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Citation: *The Journal of Chemical Physics* **17**, 819 (1949); doi: 10.1063/1.1747405

View online: <http://dx.doi.org/10.1063/1.1747405>

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Diamagnetic Susceptibilities of Mercuric and Mercurous Ions

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(Received January 3, 1949)

Magnetic susceptibilities of a number of pure mercuric and mercurous salts of inorganic and organic acids have been measured and it has been shown that Ikenmeyer's relation does not hold true in these compounds. A linear relation has been established between the molecular susceptibilities of salts of Mg, Zn, Cd, and Hg (*ic*) containing the same anion and the number of electrons contained in the cations. The significance of this relation is discussed in detail primarily with a view to finding out the susceptibilities of mercuric and mercurous ions.

A STUDY of the literature shows that a number of widely different theoretical and experimental values have been assigned to the susceptibility of an ion or an atom by various authors. These divergences may be attributed to (i) the use of different methods for the evaluation of $\Sigma \bar{r}^2$ in calculating the theoretical values, (ii) the choice of a value of the susceptibility of an ion from a number of widely different reported values on a more or less arbitrary principle for the calculation of the values of the susceptibilities of other ions on the additivity basis, (iii) the inaccuracy of the methods employed for the measurement of the susceptibilities, and (iv) the use of substances of different purities by different workers for measurement. Systematic investigations have been carried out by Prasad, Dharmatti, and co-workers¹ on the magnetic properties of a large number of Ca, Sr, Ba, Mg, Zn, and Pb salts of inorganic and organic acids for the determination of the susceptibilities of these cations, on the basis that the molecular susceptibility of a heteropolar salt is the sum of susceptibilities of the constituent ions. In order to obviate errors caused by the choice of a particular value for an anion as a standard, they subtracted all the known values of several anions from the molecular susceptibilities of the compounds and have taken an arithmetic mean of the values thus obtained as the standard value for the cation. They found that the mean value of the susceptibility for the cation deduced from salts of inorganic acids is lower than that deduced from its salts of organic acids.

The present investigation deals with the measurement of the susceptibilities of a large number of inorganic and organic salts of mercuric and mercurous mercury. The ionic susceptibility of divalent mercury, given in the *International Critical Tables*, is -33.4×10^{-6} [Pascal], while Kido's² values are -36.6×10^{-6} and -40.3×10^{-6} for the mercuric and mercurous ions (calculated for the unit Hg^+), respectively. The theoretical values, calculated for the mercuric ion, according to Slater's and Angus' methods, are -47.77

$\times 10^{-6}$ and -47.57×10^{-6} , respectively, thus showing that there is a great divergence between the various theoretical and experimental values. This calls for a confirmation of the reported experimental values for these ions.

EXPERIMENTAL

The susceptibilities of the compounds were measured by using a modified Gouy's balance, specially constructed by Prasad and co-workers¹ for their investigations. The details of the design and the necessary precautions to be taken are described by Prasad, Dharmatti, and Gokhale.^{1a}

All the salts used in this investigation were chemically pure. Most of the compounds were of Merck's extra pure quality stored up for this work and those which could not be obtained in the purest form were prepared in the laboratory and their purity was ascertained before use.

RESULTS

The results obtained for mercuric salts are given in Tables I(a) and I(b) and for mercurous salts in Tables II(a) and II(b). In these tables, column I gives the chemical formulas of the substances—together with their analysis in the case of the substances prepared in the laboratory. Column 2 gives the total number of electrons (Z) in the compounds. The observed values of the specific susceptibilities (χ_a) and the molecular susceptibilities (χ_m) are given in the third column, one below the other. The only hydrated salt investigated was mercurous nitrate. χ_m value given for this compound in column 3 is that of the anhydrous salt and has been obtained by subtracting the susceptibility value for two molecules of water from the molecular susceptibility value of the hydrated salt. Columns 4 and 5 give, respectively, the experimental values obtained by previous workers and those computed for the salts by adding up the susceptibility values of anions and cations reported by the same authors. The values computed by using the theoretical ionic values of Pauling, Slater, and Angus are given in the last column and have been indicated by letters P , S , and A , respectively. For the organic compounds, the method of Angus and Farqu-

¹ Prasad, Dharmatti, and Kanekar, *Proc. Acad. Sci.* **16**, 307 (1942). ^a Prasad, Dharmatti, and Gokhale, *ibid.* **20**, 224 (1944).

^b Prasad, Dharmatti, and Amin, *ibid.* **26**, 312 (1947). ^c Prasad, Dharmatti, and Khanolkar, *ibid.* **26**, 328 (1947).

² Kido, *Sci. Rep. Tohoku. Imp. Univ.* **21**, 149 (1922); **21**, 288-97 (1932).

TABLE I(a). Mercuric salts of inorganic acids.

Compounds	Z	Author's values	Other workers	Computed, using the experimental ionic values of the constituents by the same author	χ_m	Computed from theoretical ionic values
HgCl ₂	114	0.3028 82.21	65.16(4) 51.59(5) 80.90(2) 86.30(6)	73.6 Pascal		Hg ⁺² +2(Cl) ⁻¹ 113.00(P) 99.35(S) 93.29(A)
HgBr ₂	150	0.2914 105.10	93.74(4) 108.10(5) 109.20(6)	106.00 Kido 94.40 Pascal		Hg ⁺² +2(Br) ⁻¹ 163.00(P) 127.79(S) 120.87(A)
HgI ₂	186	0.2931 133.20	123.70(6) 134.10(2)	143.00 Kido 122.60 Pascal		Hg ⁺² +2(I) ⁻¹ 215.00(P) 167.43(S) 158.21(A)
HgO	88	0.2343 50.76	51.99(5) 52.70(6) 52.64(7)			Hg ⁺² +O ⁻² 67.60(P) 60.92(S) 58.82(A)
HgS	96	0.2382 55.44	53.42(5)			Hg ⁺² +S ⁻² 95.00(P) 85.18(S) 80.20(A)
HgSO ₄	128	0.2484 73.70	64.80(2)	75.60 Kido 67.00 Pascal		Hg ⁺² +(SO ₄) ⁻² 106.80(P) 101.78(S) 93.88(A)
Hg(NO ₃) ₂	142	0.2391 77.61	74.00(2)	76.80 Kido 61.80 Pascal		Hg ⁺² +2(NO ₃) ⁻¹ 130.82(P) 126.89(S) 115.29(A)
Hg(CN) ₂	106	0.2613 66.00		69.80 Kido 55.00 Pascal		Hg ⁺² +2(CN) ⁻¹ 99.30(P) 85.95(S) 87.79(A)
Hg(CNS) ₂	138	0.3046 96.51		112.80 Kido 86.60 Pascal		Hg ⁺² +2(CNS) ⁻¹ 179.30(P) 170.77(S) 153.05(A)
HgCrO ₄	136	0.0396 12.54				Hg ⁺² +(CrO ₄) ⁻² 112.00(P) 105.87(S) 97.72(A)
Hg found: 55.49%						
Hg theory: 55.64%						
Hg found: 43.92%						
Hg theory: 44.12%						
Hg found: 63.19%						
Hg theory: 63.31%						
Hg found: 63.16%						
Hg theory: 63.36%						

harson³ was followed. Throughout this paper all the susceptibility values are expressed in -1×10^{-6} c.g.s. unit.

DISCUSSION OF RESULTS

It will be observed from the above tables that the molecular susceptibilities of many compounds obtained by the authors agree quite well with those found by previous workers. Further, in general, there is a large difference between the authors' values of χ_m and those computed from theoretical values, especially in the case of the mercurous salts. These theoretically computed values represent the sum of the susceptibilities of the free ions which are not influenced by external factors, whereas when a compound is formed the ions are influenced by one another and this causes an alteration in the effective external charge distribution of the ions and hence the departure from strict additivity. It will be noticed from the tables that the agreement between the experimental values and those computed in column

5 by adding up the cation and anion values given by the same author is fairly good.

(a) Graphical Discussion of the Molar Susceptibilities

Prasad and co-workers¹ have shown that when the molecular susceptibilities of compounds containing the cations belonging to a particular group or subgroup in the periodic table are plotted against the total number of electrons in the compounds, the plots obtained form a pattern which is characteristic of the cations of the group or the subgroup. This has been found to be true in the case of salts of (i) Ca, Sr, Ba;^{1a} (ii) Mg, Zn, Cd;^{1b} and Tl and Pb.^{1c} Hence, the values of the susceptibilities of the mercuric salts were plotted against the total number of electrons in the compounds and the graph obtained is shown in Fig. 1, along with similar graphs for salts of Mg, Zn, and Cd. The susceptibility values of Mg and Zn salts used for plotting these graphs have been taken from the data of Prasad, Dharmatti, and Amin^{1b} and the values for Cd salts have been taken from an unpublished work done in the laboratory. It is clearly seen from the figure that all the graphs are similar in nature. Since magnetic susceptibility is essentially a physical property, depending on the electrons in the atoms, it is reasonable to expect a similarity in the magnetic behavior of the salts of a particular group of cations having similar electronic configuration.

TABLE I(b). Mercuric salts of organic acids.

Compounds	Z	Author's values	Other workers		χ_m Computed, using the experimental ionic values of the con- stituents by the same author	Computed from theoretical ionic values
Hg(HCOO) ₂	126	0.2512 73.00	—	67.4	Pascal	Hg ⁺² +2(HCOO) ⁻¹ 88.50(P) 81.27(S) 81.07(A)
Hg found: 68.91% Hg theory: 69.02%						
Hg(CH ₃ COO) ₂	142	0.3086 98.37	100.2 (2)	100.6	Kido 91.2 Pascal	Hg ⁺² +2(CH ₃ COO) ⁻¹ 112.0 (P) 104.77(S) 104.57(A)
Hg found: 62.76% Hg theory: 62.94%						
Hg(C ₆ H ₅ COO) ₂	206	0.3974 175.90	—	168.60	Pascal	Hg ⁺² +2(C ₆ H ₅ COO) ⁻¹ 186.10(P) 178.87(S) 178.67(A)
Hg found: 45.17% Hg theory: 45.31%						
HgC ₂ O ₄	124	0.2378 68.63	—	61.34	Pascal	Hg ⁺² +(C ₂ O ₄) ⁻² 82.70(P) 75.47(S) 75.27(A)
Hg found: 69.29% Hg theory: 69.50%						
Hg(CHOHCOO) ₂	156	0.3002 104.70	—	94.28	Pascal	Hg ⁺² +(CHOHCOO) ⁻² 115.40(P) 108.17(S) 107.97(A)
Hg found: 57.31% Hg theory: 57.51%						
Hg(C ₁₈ H ₁₅ O ₂) ₂	398	0.5957 457.10	—	—	—	Hg ⁺² +2(C ₁₈ H ₁₅ O ₂) ⁻¹ 488.00(P) 480.77(S) V 480.57(A)
Hg found: 25.92% Hg theory: 26.13%						
Hg(C ₁₈ H ₁₁ O ₂) ₂	366	0.5776 410.90	—	—	—	Hg ⁺² +(C ₁₈ H ₁₁ O ₂) ⁻¹ 441.00(P) 433.77(S) 433.57(A)
Hg found: 28.02% Hg theory: 28.19%						

³ Angus and Farquharson, Proc. Roy. Soc. 136A, 579 (1932).

TABLE II(a). Mercurous salts of inorganic acids.

Compounds	Z	Author's values	Other workers	Computed, using the experimental ionic values of the constituents by the same author	Computed from theoretical ionic values
Hg ₂ Cl ₂	194	0.2440 115.20	143.46(6) 119.60(2) 108.60(5)	124.80 Kido	Hg ₂ ⁺⁺ +2(Cl) ⁻¹ 168.00(P) 147.12(S) 140.86(A)
Hg ₂ Br ₂	230	0.2576 144.50	—	150.00 Kido	Hg ₂ ⁺⁺ +2(Br) ⁻¹ 218.00(P) 175.56(S) 168.44(A)
Hg ₂ I ₂	266	0.2614 171.20	198.18(6) 160.10(2)	187.00 Kido	Hg ₂ ⁺⁺ +2(I) ⁻¹ 270.00(P) 215.20(S) 205.78(A)
Hg ₂ SO ₄	208	0.2568 127.70	122.70(2)	119.60 Kido	Hg ₂ ⁺⁺ +2(SO ₄) ⁻² 161.80(P) 149.55(S) 141.45(A)
Hg ₂ (NO ₃) ₂ 2H ₂ O	222	0.2621 121.18	118.20(2)	120.80	Hg ₂ ⁺⁺ +2(NO ₃) ⁻¹ 185.82(P) 174.66(S) 162.86(A)
Hg ₂ (BrO ₃) ₂	278	0.2393 157.30	—	—	Hg ₂ ⁺⁺ +2(BrO ₃) ⁻¹ 198.26(S) 186.32(A)
Hg ₂ (IO ₃) ₂	314	0.2449 184.00	—	—	Hg ₂ ⁺⁺ +2(IO ₃) ⁻¹ 219.00(S) 206.98(A)
Hg ₂ CrO ₄	216	0.1217 62.94	—	—	Hg ₂ ⁺⁺ +2CrO ₄ ⁻² 167.00(P) 153.64(S) 145.29(A)

(b) Ikenmeyer's Relation⁴

According to Ikenmeyer, the molar susceptibilities (χ_m) of salts are a linear function of the total number (Z) of electrons contained in their molecule, that is,

$$\chi_m = C_1 Z + C_2,$$

where C_1 and C_2 are constants. To test this relationship graphs have been plotted for the values of χ_m against Z in the case of inorganic salts of mercuric and mercurous mercury separately, and are shown in Figs. 2, 3, and 4. A study of these curves leads to the following conclusions:

(1) The Ikenmeyer's relation does not hold true for all mercuric and mercurous salts. Similar observations have been made by previous workers.

(2) The points corresponding to HgCl₂, HgBr₂, HgI₂, and Hg(CNS)₂ (Fig. 2) fall on a straight line. Similarly, the points corresponding to (i) Hg₂Cl₂, Hg₂Br₂, Hg₂I₂ (Fig. 3) also lie on a straight line: (shown by dotted lines). Thus it appears that only compounds containing anions having similar constitution obey the linear law. Such a behavior has also been found in the case of lead salts.¹⁰

(3) In the case of organic compounds (Fig. 4) of

⁴ K. Ikenmeyer, Ann. d. Physik 5, 1, 190 (1929).

TABLE II(b). Mercurous salts of organic acids.

Compounds	Author's values	Other workers	Computed, using the experimental ionic values of the constituents by the same author	Computed from theoretical ionic values
Hg ₂ (HCOO) ₂	0.2443 120.00	—	—	Hg ₂ ⁺⁺ +2(HCOO) ⁻¹ 143.50(P) 129.04(S) 128.64(A)
Hg ₂ (CH ₃ COO) ₂	0.2787 144.70	144.0 (2)	144.6 Kido	Hg ₂ ⁺⁺ +2(CH ₃ COO) ⁻¹ 167.00(P) 152.54(S) 152.14(A)
Hg ₂ C ₂ O ₄	0.2436 119.20	—	—	Hg ₂ ⁺⁺ +2(C ₂ O ₄) ⁻² 137.70(P) 123.24(S) 122.84(A)
Hg ₂ (CHOHCOO) ₂	0.2769 152.10	—	—	Hg ₂ ⁺⁺ +2(CHOHCOO) ⁻² 170.40(P) 155.94(S) 155.54(A)
Hg ₂ (C ₁₅ H ₃₁ O ₂) ₂	0.5213 504.40	—	—	Hg ₂ ⁺⁺ +2(C ₁₅ H ₃₁ O ₂) ⁻¹ 543.00(P) 528.54(S) 528.14(A)
Hg ₂ (C ₁₈ H ₃₅ O ₂) ₂	0.5036 459.20	—	—	Hg ₂ ⁺⁺ +2(C ₁₈ H ₃₅ O ₂) ⁻¹ 496.00(P) 481.54(S) 481.14(A)

both mercuric and mercurous mercury many points lie on straight lines.

The values of the slopes (C_1) of the several straight lines drawn in Figs. 2, 3, and 4 have been determined from the graphs and are given in the second and fourth columns of Table III. These values of C_1 have been used

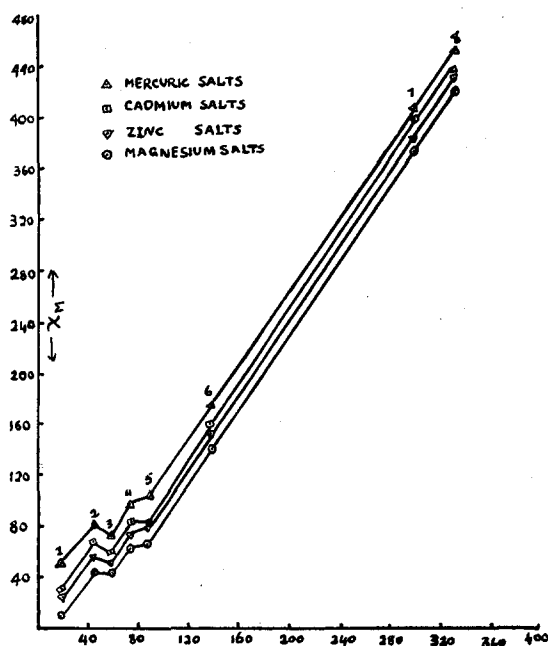


FIG. 1. (To bring out the similarity in curves very prominently, the abscissa for the same anions is kept the same in all compounds.) 1—oxide; 2—chloride; 3—sulfate; 4—acetate; 5—tartrate; 6—benzoate; 7—palmitate; 8—stearate.

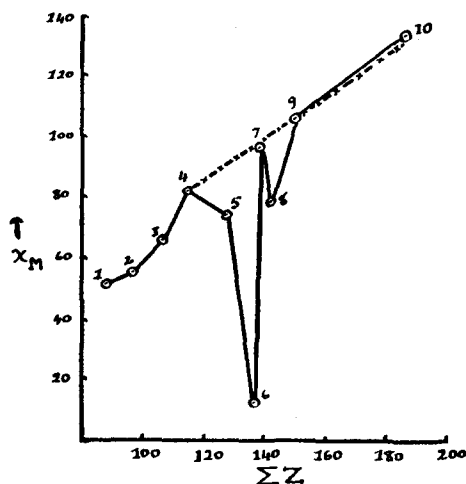


FIG. 2. Mercuric salts of inorganic acids. 1—oxide; 2—sulfide; 3—cyanide; 4—chloride; 5—sulfate; 6—chromate; 7—thiocyanate; 8—nitrate; 9—bromide; 10—iodide.

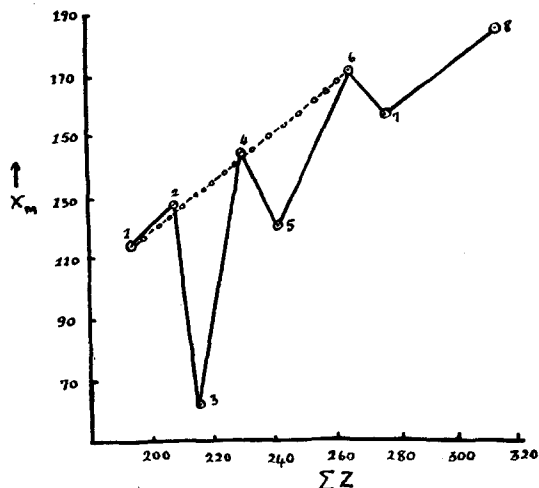


FIG. 3. Mercurous salts of inorganic acids. 1—chloride; 2—sulfate; 3—chromate; 4—bromide; 5—nitrate; 6—iodide; 7—bromate; 8—iodate.

to calculate the values of C_2 in Ikenmeyer's relation for every plotted point, and are given in the third and fifth columns of the table.

It will be seen from Table III that the values of C_1 are different for corresponding sets of inorganic salts of mercuric and mercurous mercury, showing probably that the susceptibility contributions of the anions of different groups are not the same. However, in the case of organic compounds the values of C_1 are the same for salts of both mercuric and mercurous mercury.

The values of C_2 are very nearly the same for salts of a given series, but the average value is different for each series. The values of C_2 for mercurous salts of both inorganic and organic acids are numerically higher than those for corresponding mercuric salts. Further, in both the mercuric and mercurous compounds the values of

C_2 are considerably higher for organic salts than those for inorganic ones. These results are in conformity with those found in the case of lead salts.¹⁰

From the comparison of Ikenmeyer's relation with the Pascals' law ($\chi_m = \Sigma \chi_a + \lambda$) one may infer that C_2 is of the nature of the constitutive correction constant; however, the variation of the value of C_2 from 4 to 183 for mercury salts of different series does not substantiate this view. Under these circumstances it is difficult to assign any physical meaning to C_2 at this stage.

(c) Ionic Susceptibilities of Mercuric and Mercurous Ions

1. *Statistical method.*—The ionic susceptibilities of mercuric and mercurous ions were determined by the method followed by Prasad and co-workers.¹ In this method, to give weight to all available values, various values of susceptibilities of the anions reported in the literature are collected and the values of the susceptibilities of mercuric and mercurous ions are obtained by subtracting these anion values from the molar susceptibilities. The means of such values are perhaps the most probable values of susceptibility of mercuric and mercurous ion. The mean values calculated for mercuric and mercurous ions separately from salts of inorganic and organic acids come out to be 36.92 and 37.99 and 37.21 and 41.97, respectively.

By applying a statistical test it has been found that the difference in the values for the mercuric ion obtained from inorganic and organic salts is not quite significant.

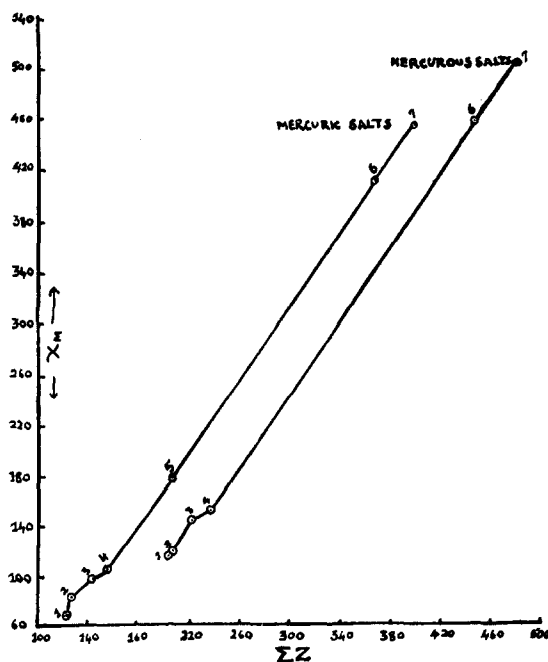


FIG. 4. Mercuric and mercurous salts of organic acids. 1—oxalate; 2—formate; 3—acetate; 4—tartrate; 5—benzoate; 6—palmitate; 7—stearate.

In the case of mercurous ion, however, the difference (3.96) is evidently significant.

(2) *Bhatnagar, Nevgi, and Ohri's method.*—Bhatnagar, Nevgi, and Ohri⁵ have suggested that as mercury forms covalent compounds it is necessary for the evaluation of cation values to take only Pascal's values of the anions, since these anion values have been derived from covalent compounds. The mean values of susceptibilities of mercurous and mercuric ions obtained from such consideration from salts of inorganic and organic acids separately have been found to be 44.03 and 42.70×2 (inorganic) and 35.20 and 41.05×2 (organic), respectively.

This method is, however, statistically not very consistent because mercury compounds are considered partly covalent and partly electrovalent, and hence it will not be justifiable to use only Pascal's values for the anions.

(3) *Graphical method.*—Prasad and co-workers^{1b} have found that almost straight line graphs are obtained when the molar susceptibilities (χ_m) of compounds having the same anions, and cations belonging to the same family of elements in periodic table, are plotted against the number of electrons (N) in the cations, that is, $\chi_m = p_1 N + p_2$, where p_1 is the tangent of the inclination (the contribution to the susceptibility (χ_m) per electron of the cation of the same group), and p_2 is the intercept of the line on the χ_m axis. This relation was also observed by Kido. Prasad and co-workers and also Kido extrapolated the straight lines to meet the χ_m axis ($N=0$); the intercepts p_2 of the lines obtained in this manner are the measure of the susceptibilities of the anion with which the cations in the group combine. The values of the anions thus obtained were utilized by these workers to deduce the values of χ -cations.

Graphs were, therefore, drawn between the molecular susceptibilities of the salts of Mg, Zn, Cd, and Hg (*ic*), having the same anion against the total number of electrons in the cations, for salts of inorganic and the organic acids and are shown in Figs. 5 and 6, respectively. The susceptibility values of the salts of Mg, Zn, and Cd used for drawing these graphs are the same as those used in Fig. 1 with the exception of the values of MgBr₂ and ZnCl₂ which are Kido's.² It will be seen that in all cases the graphs are straight lines. The straight lines are produced to meet the χ_m axis and the values of the intercepts (p_2) thus obtained have been given in column 3 of Table IV along with the slopes p_1 column (2). In order to show that the plotted points corresponding to mercuric salts definitely lie on straight lines, the molecular susceptibilities of these salts have been calculated by multiplying the values of the slope (p_1) by the number of electrons in the cation and adding the value of p_2 (the susceptibility of anions).

The values thus obtained are given in Table IV. The excellent agreement between the observed and

calculated values shows that the plotted points definitely lie on the straight lines drawn for χ_m against N .

The values of the anions obtained from the intercepts p_2 were used to calculate the susceptibility of mercuric ion and the values thus obtained are given in the last column of Table IV. The mean of these values calculated for salts of inorganic and organic acids separately comes out to be 40.19 and 38.77, respectively.

The linear relation between χ_m and N shows that the contribution per electron in the cations belonging to

TABLE III.

Compound	Mercuric compounds		Mercurous compounds	
	C ₁	C ₂	C ₁	C ₂
Chloride	0.67	+5.83	0.84	−47.7
Bromide	0.67	+4.60	0.84	−48.7
Iodide	0.67	+4.05	0.84	−52.1
Oxalate	1.43	−108.7	1.42	−170.5
Formate	1.43	−107.2	1.42	−172.5
Acetate	1.43	−104.7	1.42	−170.6
Tartrate	1.43	−118.3	1.42	−183.1
Benzoate	1.43	−118.6	—	—
Palmitate	1.43	−112.5	1.42	−174.1
Stearate	1.43	−112.1	1.42	−174.3

the group of Mg, Zn, Cd, and Hg is a fixed quantity for a particular anion; it also shows that the anion has a fixed value in combination with a particular group of cations. Hence it appears that if these two constants are known for a particular group of the cations, the molecular susceptibilities of the salts of all the elements in that group corresponding to the anion can be easily calculated.

TABLE IV.

Compounds	p_1	p_2	χ_m cal.	χ_m obs.	$\chi_{Hg^{+2}}$
Chloride	0.510	23.00	85.78	82.21	36.21
Bromide	0.500	33.00	105.00	105.10	39.10
Iodide	0.550	44.00	—	—	45.20
Oxide	0.550	6.00	48.90	50.76	44.76
Sulfate	0.520	38.00	78.56	73.70	35.70
Oxalate	0.420	36.00	68.76	68.63	32.63
Formate	0.430	19.50	72.54	73.00	34.00
Acetate	0.490	29.50	97.22	98.37	39.37
Tartrate	0.530	60.00	101.34	104.70	44.70
Benzoate	0.540	68.10	178.83	175.90	39.70
Palmitate	0.600	185.00	416.80	410.90	40.90
Stearate	0.550	208.50	459.90	457.10	40.10

For the purpose of comparison, the mean values obtained by the three methods described above are given in columns 2, 3, and 4, respectively, of Table V along with the theoretically calculated values for the mercuric and mercurous ions. The following conclusions can be drawn from Tables V(a) and V(b):

(a) Mercuric Salts

(i) The value of the mercuric ion obtained by the statistical method from salts of inorganic acids is less

⁵ Bhatnagar, Nevgi, and Ohri, Proc. Ind. Acad. Sci. 9A, 86 (1939).

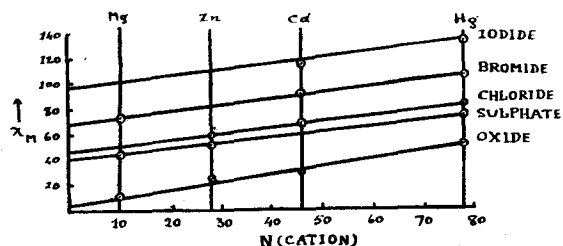


FIG. 5.

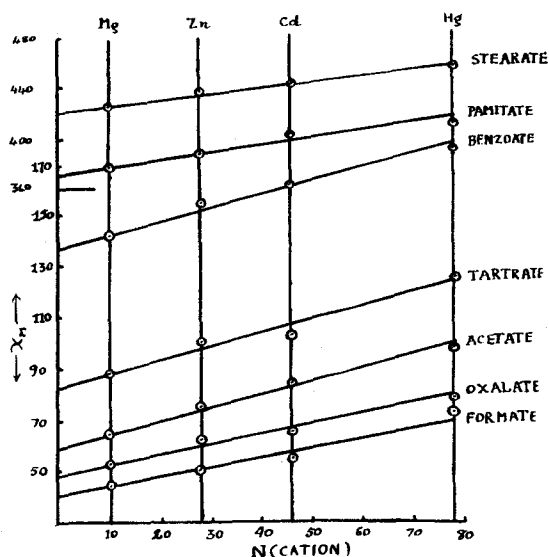


FIG. 6.

than that obtained from salts of organic acids. This is in conformity with the results obtained by Prasad and co-workers¹ for other elements of the second group. The graphical method, however, does not give results of this nature.

(ii) The theoretical values are higher than the experimental values obtained by the authors. The value obtained in the manner suggested by Bhatnagar, Nevgi, and Ohri is higher than the statistical values obtained for salts of inorganic acids but is lower for salts of organic acids.

(iii) The divergence in the values of the susceptibility of the mercuric ion deduced from inorganic salts by the statistical and graphical methods is quite small and hence a mean of the two values can be taken. This comes out to be (38.56) and can serve well as the value of the susceptibility of Hg^{+2} ions for all approximate calculations.

(b) Mercurous Salts

(i) The value of the susceptibility of the mercurous ion obtained from salts of inorganic acids by the statistical method is lower than that obtained similarly from salts of organic acids [cf. (a) (i) above].

(ii) The value obtained in the manner suggested by Bhatnagar, Nevgi, and Ohri is higher than the value

obtained by the statistical method for salts of inorganic acids but is less than that obtained by the statistical method for salts of organic acids.

(iii) The susceptibility values for mercurous ion are in general higher than that of the mercuric ion. This is probably due to the fact that in the mercurous ion two Hg atoms are combined together with common electrons, on account of which the electronic orbits are likely to have greater radii as suggested by Ehrenfest's hypothesis and hence brings about an increase in susceptibility.

(c) Ionic Radius

The ionic radii of mercuric and mercurous ions were calculated from the susceptibilities of these ions deduced from inorganic and organic salts by the statistical and the graphical methods, from the relation—

$$(\Sigma \bar{r}_e^2)^{\frac{1}{2}} : (\Sigma \bar{r}_t^2)^{\frac{1}{2}} = \bar{r}_e' : \bar{r}_t',$$

where

\bar{r}_t' = the theoretical value of the radius;

\bar{r}_e' = the experimental value of the radius (required);

$\Sigma \bar{r}_e^2$ = the mean square radius obtained from experimental ionic magnetic susceptibility;

$\Sigma \bar{r}_t^2$ = the theoretical mean square radius.

The calculated values of the radii are given in Table VI, together with the values obtained by other methods.

SUMMARY

Magnetic susceptibilities of a number of pure mercuric and mercurous salts of inorganic and organic acids have been measured by the modified form of a Gouy's balance. Values for the ionic susceptibilities of mercuric and mercurous ions have been deduced from the molecular susceptibilities of the salts on the additivity basis by subtracting all the known values of the susceptibilities of anions reported in literature and finding an arithmetic mean of the values thus obtained (1) from salts of inorganic acids and (2) from those of organic acids, separately. It has been found that the mean values obtained for the mercuric and mercurous ions from

TABLE V(a) (mercuric). Values of $\chi_{\text{Hg}^{+2}}$

Ion	Statistical method (Authors) (i)	Bhatnagar's method (ii)	Graphical method (Authors) (iii)	Theoretical	
				(Slater)	(Angus)
Hg^{++} Inorganic	36.92	44.03	40.19	47.77	47.57
Hg^{++} Organic	37.21	35.20	38.77	—	—

TABLE V(b) (mercurous).

Ion	$\chi_{\text{Hg}_2^{+2}}$	
	Statistical method (Authors)	Bhatnagar's method
Hg_2^{++} Inorganic	37.99×2	42.70×2
Hg_2^{++} Organic	41.97×2	41.05×2

salts of inorganic acids are numerically higher than those obtained from salts of organic acids but the difference in the values obtained for the mercuric ion from the two types of salts is not statistically significant. The susceptibility of mercurous ion obtained from both the salts of inorganic and organic acids is higher than that for the mercuric ion.

The graph for χ_m against N (the number of electrons in the molecule) for the mercuric and mercurous salts is definitely non-linear, if all the salts are taken into consideration. This shows that the Ikenmeyer's relation does not hold true. The pattern obtained by plotting χ_m of all mercuric salts against N is similar to the pattern for the corresponding salts of Mg, Zn, and Cd showing, thereby, a family relationship of Mg, Zn, Cd, and Hg.

A linear relation has been shown to exist between the molecular susceptibilities of salts of Mg, Zn, Cd, and Hg (*ic*) containing the same anion and the number of electrons contained in the cations. The significance of this relation has been discussed and values for the susceptibility of mercuric ion from salts of inorganic and organic acids have been deduced from this relation and have been compared with the values obtained by statistical method.

TABLE VI.

Ion	Radius	Authors	Source
Hg ⁺⁺	1.65	Author	Hg ⁺⁺ from inorganic salts of Hg ⁺⁺ (statistical method)
	1.72	Author	Hg ⁺⁺ from inorganic salts of Hg ⁺⁺ (graphical method)
	1.65	Author	Hg ⁺⁺ from organic salts of Hg ⁺⁺ (statistical method)
	1.69	Author	Hg ⁺⁺ from organic salts of Hg ⁺⁺ (graphical method)
	1.12	Goldschmidt	Hg ⁺⁺ from x-ray data
	0.66	Wyckoff	Hg ⁺⁺ from x-ray data
	1.10	Pauling	Hg ⁺⁺ from wave-mechanical concepts
	1.67	Author	Hg ₂ ⁺⁺ from inorganic salts of Hg ₂ ⁺⁺ (statistical method)
	1.75	Author	Hg ₂ ⁺⁺ from organic salts of Hg ₂ ⁺⁺ (statistical method)
	0.72	Wyckoff	Hg ₂ ⁺⁺ from x-ray data

Ionic radii for the mercuric and mercurous ions have been calculated from the values of the susceptibilities of these ions in combination with inorganic and organic anions.

One of the authors (S.S.D.) acknowledges the benefit of a very helpful discussion with Dr. W. K. Wilmarth of the University of Southern California.