

MAGNETIC STUDY OF SOME SILVER SALTS

BY MATA PRASAD, F.A.Sc., S. S. DHARMATTI, C. R. KANEKAR
AND M. G. DATAR

(*Chemical Laboratories, Royal Institute of Science, Bombay*)

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PRASAD AND CO-WORKERS¹ have determined the average values of the magnetic susceptibilities of many cations such as $\text{Ca}^{\text{++}}$, $\text{Sr}^{\text{++}}$, $\text{Ba}^{\text{++}}$, $\text{Mg}^{\text{++}}$, $\text{Zn}^{\text{++}}$, Hg (ous and ic) and Pb from the study of a large number of their salts of inorganic and organic acids. They have made a rather striking observation that the mean values of the susceptibilities of these cations obtained from salts of organic acids are higher than those obtained from salts of inorganic acids.

Comparatively few systematic investigations have been made to deduce the susceptibility of silver ion. Kido² studied a few salts of silver and reported the ionic susceptibility of silver deduced therefrom to be -26.2×10^{-6} . Pascal's value reported in the International Critical Tables is -31.0×10^{-6} , while Pauling³ has reported another value (-27.0×10^{-6}) computed from Pascal's data. All these values neither agree with one another nor is any one of them near the values calculated theoretically by the Slater's or Angus' methods (-42.35×10^{-6} and -42.11×10^{-6}). These discrepancies led the authors to measure the magnetic susceptibilities of a large number of silver salts and to determine reliable values of the susceptibility of silver ion in combination with organic and inorganic anions by using the methods of averages followed by Prasad and co-workers.

EXPERIMENTAL AND RESULTS

Twenty-one salts of silver, both of organic and inorganic acids, have been studied in the present investigation. All the salts, except silver nitrate, were prepared in a chemically pure state using extra-pure AgNO_3 (A. R. quality) as the starting substance. Since silver salts are sensitive to light, care was taken to see that they were not affected by light during the course of their preparation. For this purpose, all the operations were carried out in a dark room, illuminated by red light. All the salts were carefully analysed for their silver content. Only those specimens which were found to be chemically pure were used for the measurements of the magnetic susceptibilities.

The magnetic susceptibilities were measured on the modified form of Gouy's balance, details of which have been described by Prasad, Dharmatti

and Gokhale.¹ All measurements were made relative to a standard which was KCl ($\chi_a = -0.516 \times 10^{-6}$). All the necessary precautions such as (1) placing the specimen tube always in the same position and in such a way that one end of it lay exactly at the centre of the field and the other end in a region where the field was negligible, (2) packing the substance as uniformly and as tightly as possible in the course of every filling, and (3) keeping the field constant by keeping a rigorous check on the current feeding the magnet, were taken at the time of measurements of the susceptibilities. In order to

TABLE I A

Salt of silver	Authors' values χ_a and χ_m	χ_m other workers	χ_m computed theoretically
AgCl —found —theory	75.15% 75.26%	0.34 49.85	50.19 (2) 94.64 (4) $\text{Ag}^+ + \text{Cl}^-$ 68.19 (S) 64.97 (A)
AgNO ₂ —found —theory	69.74% 69.81%	0.272 41.86	.. $\text{Ag}^+ + \text{NO}_2^-$ 70.5 (S) 68.7 (A)
AgNO ₃ (A.R.)		0.287 48.74	46.5 (2) $\text{Ag}^+ + (\text{NO}_3)^-$ 81.93 (S) 75.97 (A)
AgBr —found —theory	57.25% 57.46%	0.328 61.63	61.97 (2) 114.6 (4) $\text{Ag}^+ + \text{Br}^-$ 82.38 (S) 78.76 (A)
AgI —found —theory	45.77% 45.96%	0.369 86.62	87.08 (2) 171.4 (4) $\text{Ag}^+ + \text{I}^-$ 102.1 (S) 97.43 (A)
Ag ₂ S —found —theory	86.98% 87.19%	0.295 73.16	.. $2\text{Ag}^+ + \text{S}^-$ 122.1 (S) 116.8 (A)
Ag ₂ CO ₃ —found —theory	78.09% 78.23%	0.293 80.89	80.5 (2) $2\text{Ag}^+ + (\text{CO}_3)^{--}$ 124.3 (S) 118.1 (A)
Ag ₂ SO ₄ —found —theory	69.11% 69.18%	0.298 92.87	91.0 (2) $2\text{Ag}^+ + (\text{SO}_4)^{--}$ 138.7 (S) 130.5 (A)
Ag ₂ CrO ₄ —found —theory	64.79% 65.04%	0.047 15.49	39.48 (5) $2\text{Ag}^+ + (\text{CrO}_4)^{--}$ 142.8 (S) 134.4 (A)
Ag ₂ SeO ₃ —found —theory	62.77% 62.9 %	0.300 100.8	99.13 (1) $2\text{Ag}^+ + (\text{SeO}_3)^{--}$ 138.4 (S) 132.1 (A)
Ag ₃ PO ₄ —found —theory	77.2% 77.3%	0.286 119.7	.. $3\text{Ag}^+ + (\text{PO}_4)^{---}$ 181.1 (S) 172.6 (A)

average the errors of packing, if any, measurements were made with three fillings of the same substance and an average of the three closely agreeing values of the susceptibility thus obtained was taken as the final value of the specific susceptibility. The results obtained for the susceptibility measurements for the salts of (i) inorganic and (ii) organic acids are given in column 2 of the Tables I A and I B, respectively. In these tables, the observed values for specific susceptibility (χ_a) and the molecular susceptibility of the salt (χ_m) are given one below the other. The values of χ_m observed by other

TABLE I B

Salt of silver	χ_a and χ_m Authors' values	χ_m computed theoretically	
CH ₃ COOAg Ag — found — theory	64.56% 64.66%	0.372 62.12	Ag ⁺ + (CH ₃ COO) ⁻ 70.88 (S) 70.62 (A)
C ₂ H ₅ COOAg Ag — found — theory	59.47% 59.67%	0.398 72.01	Ag ⁺ + (C ₂ H ₅ COO) ⁻ 82.63 (S) 82.37 (A)
AgC ₄ H ₇ O ₂ Ag — found — theory	55.17% 55.38%	0.436 84.94	Ag ⁺ + (C ₄ H ₇ O ₂) ⁻ 94.38 (S) 94.12 (A)
AgC ₇ H ₅ O ₂ Ag Benzoate Ag — found — theory	47.06% 47.17%	0.422 96.65	Ag ⁺ + (C ₆ H ₅ COO) ⁻ 108.3 (S) 108.0 (A)
AgC ₇ H ₅ O ₃ Ag — found — theory	43.81% 44.07%	0.426 104.3	Ag ⁺ + [C ₆ H ₄ (OH)COO] ⁻ 114.5 (S) 111.1 (A)
Ag ₂ C ₂ O ₄ Ag — found — theory	70.91% 71.04%	0.302 91.87	2Ag ⁺ + (COO) ₂ ⁻² 112.5 (S) 111.9 (A)
CH ₂ (COOAg) ₂ Ag — found — theory	67.72% 67.89%	0.315 100.2	2Ag ⁺ + CH ₂ (COO) ₂ ⁻² 124.2 (S) 123.7 (A)
Ag ₂ C ₄ H ₄ O ₄ Ag — found — theory	64.95% 64.03%	0.308 102.1	2Ag ⁺ + (CH ₂ COO) ₂ ⁻² 136.0 (S) 135.4 (A)
Ag ₂ C ₄ H ₄ O ₆ Ag — found — theory	59.07% 59.3%	0.343 124.9	2Ag ⁺ + (CH.OH.COO) ₂ ⁻² 145.2 (S) 144.6 (A)
Ag ₃ C ₆ H ₅ O ₇ Ag — found — theory	63.89% 64.15%	0.354 181.2	3Ag ⁺ + (CH ₂ .COO.C.OH. COO.CH ₂ COO) ⁻³ 205.6 (S) 204.9 (A)

workers for the salts of inorganic acids are given in column 3 of Table I A. The susceptibilities of the silver salts of organic acids do not appear to have been measured by any previous workers and hence column 3 is dropped in Table I B.

The molar susceptibilities of the salts were also calculated by adding up the susceptibility values of the cations and the anions according to the method followed by Angus and Farquharson.⁶ The values are given in the last column of the tables and have been designated as (S) and (A) according as Slater's or Angus' values of the ions are used for these calculations. All the susceptibility values have been expressed in terms of -1×10^{-6} c.g.s. units.

DISCUSSION OF THE RESULTS

It will be seen from Table I A that the author's values for some compounds agree with Kido's data; the values of Sugden and Meyer are in most cases high. It will also be seen that the experimental values of the molecular susceptibilities are considerably lower than the values calculated according to Angus and Farquharson's method in all cases, the difference between the two being much more in the case of the salts of inorganic acids than in the case of salts of organic acids. The theoretical values of the susceptibilities of ions correspond to those of free ions; bond effects are not taken into account while computing the molecular susceptibilities of salts of inorganic acids. The difference in the calculated and the observed values are so large that it is difficult to attribute them wholly to bond effects. The bond effects for atoms constituting the organic anions have, however, been taken into account in calculating the molecular susceptibilities of salts of organic acids, since Pascal's values which have been used for these calculations include them and even then, the calculated values are higher than the observed ones. This indicates that the theoretical values for the cations and anions used for these computations may not be quite applicable in these cases.

IONIC SUSCEPTIBILITY OF SILVER ION

For the calculation of the ionic susceptibility of silver ion by the method of Prasad and co-workers, various values of the anions reported in literature have been subtracted from the molecular susceptibilities of the silver salts and a mean of all the values thus obtained has been calculated from (i) salts of inorganic acids and (ii) those of organic acids. The values of the susceptibilities of the anions used for these calculations have been shown in Table II for ready reference.

The mean values of the ionic susceptibility of silver deduced from the salts of (i) inorganic and (ii) organic acids are 29.13 and 31.75 respectively. The latter value is higher than the former; the difference between the two values has been found to be statistically significant. This conclusion is in agreement with the findings of Prasad and co-workers.

TABLE II A

Inorganic Anions

Anion	χ_{Anion}	Anion	χ_{Anion}
NO ₃ '	14.2 I.C.T. (7) 20.1 Kido (2) 18.2 Pauling (3) 18.1 Rao and Sriraman (8) 18.4 Raychaudhuri and Sengupta (9) 19.5 Rao and Sriraman (8) 18.9 Trew (10) 18.0 Sugden (4)	I'	44.6 Pascal (I.C.T.) (7) 53.2 Kido (2) 45.0 Sugden (4) 49.25 Ikenmeyer (13) 50.2 Reicheneder (14) 49.5 Weiss (Hocart) (12) 60.5 Joos (11) 48.6 Pauling (3) 50.6 Trew (10) 51.2 Leiterer (17) 49.8 Weiss (Pascal) (12a) 50.8 " (Reicheneder) (12b) 55.7 Brindley and Hoare (15a) 50.6 " (15) 50.8 Veiel (18)
Cl'	20.1 I.C.T. (7) 19.5 Joos (11) 23.1 Weiss (Hocart) (12) 20.4 Ikenmeyer (13) 21.9 Reicheneder (14) 23.1 Weiss (Pascal) (12a) 25.3 Brindley (15) 24.0 " (15a) 20.0 Sugden (4) 22.1 Kido (2) 23.1 Abonnenc (16) 24.2 Brindley and Hoare (15a) 22.2 Leiterer (17) 21.8 Veiel (18) 24.1 Pauling (3) 23.4 Trew (10) 23.0 Weiss (Reicheneder) (12b)	CO ₃ ''	22.1 I.C.T. (7) 28.1 Kido (2) 30.2 Pauling (3) 29.5 Trew (10)
		PO ₄ '''	35.4 I.C.T. (7) 47.2 Kido (2) 47.1 Pauling (3)
		NO ₂ '	8.0 Rao and Sriraman (8) 11.4 " (8) 15.0 Kido (2) 14.1 Raychaudhuri and Sengupta (9)
Br'	30.6 I.C.T. (7) 37.1 Kido (2) 34.8 Ikenmeyer (13) 32.5 Reicheneder (14) 34.7 Kido (2) 33.6 Weiss (Reicheneder) (12b) 31.0 Sugden (4) 34.6 Pauling (3) 33.9 Weiss (Hocart) (12) 39.5 Joos (11) 37.5 Brindley (15) 34.5 " and Hoare (15a) 34.6 Trew (10) 33.0 Veiel (18) 31.4 Farquharson (19) 34.7 Weiss (Pascal) (12a) 33.4 Leiterer (17) 34.1 Flordal and Frivold (20)	CrO ₄ ''	-21.86 Bhatnagar (5) -33.0 Trew (10) -35.2 " (10)
		SO ₄ ''	33.6 I.C.T. (7) 39.0 Kido (2) 41.6 Pauling (3) 37.0 Sugden (4) 40.1 Trew (10)
		SeO ₃ ''	47.5 Kido (2) 44.9 Rao and Sriraman (8) 52.7 " (8)
		S''	15.6 I.C.T. (7)

TABLE II B

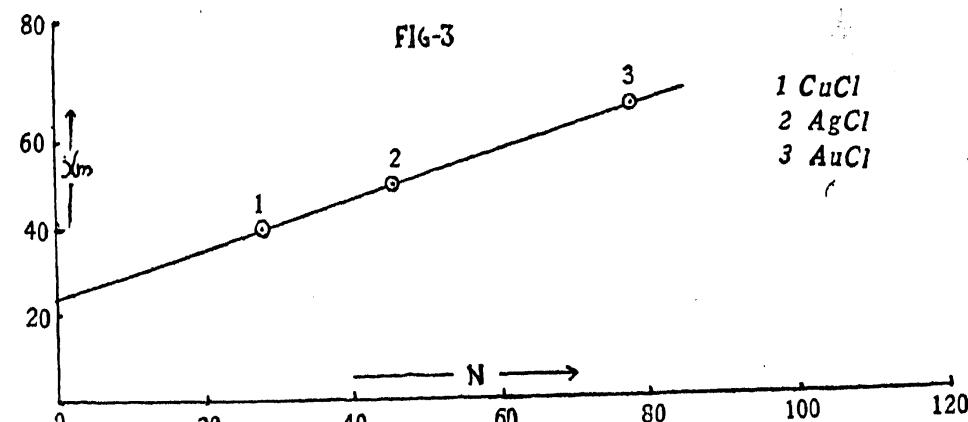
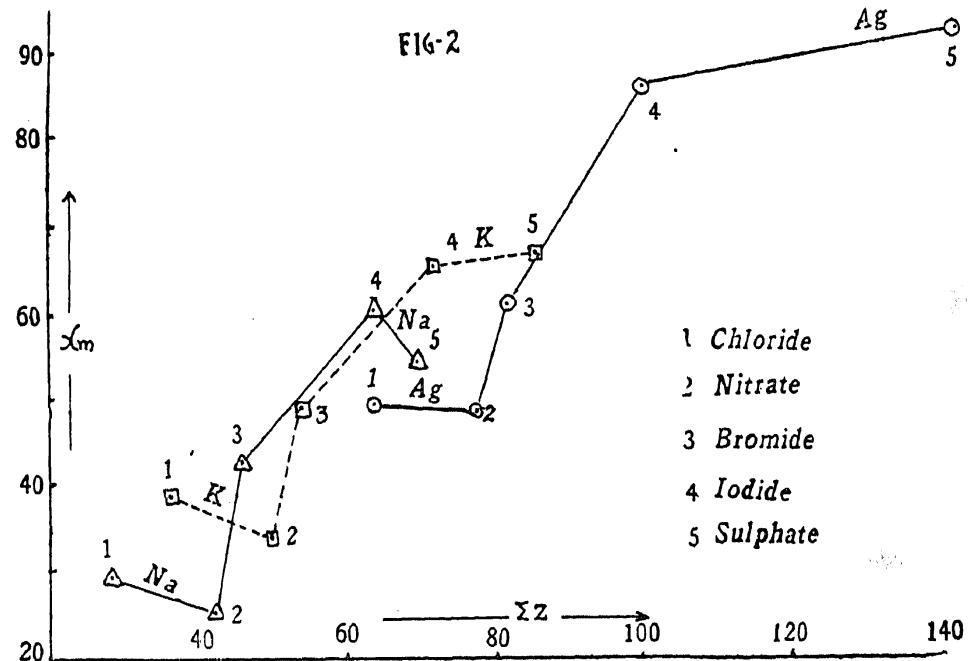
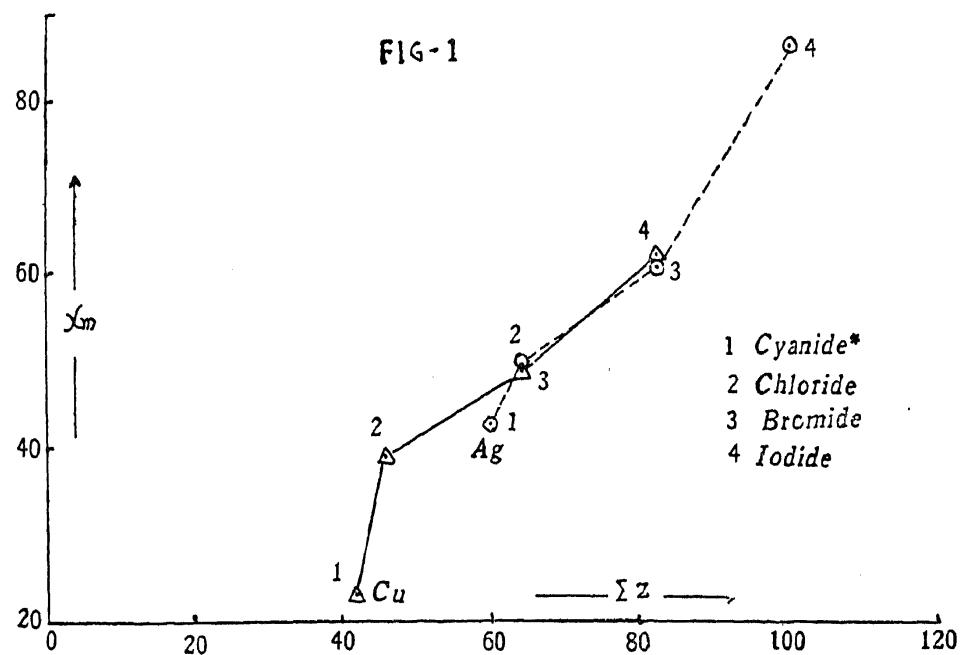
Organic Anions

Anion	χ_{Anion}	Anion	χ_{Anion}
Acetate	28.9 I.C.T. (7) 32.0 Kido (2) 31.4 , (2) 30.0 Hollens and Spencer (21) 30.0 Trew (10) 29.8 Rao and Sriraman (8) 30.2 , (8) 28.76 Pascal's corrected data	Benzoate	67.6 Pascal's corrected data 66.1 Trew (10)
Oxalate	27.9 I.C.T. (7) 28.5 Hollens and Spencer (21) 27.94 Pascal's corrected data	Malonate	39.8 Pascal's corrected data
Succinate	51.6 I.C.T. (7)	Salicylate	74.4 I.C.T. (7) 71.44 Pascal's corrected data
Tartrate	62.36 I.C.T. (7) 63.8 Pascal's corrected data 60.88 Trew (10)	Propionate	40.62 Pascal's corrected data
		Butyrate	52.48 Pascal's corrected data
		Citrate	81.9 Pascal's corrected data

(a) A comparison of the diamagnetism of silver salts with that of Cuprous Salts

It is well known that the elements belonging to the same group of the periodic table have similar physical and chemical properties. Magnetic susceptibility is a physical property depending upon the electronic structure of the atom. Hence it is reasonable to expect a similarity in the magnetic behaviour of the corresponding salts of elements belonging to the same group. Prasad and co-workers have shown that on plotting the χ_m values of the corresponding salts of cations belonging to the same group or sub-group of the periodic table against ΣZ , the total nuclear charge in each compound, patterns are obtained which are strikingly similar for a particular group or sub-group of the cations. Thus, they have shown that the patterns obtained by plotting the values of χ_m of the corresponding salts of (i) Ca, Sr, Ba (ii) Mg, Zn, Cd and Hg are strikingly similar. Cu, Ag and Au belong to the same sub-group in the periodic table hence an attempt was made to examine the findings of Prasad and co-workers in the case of the compounds of these elements. Values for a few cuprous salts have been reported by Khanna.²² Sufficient data for the susceptibilities of gold salts is not available and therefore, a comparison of only cuprous and silver salts could be made. Hence the values of the molecular susceptibilities of the salts of Cu as reported by Khanna and those of the corresponding silver salts determined by the authors have been plotted against ΣZ and the curves obtained are shown in

Fig. 1. It will be observed from the figure that even with the scanty data available for cuprous salts, the patterns obtained are quite similar.



* The Susceptibility of Silver Cyanide used in this graph has been obtained by Kido (2).

(b) *Comparison of the magnetic behaviour of silver salts with alkali salts*

Since silver is included along with alkali metals in Group I, an attempt has been made to ascertain how far the magnetic behaviour of the salts of silver is similar to that of the corresponding alkali salts. For this purpose, the values of χ''' for the corresponding salts of silver, sodium and potassium have been plotted against ΣZ , and the pattern obtained in each case is shown in Fig. 2.

The similarity of the patterns obtained for sodium and potassium salts is quite striking and substantiates the findings of Prasad and co-workers. Further, it will be noticed that the pattern for the alkali salts is not altogether dissimilar to that for the corresponding silver salts. This may be due to the fact that the alkali metals belong to one sub-group in Group I of the periodic table while silver is in the other sub-group.

RELATION BETWEEN χ_m AND N

Kido has observed a linear relation between the molecular susceptibilities (χ_m) of alkali salts containing the same anion and the number of electrons (N) in the cations. Prasad and co-workers have confirmed this relation for many compounds of elements belonging to I and II groups of the periodic table and have developed it for the calculation of the susceptibilities of ions.

The authors have attempted to examine this relation for the chlorides of Cu, Ag and Au. For this purpose, the molecular susceptibilities of CuCl and AuCl as reported by Khanna and Kido respectively (Column 1, Table III) and that of AgCl observed by the authors have been plotted against the total number of electrons in the cations. The plotted points (Fig. 3) lie on a straight line which satisfies the equation

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

where C_1 is the slope of the straight line and C_2 its intercept on the χ_m axis.

The slope of the straight line evidently signifies the contribution of the susceptibility per electron in the cation to the molecular susceptibility of the halide. The intercept, C_2 represents the susceptibility contribution when the number of electrons in the cation is zero. Since the susceptibility of an ion is, according to Langevin, a function of $\sum r^2$ which will depend on the number of electrons in the ion, it will be zero, where N is zero. Further, since $\chi_m = \chi_{cation} + \chi_{anion}$ (Pascal's law), at the point in the straight line where it meets χ_m axis, that is, when N is zero, χ_m will be equal to χ_{anion} . The intercept C_2 on the χ_m axis would, thus, be the

TABLE III

Compound	χ_m	$\chi_{\text{Cl}'}$	$\chi_{\text{cation}} (\text{graphical})$	$\chi_{\text{cation}} (\text{statistical})$
CuCl	..	39.64	15.95	17.4
AgCl	..	49.85	25.85	27.6
AuCl	..	67.02	43.45	44.43

susceptibility of the anion. It must be mentioned that the intercept has no physical significance, since it assumes that at that point the cation does not exist; actually, one cannot have two opposite ions isolated in this way. Even then, this method of interpreting the relation of χ_m and N gives a method for determining the susceptibility of the anion. Knowing the susceptibility of the anion the susceptibility of the cations, Cu, Ag, Au in combination with the chloride ion can be calculated from the $\chi_m - N$ relation in two ways: (i) by subtracting the susceptibility of the anion from the molecular susceptibility of the corresponding salt, (ii) by multiplying the slope of the straight line by the number of electrons in the cation. The values calculated by the second method are however more reliable as they are free from small experimental errors involved in the measurements of the experimental values of individual salts; these errors are obviously smoothed out in drawing the graphs. Values calculated for the susceptibilities of the chloride and for Cu, Ag and Au ions by the second method are given in the following table. The values of the cations have been compared with the average values obtained by subtracting all the known values of the susceptibility of the chloride ion from the molar susceptibilities of their chlorides.

The agreement of the graphical value with the average values is quite satisfactory. The graphical value of the anion is also in quite good agreement with many of the reported values of the susceptibilities of the chloride ion (Table II). This shows that the method of evaluating the susceptibilities of ions from the $\chi_m - N$ relation gives quite satisfactory results. This method could not, however, be used for all the salts of silver as the data for the susceptibilities of the corresponding salts of Cu and Au required for this purpose is not available.

The graphical method has one advantage over other methods, namely, that it depends solely on the accuracy of the experimental values of the molar susceptibilities of the salts considered and does not depend on the use of values of ions reported in the literature which are often widely diver-

gent from each other (*cf.* Table II). To avoid the difficulty of choosing any particular value as correct for determining the values of the susceptibilities of other ions, Prasad and co-workers used the method of averages for the determination of the susceptibilities of cations. Though this method appears to be an improvement, the graphical method seems to be better, since it does not involve any assumptions.

IONIC RADIUS OF SILVER

The ionic radius of Ag has been calculated from the mean values of ionic susceptibilities from salts of inorganic and organic acids, following the method adopted by Trew.²³ These values have been compared with (i) those obtained by Davey, Wyckoff and Goldschmidt from the experimental data of crystal structure, (ii) that of Günther Schulze from the molar volumes of permutites, (iii) that of Bragg deduced for atoms arranged in closest packing and (iv) with Pauling's theoretical value (*cf.* Table IV).

TABLE IV
Ionic Radius (A°)

Ion	Authors' value		Values of other workers					
	Inorganic salts	Organic salts	Bragg (24)	Wycoff (24)	Davey (24)	Pauling (24)	Goldschmidt (24)	Günther Schulze (24)
Ag ⁺ ..	1.55	1.62	1.77	1.65	1.18	1.28	1.13	1.78

It will be observed from Table IV that the values of the ionic radius deduced from the susceptibility measurements are higher than the values of Davey, Pauling and Goldschmidt and slightly lower than the values obtained by Bragg and Schulze.

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