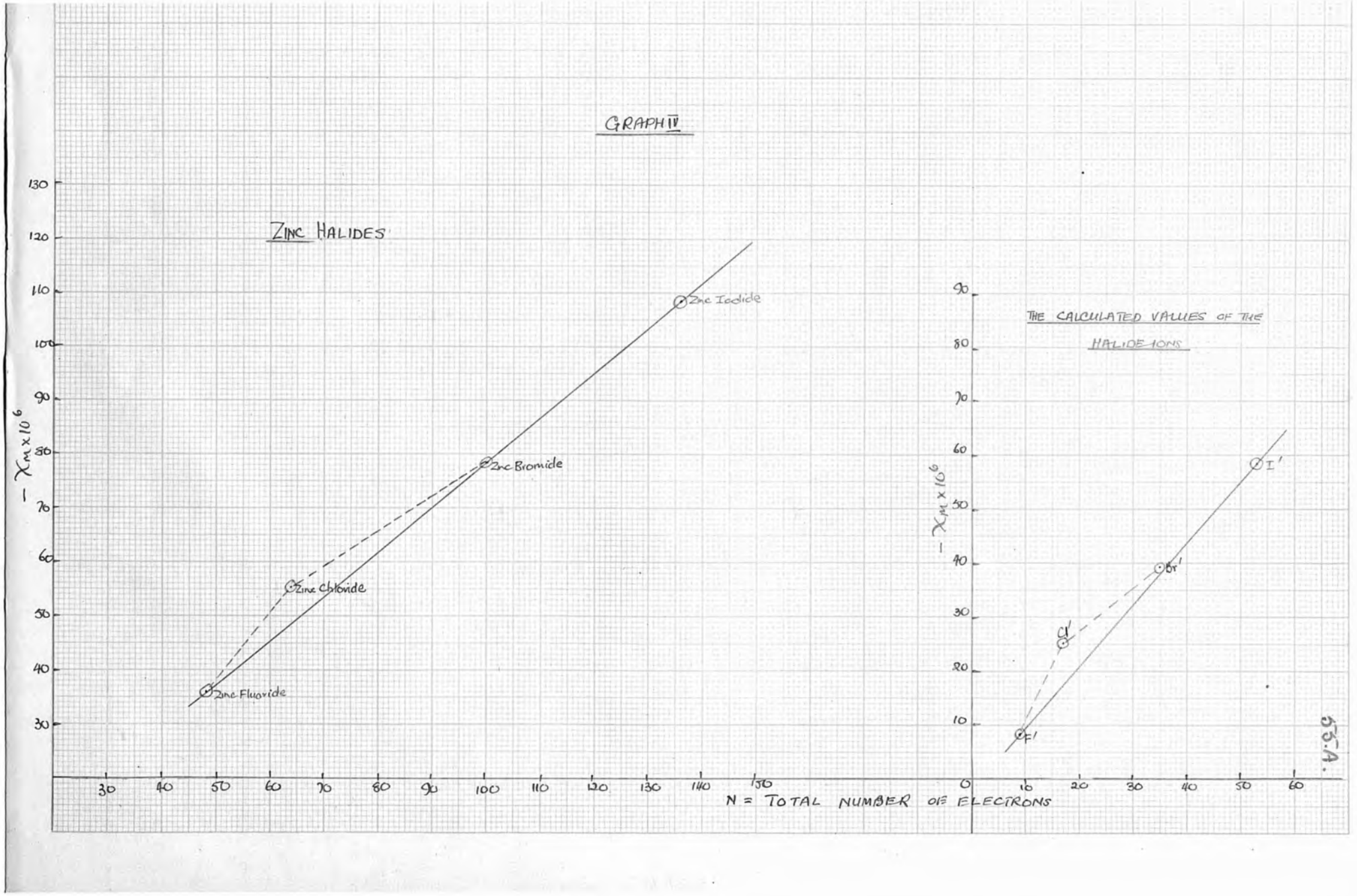
This similarity in structure and their straight line relationship between Xm and N, conforms to the hypothesis of a relationship between co-ordination number and magnetic suscpetibility.

THE ZINC HALIDES

When a graph is plotted, of the susceptibilities of the four zinc halides, and their total number of electrons, it is found that the fluoride, bromide and iodide lie on a straight line, but the value of Xm for zinc chloride is too high (Graph IV) P.55A

Ikenmeyer[1] in his work on the alkali halides observed this phenomenon but concluded the discrepancy was wrong and based his calculations on a flattened curve. The values of Xm for the chlorides were made to correspond with the values for the other halides.

Spencer[2] and Hollens[3] in their work on the cadmium compounds found that the value of Xm for $Cd Cl_2$ was too high to fall on to the straight line which passed through the other halide values. A similar result was obtained by Trew[4] in her work on thallium compounds


GRAPH IV
ZINC HALIDES
Zinc Iodide
Zinc Bromide
Zinc Chloride
Zinc Fluoride
$-\chi_m \times 10^6$
N = TOTAL NUMBER OF ELECTRONS
THE CALCULATED VALUES OF THE HALIDE IONS
F'
Cl'
Br'
I'
$-\chi_m \times 10^6$
55·A·

When a graph is plotted of the calculated values of Xm for the halide ions against their atomic numbers, the form of the line is unaltered. Ikenmeyer's flattening of the curve was not justified, since it is apparent that the discrepancy is due to some innate difference in the chlorine ion.

THE ORGANIC SALTS OF ZINC

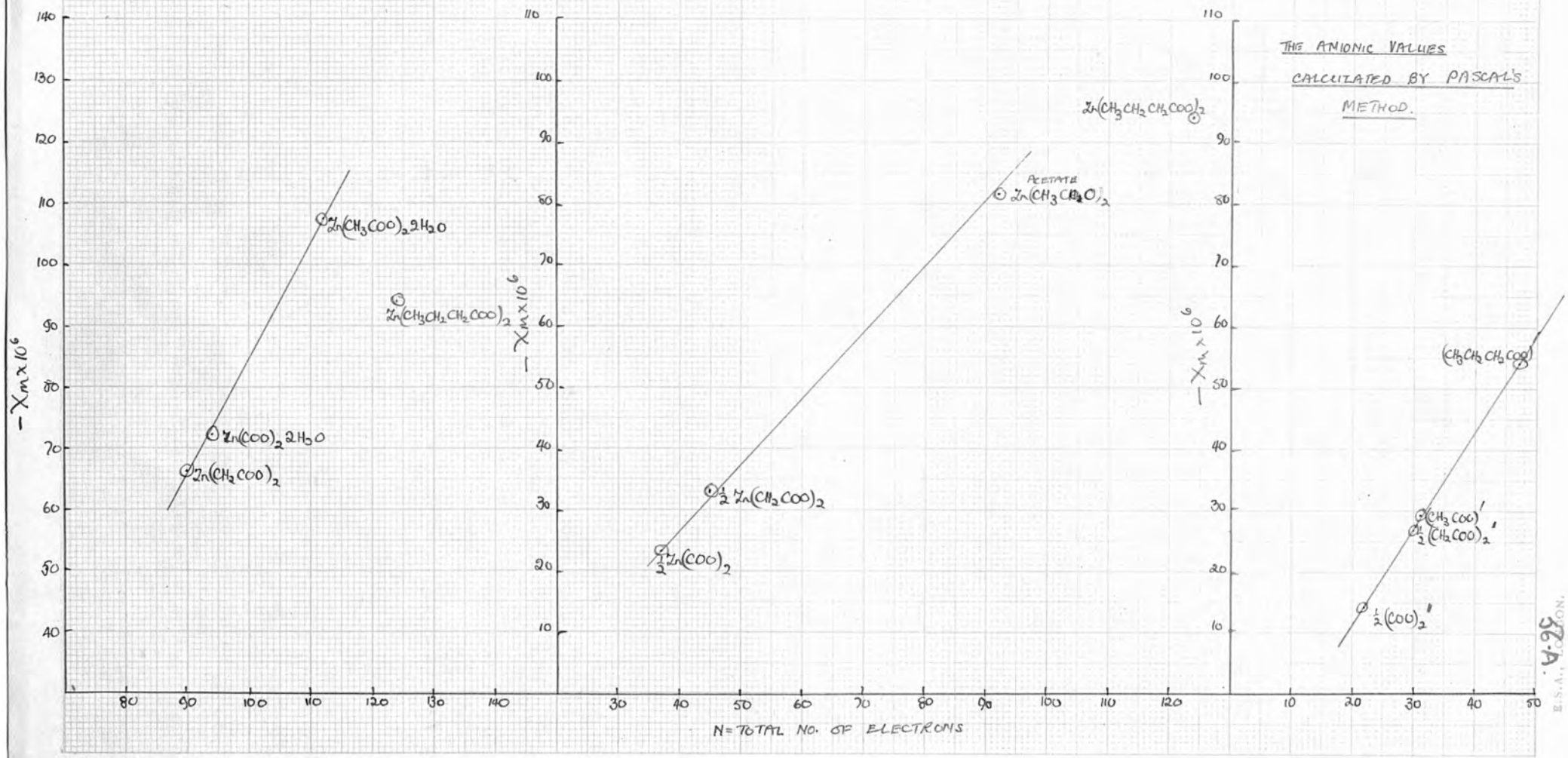
The values of Xm for the acetate, butyrate, oxalate and succinate ions were calculated by Pascal's method, using his values for Carbon, Oxygen and Hydrogen. The acetate and butyrate ions are monovalent, whilst the oxalate and succinate ions are divalent. The values of Xm for $(CH_3COO)'_2$ $(CH_3CH_2CH_2COO)'$ $\frac{1}{2}(COO)''_2$ and $\frac{1}{2}(CH_2COO)''_2$ were plotted as ordinates and the total numbers of electrons of the ions as abscissae. It was found that the points thus obtained were colinear. (Graph Vc) Page 56 A.

Values of Xm were experimentally found for zinc acetate dihydrate, zinc oxalate.dihydrate, zinc butyrate and zinc succinate. From these were deducted values of anhydrous zinc acetate, $\frac{1}{2}$ (anhydrous zinc oxalate) and $\frac{1}{2}$ (zinc succinate) taking $X_{H_2O} = -13.0 \times 10^{-6}$ These values were plotted against the total number of electrons. The points obtained were found to be colinear except zinc butyrate (Graph Vb). This shows that the values of Xm for the zinc ion in these compounds is constant, but on calculation it was found to be too high. This phenomenon has been observed by Trew[4] in the organic salts of Thallium. This may be due to an inherent property of organic radicles or it may be due to the incomplete ionisation of such compounds.

The anomaly of the butyrate may be due to the 3% of impurity it was found to contain. If this impurity, which was not isolated, was paramagnetic the low value of the compound would be explained Owing to the impurity of the compound no reliance can be placed upon the value of the susceptibility obtained.

GRAPH V

THE ORGANIC SALTS OF ZINC.



36-A.

The value of X_m for the actual organic salts measured were plotted against the total number of electrons they contained. Again the acetate, oxalate and succinate were colinear.

THE VALUE OF X_m FOR THE $>CH_2$ GROUP

Since both zinc oxalate and zinc succinate were measured it is possible to obtain a value for the susceptibility of the $>CH_2$ group.

Zinc oxalate dihydrate

$Zn(COO)_2.2H_2O$ $\quad Xm = -.72.36 \times 10^{-6}$

$\therefore$ $Zn(COO)_2$ $\quad Xm = -46.36 \times 10^{-6}$

Zinc succinate

$Zn(CH_2.COO)_2$ $\quad Xm = -66.21 \times 10^{-6}$

$\therefore$ $(>CH_2)_2 = (66.21 - 46.36) \times 10^{-6}$

$= -19.85 \times 10^{-6}$

$\therefore$ Susceptibility of the $>CH_2$ group $= -\underline{9.93 \times 10^{-6}}$

A value of this group can be calculated by Pascal's method.

$Xm\ >CH_2 = -\{6.2 + (2 \times 3.0)\} \times 10^{-6}$

$= -12.2 \times 10^{-6}$

$\therefore$ Susceptibility of CH_2 group by Pascal's method

$= -12.2 \times 10^{-6}$

THE EFFECT OF SUBSTITUTING CHLORINE IN THE SIDE CHAIN OF THE SALT OF A FATTY ACID

The effect of substituting chlorine in the side chain of the salt of a fattyaacid was estimated from the values obtained for the susceptibilities of zinc acetate and zinc trichloracetate. Zinc acetate dihydrate:

$Zn(CH_3.COO)_2.2H_2O$ $\quad Xm = -107.5 \times 10^{-6}$

Zinc trichloracetate dihydrate:

$Zn(CCl_3.COO)_2.2H_2O$ $\quad Xm = -184.5 \times 10^{-6}$

By the subtraction of the first of these values from the second a value is obtained which is the effect produced by the substitution of six chlorine atoms for six hydrogen atoms.

i.e. $2(CCl_3 - CH_3) = -77.0 \times 10^{-6}$

Therefore the effect of substituting one atom of chlorine for one atom of hydrogen is -12.8×10^{-6}

By using this value together with Pascal's method of calculating susceptibilites, a value can be found for the susceptibility of methyl chloride. This compound has already been measured[21], so the calculated and experimental values can be compared.

Pascal's value for the bond $\equiv C - H$ is -3.0×10^{-6}

If this value is correct then the bond $\equiv C - Cl$ would have a susceptibility = -15.9×10^{-6}

From this can be calculated the molar susceptibility of methyl chloride $CH_3 Cl$

CH_3Cl $Xm = -\{6.2 + (3 \times 3.0) + 15.8\} \times 10^{-6}$

$Xm = -31.0 \times 10^{-6}$

But the value of Xm for methyl chloride given in I.C.T.[21] is

$\underline{Xm = -31.96 \times 10^{-6}}$

Thus the effect of substituting an atom of chlorine for an atom of hydrogen in the side chain of an aliphatic organic compound is found to produce a change in susceptibility equal to -12.8×10^{-6} That is its diamagnetism is increased by 12.8×10^{-6}

THE ADDITIVITY SHOWN BY A SERIES OF SIMILAR COMPOUNDS

Measurments of the susceptibilities of anhydrous zinc sulphate, hydrated zinc sulphate and zinc ammonium sulphate were made, and the degree of obedience to the law of additivity was calculated.

ANHYDROUS ZINC SULPHATE

$Zn SO_4$ $Xm = (-0.297 \times 161.43) \times 10^{-6} = -47.94 \times 10^{-6}$

Xm for $7H_2O = -(7 \times 13.0 \times 10^{-6}) = -90.76 \times 10^{-6}$

If the hydrated salt is additive then the susceptibility of $Zn SO_4 7H_2O$ equals

$-(90.76 + 47.94) \times 10^{-6} = \underline{Xm = -138.70 \times 10^{-6}}$

ZINC AMMONIUM SULPHATE

$Zn\ SO_4\ (NH_4)_2\ SO_4 6H_2O$ $Xm = -(0.484 \times 401) \times 10^{-6}$

$= -195.6 \times 10^{-6}$

Spencer and Sister Mary Cecilia, working in these laboratories have found (from an unpublished work) that the susceptibility of ammonium sulphate is -71.57×10^{-6}

The value of Xm for $Zn\ So_4\ 6H_2O$ is therefore

$-(195.6 - 71.57) \times 10^{-6} = -124.03 \times 10^{-6}$

$\therefore$ Value of Xm for $Zn\ SO_4\ 7H_2O = -(124.03 + 13.0) \times 10^{-6}$

$ZnSO_4\ 7H_2O$ Xm $= -137.03 \times 10^{-6}$

ZINC SULPHATE HEPTAHYDRATE

$ZnSO_4\ 7H_2O$ $Xm = -(0.468 \times 287.5) \times 10^{-6}$

$= -134.7 \times 10^{-6}$

$Zn\ SO_4\ 7H_2O$ $Xm = -134.7 \times 10^{-6}$

These three values give a mean value of Xm for $Zn\ SO_4\ 7H_2O$ of $-136.6 \pm 2.0 \times 10^{-6}$

The susceptibilities of the compounds are therefore additive.

The susceptibilities of zinc chloride and zinc ammonium chloride were also found experimentally.

ZINC CHLORIDE

$ZnCl_2$ $Xm = -(0.406 \times 136.29) \times 10^{-6}$

$Xm = -55.34 \times 10^{-6}$

But Stoner's[13] value for Xm for ammonium chloride is -34.3×10^{-6}

$\therefore$ Xm $4NH_4Cl = -137.2 \times 10^{-6}$

$\therefore$ If the compounds are additive the susceptibility of zinc ammonium chloride should be

$-(55.34 + 137.2) \times 10^{-6} = -192.54 \times 10^{-6}$

ZINC AMMONIUM CHLORIDE

$ZnCl_2\ 4NH_4Cl$. The experimental value for the double salt was found to be

$Xm = - (0.563 \times 350.29) \times 10^{-6}$

$Xm = - 197 \times 10^{-6}$

The mean value for zinc ammonium chloride from these two compounds is therefore:

$$Xm = - 194.9 \pm 2.4 \times 10^{-6}$$

The susceptibilities of these compounds are therefore also additive.

THE ZINC SALTS OF THE PHOSPHORIC ACIDS.

The behaviour of these salts was found to be completely anomalous. The value of Xm obtained for zinc phosphite, when plotted on Graph II lies in an intermediate position between lines (I) and (II). Anhydrous zinc phosphate and zinc ammonium phosphate, although diamagnetic have values of Xm that are much too low. The values for the zinc ion obtained from them, using -37.55×10^{-6} for the phosphate ion are paramagnetic.

ZINC AMMONIUM PHOSPHATE:

$$Xm = - 26.56 \times 10^{-6}$$

Value of zinc ion $X = +24.99 \times 10^{-6}$

ANHYDROUS ZINC PHOSPHATE

$$Xm = -40.55 \times 10^{-6}$$

Value of X for zinc ion $= +11.52 \times 10^{-6}$

Zinc phosphite

$ZnHPO_3\ 2\frac{1}{2}H_2O$ $Xm = -78.86 \times 10^{-6}$

I.C.T. value for $Na_2HPO_3 = -56.87 \times 10^{-6}$, using this value the susceptibility of the zinc ion is $+ 0.75 \times 10^{-6}$

Zinc pyrophosphate and zinc orthophosphate quadrihydrate were also measured, these compounds were found to be paramagnetic.

$Zn_2P_2O_7$ $Xm = +58.37 \times 10^{-6}$

$Zn_3(PO_4)_2\ 4H_2O$ $Xm = +28.87 \times 10^{-6}$

From the value for the hydrated saltva second value for the susceptibility of the anhydrous salt can be found, assuming that the water exerts an additive diamagnetic effect.

$Zn_3(PO_4)_2$ $Xm = +80.87 \times 10^{-6}$

There is no apparent connection between these values or the value for the zinc ion which they give. It is probable that the compounds are non-polar and so the value of the ion cannot be considered.

When $-Xm \times 10^{-6}$ is plotted against the total number of electrons, Graph VII (Page 61A) is obtained. They seem to lie irregularly and without any apparent relations with each other.

The equations of the two lines drawn are

(I) $-Xm \times 10^{+6} = 0.20N + 8.8$

$-Xm \times 10^{6} = 0.592N + 28.4$

No three of the points are colinear.

Page 61B

The points can be plotted on a four quadrant graph (Graph VIII) Some regularity is now apparent, and the six points lie on two straight lines. The equations of the lines are found to be

Line (I) $-Xm \times 10^{6} = -0.614N + 23.8$

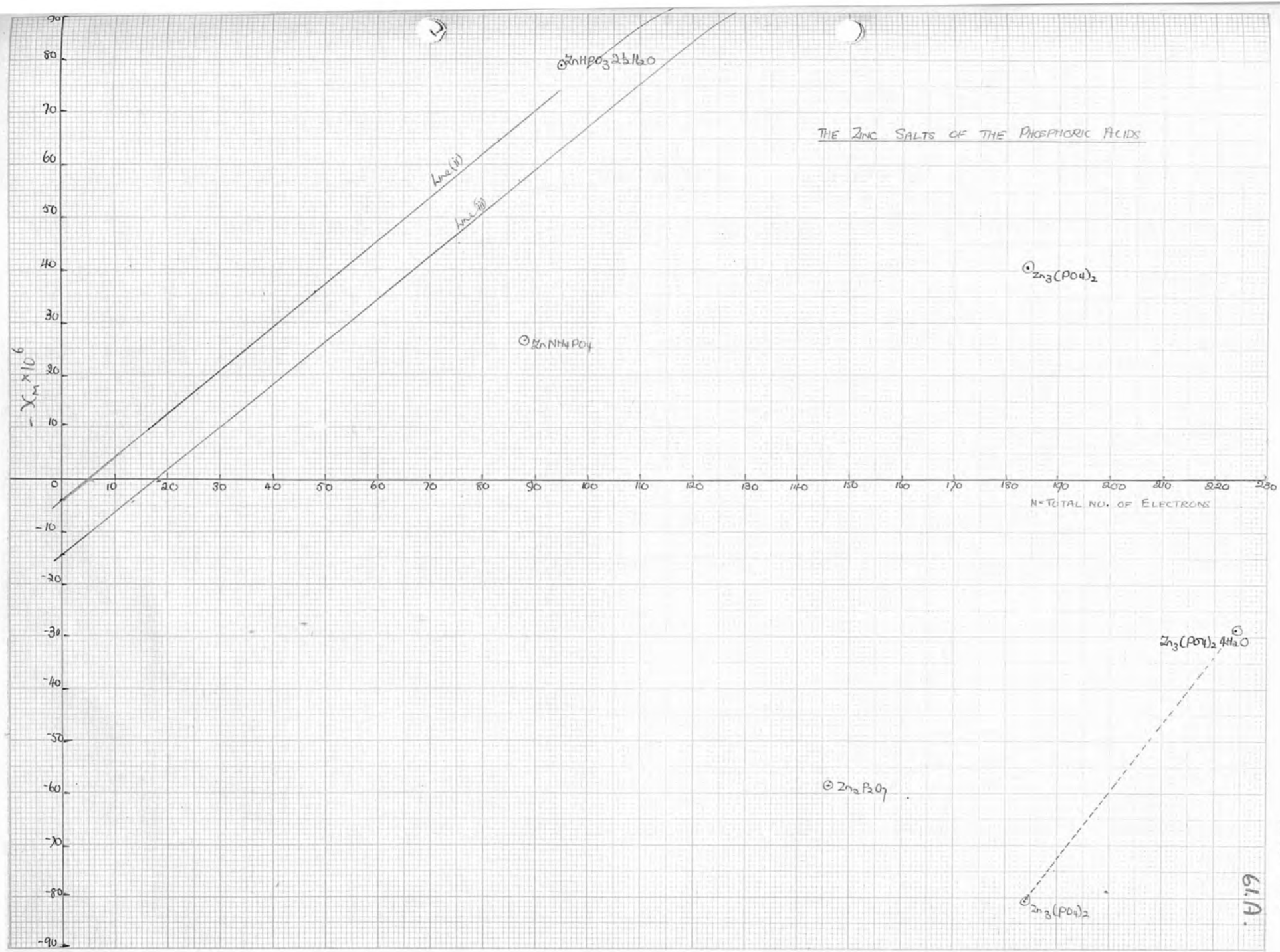
Line (II) $-Xm \times 10^{6} = -0.170N + 10.2$

The colinear nature of the points suggest that the reason for their anomalous behaviour of the compounds is regular and that it is inherent in the type of compound.

The reason must be intimately connected with the zinc atom since the phosphates of cadmium[3] and thallium[4] have been found to behave normally.

It is also found that zinc butyrate lies on line (I). This may mean that its apparently low value may be due, not to some paramagnetic impurity, but to a similar cause to that producing the anomalous behaviour of the phosphates.

The straight line property of the graph suggests that although some of the compounds are diamagnetic and some paramagnetic, the cause of the anomaly is similar in all of them.


THE ZINC SALTS OF THE PHOSPHORIC ACIDS
$\chi_M \times 10^6$
N = TOTAL NO. OF ELECTRONS
$ZnHPO_3 2\frac{1}{2}H_2O$
$Zn_3(PO_4)_2$
$ZnNH_4PO_4$
$Zn_2P_2O_7$
$Zn_3(PO_4)_2 4H_2O$
$Zn_3(PO_4)_2$
Line (i)
Line (ii)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
10
20
30
40
50
60
70
80
90
100
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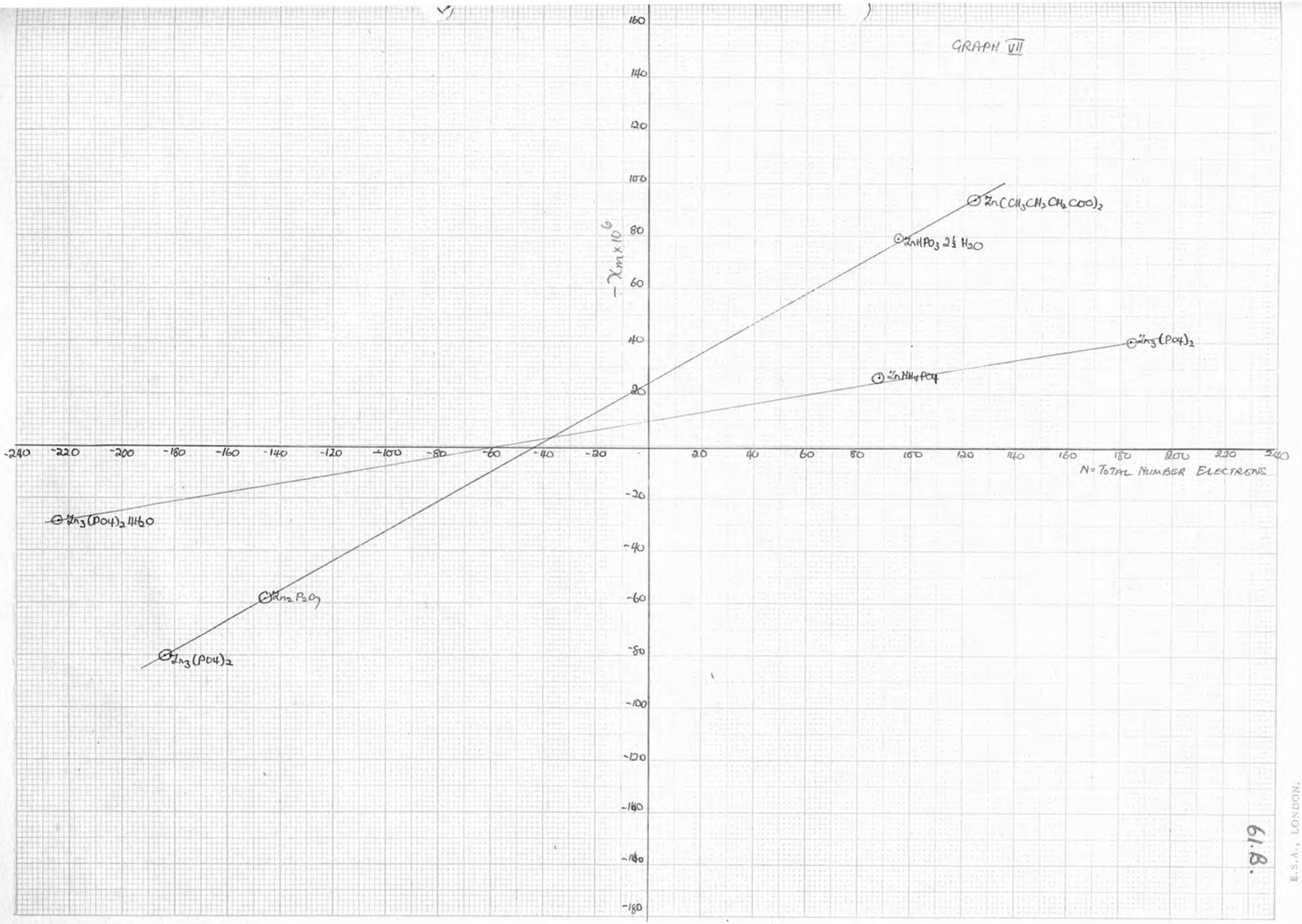
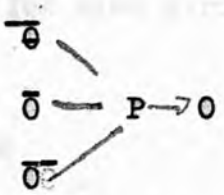
120
130
140
150
160
170
180
190
200
210
220
230

GRAPH VII



61.8.

Paramagnetism is associated, as a rule, with the transition elements and is due to their incomplete inner levels. Zinc has thirty extranuclear electrons which are considered to lie in the K L M & N levels, 2.8 . 18.2; the K L & M levels being complete whilst thevtwo electrons on the N level are the valency electrons. The Zinc ion Zn^{++} has 28 electrons 2.8.18 all the levels being complete. The phosphate ion $(PO_4)^{'''}$ has 50 electrons and has all its inner levels complete.



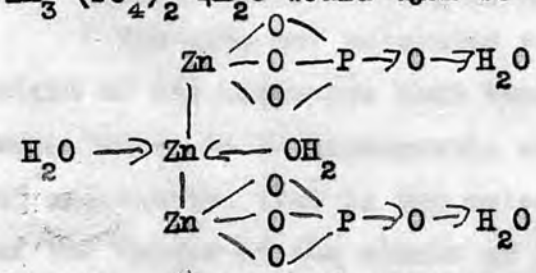
The salt $Zn_3(PO_4)_2$ whether it is polar or covalent should have no odd electrons and

its susceptibility would be expected to have the normal diamagnetic value.

Two values of Xm for $Zn_3(PO_4)_2$ were obtained, one by measurement which was diamagnetic but too low, and one by extrapolation from the hydrated salt, which was paramagnetic.

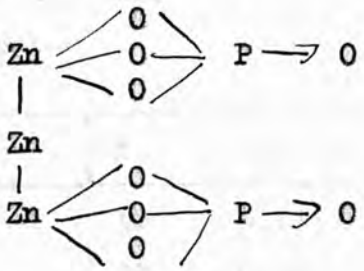
If, by some unknown force, two electrons from the M level of the zinc atom were pulled out into the N level to act as valency electrons then the M shell would contain only 16 electrons and paramagnetism would be expected.

If this happened Zinc would have four valency electrons and thus be capable of four covalent links. A probable structure of $Zn_3(PO_4)_2\ 4H_2O$ would then be

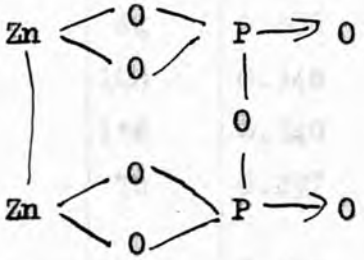


and the structure of anhydrous zinc phosphate obtained by

extrapolation from this compound would be



There is no probable structure for zinc pyrophosphate accounting for quadrivalent zinc.



This structure has no foundation or any probable reason.

The idea of two electrons being pulled out into the valency shell, when the inner levels are complete, is without precedent. The hypothesis also seems unlikely to be correct since there is a relation between zinc phosphite, which is diamagnetic and would therefore have its inner levels complete, and zinc pyrophosphate which is paramagnetic.

There is however some fundamental difference in this series of compounds which causes the ordinary laws of diamagnetism to break down. If zinc butyrate is anomalous due to the same cause then the difference must lie in the zinc atom.

THE CONCLUSIONS AND A SUMMARY OF RESULTS.

The mass and molecular susceptibilities of zinc and twenty-eight of its compounds have been found. Most of these compounds were found to be diamagnetic and to obey approximately the law of additivity, that is the molecular susceptibility is the sum of the values of the atomic or ionic susceptibility of the constituents of the compounds. Anomalies were found however,

including the organic salts which, as a rule gave too high a value for the zinc ion.

Values obtained:-

COMPOUND	N	-10^6 X	-10^6 Xm	-10^6 Zinc Ion
Zinc	30	0.137	8.96	–
Zinc oxide	38	0.343	27.78	–
Zinc Hydroxide	48	0.267	26.54	–
Zinc Fluoride	48	0.344	35.91	15.91
Zinc Chloride	64	0.406	55.34	10.74
Zinc Bromide	100	0.348	78.38	10.38
Zinc Iodide	136	0.340	108.50	8.5
Zinc Sulphate	78	0.297	47.82	14.42
Zinc Sulphate $7H_2O$	148	0.468	134.7	10.58
Zinc Ammonium Sulphate	208	0.484	194.0	11.27
$ZnCl_2 4NH_4Cl$	176	0.563	197.2	15.2
$ZnCO_3 \frac{1}{4}H_2O$	62.5	0.272	35.34	9.30
$Zn(NO_3)_2 4H_2O$	132	0.394	103.0	9.16
$ZnSO_3 2\frac{1}{2}H_2O$	95	0.302	57.82	10.3
$Zn_3(PO_4)_2 4H_2O$	224	-0.063	-28.87	-
$Zn_3(PO_4)_2$	184	0.105	40.55	-
$Zn\ NH_4\ PO_4$	88	0.149	26.56	-
$Zn_2P_2O_4$	146	-0.192	-58.37	-
$Zn\ HPO_3 2\frac{1}{2}H_2O$	95	0.414	78.86	-
$Zn_2Fe(CN)_6$	134	0.365	124.8	20.6
$Zn_3[Fe(CN)_6]_2$	298	-5.28	-3273	-
$Zn(CH_3.COO)_2 2H_2O$	112	0.491	107.5	22.1
$Zn(CCl_3.COO)_2 2H_2O$	208	0.433	184.5	22.3 *
$Zn(CH_3CH_2CH_2.COO)_2$	124	0.393	94.21	-
$Zn(COO)_2\ 2H_2O$	94	0.382	72.36	17.36
$Zn(CH_2COO)_2$	90	0.365	66.21	12.81
$ZnO_2C_6O_3 2H_2O$	154	0.060	19.05	-
$ZnHg(CNS)_4$	226	0.397	197.7	-
$Zn(IO_3)_2$	184	0.250	103.8	13.8

* This value was obtained using $\chi C - Cl = 15.8$

The susceptibility of zinc and the susceptibilities of five of its compounds had already been measured. These compounds have been remeasured and the values revised.

COMPOUND	$-X \times 10^6$	I.C.T. $-X \times 10^6$
Zinc	0.137	0.157
Zinc oxide	0.343	0.362
Zinc Hydroxide	0.267	0.487
Zinc Chloride (I.C.T. Aq)	0.406	0.470
Zinc Bromide	0.348	0.40
Zinc Sulphate $ZnSO_4 7H_2O$	0.468	0.480

The values of X obtained were all lower than those previously obtained.

From the susceptibilities of the compounds obtained a mean experimental value of the susceptibility of the zinc ion Zn^{++} was found. Experimental value of the zinc ion $X = -12.40 \times 10^{-6}$. This value was compared with the theoretical value calculated by three methods. The agreement between the experimental value and the value calculated by the Brindley-Slater method was found to be very good.

Brindley-Slater $\begin{cases} X = -12.72 \times 10^{-6} \\ X = -12.81 \times 10^{-6} \end{cases}$

The values from which the mean experimental value is calculated vary between 8.5×10^{-6} and 17.36×10^{-6}.

From a consideration of the molecular susceptibilities of the compounds measured it was found that there is a probable relationship between susceptibility and co-ordination number.

When Xm was plotted against total number of electrons it was found that the compounds which were colinear were those which had the zinc atom in a similar state of co-ordination, e.g., the binary compounds were colinear and those in which the zinc atom was probably in the state $>Zn<$ were also colinear.

This relationship would be connected with Goldschmidt's relationship between change in co-ordination number and interatomic radius.

The zinc halides were measured and on plotting their graph it was found that they were not colinear. The value of Xm for $ZnCl_2$ was too high. This high value for zinc chloride is consistent with the values obtained for KCl and TlCl. It is also noticeable that the specific susceptibilities of ZnF_2, $ZnBr_2$, ZnI_2 are approximately constant whilst $ZnCl_2$ is much higher.

ZnF_2 $X = -0.344 \times 0^{-6}$
$ZnCl_2$ $X = -0.406 \times 10^{-6}$
$ZnBr_2$ $X = -0.348 \times 10^{-6}$
ZnI_2 $X = -0.340 \times 10^{-6}$

Ikenmeyer flattened the curve of the halides, but this flattening is not justifiable as the high values of the chlorides appears to be due to an inherent difference in the chloride ion.

From the susceptibilities of the organic salts measured, the value of the group $>CH_2$ has been calculated, and also the effect of substituting a chlorine atom for a hydrogen atom in the side chain of a fatty acid has been estimated.

$>CH_2$ $X = -9.93 \times 10^{-6}$

Pascal's value for $>CH_2$ $X = -12.2 \times 10^{-6}$

The change $\geq C - H$ to $\geq C - Cl$ causes an increase in diamagnetic susceptibility equal to $X = -12.8 \times 10^{-6}$.

The zinc salts of the oxyacids of phosphorus were found to behave in an anomalous manner. Some of the salts were diamagnetic but had a value much lower than was expected, whilst the hydrated orthophosphate and the pyrophosphate were paramagnetic. There was found to be some regularity in these compounds, showing that the cause of the anomaly is similar throughout the series. The susceptibility of zinc butyrate agrees with those compounds and the cause of its low value may be similar. It is interesting that the total number of electrons in the phosphate ion $(PO_4)'''$ and in the butyrate ion $(CH_3.CH_2.CH_2.COO)'_2$ are the same. The anomaly has not been adequately explained.

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REFERENCES

1. Ikenmeyer Ann der Phys 1.169. 1929
2 Sugden J.C.S. 1932 161
3. Spencer and Hollens J.C.S. 1935 495
4. Trew Trans. Faraday Soc: 1936 XXXII 188
5. Honda Ann. der Phys. 32. 1027. 10'
6. Owen Ann. der Phys. 37. 657. 12
6. Meslin Ann. de Chim. et de Phys, 7. 145. '06
7. Endo Science Reports Tohoku Series 1. 14 479
8. Wilson Proc. Royal Soc.
9. Meyer Ann. der Phys. 68. 325. 1899
   69. 236. 1899. 1.664. 1900
10. König Ann der Phys 31 231 1887
11. Sugden Trans. Chem. Soc. 1932 161
    Trew and Watkins Trans. Faraday Soc. 1933·29·1310
12. Langevin Ann. des Chim et de Phys. (8)·5·70·1905
13. Stoner - Magnetism and matter
14. Slater Phys. Rev. 34.1293. 1929
    36. 57. 1931
15. Zener Phys. Rev. 36. 51 1930
16. Ikenmeyer Ann. der Phys. 1 .169 1929
17. Brindley Phil. Mag. 11.786 1931
18. Angus Proc. Roy. Soc. 136 569 1932
19. Goldschmidt Trans. Faraday Soc. 1929. 253
20. Sidgwick Electronic Theory of Valency P,195
21. Pascal Compt. Rend. 147 56, 242, 742, :08