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J. Am. Chem. Soc., **1928**, 50 (4), 1036-1045 • DOI: 10.1021/ja01391a014

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 160]

THE INFLUENCE OF RELATIVE IONIC SIZES ON THE PROPERTIES OF IONIC COMPOUNDS

BY LINUS PAULING

RECEIVED JANUARY 4, 1928

PUBLISHED APRIL 5, 1928

Introduction

The simple method used by Born¹ to calculate the crystal energy of an ionic crystal has been widely applied for evaluating the electron affinities of atoms, the heats of solution of ions and in other similar problems in chemical thermodynamics. The repulsive potential is assumed to vary inversely with a high power of the interionic distance, so that the crystal energy per molecule may be written

$$\Phi = -\frac{z^2e^2 A}{r} + \frac{B}{r^n} \quad (1)$$

in which ze is the charge of an ion, r a characteristic interionic distance, and A and B are constants for a given crystal. The Madelung constant A may be calculated for any given ionic arrangement from the laws of electrostatics, and B is chosen so that at equilibrium, where $d\Phi/dr = 0$, r will have the value R found experimentally for the crystal under consideration. The crystal energy at equilibrium is

$$U = -\frac{z^2e^2 A}{R} \left(1 - \frac{1}{n}\right) \quad (2)$$

The repulsion exponent n is usually placed equal to 9, an average of the values obtained from the experimentally measured compressibilities of the alkali halides.

For the theoretical treatment of many phenomena it is necessary to know the relative magnitude of the repulsive forces between unlike ions and those between like ions. Moreover, it is often desired to make calculations for non-existent crystals, or other crystals for which R (and hence B) has not been experimentally determined. With the development of our knowledge of the sizes of ions it has become possible to express the interionic forces in a crystal in terms of radii of the ions in the crystal.² The resultant equation for the crystal energy is of the type of Equation 1, and it has the same limits of accuracy (1 or 2%). Like Born's equation, it is held to represent the actual crystal only to a first approximation; and it cannot be used in treating second order effects. On applying the equation it has been found that many properties of crystals depend not only on the distance between neighboring ions in the crystal (the

¹ Born, "Atomtheorie des Festen Zustandes," Teubner, 1923, p. 749.

² A detailed account of this work is given in a paper to be published in the *Z. Krist.* The present article contains only a description of the applications of interest to chemists.

"radius sum"), but also on the *relative* sizes of cation and anion (the "radius ratio"). The previously unrecognized effect of the radius ratio has been shown to account for a number of irregularities in the properties of the alkali halides formerly adduced as evidence for the existence of important deformation phenomena.

The Alkali Halides: Deviation of Interionic Distances from Additivity

By applying the perturbation theory of the new quantum mechanics to a simple model susceptible to quantitative treatment, it can be shown that the potential energy of two ions A and B , a distance r_{AB} apart, may be approximately written (neglecting polarization) as

$$\varphi = \frac{z_A z_B e^2}{r_{AB}} + \beta_{AB} \frac{(r_A + r_B)^n}{r_{AB}^n} \cdot B_0 \quad (3)$$

in which r_A and r_B are "standard radii" characteristic of the ions, B_0 is a constant for all ions, and β_{AB} has certain values obtained from the model (in particular, 1 for $M^+ - X^-$, 0.75 for $X^- - X^-$ and 1.25 for $M^+ - M^+$). On introducing this expression for the potential energy of each pair of ions in a sodium chloride type crystal (taking into consideration the repulsive potential between each ion and the adjoining six unlike and twelve like ions), there results for the equilibrium interionic distance R , the equation

$$R = (r_+ + r_-)^{\frac{n}{n-1}} \cdot F(\rho) \quad (4)$$

with

$$F(\rho) = \left\{ \frac{(1 + \rho)^n + \beta_{++} (\sqrt{2} \rho)^n + \beta_{--} (\sqrt{2})^n}{(1.75)^n + \beta_{++} (\sqrt{2} \cdot 0.75)^n + \beta_{--} (\sqrt{2})^n} \right\}^{\frac{1}{n-1}} \quad (4a)$$

in which B_0 and the standard radii have been so chosen that $R = (r_+ + r_-)^{\frac{n}{n-1}}$ for the radius ratio ρ equal to 0.75. This function, calculated for $\beta_{++} = 1.25$, $\beta_{--} = 0.75$ and $n = 9$, is represented in Fig. 1.

The deviation of interionic distances in the alkali halide series from additivity is well known.³ The most pronounced deviations, those of the lithium salts, were explained by Landé⁴ and Wasastjerna⁵ as arising from the mutual contact of the anions; if the ions are considered as rigid spheres, contact between the anions occurs for $\rho = 0.414$, causing the interionic distance to increase as shown by the broken line in Fig. 1. It has also been pointed out⁶ that for actual mutually repelling ions an increase in the interionic distance will take place at values of ρ even somewhat larger than 0.414, for repulsion both between anion and cation and

³ See Fajans and Grimm, *Z. Physik*, **2**, 299 (1920); Fajans and Herzfeld, *ibid.*, **2**, 309 (1920).

⁴ Landé, *ibid.*, **1**, 191 (1920).

⁵ Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.*, **38**, 1 (1923).

⁶ Pauling, *THIS JOURNAL*, **49**, 765 (1927).

between anion and anion will be operative; this effect of "double repulsion" provides a qualitative explanation of further deviations from additivity shown by the alkali halides. It will be seen from Fig. 1 that the quantitative considerations of this paper substantiate these views. $F(\rho)$ is roughly unity for ρ larger than 0.70; it approximates the anion-contact curve for small values of ρ , and for values in the neighborhood of 0.414 it is considerably higher than the rigid-sphere curve, showing the effect of double repulsion.

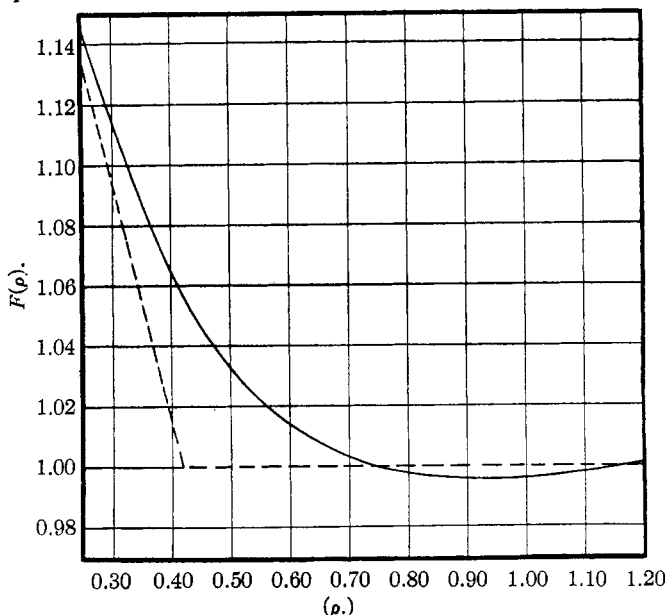


Fig. 1.—The correction factor $F(\rho)$ giving the dependency of interionic distance in sodium chloride type crystals on the radius ratio ρ (solid line). The broken line shows the form of this function for $n = \infty$; that is, for solid spheres.

It is, moreover, possible to select values of r_+ and r_- for the alkali and halide ions such that the interionic distances as calculated by Equation 4 are in complete agreement with experiment for all the alkali halides. In this calculation n was given the value 9 and β_{++} and β_{--} the values 1.25 and 0.75 throughout. The values of r_+ and r_- used are given in Table I.

TABLE I
STANDARD RADII FOR THE ALKALI AND HALIDE IONS

	r_+ , Å.		r_- , Å.
Li ⁺	0.574		
Na ⁺	0.873	F ⁻	1.225
K ⁺	1.173	Cl ⁻	1.589
Rb ⁺	1.294	Br ⁻	1.702
Cs ⁺	1.434	I ⁻	1.867

Those for K^+ and Cl^- and for Rb^+ and Br^- were chosen such that their ratios agree with the ratios of previously derived size screening constants,⁷ and the remaining r 's were then taken to cause agreement with the experimental data.

TABLE II

THE RADIUS RATIO ρ , THE CORRECTION FACTOR $F(\rho)$ AND THE CORRECTED INTERIONIC DISTANCE $R_{0.75}$ FOR THE ALKALI HALIDES

		F^-	Cl^-	Br^-	I^-
Li^+	ρ	= 0.464	0.357	0.334	0.304
	$F(\rho)$	= 1.042	1.082	1.094	1.111
	$R_{0.75}$	= 1.927 Å.	2.373 Å.	2.513 Å.	2.720 Å.
Na^+	ρ	= 0.713	0.550	0.513	0.468
	$F(\rho)$	= 1.002	1.023	1.029	1.041
	$R_{0.75}$	= 2.302 Å.	2.753 Å.	2.894 Å.	3.106 Å.
K^+	ρ	= 0.959	0.739	0.689	0.629
	$F(\rho)$	= 0.995	1.001	1.005	1.010
	$R_{0.75}$	= 2.675 Å.	3.138 Å.	3.278 Å.	3.494 Å.
Rb^+	ρ	= 1.057	0.815	0.760	0.694
	$F(\rho)$	= 0.997	.997	.999	1.004
	$R_{0.75}$	= 2.827 Å.	3.288 Å.	3.436 Å.	3.650 Å.
Cs^+	ρ	= 1.172	0.903	0.843	0.769
	$F(\rho)$	= 0.999	.995	.996	.999
	$R_{0.75}$	= 3.008 Å.	3.471 Å.	3.617 Å.	3.832 Å.

The corresponding values of the radius ratio and of the correction factor $F(\rho)$ for the alkali halides are given in Table II. In addition there are given values of $R_{0.75}$ obtained from Equation 4 by placing $F(\rho) = 1$. These are the interionic distances the crystals would show if the radius ratio effect did not exist. By multiplying $R_{0.75}$ by $F(\rho)$ we obtain the calculated values of the interionic distance in the alkali halides as given by Equation 4. For comparison the calculated and observed values are given together in Table III.

TABLE III

MEASURED AND CALCULATED INTERIONIC DISTANCES IN THE ALKALI HALIDE CRYSTALS^a

	F^- , Å.	Cl^- , Å.	Br^- , Å.	I^- , Å.
Li^+	2.008	2.567	2.747	3.022
	2.009	2.566	2.745	3.025
Na^+	2.307	2.815	2.979	3.233
	2.310	2.814	2.981	3.231
K^+	2.663	3.140	3.293	3.527
	2.664	3.140	3.293, 3.289	3.526
Rb^+	2.817	3.277	3.434	3.663
	2.815	3.268, 3.285	3.434	3.663
Cs^+	3.005	3.455	3.604	3.828
	3.005	(3.580) ^b	(3.715) ^b	(3.95) ^b

^a The upper figure in each case is the calculated one. For literature citations see ref. 2.

^b Cesium chloride structure.

⁷ Pauling, *Proc. Roy. Soc. (London)*, **114A**, 181 (1927); *THIS JOURNAL*, **49**, 765 (1927).

The average difference is $\pm 0.001 \text{ \AA.}$, within the experimental error, so that the agreement can be said to be complete. The deviations from additivity to be accounted for are as large as 0.150 \AA. , and in the case of lithium iodide the correction due to $F(\rho)$ is 0.302 \AA. No arbitrary parameters other than the r 's were introduced in this calculation, for n , β_{++} and β_{--} were previously determined. Hence by means of nine variables (the r 's) seventeen equations giving the interionic distances are satisfied, as well as the two equations giving the previously determined ratios r_{+}/r_{-} for $\text{K}^{+}/\text{Cl}^{-}$ and $\text{Rb}^{+}/\text{Br}^{-}$. This may be compared with the results of Fajans and Herzfeld, who, using the model of the static cubical ion, calculated eleven interionic distances (not including the lithium salts, which show the greatest deviation) with an average error of 0.004 \AA. by the use of seven arbitrarily chosen radii.

The calculated values for the cesium halides give closely the distances to be expected for these substances crystallizing with the sodium chloride structure. Under ordinary conditions these salts (except the fluoride) have the cesium chloride arrangement, with the interionic distances shown in the table. The increase in R in going from the sodium chloride to the cesium chloride structure is from these figures, 3.03, 3.08 and 3.19% for the chloride, bromide and iodide of cesium, agreeing with the increase of 3% deduced by Goldschmidt⁸ from the measured distances in the two forms of the ammonium halides. The theoretical interpretation of this increase is discussed elsewhere.²

Melting Points, Boiling Points and Related Properties

The effect of the radius ratio on other properties of the alkali halides can be similarly discussed. In some cases the radius ratio is of no importance; thus the interatomic distance in a gaseous diatomic salt molecule is not a function of it (for only the radius sum enters in the equation expressing the potential energy of two ions), nor is the energy of formation of such a molecule from free ions. In order to separate the effect of the radius ratio from other effects we shall define for each substance a corresponding hypothetical standard substance; namely, one with the same radius sum $r_{+} + r_{-}$, and the same ionic properties otherwise, but with the standard radius ratio $\rho = 0.75$. The properties attributed to this hypothetical substance will be designated as corrected for the radius ratio effect or, briefly, corrected.

The effect of the radius ratio on interionic distances is shown in Fig. 2, in which the actual interionic distances (Table III) are connected by solid lines, and the corrected ones ($R_{0.75}$ of Table II) by broken lines. It will be seen that the corrected distances show some regularities not exhibited

⁸ Goldschmidt, *Skrifter Det Norske Videnskaps-Akademi i Oslo*, 1926, No. 2; 1927, No. 8.

by the actual ones; thus the approximate equality of the differences Cs^+-Rb^+ and Rb^+-K^+ is shown also by the much larger differences K^+-Na^+ and Na^+-Li^+ .

The related properties density and molecular volume are, of course, also similarly affected by the radius ratio, the percentage corrections being roughly three times as large as those for the interionic distances.

The properties to be expected of the hypothetical alkali halides with $\rho = 0.75$ are the following. The interionic distances in the crystals should conform nearly to additivity, as is shown in Fig. 2. The crystal energy, which is inversely proportional to the interionic distance, should show a corresponding regularity. A large number of properties of salts depend essentially on the crystal energy—the heat of fusion, heat of sublimation, melting point, boiling point, solubility, etc. All of these properties in the case of the hypothetical alkali halides would exhibit a regular dependency on the interionic distance, and hence the curves showing any one of these properties should be similar to the dotted lines in Fig. 2. The properties of the actual alkali halides deviate very much from this expected regularity; the observed melting points, for example, shown on the left side of Fig. 3, deviate greatly from inverse proportionality with the interionic distances.

The quantitative explanation of such discrepancies is again provided by the radius ratio effect. The crystal energy of each hypothetical alkali halide with $\rho = 0.75$ (the corrected crystal energy) and that of the actual crystal may be obtained from Equation 2 with the aid of the data of Tables II and III. The difference ΔU between the actual and the corrected crystal energy is given by the equation

$$\Delta U = -z^2e^2 A \left(1 - \frac{1}{n}\right) \left(\frac{1}{R} - \frac{1}{R_{0.75}}\right)$$

Values of this quantity are given in Table IV.

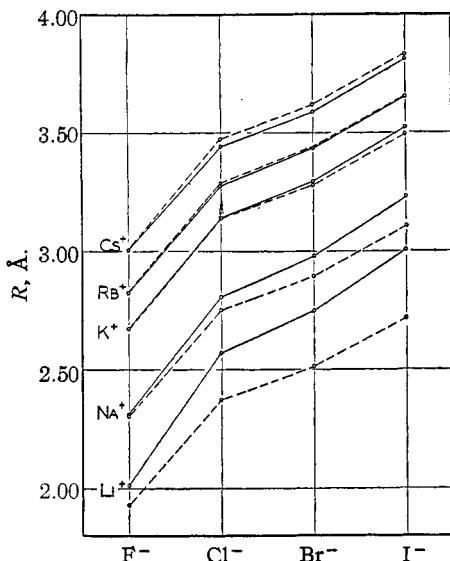


Fig. 2.—The points connected by solid lines give the actual interionic distances for alkali halide crystals with the sodium chloride arrangement, and those connected with broken lines interionic distances corrected for the radius ratio effect; that is, calculated for hypothetical substances with the same radius sums as the alkali halides but with the standard radius ratio $\rho = 0.75$.

TABLE IV
THE EFFECT OF THE RADIUS RATIO ON CRYSTAL ENERGY, BOILING POINTS AND MELTING POINTS

		F ⁻	Cl ⁻	Br ⁻	I ⁻
Li ⁺	ΔU	= 10.8	16.4	17.6	18.8
	ΔT_{BP}	= 138°	209°	225°	240°
	ΔT_{MP}	= 270°	410°	440°	470°
Na ⁺	ΔU	= 0.5	4.1	5.1	6.5
	ΔT_{BP}	= 7°	52°	65°	83°
	ΔT_{MP}	= 13°	102°	127°	162°
K ⁺	ΔU	= -0.9	0.1	0.7	1.4
	ΔT_{BP}	= -11°	1°	9°	18°
	ΔT_{MP}	= -22°	3°	18°	35°
Rb ⁺	ΔU	= -0.6	-0.5	-0.1	0.5
	ΔT_{BP}	= -8°	-7°	-1°	7°
	ΔT_{MP}	= -15°	-13°	-3°	13°
Cs ⁺	ΔU	= -0.2	-0.7	-0.5	-0.1
	ΔT_{BP}	= -3°	-9°	-7°	-1°
	ΔT_{MP}	= -5°	-18°	-13°	-3°

The energy difference ΔU is largest for lithium iodide, amounting to 11% of the total energy. The same energy quantity is required to correct the heat of sublimation, as the energy of a gaseous molecule is not a function of the radius ratio.

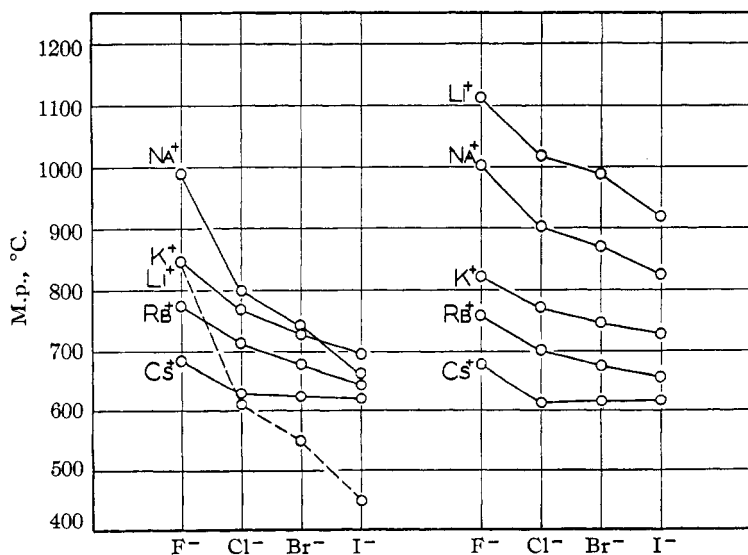


Fig. 3.—The points on the left are the observed melting points of the alkali halides; those on the right are corrected for the radius ratio effect.

The heat of sublimation at room temperature is equal to the sum of the heat of fusion at the melting point, the heat of vaporization at the

boiling point and the difference between the heat capacity of the solid and liquid and that of the vapor, integrated from room temperature to the boiling point; so that these quantities are also subject to correction for the radius ratio effect. For potassium chloride 10% of the total heat of sublimation is heat of fusion, 60% heat of vaporization and 30% results from the heat-capacity difference. It would perhaps be reasonable to divide the correction energy in these proportions; however, it is to be expected that the transition from crystal to liquid would work to destroy the coördination character of the ionic aggregation, causing the heat of fusion to assume a larger share of the correction energy, and that furthermore the coördination surviving in the liquid would decrease rapidly with increasing temperature, so that the heat content of the liquid would also assume more than its share of ΔU .⁹ The following calculations were made by apportioning 15% of ΔU to the heat of fusion and 30% to the heat of vaporization, these proportions being chosen partially to produce satisfactory results in the consideration below of boiling points and melting points.

These heat quantities themselves are not sufficiently accurately known throughout the series to provide material for the direct test of this effect. The boiling point of a substance is, however, related to its heat of vaporization by Trouton's rule, according to which the entropy of vaporization is a constant. For the alkali halides this constant has the value 23.5 cal./mole degree, found from the experimental values of the heat of vaporization and the boiling points. If the corrected boiling points be so calculated, then the correction, in degrees, is

$$\Delta T_{BP} = \frac{0.30 \Delta U}{0.0235} \quad (5)$$

Similarly we may assume that the entropy of fusion is constant (Richards' rule), with the value 6.0 cal./mole degree. The resultant melting point correction is then

$$\Delta T_{MP} = \frac{0.15 \Delta U}{0.0060} \quad (6)$$

The values of ΔT_{BP} and ΔT_{MP} obtained by the use of the previous results for ΔU are also given in Table IV.

The observed melting points and boiling points of the alkali halides¹⁰ (Figs. 3 and 4, left side) show large irregularities, and correspond only very roughly with the crystal distances, to which, if the radius ratio be not considered, they should be closely related. Thus the boiling points

⁹ This would cause the salts for which ΔU is large to show low values of the heat capacity and of the thermal coefficient of expansion in the fused state.

¹⁰ We apply these considerations also to the cesium salts, three of which have at room temperature the cesium chloride structure. This can, of course, have no effect on the boiling point; and it is furthermore probable that the salts undergo transformation to the sodium chloride structure before reaching the melting point.

and melting points of all the lithium salts lie below those of the corresponding sodium salts; those of lithium iodide being, in fact, the lowest of all for the alkali halides. These irregularities have been previously explained¹¹ as resulting from the influence of deformation of the ions in the gaseous molecule, which would tend to decrease the heat of sublimation and hence to lower the boiling point and melting point. Our calculations show, however, that they result mainly from the radius ratio effect. The corrected melting points (Fig. 3) are entirely regular and correspond closely to the crystal distances. Indeed, since in the fused salt a coordination structure only somewhat less pronounced than that for the crystal exists, the electric field is extremely small at the center

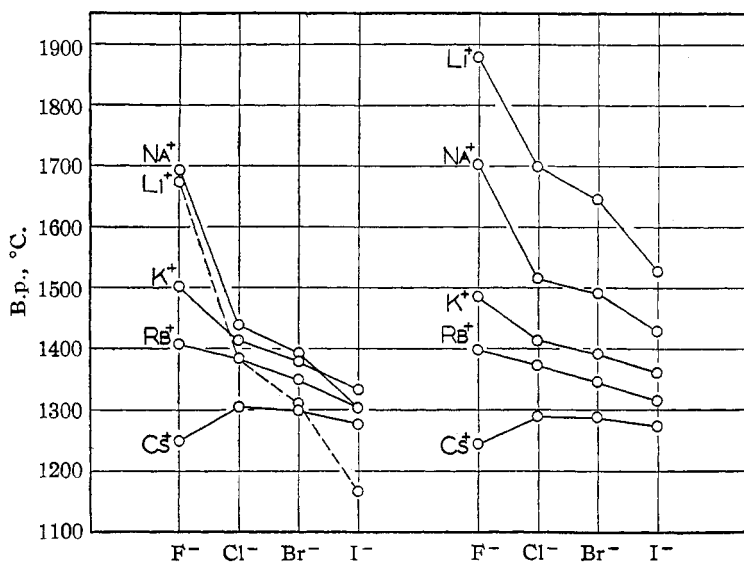


Fig. 4.—The points on the left are the observed boiling points of the alkali halides; those on the right are corrected for the radius ratio effect.

of each ion, and only poles of high order (no electric dipoles) will be formed; so that the heat of fusion and the melting point would not be expected to vary appreciably with the polarizability or deformability of the ions. On the other hand, some influence of the polarization of the ions in the vapor molecule on the heat of vaporization and boiling point is to be expected, although not so large as that previously postulated. The boiling points corrected for the radius ratio effect (Fig. 4) are not completely regular, even though a favorable value of the fraction of ΔU to be attributed to heat of vaporization has been chosen. It is not possible to eliminate the inverted order of the cesium halides by any choice of fraction of ΔU . This small residual effect is no doubt to be attributed to deformation.

¹¹ Fajans, *Z. Krist.*, **61**, 18 (1925).

Thus we may conclude that the major anomalies in the melting points and boiling points of the alkali halides result from the influence of the relative sizes of cation and anion, and that deformation phenomena play only a minor role.

Further Radius Ratio Effects

The action of the radius ratio in influencing the axial ratio of tetragonal crystals with the rutile and anatase structures has been evaluated, and shown to agree well with the results of observation.² The radius ratio is also of significance for the relative stability of alternative crystal structures, for the variation of interionic distance accompanying transition from one structure to another,² for hydrate and ammoniate formation and for the solubility of salts; in short, for all properties dependent on the crystal energy. The potential expressions of this paper are now being applied to the problems of ion formation, valence and the structure of ionic complexes.

Summary

With the aid of an expression for the mutual energy of ions in terms of standard ionic radii it is shown that the ratio of cation radius to anion radius influences the properties of ionic substances. Irregularities in interionic distances, melting points and boiling points of the alkali halides are explained as resulting from this effect.

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[CONTRIBUTION FROM THE MARTIN MALONEY CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY OF AMERICA]

ADSORPTION OF SULFUR DIOXIDE BY TITANIA GEL

BY SIMON KLOSKY AND A. J. BURGGRAFF¹

RECEIVED JANUARY 9, 1928

PUBLISHED APRIL 5, 1928

The object of this investigation was to determine whether a porous body similar to silica gel, but with a more specific attraction for sulfur dioxide, would adsorb it according to Patrick's condensation formula.

Material

The titania gel was prepared in quantity according to the method of Klosky and Marzano.² The sulfur dioxide was taken from the metal tanks which are sold in industry. Its purity was tested by absorbing a known volume in concentrated sodium hydroxide. The gas was completely adsorbed by the sodium hydroxide.

¹ Extract from Doctor's Dissertation, 1927.

² Klosky and Marzano, *J. Phys. Chem.*, **29**, 1125 (1925).