

# DIAMAGNETIC SUSCEPTIBILITIES OF MAGNESIUM AND ZINC IONS

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ON the basis of electronic theory, and quantum and wave mechanics it has been established that the diamagnetic susceptibility of an ion is given by

$$\chi_a = -2.83 \times 10^{10} \sum_n \bar{r}^2 \text{ e.m.u.}$$

Van Vleck,<sup>1</sup> Pauling,<sup>2</sup> Stoner,<sup>3</sup> Slater<sup>4</sup> and Angus<sup>5</sup> have deduced independently several expressions for  $\sum_n \bar{r}^2$  and have used them to calculate the diamagnetic susceptibilities of several ions. These are known as theoretical values after their names, and differ from one another appreciably in some cases.

The experimental verification of these values has been attempted on the basis that the molecular susceptibility of a heteropolar salt is the sum of the ionic susceptibilities of the constituent ions. For this purpose a certain value of susceptibility has been assigned to one particular ion. The following are some of the values (in units of  $-1 \times 10^{-6}$ ) which have been taken as standards.

$$\begin{aligned}\chi_{K^+} &= 15.5 \text{ (Joos)}^6; \quad \chi_{Cl^-} = 19.5 \text{ (Joos)}^6; \\ \chi_{Cs^+} &= 45.75 \text{ (Ikenmeyer)}^6; \\ \chi_{I^-} &= 49.25 \text{ (Ikenmeyer)}^6; \quad \chi_{H^+} = 0 \text{ (Reicheneder)}^6; \\ \chi_{Li^+} &= 0.70 \text{ (Hoare and Brindley)}^6.\end{aligned}$$

Using these values or others derived from them, experimental values of the susceptibilities of several ions have been determined by different workers.

A review of the literature shows that values of the susceptibilities widely different from one another have been recorded for the same ion. Angus<sup>7</sup> also remarks in the Annual Report of the Chemical Society, "From such a diversity of methods a diversity of values is obtained which, at present, cannot be satisfactorily sorted out".

Looking to the fact that, "A satisfactory table of ionic susceptibilities has a considerable value" (*cf.* Stoner), attempts have been made by some workers to arrive at a set of correct ionic susceptibilities. Amongst these, a systematic study of cadmium compounds has been made by Hollens and Spencer,<sup>9</sup> of thallium compounds by Trew,<sup>10</sup> and of compounds of bismuth

(trivalent), rubidium and thallium by Bhatnagar and co-workers.<sup>11</sup> In order to circumvent the arbitrariness involved in using one particular value of the susceptibility of an anion Nevgi<sup>11a</sup> has subtracted all the known values of the anions from the molecular susceptibilities of the salts containing the same cation and have taken the arithmetic mean of the values thus obtained as the most probable value of the cation. The same procedure has been followed by Prasad and co-workers<sup>12, 13</sup> in deducing the ionic susceptibilities of barium, calcium and strontium ions.

Prasad and co-workers found that the theoretical susceptibilities of calcium, strontium and barium ions calculated according to Slater's and Angus' methods are in fair agreement with the experimental values deduced from salts of inorganic acids but are less than those deduced from the salts of these cations with organic anions. Some such observations were also made by Trew<sup>10</sup> in the case of thallium salts.

The present work was conducted with a view to establish the general validity of the conclusions mentioned above. For this purpose the magnetic susceptibilities of magnesium and zinc salts of several inorganic and organic acids were determined. The choice of the salts of these two elements was based on the fact that they belong to the same group in the periodic table as calcium, strontium and barium, but still form a separate sub-group with cadmium and mercury.

#### EXPERIMENTAL

The susceptibilities were measured by using a modified Gouy's balance. Many changes were introduced in this balance, including a new magnet, in order to increase the sensitivity and the accuracy of the balance.

Machine drawn pyrex-glass tubes with ground glass stopper were used as the containers of substances. The substances to be investigated were used in the form of fine powders and were well pressed uniformly (upto a certain mark made on the tube) to satisfy the theoretical conditions.

At the end of each measurement the specimen tube was thoroughly cleaned with water, chromic acid solution, distilled water and absolute alcohol and finally well dried before using it for the next measurement. All the compounds studied were experimented upon in two different ways: (i) two independent readings were taken for different packings in a given tube, each of these readings being taken three times, (ii) the same procedure was repeated in another tube. KCl (Merck's A. R. quality) was used as the standard substance. The magnetic susceptibility was calculated from the usual relation.

Great stress was laid on the purity of the substances used. They were either Merck's extra pure or A.R. quality or B.D.H. A.R. quality chemicals or were prepared in the laboratory; in the latter case their purity was ascertained before use.

## RESULTS

The results obtained for Magnesium salts are given in Tables I (a) and I (b) and for Zinc salts in II (a) and II (b). In these tables column 1 gives the chemical formulæ of substances along with their analysis in the case of substances prepared in the laboratory, and column 2 gives the total number (N) of electrons in the compounds. Some of the salts investigated were hydrated, hence the values ( $\chi_m$ ) actually measured are those of hydrated salts. For the purpose of discussion, these values have been reduced to that of anhydrous salts ( $\chi_{ma}$ ) by subtracting the susceptibility for molecules of water ( $\chi_{H_2O} = 12.96$ ) from the molecular susceptibilities of hydrated salts. Such a procedure may not be justified, since the exact effect of water

TABLE I (a)

*Magnesium salts of Inorganic Acids*

Compounds	N	Authors' values	$\chi_{ma}$ Other workers	$\chi_{ma}$ Computed experimentally	$\chi_{ma}$ Computed theoretically
1	2	3	4	5	6
MgO ..	20	0.253 .. 10.20	10.08(15)	13.46(15)	Mg <sup>+2</sup> +O <sup>-2</sup>  15.80 (P) 16.33 (S) 14.14 (A)
MgCO <sub>3</sub> ..	42	0.3844 .. 32.41	6.99(16) 32.10(14) 33.73(15) 27.62(17) 43.00(15)	32.3 (15) 32.4 (14) 33.5 (2)	Mg <sup>+2</sup> +(CO <sub>3</sub> ) <sup>-2</sup>  41.15 (P) 42.78 (S) 36.79 (A)
MgSO <sub>4</sub> ·7H <sub>2</sub> O ..	60	0.5463 134.60 43.88	41.00(14) 45.11(15) 54.18(15) 43.34(18) 43.34(18) 74.59(18) 46.58(17)	43.7 (15) 43.3 (14) 44.9 (2)	Mg <sup>+2</sup> +(SO <sub>4</sub> ) <sup>-2</sup>  55.00 (P) 57.19 (S) 49.20 (A)
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O ..	130	0.4987 167.0 115.16		101.1 (15) 107.3 (14)	3Mg <sup>+2</sup> +2(PO <sub>4</sub> ) <sup>-3</sup>  113.80 (P) 118.06 (S) 101.75 (A)

TABLE I (b)

*Magnesium salts of Organic Acids*

Compounds	N	Authors' values	$\chi_{ma}$ Computed experimentally	$\chi_{ma}$ Computed theoretically
MgC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O Mg Found 16.39% Mg Theory 16.58%	56	0.4554 67.59 41.67	38.04(15)	Mg <sup>+2</sup> + (C <sub>2</sub> O <sub>4</sub> ) <sup>-2</sup> 30.90 (P) 30.88 (S) 30.59 (A)
Mg(HCOO) <sub>2</sub> ·2H <sub>2</sub> O Mg Found 16.16% Mg Theory 16.36%	58	0.4638 69.74 43.82	43.9 (15) 44.7 (14)	Mg <sup>+2</sup> + 2(HCOO) <sup>-1</sup> 36.70 (P) 36.68 (S) 36.39 (A)
Mg(CH <sub>2</sub> ) <sub>2</sub> (COO) <sub>2</sub> ·3H <sub>2</sub> O Mg Found 12.32% Mg Theory 12.63%	72	0.5320 103.6 64.72	61.16(15)	Mg <sup>+2</sup> + (CH <sub>2</sub> COO) <sub>2</sub> <sup>-2</sup> 54.40 (P) 54.38 (S) 54.09 (A)
Mg(CH <sub>3</sub> COO) <sub>2</sub> ·4H <sub>2</sub> O	74	0.5420 116.22 64.38	67.9 (15) 68.3 (14) 67.1 (14)	Mg <sup>+2</sup> + 2(CH <sub>3</sub> COO) <sup>-1</sup> 60.20 (P) 60.18 (S) 59.89 (A)
Mg(CHOH) <sub>2</sub> (COO) <sub>2</sub> ·5H <sub>2</sub> O Mg Found 9.08% Mg Theory 9.37%	88	0.5049 132.5 67.70	64.84(15)	Mg <sup>+2</sup> + (CHOHCOO) <sub>2</sub> <sup>-2</sup> 63.60 (P) 63.58 (S) 63.29 (A)
Mg(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> ·3H <sub>2</sub> O Mg Found 7.62% Mg Theory 7.68%	138	0.5638 180.6 141.72	145.3 (15)	Mg <sup>+2</sup> + 2(C <sub>6</sub> H <sub>5</sub> COO) <sup>-1</sup> 134.30 (P) 134.28 (S) 133.99 (A)
Mg(C <sub>6</sub> H <sub>4</sub> OHCOO) <sub>2</sub> ·4H <sub>2</sub> O Mg Found 6.539% Mg Theory 6.637%	154	0.5597 207.30 155.46	152.98(15)	Mg <sup>+2</sup> + 2(C <sub>6</sub> H <sub>4</sub> OHCOO) <sup>-1</sup> 143.5 (P) 143.48 (S) 143.19 (A)
Mg <sub>3</sub> (CH <sub>2</sub> COO·COH·COO· CH <sub>2</sub> COO) <sub>2</sub> ·14H <sub>2</sub> O Mg Found 10.12% Mg Theory 10.49%	230	0.5125 360.40 178.96	188.64(15)	3Mg <sup>+2</sup> + 2(CH <sub>2</sub> COO·C· OHCOO·CH <sub>2</sub> COO) <sup>-3</sup> 166.60 (P) 166.54 (S) 165.67 (A)

of hydration on the compounds is still doubtful, but for purposes of comparison it should not matter much, since the correction is of a small order. The observed values of the specific susceptibilities ( $\chi_a$ ), the molecular susceptibilities ( $\chi_m$ ), and the molecular susceptibilities of anhydrous salts ( $\chi_{ma}$ ), are given in the third column of the Tables one below the other in the order mentioned. Columns 4 and 5 give, respectively, the experimental values obtained by the previous workers, and those computed by summing up the

values of anions and cations obtained by the same author. Since no determinations of susceptibilities of organic compounds have been made by previous workers, column 4 has been dropped in Tables I (b) and II (b); only zinc acetate  $\text{Zn}(\text{CH}_3\text{COO})_2$  has been studied by Kido and its value has been entered in column 3 along with the authors' values. All the values of susceptibilities are expressed in this paper in units of  $-1 \times 10^{-6}$ .

TABLE II (a)  
*Zinc salts of Inorganic Acids*

Compounds	N	Authors' values	Other Workers	$\chi_{ma}$ Computed experimentally	$\chi_{ma}$ Computed theoretically
$\text{ZnCO}_3$	60	0.3424 .. 42.93	42.2 (14) 47.15(17)	35.7 (15) 40.9 (14)	$\text{Zn}^{+2} + (\text{CO}_3)^{-2}$ 48.95 (P) 55.17 (S) 49.35 (A)
$\text{ZnO}$	38	0.3058 .. 24.88	21.15(15) 26.85(18) 29.46(15)	16.86(15)	$\text{Zn}^{+2} + \text{O}^{-2}$ 23.60 (P) 28.72 (S) 26.70 (A)
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	78	0.4967 142.8 52.08	47.23(15) 43.62(18) 61.68(18) 44.60(14) 43.58(16) 52.48(17)	47.1 (15) 51.8 (14)	$\text{Zn}^{+2} + (\text{SO}_4)^{-2}$ 62.80 (P) 69.58 (S) 61.76 (A)
$\text{Zn}_3(\text{PO}_4)_2$	184	0.3663 .. 141.5	..	111.3 (15) 119.46(14)	$3\text{Zn}^{+2} + 2(\text{PO}_4)^{-3}$ 137.20 (P) 155.23 (S) 139.43 (A)
$\text{ZnSeO}_3$	88	0.2814 .. 54.19	..	60.3(14)	..

#### DISCUSSION OF RESULTS

It will be noticed from the above Tables that the  $\chi_{ma}$  values of some compounds obtained by the authors agree well with those found by the previous workers. Values of  $\chi_{ma}$  calculated according to the method developed by Angus and Farquharson<sup>19</sup> by summing up the susceptibilities of the constituent atoms in the required ionic state (*cf.* column 6) show that in many cases they are widely different from the experimental values. Similar observations were made by Prasad, Dharmatti and Gokhale.<sup>13</sup> However, the agreement between the experimental values and those computed by

TABLE II (b)  
*Zinc salts of Organic Acids*

Compounds	N	Authors' values	$\chi_{ma}$ Computed experimentally	$\chi_{ma}$ Computed theoretically
Zn(COO) <sub>2</sub> ·2H <sub>2</sub> O Zn Found 34.11% Zn Theory 34.5 %	74	0.4097 77.61 51.69	41.44(15)	Zn <sup>+2</sup> + (C <sub>2</sub> O <sub>4</sub> ) <sup>-2</sup> 38.17 (P) 43.27 (S) 43.15 (A)
Zn(HCOO) <sub>2</sub> ·2H <sub>2</sub> O Zn Found 34.28% Zn Theory 34.39%	76	0.4004 .. 50.73	47.3 (15) 53.2 (14)	Zn <sup>+2</sup> + 2(HCOO) <sup>-1</sup> 44.5 (P) 49.07 (S) 48.95 (A)
Zn(CH <sub>2</sub> ) <sub>2</sub> (COO) <sub>2</sub> Zn Found 35.91% Zn Theory 36.04%	90	0.4033 .. 73.14	65.16(15)	Zn <sup>+2</sup> + (CH <sub>2</sub> COO) <sub>2</sub> <sup>-2</sup> 62.20 (P) 66.77 (S) 66.65 (A)
Zn(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O	92	0.4600 100.9 74.98 76.8(14)	71.3 (15) 74.8 (14)	Zn <sup>+2</sup> + 2 CH <sub>3</sub> COO <sup>-1</sup> 68.00 (P) 72.57 (S) 72.45 (A)
Zn(CHOH) <sub>2</sub> (COO) <sub>2</sub> ·2H <sub>2</sub> O Zn Found 25.86% Zn Theory 26.20%	106	0.4244 105.9 79.98	68.24(15)	Zn <sup>+2</sup> + (CHOHCOO) <sub>2</sub> <sup>-2</sup> 71.40 (P) 75.97 (S) 75.85 (A)
Zn(C <sub>6</sub> H <sub>4</sub> ·COO·COO) Zn Found 28.26% Zn Theory 28.38%	114	0.4204 .. 96.42	94.64(15)	Zn <sup>+2</sup> + (C <sub>6</sub> H <sub>4</sub> COO·COO) <sup>-2</sup> 87.5 (P) 92.07 (S) 91.95 (A)
Zn(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> Zn Found 20.92% Zn Theory 21.25%	156	0.5006 .. 154.0	148.7 (15)	Zn <sup>+2</sup> + 2(C <sub>6</sub> H <sub>5</sub> COO) <sup>-1</sup> 142.1 (P) 146.67 (S) 146.55 (A)
Zn(C <sub>6</sub> H <sub>4</sub> OHCOO) <sub>2</sub> ·3H <sub>2</sub> O Zn Found 16.49% Zn Theory 16.61%	172	0.5129 201.90 163.02	152.88(15)	Zn <sup>+2</sup> + 2(C <sub>6</sub> H <sub>4</sub> OHCOO) <sup>-1</sup> 151.30 (P) 155.87 (S) 155.75 (A)
Zn <sub>3</sub> (CH <sub>2</sub> ·COO·COH·COO· CH <sub>2</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O Zn Found 31.96% Zn Theory 32.13%	284	0.4032 246.10 220.18	188.34(15)	3Zn <sup>+2</sup> + 2(CH <sub>2</sub> ·COO·COH COO·CH <sub>2</sub> COO) <sup>-3</sup> 190.00 (P) 203.71 (S) 203.35 (A)

adding the cation and anion values given by the same author is fairly good (cf. columns 3 and 5).

(a) *Electronic Isomers*

Bhatnagar and co-workers<sup>20</sup> have empirically shown that the molecular susceptibility of a salt is given by

$$\chi_{ma} = -2.832 \times 10^{10} \cdot \bar{r}^{22} \cdot K,$$

where the numerical factor K should have the same value for a set of electronic isomers. This relation can be used to calculate the value of  $\chi_{ma}$  of a compound if its  $\bar{r}^2$  and K of its series of isomers are known. The authors have used this relation to calculate the molecular susceptibilities of some of the compounds studied in this investigation. For this purpose the  $\chi_{ma}$  values of the isomers are taken from International Critical Tables, 1929, Landolt Bornsteins Physikalische Chemischen tabellen, 1930, and from other available literature. The values of  $\bar{r}^2$  have been estimated by using Bragg's theory<sup>21</sup> of closest packing. The values of K and  $\chi_{ma}$  for some salts of Magnesium and Zinc calculated for different isomers are given in columns 6 and 7 of Table III.

TABLE III

No. of atoms	Total No. of Electrons	Electronic Isomers	$\chi_{ma}$ (Observed)	Radius in A. U.	K	$\chi_{ma}$ Calculated
5	42	MgCO <sub>3</sub>	32.41*	1.606	..	18.67
		NaNO <sub>3</sub>	25.60(18)	1.88	2.557	..
6	60	MgSO <sub>4</sub>	43.88*	1.714	..	52.35
		AlPO <sub>4</sub>	49.33	1.664 1.946	6.292 4.598	38.25 ..
5	60	ZnCO <sub>3</sub>	42.93*	1.530	..	17.57
		KClO <sub>3</sub>	36.81(15)	2.219	2.650	..
5	88	ZnSeO <sub>3</sub>	54.19*	1.678	..	33.43
		NaIO <sub>3</sub>	51.77(17)	2.088	4.192	..
2	38	ZrO	24.88*	1.97	..	20.01
		Libr	37.3(18)	2.69	1.82	..
2	20	MgO	10.2*	2.07	..	16.03
		LiCl	24.3(15)	2.55	1.32	..
6	78	ZnS(O <sub>4</sub> )	52.08*	1.646	..	23.60
		K <sub>2</sub> SO <sub>3</sub>	63.70(14)	2.704	3.076	..

\* Authors' values.

It is clearly seen from this Table that the values of  $\chi_{ma}$  calculated from the K value of its isomer are far different from the experimental ones. Similar disagreement has been found in the case of other salts as well.<sup>13</sup>

(b) Graphical discussion of the results of molar susceptibilities

From the study of the halides of alkali and alkaline earth metals Ikenmeyer<sup>23</sup> has shown that the molecular susceptibility is a linear function of the sum of the nuclear charges of the atoms constituting the molecules and can be expressed in the form  $-\chi_{ma} = C_1 \Sigma Z + C_2$  where  $\Sigma Z$  is the sum of the electrons in the compound and  $C_1$  and  $C_2$  are specific constants for a given series of salts. To verify this relation values of  $\chi_{ma}$  were plotted against  $\Sigma Z$  by Kido,<sup>14</sup> Trew,<sup>10</sup> and Prasad, Dharmatti and co-workers.<sup>12, 13</sup> Kido<sup>14</sup> found that the curves were definitely linear. Trew noticed some deviation from linearity and explained them as 'specific effects due to the crystalline forms of compounds investigated'. Prasad, Dharmatti and co-workers<sup>12,13</sup> not only found definite divergences from the linear relation but observed a pattern in these curves, which was repeated in the same way for the same salts of calcium, strontium and barium and thereby established the family relationship of the three elements from a new view point.

Values of  $\chi_{ma}$  for the same salts of magnesium and zinc were plotted against  $\Sigma Z$  by the authors and the graphs marked as (a) and (b), obtained are shown in Fig. 1. The non-linearity of the graphs definitely shows that

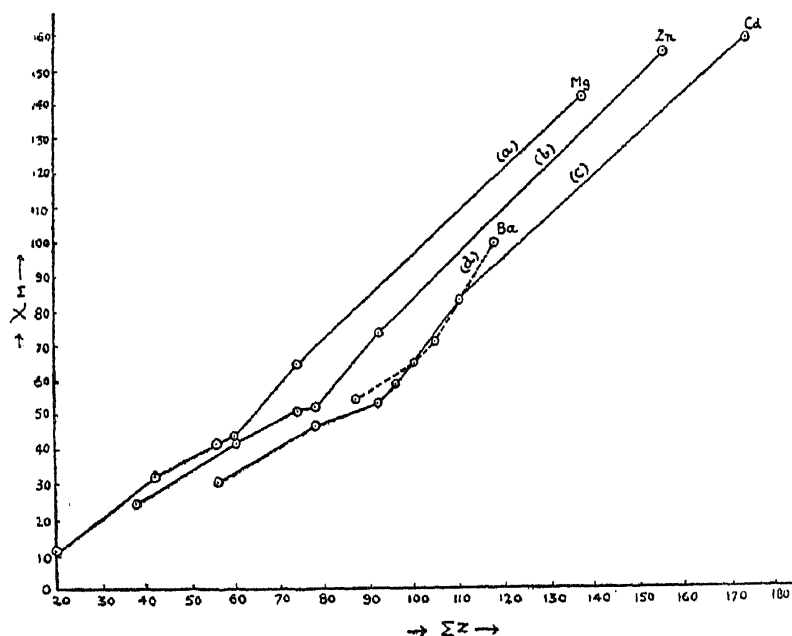


FIG. 1

Ikenmeyer's relation is not generally true and supports the observations of Prasad, Dharmatti and co-workers. The observed divergences may be due to different susceptibility contributions of the different anions.

Values of  $\chi_{ma}$  have been plotted against  $\Sigma Z$  for the same salts of cadmium and barium as those of magnesium and zinc in Fig. 1 and are marked as (c) and (d). The values of  $\chi_{ma}$  for cadmium salts were taken from Hollens



and Spencer<sup>9</sup> and those for barium from Prasad, Dharmatti and Kanekar.<sup>12</sup> It will be noticed that the plots for salts of magnesium, zinc and cadmium are of the same pattern while that of barium is definitely different. This is expected from the chemical analogy and the family characteristics of magnesium, zinc and cadmium.

When, however, the values of  $\chi_{ma}$  were plotted against  $\Sigma Z$  separately for inorganic and organic salts of magnesium and zinc, the curves shown in Fig. 2 were obtained. These are very nearly straight lines in all the four

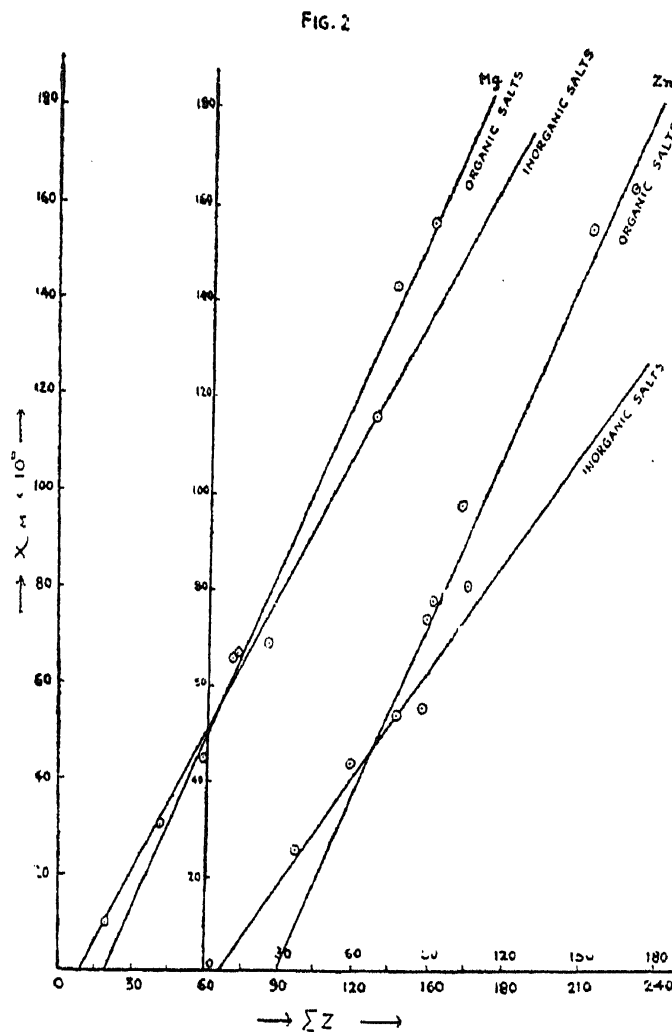


FIG. 2

cases. The linear relationship between  $\chi_{ma}$  and  $\Sigma Z$  suggested by Ikenmeyer is therefore true in the case of magnesium and zinc compounds when the organic and the inorganic salts are considered separately. Another important feature which will be noticed in Fig. 2 is that the slopes of the lines relating to the organic compounds are higher than those for the inorganic ones, showing thereby that the contribution per electron is higher in the case of organic salts than in the inorganic ones.

Further, when the values of  $\chi_{ma}$  for salts containing the same anions were plotted against the number of electrons (N) in magnesium, zinc, and cadmium ions, the graphs obtained, shown in Fig. 3, were a set of nearly

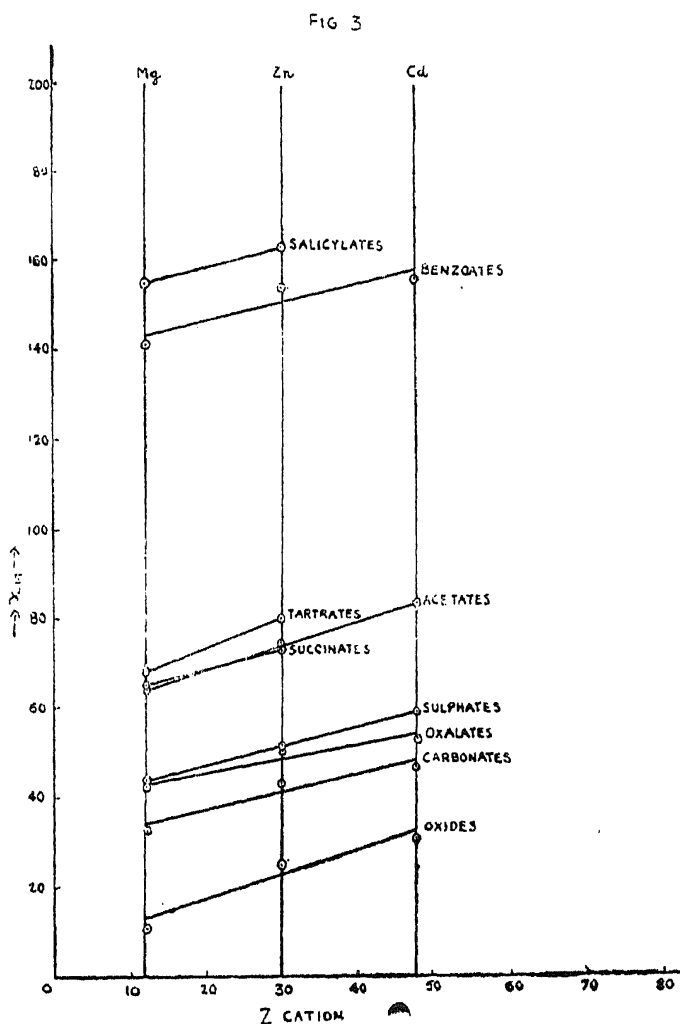


FIG. 3.

parallel straight lines. These lines have been smoothened out to some extent in the same manner as followed by Prasad, Dharmatti and Gokhale.<sup>13</sup> The values of  $C_1$  and  $C_2$  in the equation,  $-\chi_{ma} = C_1N + C_2$  for these lines, have been evaluated for different anions and are given in Table IV. Although

TABLE IV

Anions	Values for the Mg-Zn-Cd Series	
	$C_1$	$C_2$
Benzoates ..	0.5286	67.65
Phosphates ..	0.4781	48.00
Acetates ..	0.5150	29.00
Sulphates ..	0.4477	38.10
Oxalates ..	0.4202	36.50
Carbonates ..	0.4469	27.00
Oxides ..	0.6138	3.00
Formates ..	0.3838	19.20
Succinates ..	0.4677	58.80
Tartrates ..	0.6829	59.20
Citrates ..	0.7633	84.90

all the values of  $C_1$  are not the same as required by the parallelism of all the lines, yet they do not deviate much from the mean, excepting in one or two cases.

TABLE V  
*Ionic susceptibilities of magnesium*

Compound	$\chi_{ma}$ Authors	$\chi_{anion}$ Other workers	$\chi_{Mg^{++}}$
(a) Values $Mg^{++}$ from magnesium salts of inorganic acids			
MgO ..	10.2	3.36(15)	6.84
MgCO <sub>3</sub> ..	32.41	22.20(15)	10.21
		28.10(14)	4.31
		24.59(17)	7.82
		29.50(10)	2.91
MgSO <sub>4</sub> ..	43.88	33.60(15)	10.28
		39.00(14)	4.88
		37.00(10)	6.88
		39.00(10)	4.88
		40.10(10)	3.78
		37.50(17)	6.38
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ..	115.16	47.20(11)	6.92
		40.43(17)	11.43
		35.40(15)	14.79
		43.49*	9.39
(b) Values of $Mg^{++}$ from magnesium salts of organic acids			
Magnesium formate ..	43.82	16.9*	10.02
		20.2 (14)	3.42
		17.3 (27)	9.22
		17.6 (27)	8.62
Magnesium acetate ..	64.38	28.90(15)	6.58
		32.00(14)	0.38
		30.00(10)	4.38
		30.00( 9)	4.38
		29.80 27)	4.78
		31.40(14)	1.58
		30.20(27)	3.98
		28.76*	6.86
Magnesium benzoate ..	141.72	67.60*	6.52
		66.10(10)	9.52
Magnesium citrate ..	178.96	79.17*	6.87
Magnesium oxalate ..	41.67	27.94*	13.73
		28.50( 9)	13.17
Magnesium salicylate ..	155.45	72.69*	10.07
Magnesium succinate ..	64.72	51.66*	13.06
Magnesium tartrate ..	67.90	63.80(10)	3.90
		60.88*	6.82

\* These values are obtained by adding Pascal's corrected values for various constituents.

TABLE VI  
*Ionic susceptibilities of zinc ion*

Compound	$\chi_{ma}$ Authors	$\chi_{anion}$ Other workers	$\chi_{Zn^{++}}$
(a) Values of $Zn^{++}$ from zinc salts of inorganic acids			
ZnO ..	24.88	3.36(15)	21.52
ZnCO <sub>3</sub> ..	42.93	22.20(15) 28.10(14) 24.59(17) 29.50(10)	20.73 14.83 18.34 13.43
ZnSO <sub>4</sub> ..	52.08	33.60(15) 39.00(14) 37.00(10) 39.00(10) 40.10(10) 37.50(17)	18.48 13.08 15.08 13.08 11.98 14.58
Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ..	141.5	47.20(11) 40.43(17) 35.40(15) 43.49*	15.70 20.21 23.57 18.17
ZnSeO <sub>3</sub> ..	54.19	44.90(27) 47.50(14) 39.59**	9.29 6.69 14.60
(b) Values of $Zn^{++}$ from zinc salts of organic acids			
Zinc formate ..	50.73	16.9* 20.2 (14) 17.3 (27) 17.6 (27)	16.93 10.33 16.13 15.53
Zinc acetate ..	74.98	28.90(15) 32.00(14) 30.00(10) 30.00( 9) 29.80(27) 31.40(14) 30.20(27) 28.76*	17.18 10.98 14.98 14.98 15.38 12.18 14.58 17.46
Zinc benzoate ..	154.00	67.60* 66.10(10)	18.62 21.80
Zinc citrate ..	220.18	79.17*	20.61
Zinc oxalate ..	51.69	27.94* 28.50( 9)	23.75 23.19
Zinc salicylate ..	163.02	72.69*	17.64
Zinc succinate ..	73.14	51.66*	21.48
Zinc tartrate ..	79.98	63.80(10) 60.88*	16.18 19.10
Zinc phthalate ..	96.42	81.14	15.28

\* These values are obtained by adding Pascal's corrected values for various constituents.  
\*\* Mean value obtained from some selenites.

(c) *Ionic Susceptibility*

The susceptibilities of magnesium and zinc ions were deduced by subtracting all the known experimental values of anions of various other workers from the molecular susceptibilities of the salts studied in this investigation. The anion values used are given in column 3 of Tables V and VI. The values thus obtained are given in the last column of these Tables. No distinction has been made, as has been done in the previous publications from this laboratory,<sup>13</sup> between the solid and the solution data in evaluating the ionic susceptibilities, since the results are not much affected by such a distinction. Two separate means were taken for values of  $\chi_{Mg^{++}}$  and  $\chi_{Zn^{++}}$  given in the last columns of Tables V and VI, one deduced from inorganic salts and the other from the organic ones. These mean values are given in column 2 of Table VIII.

Another method was followed for the evaluation of the ionic susceptibilities of magnesium and zinc ions. Values of  $C_2$  (Table IV), obtained by producing the smoothed straight lines shown in Fig. 3 to meet the  $\chi_{ma}$  axis were taken to be the values of the susceptibilities of the respective divalent anions. Subtracting these anion values from the molecular susceptibilities of these magnesium and zinc salts, the ionic susceptibilities of  $Mg^{++}$  and  $Zn^{++}$  were deduced from each salt. The results obtained from the inorganic and the organic salts are given under two separate heads in Table VII.

TABLE VII

Anion	$\chi_{anions}$	$\chi_{Mg^{++}}$	$\chi_{Zn^{++}}$
(a) Inorganic Salts			
Oxide	3.00	7.20	21.88
Carbonate	27.00	5.41	15.93
Sulphate	38.10	5.78	13.98
Phosphate	49.50	5.39	14.17
(b) Organic Salts			
Oxalate	36.50	5.17	15.19
Acetate	29.00	6.38	16.98
Benzoate	67.65	6.42	19.70
Salicylate	75.00	5.46	13.02
Formate	19.20	5.42	12.33
Succinate	58.80	5.92	14.34
Tartrate	59.20	8.50	20.78
Citrate	77.00	8.32	22.06

The mean values of ionic susceptibilities deduced for magnesium and zinc ions from the inorganic and organic salts from the above Table are given in the third column of Table VIII.

TABLE VIII

Ions	$\chi_{\text{ion}}$ from Tables V & VI	$\chi_{\text{ion}}$ from Table VII
Mg <sup>++</sup> Inorganic ..	7.45	5.95
Mg <sup>++</sup> Organic ..	7.04	6.45
Zn <sup>++</sup> Inorganic ..	15.74	16.49
Zn <sup>++</sup> Organic ..	17.01	16.80

The values of susceptibilities for magnesium ion theoretically calculated according to Slater<sup>4</sup> and Angus<sup>5</sup> are 3.11 and 2.88, respectively, while those for zinc ion are 15.82 and 15.46. On comparing these values with those obtained in this investigation it is clear that the calculated values for magnesium ion are much lower than the experimental ones, while they are nearly the same as deduced from inorganic and organic salts in the case of zinc ion.

It appears from the above Table that the mean values of the susceptibilities of Magnesium and Zinc ions deduced from salts of organic acids are higher than those obtained from salts of inorganic acids, as it happens to be in the case of calcium, strontium and barium ions.<sup>12,13</sup> But when these results were subjected to statistical analysis, the differences between the two values were found to be insignificant. Hence these results can only have a qualitative meaning in support of the results of the aforesaid workers.<sup>12,13</sup>

Prasad, Dharmatti and Kanekar<sup>12</sup> have observed that as the number of carbon atoms in barium salts of organic acids increases, there is an increase in the susceptibility of the cation. The results obtained by Prasad, Dharmatti and Gokhale<sup>13</sup> also indicate the same trend. Hence the mean of all the values of  $\chi_{\text{Mg}^{++}}$  and  $\chi_{\text{Zn}^{++}}$  deduced from salts of different organic acids [cf. last column of Tables V (b) and VI (b)] were obtained and are given in the last column of Table IX which also gives the number of carbon atoms (column 2) and the total number of electrons (column 3) in the salts of the two elements.

It is clear from the results given in the above Table that the ionic susceptibility of a cation does not bear any quantitative relation with the number of carbon atoms in the anion.

TABLE IX

Compounds	No. of C-atoms	No. of Electrons	Observed $\chi_{ma}$	$\chi_{cation}$
(a) Magnesium salts				
Oxalate ..	2	56	41.67	13.45
Formate ..	2	58	43.82	7.82
Succinate ..	4	72	64.72	13.06
Acetate ..	4	74	64.38	4.11
Tartrate ..	4	88	67.7	5.36
Citrate ..	12	200	178.96	6.87
Benzoate ..	14	138	141.72	8.02
Salicylate ..	14	154	161.46	10.07
(b) Zinc salts				
Oxalate ..	2	74	51.69	23.47
Formate ..	2	76	50.73	14.73
Succinate ..	4	90	73.14	21.48
Acetate ..	4	92	74.98	16.82
Tartrate ..	4	106	79.98	17.64
Phthalate ..	8	114	95.59	15.28
Citrate ..	12	284	220.18	20.61
Benzoate ..	14	156	154.00	20.21
Salicylate ..	14	172	157.02	17.64

## (d) Ionic Radius

Ionic radii of magnesium and zinc ions were calculated from the susceptibilities of these ions deduced from inorganic and organic salts from the relation,

$$\sqrt{\frac{\Sigma r_e^2}{\Sigma r_t^2}} = \frac{r'_e}{r'_t}$$

where  $\Sigma r_e^2$  is computed from the known value of  $\chi_{ion}$  from Langevin's equation,  $\Sigma r_t^2$  is calculated theoretically from Slater's approximate wave function, and  $r'_t$  is the effective radial electron density of the outermost shell. The calculated values of radii are given in Table X. For the sake of comparison the values of radii of magnesium and zinc ions obtained by other methods are also included in this Table.

TABLE X

Ions	Author's calculated values of ionic radius in Å. U.	Values of Ionic radius by other workers from X-ray data in Å. U.		
		Wyckoff <sup>25</sup>	Bragg <sup>24</sup>	Clark <sup>26</sup>
Mg <sup>++</sup> (Inorganic) ..	0.9645	0.75	0.75	0.65
Mg <sup>++</sup> (Organic) ..	0.9833			
Zn <sup>++</sup> (Inorganic) ..	1.233	0.83	..	0.74
Zn <sup>++</sup> (Organic) ..	1.263			

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