

# DIAMAGNETIC SUSCEPTIBILITY OF CADMIUM ION

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PRASAD and co-workers<sup>1</sup> have determined the average values of the susceptibilities of many ions in combination with inorganic and organic anions with a view to compare them with those calculated theoretically by Slater's<sup>2</sup> and Angus's<sup>3</sup> methods. Their work includes a detailed study of all the ions of the second group of the periodic table with the exception of the cadmium ion. The ionic susceptibility of cadmium reported in the I.C.T. is 20.0\* while the values deduced by Kido<sup>4</sup> and Hollens & Spencer<sup>5</sup> are 20.3 and 24.85, respectively. All these values are very much lower than those calculated by the Slater's and Angus' methods (34.25 and 33.9, respectively). The object of the present paper is to examine this discrepancy and to complete the data of the susceptibilities of ions of the second group.

## EXPERIMENTAL

The salts used in this investigation were either of Merck's extra-pure quality or were prepared in pure state in these laboratories. The latter were carefully analysed and only those specimens which were found to be of the required purity were used for the measurement of the susceptibilities. The results of analyses are given in column 2 of Tables I(a) and (b). A modified form of the Gouy's balance was used for these measurements, the method being the same as that described by Prasad, Dharmatti and Gokhale.<sup>1</sup> All the precautions detailed in that paper were taken at the time of the measurements. KCl ( $\chi_a = 0.516$ ) was used as the standard substance. The results obtained are a mean of six independent readings, three being taken with one specimen tube and the remaining three with another tube. This procedure averages out errors due to (1) the packing of the substances uniformly and tightly in the specimen tube and (2) the non-uniformity of specimen

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\* All the susceptibility values are expressed in  $-1 \times 10^{-6}$  c.g.s. units.

tubes, if any. The results obtained for salts of inorganic and organic acids are given in Tables I(a) and (b), respectively. In these tables,

$\chi_a$  = the specific susceptibility,

$\chi_m$  = the molecular susceptibility,

$\chi_{ma}$  = the molecular susceptibility of the anhydrous salt.

$\chi_{ma}$  is obtained by deducting the susceptibility of molecules of water of crystallisation ( $\chi_{H_2O} = 12.96$ ) from the molecular susceptibility of the hydrate, assuming strict additivity. The values of  $\chi_m$  and  $\chi_{ma}$  are given one below the other.

For comparison, the experimental values obtained by previous workers are given in column 6 of the tables.

TABLE I(a)

Compound	Analysis % Cd			Authors' Value		Values of other workers	
	Ob- served	Calcu- lated		$\chi_a$	$\chi_m$	$\chi_m$	Reference
CdO	.. ..	..	0.2320	29.80	30.70		Hollens and Spencer <sup>5</sup>
Cd(OH) <sub>2</sub>	.. 76.18	76.76	0.2805	41.08	40.60		do
CdCl <sub>2</sub>	.. 61.21	61.31	0.3749	68.92	68.74 67.50 58.65		do Kido <sup>4</sup> I.C.T.
CdBr <sub>2</sub> ·4H <sub>2</sub> O	.. 32.58	32.63	0.3964	136.49 84.65*	103.5 93.00 87.10 92.10		I.C.T. Kido <sup>4</sup> Hollens and Spencer <sup>5</sup> Flordal and Frivold <sup>11</sup>
CdI <sub>2</sub>	.. 30.68	30.68	0.3139	115.00	112.7 117.20 117.20		Kido <sup>4</sup> Hollens and Spencer <sup>5</sup> I.C.T.
CdS	.. ..	..	0.3531	51.02	49.57		Hollens and Spencer <sup>5</sup>
CdSO <sub>4</sub>	.. ..	..	0.2858	59.60	58.60 59.23 45.87		Kido <sup>4</sup> Hollens and Spencer <sup>5</sup> Ray Chaudhari <sup>12</sup>
Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	.. ..	..	0.3684	113.70 61.86*	114.50		Hollens and Spencer <sup>5</sup>
CdCrO <sub>4</sub>	.. 49.61	49.20	0.0736	16.81			
Cd(IO <sub>3</sub> ) <sub>2</sub>	.. 24.03	24.31	0.2403	111.10	108.4		Hollens and Spencer <sup>5</sup>
Cd <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	.. ..	..	0.3122	164.60	159.20		Hollens and Spencer <sup>5</sup>
CdCO <sub>3</sub>	.. ..	..	0.2960	51.05	52.6 46.72 47.34		Kido <sup>4</sup> Hollens and Spencer <sup>5</sup> Prasad and Desai <sup>1</sup>

TABLE I (b)

Compound	Analysis % Cd		Author's Value		Values of Other Workers	
	Observed	Calculated	$\chi_a$	$\chi_m$	$\chi_m$	Reference
$\text{CdH}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	.. 47.19	47.12	0.3410	81.31 55.39*		
$\text{Cd}(\text{CH}_3\text{COO})_2$	.. ..	..	0.3629	83.66	83.66 84.30	Hollens and Spencer <sup>5</sup> Kido <sup>4</sup>
$\text{Cd}(\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COO})_2$	.. 43.71	43.41	0.4260	110.10		
$\text{Cd}(\text{C}_{16}\text{H}_{31}\text{O}_2)_2$	.. 17.8	18.0	0.6455	402.05		
$\text{Cd}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	.. 16.9	16.9	0.6491	440.63		
$\text{Cd}(\text{CH}_2)_2 \cdot (\text{COO})_2$	.. ..	..	0.3123	71.32		
$\text{Cd}(\text{CHOHCOO})_2$	.. 43.76	43.13	0.3171	82.58		
$\text{CdC}_2\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$	.. 45.0	44.8	0.3705	92.75 66.83*	58.50	Hollens and Spencer <sup>5</sup>
$\text{CdC}_2\text{O}_4$	.. 55.91	56.08	0.2765	55.39	53.13	Hollens and Spencer <sup>5</sup>
$\text{Cd}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 2\text{H}_2\text{O}$	.. 28.59	28.78	0.4789	187.02 161.10*	184.90	Hollens and Spencer <sup>5</sup>
$\text{Cd}(\text{C}_6\text{H}_4\text{OHCOO})_2 \cdot \text{H}_2\text{O}$	27.75	27.78	0.4554	186.16 171.20*		
$(\text{CdC}_3\text{H}_7\text{COO})_2 \cdot \text{H}_2\text{O}$	.. 36.6	36.0	0.4730	144.04 131.08*		

\* The molecular susceptibility of the anhydrous salt calculated from the  $\chi_m$  of the hydrate.

### DISCUSSION OF RESULTS

It will be seen from Tables I (a, b) that the values obtained by the authors are generally in fair agreement with other reported values, especially with those obtained by Kido.<sup>4</sup> It is remarkable that even though, in many cases, the authors' values agree fairly well with those obtained by Hollens and Spencer<sup>5</sup> their values are definitely lower for some salts. In cases in which authors' values differ much from those of other workers, the authors have carefully repeated the measurements with fresh samples and have established the reproducibility of the results.

### Ionic Susceptibility of Cadmium

(a) *Method of averages.*—The susceptibility of cadmium ion has been determined, in the first instance, by the method of averages followed by Prasad and co-workers. For this purpose, various values of the anions

reported in the literature (*cf.* Table II) were subtracted from the molecular susceptibilities of the cadmium salts and from the values of the susceptibility of cadmium ion, thus obtained, mean values calculated for this ion in combination with (i) inorganic and (ii) organic anions were found to be 20.82 and 25.32, respectively. The difference between the two values has been found to be significant from a standard statistical test. These results substantiate the observation of Prasad and co-workers that the susceptibility of a cation deduced from salts of organic acids by the statistical method is higher than that obtained from salts of inorganic acids.

TABLE II

For the several values of the susceptibilities of the chloride, bromide, iodide, sulphide, sulphate, nitrate, carbonate, phosphate, chromate, benzoate, oxalate, tartrate, malonate, succinate, acetate, salicylate, propionate and butyrate ions refer to Prasad, Dharmatti, Kanekar and Datar (under publication).

Ion	$\chi_{\text{ion}}$
O <sup>2-</sup> ..	4.61 Pascal <sup>6</sup> 3.36 do
IO <sub>3</sub> <sup>-</sup> ..	52.20 Kido <sup>4</sup> 47.30 Rao and Sriraman <sup>8</sup> 45.00 Hollens and Spencer <sup>5</sup> 51.40 Trew <sup>7</sup> 46.75 Prasad and Desai <sup>1</sup>
OH <sup>-</sup> ..	8.50 Kido <sup>4</sup>
(HCOO) <sup>-</sup> ..	16.90 Pascal's data <sup>6</sup> 20.2 Kido <sup>4</sup> 17.30 Rao and Sriraman <sup>8</sup> 17.60 do
(C <sub>17</sub> H <sub>35</sub> COO) <sup>-</sup> ..	207.50 (Walvekar) <sup>9</sup>
(C <sub>15</sub> H <sub>31</sub> COO) <sup>-</sup> ..	183.50 (Walvekar) <sup>9</sup>

Both the mean values for the susceptibility of Cd<sup>++</sup> are definitely lower than those calculated by the Slater's or Angus' methods. It may, at first sight, appear that the difference between the observed and the theoretically calculated values can be accounted for by the fact that there arises a temperature-independent paramagnetism in the solid state which is not generally taken into account in calculating the susceptibilities of free ions.

If the additivity law of ions is valid, the magnitude of the factor due to the paramagnetism independent of temperature will be very small and

would cause only a small increase in the observed value of the diamagnetic susceptibility of the ion. This cannot account for the large difference in the observed and the calculated values. Trew<sup>13</sup> has also observed a similar difference between the theoretical and observed values of the susceptibility of thallium ion. She finds that the Slater's calculations agree with experimental results for ions of elements of atomic Nos. 12-20 and Angus' values for those of Nos. 20-28 but are a bit too high for the heavy ions. Probably Slater's and Angus' calculations of the screening constant do not hold for such heavy ions as cadmium.

(b) *Graphical Method.*—The method of averages used in determining the susceptibility of cadmium ion avoids the arbitrary procedure of selecting a particular anion value as correct from among a number of widely divergent values and may, therefore, be considered to give satisfactory values of the susceptibility of cations. However, since the values of anions reported in the literature are obtained by fixing some value of anion as standard on some assumptions, theoretical or otherwise, the method of averages cannot be considered to be free from the errors involved in these assumptions. Hence it would be necessary to have a method of determining the susceptibility of ions which will depend merely on the accuracy of the experimental results of molecular susceptibilities. Kido<sup>4</sup> and Prasad and co-workers have observed a linear relation between the molar susceptibilities ( $\chi_m$ ) of compounds having the same anion and cations belonging to the same family of elements in the periodic table and the number of electrons (N) in the cations. These workers have employed this relation for the evaluation of the susceptibilities of several ions. This method appears to be a better method than the earlier method of averages, Prasad, Dharmatti and Ghose<sup>1</sup> found that the  $\chi_m$ -N relation for salts of Mg, Zn, Cd and Hg having a common anion was definitely linear. They used this relation to obtain the susceptibility of Hg ion. For drawing the graphs these authors used the susceptibilities of corresponding cadmium salts determined by one of us (R.A.B.). The present authors have drawn similar graphs for the carbonates, phosphates, salicylates, butyrates, propionates and malonates of these metals (Fig. 1). It will be observed that the graphs are straight lines. In order to confirm that the plotted points definitely lie on straight lines, values were calculated from the relation  $\chi_m = \text{slope of the straight line} \times \text{number of electrons in the cation} + \text{intercept of the line on the } \chi_m \text{ axis}$ . The good agreement found between the observed and the calculated values establishes that the relation between  $\chi_m$  and N is definitely linear in the case of these salts as well.

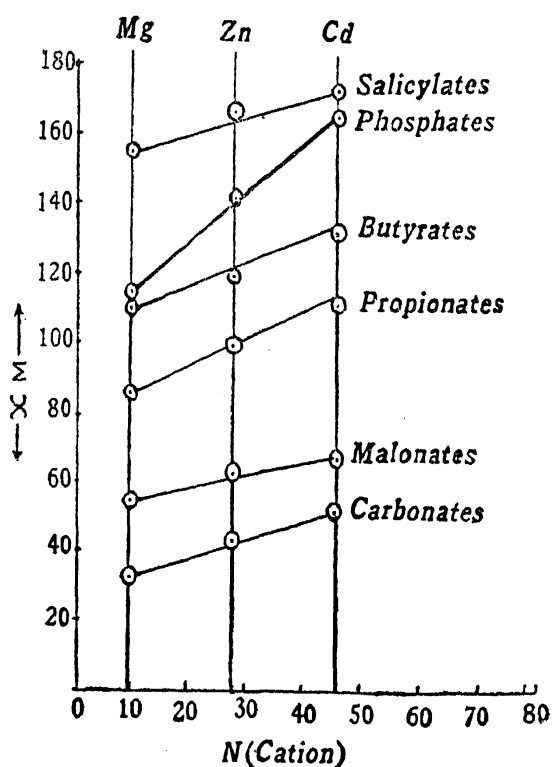


FIG. 1

The linear relation has been used for the evaluation of the susceptibilities of ions in the following manner: (1) the value of the intercept is the measure of the susceptibility of the anion and (2) the susceptibility of the cation is calculated by (a) subtracting the susceptibility of the anion from the molar susceptibility of the salt and is designated as  $\chi_A$ , and (b) by multiplying the slope of the straight line ( $\partial\chi_m/\partial N$ ) by  $N$ , the number of electrons in the cation (since, intercept =  $\chi_{\text{anion}}$ ;  $\chi_m = (\partial\chi_m/\partial N) \cdot N + \chi_{\text{anion}}$  and  $\chi_m = \chi_{\text{anion}} + \chi_{\text{cation}}$ ), and is designated as  $\chi_B$ .

Values calculated in this way for the various anions in combination with Mg, Zn, Cd, and Hg ions are shown in Table III, Column 3.

It will be seen that the values of  $\chi_{\text{anions}}$  are of the same order as those reported by various workers (Table II). This indicates that the graphical method gives quite reliable values. The values of  $\chi_A$  and  $\chi_B$  in combination with an anion are not far different from each other. The  $\chi_B$  values are, however, more correct than  $\chi_A$  values which contain small experimental errors involved in the measurement of the molecular susceptibilities of the individual salts. A mean of all the  $\chi_B$  values deduced from the various salts of inorganic acids has been taken and given at the end of the table, since these values do not differ from the mean values by more than the experimental error (5%). Also it will be observed that the mean value is higher than that calculated by the method of averages and far lower than those calculated by Slater's and Angus' methods.

TABLE III

Compound	Slope	$\chi_{\text{anion}}$	$\chi_A$	$\chi_B$
Oxide ..	0.550	6.00	23.80	25.30
Chloride ..	0.510	23.00	22.49	23.46
Bromide ..	0.560	33.00	24.63	23.00
Iodide ..	0.550	44.00	27.00	25.30
Sulphate ..	0.520	38.00	21.60	23.92
Carbonate ..	0.520	26.50	24.52	23.92
Phosphate ..	0.490	50.00	21.53	22.54
Mean ..			23.79	23.92
Oxalate ..	0.420	36.00	19.39	19.32
Formate ..	0.430	19.50	16.39	19.78
Acetate ..	0.490	29.50	24.66	22.54
Tartrate ..	0.531	60.00	22.58	24.39
Benzoate ..	0.540	68.10	24.90	24.84
Palmitate ..	0.600	185.00	32.05	27.61
Stearate ..	6.550	208.50	23.63	25.30
Butyrate ..	0.659	51.50	28.08	30.31
Propionate ..	0.692	39.75	30.60	31.83
Salicylate ..	0.440	75.00	21.20	20.24
Malonate ..	0.350	52.00	14.83	16.10

The values of  $\chi_A$  and  $\chi_B$  are, however, different in combination with different organic anions. This means that the susceptibility of cadmium ion is not a fixed quantity but varies from salt to salt when this ion combines with organic anions. Probably, this peculiarity is exhibited even in salts of cadmium with inorganic anions but is not so marked as in the case of organic anions. A mean of such widely varying values of  $\chi_{\text{Cd}^{++}}$  obtained from salts of organic acids has, therefore, no significance.

The observed variations in the values of the susceptibility of cadmium ion deduced from various salts may be due to several reasons. Since the crystal structure and the co-ordination number of cadmium for different cadmium salts are different, these differences would, to some extent, cause variations in the values of the ionic susceptibility of cadmium deduced from these salts. It is also possible that the susceptibility of cadmium ion may depend on the nature and the size of the anion with which it combines. The values of  $\chi_{\text{Cd}^{++}}$  obtained from the graph (Table III) tend to indicate the plausibility of this explanation. The values of  $\chi_{\text{Cd}^{++}}$  are found to increase with increase in the size of the anion; however, no definite relation has been observed between these values and the number of carbon atoms in the organic anion.

The authors have also plotted the values of  $\chi_{ms}$  of salts of (i) inorganic and ii) organic acids against total number of electrons in the molecules of the

salts. The graphs (Fig. 2) obtained show that Ikenmeyer's relation<sup>10</sup> is not obeyed by all salts. This result is in conformity with the observations of Prasad and co-workers. Prasad, Dharmatti and Ghose<sup>1</sup> have observed

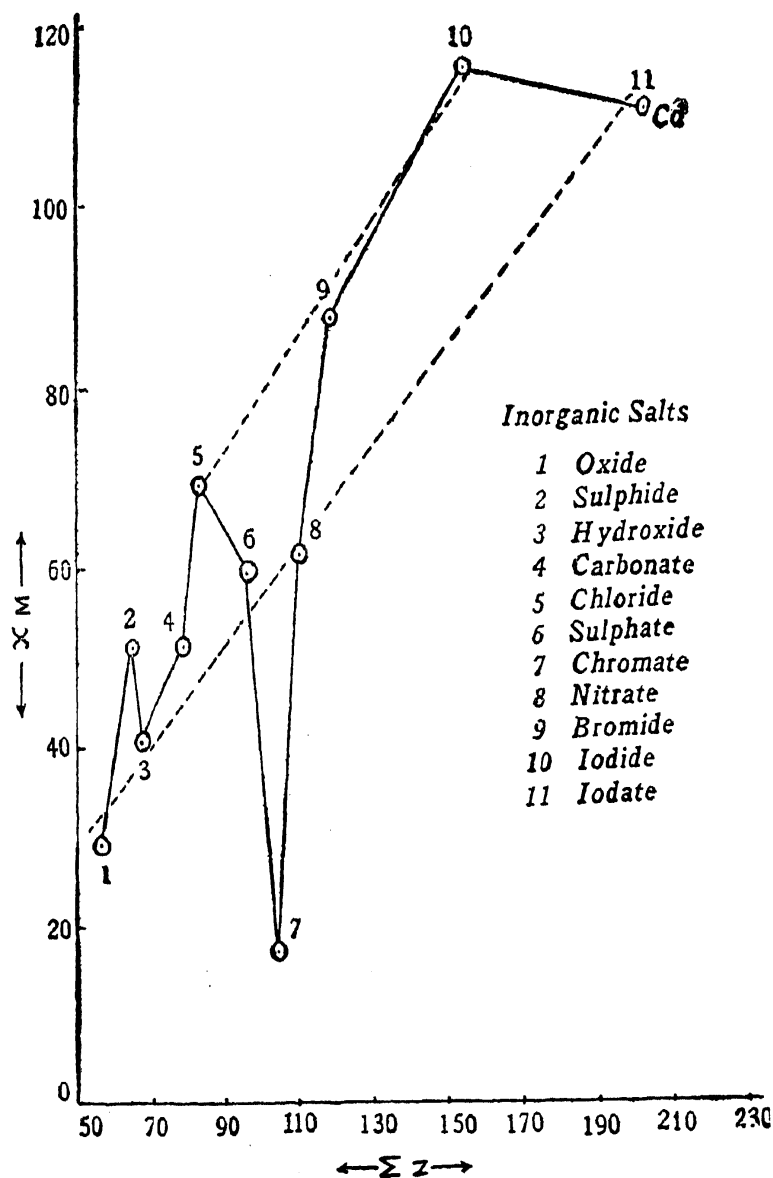


FIG. 2a

that the patterns obtained by plotting the values of  $\chi_m$  of the corresponding salts of Mg, Zn, Cd and Hg against  $\Sigma Z$  are strikingly similar. The data of the molecular susceptibilities of cadmium salts used by them for drawing this graph is the same as that reported in this paper.

A closer examination of the graphs in Fig. 2 reveals that the points corresponding to (i)  $\text{CdCl}_2$ ,  $\text{CdBr}_2$ ,  $\text{CdI}_2$  and (ii)  $\text{CdO}$ ,  $\text{CdCO}_3$ ,  $\text{CdSO}_4$ ,  $\text{Cd}(\text{IO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$  appear to lie on straight lines. Neglecting little divergences a mean straight line (iii) is also drawn through the plotted points for organic salts. The inclinations ( $C_1$ ) and the intercepts ( $C_2$ ) of these straight lines on  $\chi_m$  axis, given in Table IV, are very different from each other.



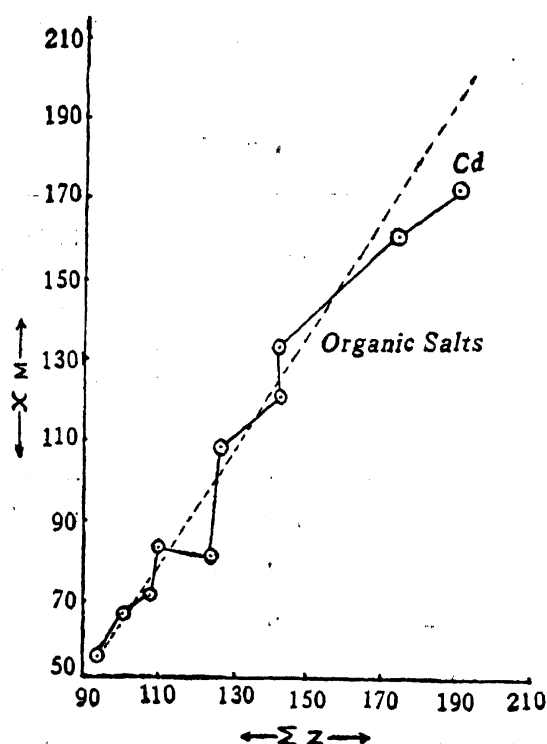


FIG. 2b

TABLE IV

$C_1$	$C_2$
(i) $0.520 \times 10^{-6}$	8.31
(ii) $0.63 \times 10^{-6}$	15.19
(iii) $1.505 \times 10^{-6}$	-93.39

Ikenmeyer's relation reduces to,

$$\chi_m = C_2 \text{ when } \Sigma z \text{ is zero.}$$

The existence of an intercept  $C_2$  means that there is some contribution of susceptibility to the molar susceptibility of a salt even when the number of electrons in the molecule is zero. This is possible if  $C_2$  is considered as a correction constant like those given by Pascal<sup>6</sup> for various linkages in carbon compounds. However, the values of  $C_2$  given above are so large that it is difficult to attribute such a significance to them.

### *Ionic Radius*

The ionic radius of  $\text{Cd}^{++}$  has been calculated from the observed values for the susceptibility of the ion from salts of inorganic and organic acids.

The results obtained are given in Table V along with the values obtained by other workers by other methods.

TABLE V

Ionic radii calculated from $\chi_{Cd^{++}}$ (Authors)			Ionic radii of Cadmium (Other workers)	
Inorganic		Organic	Goldschmidt	Pauling (Theoretical)
Statistical Method	Graphical Method	Statistical Method		
1.28 Å	1.38 Å	1.41 Å	1.03 Å	0.97 Å

## SUMMARY

1. The magnetic susceptibility of a number of cadmium salts of inorganic and organic acids have been measured on the modified form of Gouy's balance.

2. The susceptibility of the cadmium ion has been deduced by the statistical method both from salts of inorganic acids and organic acids; the mean value of the ion obtained from the latter type of salts is significantly higher than that obtained from the former type.

3. From the  $\chi_m$ -N graphs, the susceptibility values of anions and cadmium ion in combination with these anions have been determined. The values for the susceptibility of cadmium ion have been calculated in two ways: (i) by multiplying the slopes of the straight lines obtained by plotting  $\chi_m$ -N graphs, by the number of electrons in the cadmium ion, and (ii) by subtracting the values of the anions (obtained from the intercepts) from the molecular susceptibilities of cadmium salts. The former values are more correct. The susceptibility of cadmium ion obtained graphically from various salts of inorganic acids is fairly constant but varies in combination with organic anions.

4. Ionic radius of cadmium has been calculated from the average values for the susceptibility of the ion from salts of inorganic and organic acids.

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