MAGNETIC SUSCEPTIBILITIES OF CALCIUM AND STRONTIUM IONS

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Prasad, Dharmatti and Kanekar[1] have recently measured the susceptibilities of a number of barium salts of inorganic and organic acids, and using the available values of the anions they have determined the ionic susceptibility of barium. They found that the values calculated from the salts of inorganic acids agree well with those theoretically calculated according to Slater's[2] and Angus's[3] methods, and that the values deduced from the susceptibilities of salts of organic acids are higher than these values. This paper gives the results of the measurements of susceptibilities of calcium and strontium salts of several inorganic and organic acids. The data obtained have been utilised to calculate the susceptibilities of calcium and strontium ions, using all the possible available values of anions and assuming the applicability of the additivity law. The results obtained have been statistically examined and the significance of the observed differences in their values deduced by using values for anions from different sources has been determined. The ionic susceptibilities evaluated from the data on inorganic salts have been compared with those deduced from the data on salts of organic acids with a view to examine the findings of the previous workers. Ionic radii of calcium and strontium ions have also been estimated from their ionic susceptibilities and the values thus obtained have been compared with those obtained on the basis of other considerations.

The susceptibilities of many of the compounds studied in this investigation do not seem to have been measured so far; thus the data given in this paper consists of (*i*) the unknown values of the susceptibilities of many known compounds and (*ii*) the revised values of the susceptibilities of compounds, investigated previously by other workers. A large number of salts of calcium and strontium has been used in this investigation since the accuracy of the deduced values of the ionic susceptibilities is higher, greater is the number of salts whose susceptibilities are used for averaging, wherever such a procedure is valid.

The values of the susceptibilities of some salts have also been computed from Bhatnagar's theory of electronic isomers[4] and compared with the experimental values.

Some of the previous workers have deduced the susceptibilities of salts from measurements made on their solutions in water but in thisi nvestigation all the measurements have been made on solid compounds mainly because the theoretical position regarding the state of ionisation in solution and the effect of ions on the molecules of the solvent is not satisfactorily settled.[5]

Experimental

The measurement of the susceptibilities was made by a magnetic balance of Gouy type in which several refinements were introduced. Some of the important features are described in this paper and complete details are being published elsewhere.

The electromagnet employed so far in our previous investigations used to get heated, and the errors introduced thereby were avoided by a number of adjustments. Consequently a magnet was designed which with a low current (0·7 amps.) at 230 volts could give fairly high fields necessary for susceptibility measurements. The windings (Helico solenoidal) of the magnet were made in eight sections and the total resistance of the windings was 270 ohms. at 30°. The yoke of the magnet was made of the best quality dynamo steel of low hysteresis. The semi-angle of the pole pieces was 27° 22′ and the area of the pole pieces was 1 square inch. It was observed that the magnet showed no rise of temperature for half an hour's continuous run when kept open in a room, but in the casing of the magnetic balance the temperature rose by 0·1°. The field between a pole gap of 1 cm. was found to be 7,500 gauss.

In order to maintain constant current through the electromagnet the voltage fluctuations were guarded by introducing two series rheostats of 100 ohms rated at 1 amp. each, as ballast resistances.

The sensitivity of the balance was adjusted to 4 divisions per mg. The upthrust of the tube carrying the substance whose susceptibility was required was measured by means of the shift of a 5 mg. rider. This gave an accuracy of 0·0001 gm. in weight measurements.

The tube used for containing substances was machine drawn. It was made of 1/16″ pyrex glass, was 3·5 cm. long and 0·6 cm. wide (inside diameters) and its capacity was about 3·0 c.c. This tube was suspended by an arrangement which satisfies practically all the theoretical conditions. The general disposition of the several parts of the apparatus was such that its working was quite easy and convenient.

The substance to be investigated was first crushed into a fine powder and dried, and then introduced into the tube through a thistle-shaped funnel

by the aid of a rod, upto a certain mark made on the tube. The substance was pressed home by means of a ram-rod so that the theoretical condition of closest and uniform packing is reached as approximately as possible. The tube was closed by a ground-glass stopper soon after filling to prevent any contamination of the substance with moisture.

After each experiment the substance was taken out of the tube by means of a small glass spade and the tube was cleaned with tap water, dilute chromic acid, distilled water, and absolute alcohol and then dried before use.

Method of Working

Every compound studied was experimented upon in two different ways: (*i*) two readings were taken for different packings in a given tube, each of these readings being the mean of four observations and (*ii*) the same procedure was repeated in another tube. The shift values employed for the calculation of molar susceptibilities were thus the mean of sixteen readings. The result was the mean of four susceptibility values. This procedure was good enough to smooth out errors due to heterogeneity or looseness of packing. By way of check on the procedure, empty tube readings were taken in between every set of observations and the balance was periodically calibrated with Kahlbaum's or Merck's extra pure KCl, Te and Se.

The magnetic susceptibility was calculated from the relation

$$\chi = \frac{1}{m}\left[(\chi_1 m_1 - \chi_a m_{a1})\frac{d_2 - d_a}{d_1 - d_a} + \chi_a m_a\right]$$

where the terms involved have the usual meaning.

In any set of experiments the shift values of the rider for a filled tube were found to be nearly the same for all observations. This shows that the packing was of nearly the same closeness throughout, the volumes to which the tubes were filled were nearly the same, and there were no fluctuations due to heating. The maximum variations in the shift values were of the order of about 1 per cent. for several substances used in this investigation. The reproducibility of the results was therefore high; the average error in the susceptibility values was nearly 5 per cent.

Substances Used

The compounds studied are the calcium and strontium salts of inorganic and organic acids. Some of these were either Kahlbaum's or Merck's products of extra pure quality [indicated as (1) and (2), respectively in Tables I and II] and others were either purified by recrystallisation or prepared in the laboratory and were analysed for their purity before use.

Results

The results obtained are given in Tables I and II in which the quality of the substances used is given in column 1, and N, the total number of electrons in the molecules of the anhydrous compound in column 2. In order to compare the observed values (column 3) with the experimental values obtained by previous workers (column 4) and with those computed by summing the experimental values of cations and anions derived by the same worker (column 5) the observed molar susceptibilities for the anhydrous salts were obtained from the values of the hydrated susbtances by subtracting the accepted values (12·96), the molar susceptibility of water, for every molecule of water of hydration. The same procedure has been followed by Kido and other workers. This, however, takes away some of the rigour of the investigation as it tacitly assumes an additivity for the susceptibility of the water of crystallisation, but the effect of hydration in compounds containing water of crystallisation is not so simple, for the surrounding water molecules of co-ordination become saturated and distorted (*cf.* Sack[6]). Raichaudhari[7] and others have attempted to correlate the change of susceptibility due to the presence of water molecules of co-ordination with the corresponding heats of hydration, but an exact quantitative description of the phenomenon is not known. In the absence of such a relation, the process of subtracting seems justifiable and may be adopted. The values of specific susceptibilities (χ_a) and molar susceptibilities (χ_m) of salts and molar susceptibilities of anhydrous salts (χ_{ma}) are given in the third column of the tables.

All susceptibility values given in this paper are expressed in units of (-1×10^{-6}) c.g.s. units.

Discussion of Results

It will be seen from the above tables that the values of the susceptibilities of many substances obtained by the authors are in fair agreement with those found by some of the previous workers (*cf.* columns 3 and 4 of Tables I and II) within the limits of error found in this investigation. The observed differences in the other cases may either be due to (*i*) impurities in the substances used, or (*ii*) different physical state of the substances employed, or (*iii*) the data being obtained from measurements on solutions in cases wherein the solution law is not rigorously applicable.

Angus[3] and Farquharson[8] have developed a method for the calculation of the susceptibilities of ions containing more than one dissimilar atom by summing up the susceptibilities of the constitutent atoms in the desired ionic state. Thus according to this method the susceptibility of the sulphate ion is

TABLE I

Compounds	N	Authors' values	χ_{ma} Other workers		χ_{ma} Computed experimentally	χ_{ma} Computed theoretically
(a) Calcium salts of inorganic acids						
$CaBr_2\,3H_2O$ (1)	90	$\chi_a = 0{\cdot}453$ $\chi_m = 115{\cdot}1$ $\chi_{ma} = 76{\cdot}22$	Luther	54·55	73·2 (Pascal) 73·48 (Pascal) 78·4 (Hoccart) 80·6 (Ikenmeyer) 79·6 (Weiss) 72·0 (Brindley) 75·9 (Kido)	$Ca^{+2}+2\,Br^{-1}$ 121·3 91·58 83·72
$CaCO_3$ (2)	50	$\chi_a = 0{\cdot}37$ $\chi_m = 37{\cdot}37$ $\chi_{ma} = 37{\cdot}37$	Pascal Dhawan Kido Raman & Krishnan— Aragonite Calcite	38·2 14·01 35·5 40·08 37·8	34·4 (Pascal) 34·6 (Kido)	$Ca^{+2}+C^{+4}+3\,0^{-2}$ 51·25 50·98 44·32
$CaCl_2$ (anhydrous) (1) ..	54	$\chi_a = 0{\cdot}480$ $\chi_m = 53{\cdot}4$ $\chi_{ma} = 53{\cdot}4$	Quincke (aq. sol.) Königsberger (aq. sol.) Meyer (solid) Ikenmeyer (aq. sol.) Hoccart (aq. sol.) (solid)	41·41 43·43 49·49 51·7 55·6 54·45	51·4 (Pascal) 56·8 (Hoccart) 51·8 (Ikenmeyer) 57·6 (Weiss) 58·0 (Brindley) 50·7 (Kido)	$Ca^{+2}+2\,Cl^{-1}$ 71·30 62·96 56·14
$CaCrO_4 \cdot 2\,H_2O$ Ca found = 20·17% Ca theory = 20·9%	76	$\chi_a = 0{\cdot}0468$ $\chi_m = 9{\cdot}030$ $\chi_{ma} = 16{\cdot}89$	..		..	$Ca^{+2}+Cr^{+6}+4\,0^{-2}$ 70·30 69·48 60·57
CaF_2 (1) (2)	38	$\chi_a = 0{\cdot}339$ $\chi_m = 26{\cdot}5$ $\chi_{ma} = 26{\cdot}5$	Meyer Voigt & Kinoshita Ishiwara Pascal	23·4 15·6 22·25 28·1	23·1 (Pascal) 24·8 (Pascal) 23·2 (Pascal) 38·8 (Ikenmeyer) 34·0 (Brindley) 30·9 (Kido)	$Ca^{+2}+2\,F^{-1}$ 29·5 27·98 24·92
$Ca(OH)_2$ (2)	38	$\chi_a = 0{\cdot}300$ $\chi_m = 22{\cdot}23$ $\chi_{ma} = 22{\cdot}23$	Meyer Kido	28·9 21·3	18·74 (Pascal)	$Ca^{+2}+2\,(OH)^{-1}$ 38·5 37·68 32·92

$Ca(NO_3)_2$ (1)	82	$\chi_a = 0{\cdot}287$ $\chi_m = 47{\cdot}1$ $\chi_{ma} = 47{\cdot}1$	Kido	46·0	39·6 (Pascal) 46·7 (Kido)	$Ca^{+2}+6O^{-2}+2\,N^{+5}$ 89·12 90·46 78·14
CaO (2)	28	$\chi_a = 0{\cdot}270$ $\chi_m = 15{\cdot}14$ $\chi_{ma} = 15{\cdot}14$	Meyer Dhawan	15·13 15·74	15·81 (Pascal)	$Ca^{+2}+O^{-2}$ 25·9 24·53 21·67
$CaSO_4 \cdot 2\,H_2O$ Ca found = 23·3% Ca theory = 23·35%	68	$\chi_a = 0{\cdot}433$ $\chi_m = 74{\cdot}6$ $\chi_{ma} = 48{\cdot}68$	Meyer Pascal Dhawan Kido	51·8 49·6 51·73 46·8	44·8 (Pascal) 45·5 (Kido)	$Ca^{+2}+S^{+6}+4\,O^{-2}$ 65·1 65·39 56·73

(*b*) *Calcium salts of organic acids*

$(CH_3COO)_2Ca$ Ca found = 25·31% Ca theory = 25·4%	82	$\chi_a = 0{\cdot}433$ $\chi_m = 68{\cdot}4$ $\chi_{ma} = 68{\cdot}4$	Kido	70·5	69·0 (Pascal) 70·5 (Kido) 69·3 (Kido)	$Ca^{+2}+2(CH_3COO)^{-1}$ 70·82 68·9 67·94
$(HCOO)_2Ca$ Ca found = 30·78% Ca theory = 30·8%	66	$\chi_a = 0{\cdot}348$ $\chi_m = 45{\cdot}3$ $\chi_{ma} = 45{\cdot}3$	Rao & Sriraman Rao & Sriraman (aq. sol.)	39·5 39·9	45·0 (Pascal) 46·9 (Kido)	$Ca^{+2}+2\,(HCOO)^{-1}$ 47·1 45·18 44·22
$(C_3H_5O_3)_2Ca \cdot 5\,H_2O$ (2)	114	$\chi_a = 0{\cdot}609$ $\chi_m = 187{\cdot}5$ $\chi_{ma} = 122{\cdot}7$	..		..	$Ca^{+2}+2(C_3H_5O_3)^{-1}$ 103·76 101·84 100·88
CaC_2O_4 Ca found = 31·29% Ca theory = 31·35%	64	$\chi_a = 0{\cdot}346$ $\chi_m = 44{\cdot}3$ $\chi_{ma} = 44{\cdot}3$	..		39·16 (Pascal)	$Ca^{+2}+(C_2O_4)^{-2}$ 41·24 38·38 39·32
$(C_6H_4OHCOO)_2Ca \cdot 3\,H_2O$ Ca found = 9·98% Ca theory = 10·9%	162	$\chi_a = 0{\cdot}546$ $\chi_m = 200{\cdot}9$ $\chi_{ma} = 162{\cdot}02$	..		153·08 (Pascal	$Ca^{+2}+2(C_6H_4OHCOO)^{-1}$ 154·64 151·76 152·76
$CaC_4H_4O_6 \cdot 4\,H_2O$ Ca found = 15·38% Ca theory = 15·40%	96	$\chi_a = 0{\cdot}464$ $\chi_m = 120{\cdot}2$ $\chi_{ma} = 68{\cdot}36$	..		65·94 (Pascal)	$Ca^{+2}+(C_4H_4O_6)^{-2}$ 74·18 72·26 71·30

TABLE II

Compounds	N	Authors' values	χ_{ma} Other workers		χ_{ma} Computed experimentally	χ_{ma} Computed theoretically
(a) Strontium salts of inorganic acids						
$SrBr_2$ (2)	108	$\chi_a = 0{\cdot}352$ $\chi_m = 86{\cdot}63$ $\chi_{ma} = 86{\cdot}3$	Meyer Meyer Meyer Ikenmeyer (aq. sol.)	76·6 96·25 76·6 87·3	81·6 (Pascal) 81·88 (Pascal) 86·7 (Hoccart) 95·0 (Ikenmeyer) 85·0 (Kido)	$Sr^{+2}+2\ Br^{-1}$ 136·00 101·70 93·49
$SrCO_3$ (2)	68	$\chi_a = 0{\cdot}322$ $\chi_m = 47{\cdot}23$ $\chi_{ma} = 47{\cdot}23$	Pascal Dhawan Kido	46·6 25·25 44·2	42·8 (Pascal) 43·7 (Kido)	$Sr^{+2}+(CO_3)^{-2}$ 65·95 61·13 54·09
$SrCl_2$ (2)	72	$\chi_a = 0{\cdot}402$ $\chi_m = 63{\cdot}6$ $\chi_{ma} = 63{\cdot}6$	Königsberger (aq. sol.) Meyer (solid) Meyer (solid) Ikenmeyer (aq. sol.) Ikenmeyer (aq. sol.) Kido	63·4 88·6 69·6 53·5 61·6 61·3	60·8 (Pascal) 65·1 (Hoccart) 66·2 (Ikenmeyer) 59·8 (Kido)	$Sr^{+2}+2\ Cl^{-1}$ 86·00 76·11 65·91
$SrCrO_4$ Sr found = 43·1% Sr theory = 43·13%	94	$\chi_a = -0{\cdot}0252$ $\chi_m = -5{\cdot}09$ $\chi_{ma} = -5{\cdot}09$	..		..	$Sr^{+2}+Cr^{+6}+4\ 0^{-2}$ 85·0 79·63 70·34
$Sr(OH)_2$ (2)	56	$\chi_a = 0{\cdot}417$ $\chi_m = 40{\cdot}4$ $\chi_{ma} = 40{\cdot}4$	Kido	32·1	35·68 (Pascal)	$Sr^{+2}+2\ (OH)^{-1}$ 53·2 47·83 42·62
$SrSO_4$ (2)	96	$\chi_a = 0{\cdot}328$ $\chi_m = 60{\cdot}3$ $\chi_{ma} = 60{\cdot}3$	Pascal (solid) Pascal (mean value from orthorhombic crystals) Kido (solid)	57·9 58·8 52·4	54·2 (Pascal) 54·6 (Kido)	$Sr^{+2}+S^{+6}+4\ 0^{-2}$ 79·8 75·54 66·5

$Sr(NO_3)_2 \cdot 4H_2O$ (1) ..	100	$\chi_a = 0{\cdot}359$ $\chi_m = 101{\cdot}7$ $\chi_{ma} = 57{\cdot}86$	Kido	54·7	49·0 (Pascal) 55·8 (Kido)	$Sr^{+2}+2N^{+5}+6O^{-2}$ 103·82 100·65 87·91
SrO (2)	46	$\chi_a = 0{\cdot}34$ $\chi_m = 35{\cdot}22$ $\chi_{ma} = 35{\cdot}22$	Pascal Luther	61·88 25·04	25·210 (Pascal)	$Sr^{+2}+O^{-2}$ 40·60 34·68 31·44

(*b*) *Strontium salts of organic acids*

$(CH_3COO)_2Sr \cdot \frac{1}{2}H_2O$ Sr found = 40·0% Sr theory = 40·08%	100	$\chi_a = 0{\cdot}318$ $\chi_m = 87{\cdot}7$ $\chi_{ma} = 81{\cdot}22$	Kido	79·1	78·4 (Pascal) 79·6 (Kido) 78·4 (Kido)	$Sr^{+2}+2(CH_3COO)^{-1}$ 85·52 79·05 77·71
$SrC_2O_4 \cdot H_2O$ Sr found = 45·1% Sr theory = 45·3%	82	$\chi_a = 0{\cdot}349$ $\chi_m = 67{\cdot}6$ $\chi_{ma} = 54{\cdot}64$	..		48·54 (Pascal)	$Sr^{+2}+(C_2O_4)^{-2}$ 55·94 49·47 48·13
$(HCOO)_2Sr$ Sr found = 49·0% Sr theory = 49·3%	82	$\chi_a = 0{\cdot}339$ $\chi_m = 60{\cdot}3$ $\chi_{ma} = 60{\cdot}3$	..		54·4 (Pascal) 56·0 (Kido)	$Sr^{+2}+2(HCOO)^{-1}$ 61·8 55·33 53·99
$(C_6H_4OHCOO)_2Sr \cdot 2H_2O$ Sr found = 22·0% Sr theory = 22·18%	180	$\chi_a = 0{\cdot}508$ $\chi_m = 202{\cdot}2$ $\chi_{ma} = 176{\cdot}28$	..		163·48 (Pascal)	$Sr^{+2}+2(C_6H_4OHCOO)^{-1}$ 169·34 162·82 161·54
$SrC_4H_4O_6 \cdot 4H_2O$ Sr found = 28·1% Sr theory = 28·5%	..	$\chi_a = 0{\cdot}457$ $\chi_m = 140{\cdot}5$ $\chi_{ma} = 88{\cdot}66$	..		75·34 (Pascal)	$Sr^{+2}+(C_4H_4O_6)^{-2}$ 88·88 82·41 81·07

given by the sum of susceptibilities of S^{+6} and $4O^{-2}$ ions. This value of the sulphate ion when added to the susceptibility of a cation would give the susceptibility of the particular sulphate. Angus found that the values of susceptibilities of several beryllium salts calculated according to the above-mentioned scheme by using the values of ionic susceptibilities calculated according to his method agree fairly well with those found experimentally. However, Farquharson found wide divergences between the theoretical and experimental values, which he expected and explained as due to addition reactions and the relative increase in the weak paramagnetism which is independent of temperature. He utilised these differences to calculate the relative polarities of some of the bonds. The susceptibility values of the salts used in this investigation have been calculated according to the above scheme, employing the values for various ions calculated by Pauling, Slater and Angus. These values are given in column 6 of Tables I and II under the heading χ_{ma} (theor.) in the order P, S and A. It will be seen that nearly in all cases the calculated values do not agree with the observed ones for the anhydrous salts. These observations are similar to those made by Farquharson.

Pauling has computed the values of susceptibilities for some anions regarding them as mono-nuclear systems. The sum of these values and the values of cations also calculated by him in required molecular proportions would give the susceptibility of a salt. These values differ considerably from the observed values and thus point to the uncertainty in the method of calculation adopted by Pauling.

Interesting results are obtained when the values of χ_{ma} for the same salts of calcium, strontium and barium are plotted against N. The values of χ_{ma} for barium salts are those obtained by Prasad, Dharmatti and Kanekar.[1]

The curves drawn are shown in Fig. 1. Curves of this type have been drawn by Ikenmeyer,[9] Kido,[10] Trew,[11] and Prasad, Dharmatti and Kanekar[1]; the first three found that they are linear, while the last named observed that the various points on the graph do not lie on a straight line. Trew also noticed some deviations which are explained as " specific effects due to the crystalline forms of the compounds investigated ", but it appears to the authors that the observed divergences are due to different susceptibility contributions of the different anions. It will be seen that the various curves in Fig. 1 are not linear and hence these results are not in accordance with the observations of Ikenmeyer, Kido and Trew, while they support the findings of Prasad and co-workers.

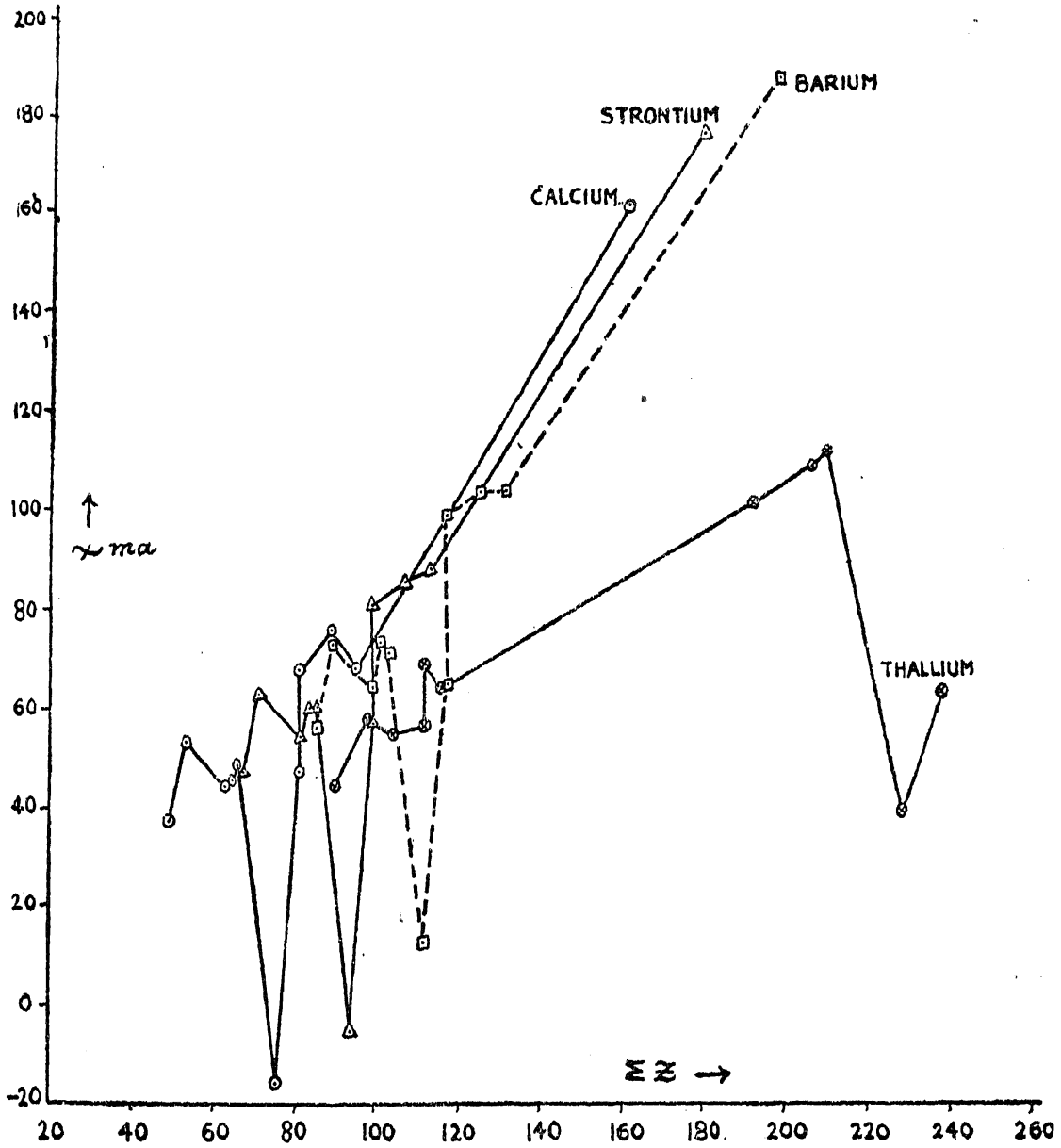

FIG. 1

Further it will be noticed that in each individual curve there is a pattern which is similar for the salts of the three elements. This similarity appears to indicate a family characteristic since the nature of the curve obtained by plotting the values of χ_{ma} for the same compounds of thallium (Trew's data), shown in the same figure, is different.

On plotting the values of χ_{ma} against N for the salts of calcium, strontium and barium containing the same anions, the curves (Fig. 2.) obtained are approximately linear the deviations from linearity are signifcant as they are probably caused by the different effects of similar bonds in different combinations. These lines have been smoothed out in the same manner as followed by Ikenmeyer[9] and the values of C_1 and C_2 in Ikenmeyer's equation $-\chi_{ma} = C_1 N + C_2$ have been evaluated. These values for different anions

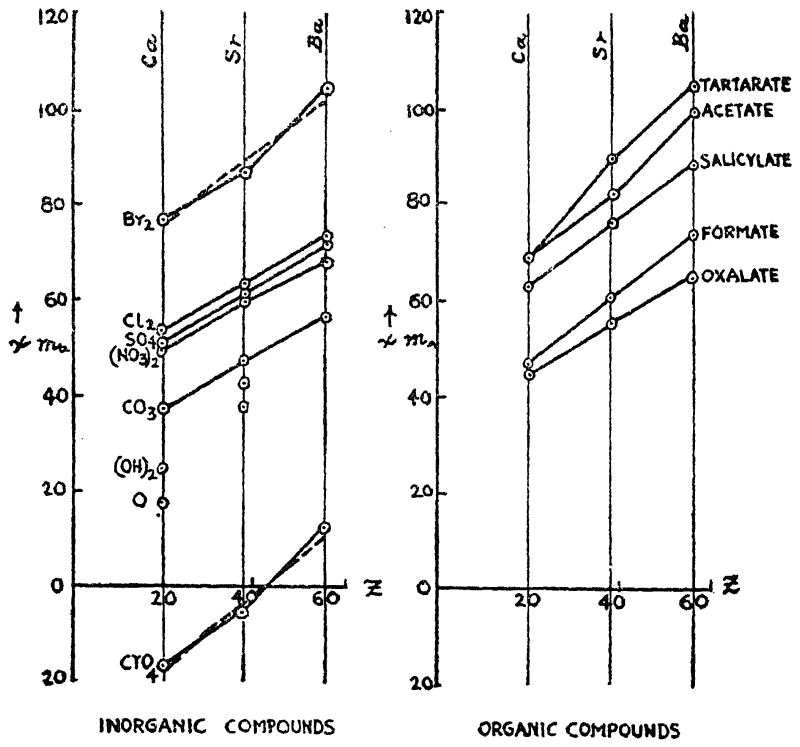

FIG. 2

are given in Table III. Van Vleck[12] has, however, pointed out that 'these linear relations should not be taken too literally as the extrapolation of these lines leads to absurd results.'

TABLE III

No.	Anions*	$C_1 \times 10^{-6}$	$C_2 \times 10^{-6}$
1	Oxides	1·15	−14·5
2	Hydroxides	1·08	−19·2
3	Fluorides	..	..
4	Carbonates	0·58	9·2
5	Chlorides	0·60	21·5
6	Oxalates	0·60	10·8
7	Formates	0·75	− 3·5
8	Sulphates	0·62	8·5
9	Chromates	0·55	−53·7
10	Nitrates	0·55	4·0
11	Acetates	0·85	− 1·0
12	Bromides	0·71	− 3·0
13	Tartrates	1·00	−26·5
14	Lactates	..	..
15	Salicylates	0·75	91·8

* Arranged in the order of increasing N values.

It will be seen from the above table that the values of C_1 do not deviate much from the mean and hence it is not unreasonable to infer that the several

lines are approximately parallel to each other. Similar observations have been made by Ikenmeyer[9] which support approximately the Pascal's law of additivity. The mean value of C_1 may be statistically interpreted as an increase in the value of χ_{ma} per unit increase of N, that is the average contribution per electron to the molar susceptibility of any of the salts of calcium, strontium and barium.

The values of C_2 differ widely for different salts and do not seem to have any physical meaning.

Ionic Susceptibility.—The experimental data is utilised to calculate the ionic susceptibilities of Ca^{++} and Sr^{++}, assuming the law of additivity and using all the values of the various anions given by previous workers. These anion values are either (1) taken from the data of previous workers, theoretical or experimental (marked *a*), or (2) deduced from such data by previous workers by appropriate considerations (marked *b*), or (3) deduced on semi-theoretical grounds, such as considerations of the structural formulæ of the anions (marked *c*), or (4) calculated by the authors as mentioned in (2) (unmarked). These values are given in column 4 of the Tables IV and V, and are classified into two parts namely, deduced from the data from (1) solids and (2) solutions. The salts of organic and inorganic acids are considered separately.

Table VI gives the mean values of χ_{ma} for Ca^{++} and Sr^{++} ions derived from (1) inorganic salts using anion values deduced drom solids, (2) inorganic salts using anion values derived from solutions, (3) organic salts using anion values derived from solids, and (4) organic salts using anion values derived from solutions. The mean in each case is an arithmetic mean as each value is tacitly assumed to be as reliable as any other. A root-mean square value was not taken because the accuracy of the additivity relation is not of such a high order as to warrant it. All the values of χ_{ma} for Ca^{++} and Sr^{++} ions have been averaged *en masse*. This procedure is slightly different from that adopted in our previous work in which average value of the cation was obtained from every conpound separately; this had an advantage in that each mean cation value could be examined separately with respect to a different molecule, but it is likely to attach undue weight to a set of values.

It appears from the above table that (*i*) the ionic susceptibility of a cation evaluated by using anion values deduced from solution data is less than that obtained when anion values deduced from data on solid salts are used, (*ii*) the cation values deduced from salts of organic acids are higher than those obtained from salts of inorganic acids, both when anion values from solid and solution data are used, and (*iii*) the values calculated according to Slater's and Angus' methods are in fair agreement with the values

TABLE IV

Compounds	χ_{ma} Authors	χ Other ions		χ Ca^{++}	
		Solid	Solution	Solid	Solution
(a) Values of $\chi_{Ca^{++}}$ ion from calcium salts of inorganic acids					
$CaBr_2$	76·22	30·5 Pascal (*a*) 30·64 Pascal (Corrected value) 33·9 Hoccart (*a*) 36·0 Brindley (*a*) 31·4 Farquharson (*a*) 31·4 Sugden (*a*) 34·7 Kido (*a*) 34·5 Hoare & Brindley (*a*) 36·29 Prasad (*b*)	38·3 Joos (*b*) 34·8 Ikenmeyer (*a*) 32·5 Reicheneder (*a*) 34·1 Weiss (*b*) 34·1 Abonnec (*a*)	15·22 14·94 8·42 4·22 13·42 13·42 6·82 7·22 3·62	— 0·38 6·62 11·22 8·02 8·02
$CaCO_3$	37·37	22·2 Pascal (*a*) 28·1 Kido (*a*) 23·89 Prasad (*b*) 18·83 Pascal's values (*c*)	..	15·17 9·27 13·48 18·54	..
$CaCl_2$	53·40	20·1 Pascal (*a*) 19·85 Bhatnagar & Luther (*a*) 23·1 Hoccart (*b*) 24·0 Brindley (*a*) 20·0 Sugden (*a*) 22·1 Kido (*a*) 24·2 Hoare & Brindley (*a*) 20·6 Prasad (*b*)	19·5 Joos (*b*) 20·4 Ikenmeyer (*a*) 21·9 Reicheneder (*a*) 23·1 Weiss (*b*) 23·9 Weiss (*b*) 23·1 Abonnec (*a*) 22·2 Leiterer (*a*) 22·2 Bhatnagar, Prakash & Hamid (*a*)	13·2 13·7 7·2 5·4 13·4 9·2 5·0 12·21	14·4 12·6 9·6 7·2 5·6 7·2 9·0 9·0
$CaCrO_4$	—16·89	—35·2 Trew (*a*) —33·0 Trew (*b*) —21·86 Bhatnagar (*b*) —25·70 (*b*) —19·61 Kanekar (*b*)	..	18·31 16·11 4·97 8·99 2·72	..

CaF_2	26·50	5·95 Pascal (*a*) 6·3 Pascal (*a*) 6·0 Pascal (*a*) 12·0 Brindley (*a*) 12·2 Kido (*a*) 9·4 Hoare & Brindley (*a*)	10·8 Joos (*b*) 13·9 Ikenmeyer (*a*)	14·60 13·9 14·5 2·5 2·1 7·7	4·9 −1·3
$Ca(OH)_2$	22·23	7·54 Pascal (*a*) 7·66 (*c*) 7·54 (*c*)	..	7·15 9·63 7·15	..
$Ca(NO_3)_2$	47·10	14·2 Pascal (*a*) 18·0 Sugden (*a*) 20·1 Kido (*a*) 18·4 Raichaudhari & Sen Gupta (*a*) 18·1 Rao & Sriraman (*a*) 16·69 Kanekar (*b*) 16·93 (*c*)	18·4 Reicheneder (*a*) 19·5 Rao & Sriraman (*a*)	8·6 11·1 6·8 10·2 10·8 13·62 13·14	10·2 8·1
CaO	15·14	4·61 Pascal (*a*)	..	5·92	..
$CaSO_4$	48·68	33·6 Pascal (*a*) 39·0 Kido (*a*) 37·0 Trew (*a*) 17·34 (*c*) 39·13 Kanekar (*b*)	..	15·08 9·68 11·68 31·34 9·55	..

(*b*) *Values of* $\chi_{Ca^{++}}$ *ion from calcium salts of organic acids*

Calcium acetate ..	68·40	28·9 Pascal (*a*) 32·0 Kido (*a*) 31·4 Kido (*a*) 30·0 Hollens & Spencer (*a*) 30·0 Trew (*a*) 29·8 Rao & Sriraman (*a*) 28·44 Kanekar (*b*) 29·62 (*c*) 29·26 (*c*)	30·2 Rao & Sriraman (*a*)	11·6 4·4 5·6 8·4 8·4 8·8 11·53 8·16 9·88	8·0
Calcium formate ..	45·30	16·9 Pascal (*a*) 20·2 Kido (*a*) 17·3 Rao & Sriraman (*a*) 15·54 Kanekar (*b*) 17·27 (*c*) 17·15 (*c*)	17·6 Rao & Sriraman (*a*)	11·5 4·9 10·7 14·22 10·76 11·0	10·1

TABLE IV—(*Contd.*)

Compounds	χ_{ma} Authors	χ Other ions		χ Ca^{++}	
		Solid	Solution	Solid	Solution
Calcium lactate ..	122·70	53·92 (*c*) 53·44 (*a*)	..	14·86 15·82	..
Calcium oxalate ..	44·30	27·94 Pascal (*a*) 28·5 Hollens & Spencer (*a*) 22·15 Kanekar (*b*) 22·19 (*c*)	..	16·36 15·8 22·15 22·11	..
Calcium salicylate ..	162·02	71·44 Pascal (*a*) 72·71 Prasad (*b*) 74·68 (*c*)	..	20·14 16·60 12·66	..
Calcium tartrate ..	68·36	62·36 Pascal 63·8 Trew 61·52 Prasad (*b*) 60·88	..	6·0 4·56 6·84 13·48	..

TABLE V

Compounds	χ_{ma} Authors	χ Other ions		χ Sr^{++}	
		Solid	Solution	Solid	Solution
(a) Values of $\chi_{Sr}{}^{++}$ ions from strontium salts of inorganic acids					
$SrBr_2$	86·30	30·5 Pascal (*a*) 30·64 Pascal (Corrected value) 33·9 Hoccart (*a*) 36·0 Brindley (*a*) 31·4 Farquharson (*a*) 31·4 Sugden (*a*) 34·7 Kido (*a*) 34·5 Hoare & Brindley (*a*) 36·29 Kanekar (*b*)	38·3 Joos (*b*) 34·8 Ikenmeyer (*a*) 32·5 Reicheneder (*a*) 34·1 Weiss (*b*) 34·1 Abonnec (*a*)	25·63 25·35 18·83 14·63 23·83 23·83 17·23 17·63 14·03	10·03 17·03 21·63 18·43 18·43
$SrCO_3$	47·23	22·2 Pascal (*a*) 28·1 Kido (*a*) 23·89 Kanekar (*b*) 18·83 Pascal's value (*c*)	..	25·03 19·13 23·34 28·4	..
$SrCl_2$	63·60	20·1 Pascal (*a*) 19·85 Bhatnagar & Luther (*a*) 23·1 Hoccart (*b*) 24·0 Brindley (*a*) 20·0 Sugden (*a*) 22·1 Kido (*a*) 24·2 Hoare & Brindley (*a*) 20·6 Kanekar (*b*)	19·5 Ioos (*b*) 20·4 Ikenmeyer (*a*) 21·9 Reicheneder (*a*) 23·1 Weiss (*b*) 23·9 Weiss (*b*) 23·1 Abonnec (*a*) 22·2 Leiterer (*a*) 22·2 Bhatnagar, Prakash & Hamid	23·4 23·82 17·4 15·6 23·6 19·14 15·2 22·41	24·6 22·8 19·8 17·4 16·8 17·4 19·2 19·2
$SrCrO_4$	−5·09	−35·2 Trew (*a*) −33·0 Trew (*b*) −21·86 Bhatnagar, Prakash & Hamid −24·7 (*b*) (*b*) −19·61 Kanekar (*b*)	..	30·11 27·91 16·77 20·61 14·52	..
$Sr(OH)_2$	40·40	7·54 Pascal (*a*) 7·66 (*c*) 7·54 (*c*)	..	25·32 25·08 25·32	..

$SrSO_4$	60·30	33·6 Pascal (*a*) 39·0 Kido (*a*) 37·0 Trew (*a*) 17·34 Trew (*c*) 39·13 Kanekar (*b*)	..	26·70 21·3 23·3 42·96 21·17	..
$Sr(NO_3)_2$	57·86	14·2 Pascal (*a*) 18·0 Sugden (*a*) 20·1 Kido (*a*) 18·4 Raichaudhari & Sen-Gupta (*a*) 18·1 Rao & Sriraman (*a*) 16·69 Kanekar (*b*) 16·93 (*c*)	18·4 Reicheneder (*a*) 19·5 Rao & Sriraman (*a*)	29·46 21·86 17·66 21·06 21·66 24·48 24·00	21·06 18·86
SrO	35·22	4·61 Pascal (*a*)	..	30·61	..

(*b*) *Values of* $\chi_{Sr^{++}}$ *ions from Strontium salts of organic acids*

Strontium acetate ..	81·22	28·9 Pascal (*a*) 32·0 Kido (*a*) 31·4 Kido (*a*) 30·0 Hollens & Spencer (*a*) 30·0 Trew (*a*) 29·8 Rao & Sriraman (*a*) 28·44 Kanekar (*b*) 29·62 (*c*) 29·26 (*c*)	30·2 Rao & Sriraman (*a*)	23·42 17·22 18·42 21·22 21·22 21·62 24·35 21·98 22·70	21·82
Strontium oxalate ..	54·64	27·94 Pascal (*a*) 28·5 Hollens & Spencer (*a*) 22·15 Kanekar (*b*) 22·19 (*c*)	..	26·7 26·14 32·49 32·45	..
Strontium formate ..	60·30	16·9 Pascal (*a*) 20·2 Kido (*a*) 17·3 Rao & Sriraman (*a*) 15·54 Kanekar (*b*) 17·27 (*c*) 17·15 (*c*)	17·6 Rao & Sriraman (*c*)	26·5 19·9 25·7 29·22 25·76 26·00	25·1
Strontium salicylate ..	176·28	71·44 Pascal (*a*) 72·71 Kanekar (*b*) 74·63 (*c*)	..	33·4 30·86 26·92	..
Strontium tartrate ..	88·66	62·36 Pascal 63·8 Trew 61·52 Kanekar (*b*) 60·88	.. ..	26·3 24·86 27·14 17·78	..

TABLE VI

Source	χ_{ma} for Ca^{++}	χ_{ma} for Sr^{++}
(1)	10·65	22·61
(2)	7·65	18·85
(3)	12·33	26·36
(4)	9·05	23·46
Slater	11·2	27·1
Angus	10·42	32·1

obtained in this investigation using anion values deduced from solid salts. The same observations have been made by Trew (11) and Prasad and co-workers.[1] In view of the important implications of the first two observations and since the numbers of the samples used for the different averages are different, the observed results were statistically examined by the usual formula for standard deviations, and it was confirmed that the observed differences in the two cases are significant.

Trew[11] and Prasad and co-workers[1] have observed that the ionic susceptibilities of cations calculated from the susceptibilities of their compounds with organic acids increase with the increase in the number of carbon atoms in the compounds. Trew has suggested that the increase in the number of carbon atoms in the compounds increases the size of the negative ions and this causes an increase in the effective ionic radius of the cation and hence an increase in the susceptibility of that ion. Looking to the importance of these observations, the data obtained on the susceptibilities of calcium and strontium salts of organic acids were also examined from the aforesaid point of view and the results obtained are given in the following table. The susceptibility values of anions used in calculating the values χ cation given in the last column of Table VII are the mean of the values given in column 5 under 'solid' in Tables IV and V.

TABLE VII

Compound	No. of carbon atoms	N	χ_{ma} (obs.)	χ cation
Calcium Oxalate	2	64	44·30	19·10
,, Formate	2	66	45·30	10·52
,, Acetate	4	82	68·40	8·52
,, Tartrate	4	96	68·36	12·28
,, Lactate	6	150	122·7	15·34
,, Salicylate	14	150	162·02	16·14
Strontium Oxalate	2	82	54·64	29·44
,, Formate	2	84	60·30	25·52
,, Acetate	4	100	81·22	21·34
,, Tartrate	4	114	88·66	32·54
,, Salicylate	14	168	176·28	30·40

Two facts emerge out from the results given above: (*i*) there is no steady increase in the value of χ cation with increasing values of either N or the number of carbon atoms, and (*ii*) there is a definite increase in the values of χ_{ma} with an increase in both N and the number of carbon atoms. These results are not exactly the same as those obtained by previous workers. It is therefore necessary that some more salts of organic acids should be examined in order to arrive at some definite conclusions. Experiments based on these lines are being carried out in this laboratory.

Electronic isomers.—The results obtained in this investigation have been compared also with those calculated according to the theory of electronic isomers suggested by Bhatnagar and Mathur,[13] who empirically generalising the Langevin-Pauli formula obtained:

$$\chi_{ma} = -\frac{Le^2}{6mc^2} K r^2 = -2{\cdot}832 \times 10^{10} K r^2$$

in which the numerical value of K is the same for electronic isomers.

For this purpose the values of K were calculated from (1) the known values of χ_{ma} obtained from the *International Critical Tables* (1929) and *Landolt-Bornstein's Physikalischechemischen Tabellen* (1936) for a set of the electronic isomers of compounds studied in this investigation, and (2) the values of r calculated on the basis of Bragg's theory of closest packing using Bragg's data as done by Bhatnagar and Mathur, from the relation:

$$K = -\chi_{ma}/2{\cdot}832 \times 10^{10} r^2.$$

Using these values of K and values of r calculated as stated above, the values of χ_{ma} for salts studied in this investigation were calculated and they are given in Table VIII.

It can be seen from Table VIII that there are large differences between the calculated values and the values obtained by the authors and other workers (*cf.* last column of the table). The disagreement between the calculated and the observed values cannot be accounted for by correcting the values of r only; it appears that some other factors have to be taken into account to reproduce the experimental results.

Ionic radius.—From the mean ionic susceptibilities of Ca^{++} and Sr^{++} their ionic radii have been calculated and are compared with the values obtained by other workers. The results obtained are shown in Table IX.

It appears from Table IX that the authors' calculated values are in better agreement with those of Slater.

TABLE VIII

Isomer				Compound studied				
Name	R (A.U.)	χ_{ma}	K	Name	R (A.U.)	χ_{ma} (cal.)	χ_{ma} (obs.)	χ_{ma} (obs.) by others (*cf.* Table I)
$BaCl_2$,,	2·262	85·3 73·50*	5·89 5·10	$CaBr_2$,,	2·023	68·25 58·9	76·22	54·55
Al_2O_3 KNO_3	1·791 2·152 2·156†	9·98 32·95	1·1 2·52 1·7†	$CaCO_3$,,	1·836	10·46 24·0 13·28†	37·37	38·2 14·01 35·5 40·08 37·8
$BeCl_2$ CS_2	1·566 1·371	47·9 41·12	6·90 7·70	CaF_2 ,,	1·726	58·3 64·9	26·50	23·4 15·6 22·25 28·1
N_2O_3	2·877	15·65	0·67	$Ca(OH)_2$	1·793	6·08	22·23	28·9 21·3
NaCl	2·825	29·2 23·98†	1·29 1·0†	CaO	2·350	20·2 15·74†	15·14	15·13 15·74
K_2CO_3	2·671 2·675†	67·4 66·02†	3·345 3·26	$CaSO_4$	1·919 1·922†	34·75 34·1†	48·68	51·8 42·54 49·6 46·34 51·73 46·8
$RbNO_3$	2·320	41·4	2·72	$SrCO_3$	2·056	32·53	47·23 29·18†	46·60 25·25 44·2
NaBr	1·934	48·3	3·62	SrO	1·973	39·9	35·22	61·88 25·04
Rb_2CO_3	2·887	74·09	3·14	$BaSO_4$	2·258	45·3	71·44	

* The observed value of $BaCl_2$ is here taken as the basis for calculation.
† Values given by Bhatnagar and Mathur.

TABLE IX

Ion	Authors' calculated values	Values of other workers	
		Wassastjerna	Slater
	Å	Å	Å
Ca^{++} (inorganic)	1·21	1·02	1·17
Ca^{++} (organic)	1·29	—	—
Sr^{++} (inorganic)	1·31	1·20	1·43
Sr^{++} (organic)	1·41	—	—

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