Formula for the Melting Points of Inorganic Compounds of Type MXO_n

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(Received March 5, 1952)

General

(**1—a**) Purpose of the present paper is to propose an expression for the melting points of the inorganic compounds of type MXO_n as the function of the ionic radius and the polarizability of the atom, where M^+ is the metal ion and XO_n^- is the anion, e. g., in the case of the alkali nitrates, M^+ denotes lithium, sodium and potassium ion etc., and XO_n^- nitrate ion, NO_3^-.

The melting points of the salts are expressed by T°K and the polarizabilities and the ionic radii of the ions, M^+ and $X^{(2n-1)+}$, are written as α and r respectively. Positive signs are suffixed to α and r of the metal ion, M^+, and the negative signs to those of the ion, $X^{(2n-1)+}$, in the negative ion. The data of the melting points which are necessary for this study have been taken out of the Landolt-Boernstein tables,(1) International critical tables(2) and the

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(1) Landolt-Boernstein Physikalisch-chemische Tabellen.

(2) International critical tables.

Smithonian physical tables.(3) Both the values of Goldschmidt(4) and of Pauling,(5) are adopted for the ionic radius. The polarizabilities of the metal ion, M^+, are taken out of the reports of Goldschmidt(6) and of Fajans.(7) The polarizabilities of the ion $X^{(2n-1)+}$ are approximately taken as equal to the cubes of the ionic radius of $X^{(2n-1)+}$. That is, α_- is set as $(r_-)^3$. The values of α given by Goldschmidt and by Fajans have also been utilized.

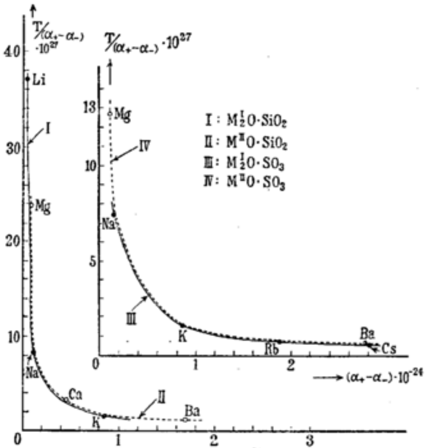

Fig. 1.

In order to find any correlation between T, α and r, these values were presented as graphs in many ways. Considering the results, a simple relation was observed, when the values of $T/(\alpha_+-\alpha_-)$ was plotted as an ordinate and $(\alpha_+-\alpha_-)$ as an abscissa. In Fig. 1, the examples of alkali-silicates, alkaliearth-silicates and alkali-sulphates etc. are given. Each line shows very similar type, and the type of the line seems to be approximately 'hyperbolic.' These 'hyperbolic' lines can also be obtained for other series of salts. No other relation has yet been obtained, which is simpler than those in Fig. 1. All the data of T, α and r, necessary for the calculation, are given in Tab. 1. In the table, the data of Pauling, Fajans and Goldschmidt are cited for α and r.

(1—b) Now we consider the series of compounds having different cations and the same anion. According to (1—a), approximate 'hyperbolic' correlation should be observed as a graph of $T/(\alpha_+-\alpha_-)$ versus $(\alpha_+-\alpha_-)$ for these compounds. Then an approximate expression (1) is obtained for these salts,

$$T^m\cdot(\alpha_+-\alpha_-)^n=A \qquad (1)$$

where m and n are the exponent of T and $(\alpha_+-\alpha_-)$ respectively and A is a constant. In order to find the values of m and n which satisfy (1), the known values of T and $(\alpha_+-\alpha_-)$ were put into (1) and the values of A were calculated for the several values of m and n. According to the results of calculation, A becomes almost constant for all the members of the series when,

$$m=1$$

$$\text{and} \qquad n=1/6. \qquad (2)$$

When these values of m and n were applied to other series, the results were also very satisfying. The calculated values of A for several series of salts are also shown in Tab. 2.

Though the values of A remains almost constant in one series of compounds, there are slight differences between the members of the series. These differences are due to the differences between the constituents of the salts. In order to find any regularity in these differences, the present author examined the correlation between the ionic radius of the atom and the values of A. When he has presented these values as a graph of A versus the reciprocal of the ionic radius of the cation, r_+,

Table 1

		Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
r_+ (10^{-8}.cm.)	Paul.	0.60	0.95	1.33	1.48	1.69	0.65	0.99	1.13	1.35
	Gold.	0.78	0.98	1.33	1.49	1.65	0.78	1.06	1.27	1.43
α_+ (10^{-24}.cm.^{3})	Faj.	0.08	0.196	0.88	1.56	2.56	0.12	0.51	0.86	1.68
	Gold.	0.067	0.197	0.29	1.90	2.85	0.114	0.57	1.38	2.8
		Al^{3+}	B^{3+}	C^{4+}	Si^{4+}	N^{5+}		P^{5+}		S^{6+}
r^- (10^{-8}.cm.)	Paul.	0.50	0.20	0.15	0.41	0.11		0.34		0.29
	Gold.	0.57		0.2	0.49	0.1~0.2		0.03~0.4		0.34

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(3) Smithonian physical tables, P. 254 (1933).

(4) V. M. Goldschmidt *Chem. Ber.* **60**, 1268 (1927).

(5) L. Pauling *J. Am. Chem. Soc.*, **49**, 765 (1927).

(6) V. M. Goldschmidt Geochemische Verteilungsgesetze der Elemente vol. **7**, 60 (1926).

(7) K. Fajans, G. Joos *Z. f. Phys.* **23**, 1 (1924).

Table 2

(1) ($M_2O\cdot B_2O_3$) α_+(G.), r_+(G), r_-(P), $\alpha_-=(0.2)^3$

Salt	T°K	A	r_-/r_+
$Li_2O\cdot B_2O_3$	1116	0.069	0.256
$Na_2O\cdot B_2O_3$	1239	0.094	0.204
$K_2O\cdot B_2O_3$	1220	0.120	0.151
($MO\cdot B_2O_3$)			
$CaO\cdot B_2O_3$	1427 (1)	0.159	0.188
	1373	0.139	〃
$SrO\cdot B_2O_3$	1373	0.145	0.157
$BaO\cdot B_2O_3$	1333	0.158	0.140

(2) ($MO\cdot Al_2O_3$) α_+(G), r_+(G), r_-(G), $\alpha_-=(0.57)^3$

Salt	T°K	A	r_-/r_+
$CaO\cdot Al_2O_3$	1960 (1)	0.167	0.54
	1873	0.159	〃
$SrO\cdot Al_2O_3$	2015 (1)	0.207	0.45
	2288	0.237	〃
$BaO\cdot Al_2O_3$	2000 (1)	0.235	0.33
	2273	0.267	〃

(3) ($M_2O\cdot CO_2$) α_+(G), r_+(G), $r_-=0.2$, $\alpha_-=(0.2)^3$

Salt	T°K	A	r_-/r_+
$Li_2O\cdot CO_2$	1005	0.065	0.256
$Na_2O\cdot CO_2$	1124	0.085	0.204
$K_2O\cdot CO_2$	1164	0.114	0.151
$Rb_2O\cdot CO_2$	1170	0.130	0.134
($MO\cdot CO_2$)			
$SrO\cdot CO_2$	1770	0.187	0.157
$BaO\cdot CO_2$	2013	0.239	0.140

(4) ($M_2O\cdot SiO_2$) α_+(G), r_+(G), r_-(G), $\alpha_-=0.04$(G)

Salt	T°K	A	r_-/r_+
$Li_2O\cdot SiO_2$	1474 (3)	0.0807	0.50
$Na_2O\cdot SiO_2$	1361 (3)	0.0997	0.40
$K_2O\cdot SiO_2$	1249 (3)	0.1218	0.294
($MO\cdot SiO_2$)			
$MgO\cdot SiO_2$	1830 (3)	0.1185	0.50
$CaO\cdot SiO_2$	1515 (3)	0.136	0.369
$SrO\cdot SiO_2$	1853 (3)	0.1946	0.307
$BaO\cdot SiO_2$	1877 (3)	0.2223	0.274
($MO_2\cdot SiO_2$) $\alpha_+=[r_+(G)]^3$, $\alpha_-=0.04$(G)			
$ZrO_2\cdot SiO_2$	2823 (3)	0.261	0.448
$HfO_2\cdot SiO_2$	2851 (3)	0.265	0.443
$UO_2\cdot SiO_2$	2881 (3)	0.323	0.371
$ThO_2\cdot SiO_2$	2882 (3)	0.372	0.351

(5-2) ($M_2O\cdot N_2O_5$) α_+(G), r_+(G) $\alpha_-=[r_-(P)]^3=0.001$

Salt	T°K	A	r_-/r_+
$NaNO_3$	581	0.443	0.12
KNO_3	614	0.0603	0.083
$RbNO_3$	583	0.0649	0.074
$CsNO_3$	683	0.196	0.067

(5-3) ($MO\cdot N_2O_5$) α_+(F), $\alpha_-=[r_-(P)]^3$, r_+(P)

Salt	T°K	A	r_-/r_+
$Ca(NO_3)_2$	834	0.0759	0.111
$Sr(NO_3)_2$	843	0.0887	0.0975
$Ba(NO_3)_2$	865	0.102	0.0817

(6) (M_3PO_4) α_+(F), r_+(P), r_-(P) $\alpha_-=[r_-(P)]^3$

Salt	T°K	A	r_-/r_+
Li_3PO_4	1110	0.061	0.57
Na_3PO_4	1613	0.119	0.35
K_3PO_4	1613	0.157	0.256

(7-3) ($M_2O\cdot SO_3$) α_+(G), r_+(G), r_-(G), $\alpha_-=[r_-(G)]^3$

Salt	T°K	A	r_-/r_+
Na_2SO_4	1157	0.085	0.35
K_2SO_4	1340	0.131	0.256
Rb_2SO_4	1325	0.147	0.228
Cs_2SO_4	1281	0.152	0.206
($MO\cdot SO_3$)			
$MgSO_4$	1393	0.0905	0.436
$CaSO_4$	1723	0.1550	0.32
$BaSO_4$	1853	0.2194	0.23

(1) and (3) of melting points shows the source of reference quotation. Other values of melting points have been taken out of reference (2).

strictly speaking, the ratio of the ionic radii, r_-/r_+, one straight line has been obtained and the following expressions (3), (4) have been given,

$$A=a-b(r_-/r_+) \qquad (3)$$

$$T\cdot(\alpha_+-\alpha_-)^{1/6}=a-b\cdot(r_-/r_+), \qquad (4)$$

where a and b are the constants of positive sign which are characteristic for one series of the salts. Thus the expression (4) is the formula for the melting points of the inorganic compounds of type MXO_n. Several examples showing the linearity functions of (3) are shown in Fig. 2 and 3.

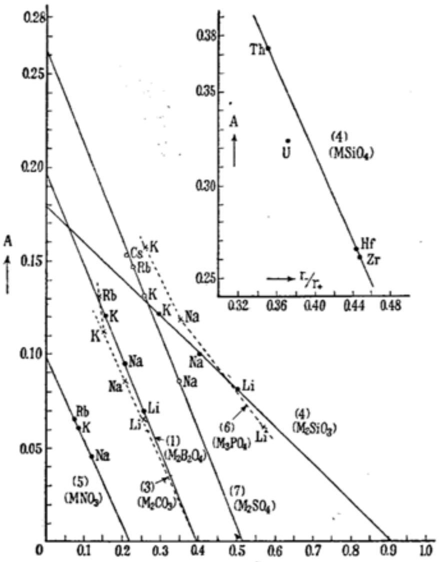

Fig. 2.

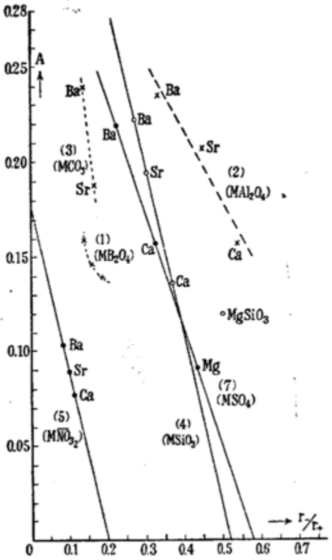

Fig. 3.

Special

(1) **Borates.**—Linear correlation of (4) is observed in the case of borates of lithium, sodium and potassium when the ionic radius of B^{3+}, r_-, is taken as 0.20, and polarizability of B^{3+}, α_-, as $(0.20)^3 = 0.008 (10^{-24}\,\text{cm}^3)$. The polarizabilities for the cations are taken from Goldschmidt's data. Such a clear-cut linear correlation was not observed in the case of bivalent métal salts, such as calcium, strontium and barium, as was shown in monovalent metal salts.

Following values of a and b for expression (4) are obtained by the graph, $a = 0.195$ and $b = 0.482$ for $M_2O \cdot B_2O_3$.

(2) **Alluminates.**—Alluminates of bivalent metals do not give a linear correlation expressed by (4). But when the ionic radius of Al^{3+}, r_-, is taken as 0.57 and the polarizabilities of the cations are taken from Goldschmidt's data, we can obtain an approximately straight line as is shown in Fig. 3. In this case, the polarizability of Al^{3+}, α_-, is set as $(0.57)^3$. When we set α_- as $(0.50)^3$, the cube of the ionic radius given by Pauling for Al^{3+}, the presented graph deviates far from a straight line. Polarizabilities taken out of the data of Fajans and Joos are unsatisfactory. Considering the results of this study, the presented graphs for most of the other series of compounds do not show clear-cut linear correlation when we take the polarizabilities out of the data of Fajans and Joos, and the ionic radii out of those of Pauling. Thus the Goldschmidt's values will be adopted for polarizabilities and ionic radii in the following calculation. When we take the melting points out of the literature (2) as 1873°K for $CaO \cdot Al_2O_3$, 2288°K for $SrO \cdot Al_2O_3$ and 2273°K for $BaO \cdot Al_2O_3$, the presented graph deviates from a straight line exceedingly, whereas, the values taken out of the literature (1) are satisfying. Thus the values given by the latter seem close to the fact, and in this case the following approximate values of a and b are obtained.

$$a = 0.350, \quad b = 0.327 \quad \text{for} \quad MO \cdot Al_2O_3.$$

This result is an example, where the applicability of the formula (4) for the examination of the observed values of melting points is demonstrated.

(3) **Carbonates.**—The ionic radius for C^{4+}, r_-, is 0.2 and α_- is set as $(0.2)^3 = 0.008$. The correlation given by the salts of lithium, sodium and potassium is approximately taken as a straight line, and the following values are obtained,

$$a = 0.178 \text{ and } b = 0.450 \text{ for } M_2O \cdot CO_2.$$

Rubidium carbonate deviates from this line.

The melting points of the bivalent metal carbonates are known only for strontium, and barium, and the linearity can not be examined in this case. But if we make a graph with the two salts, we can obtain the following values,

$$a = 0.699, \text{ and } b = 3.25 \text{ for } MO \cdot CO_2.$$

(4) **Silicates.**—When the polarizability of Si^{4+} is taken as 0.04, the silicates of lithium, sodium give closely linear correlation and in this case,

$$a = 0.183 \text{ and } b = 0.200 \text{ for } M_2O \cdot SiO_2.$$

The results are unsatisfactory when α_- is set as $(r_-)^3$.

Calcium, strontium and barium give also another linear correlation, and

$$a = 0.472, \; b = 0.904 \text{ for } MO \cdot SiO_2.$$

Magnesium compound, $MgO \cdot SiO_2$, deviates from this correlation. The present author examined also the correlation between the compounds of tetravalent metals, $MO_2 \cdot SiO_2$. When the ionic radius is taken as 0.87 for Zr^{4+}, 0.88 for Hf^{4+}, 1.05 for U^{4+} and 1.10 for Th^{4+} according to Goldschmidt, and the polalizabilities of these ions are taken as the cubes of the ionic radii respectively, thorium, hafnium and zirconium show linear correlation and in this case,

$$a = 0.975 \text{ and } b = 1.157 \text{ for } MO_2 \cdot SiO_2.$$

Uranium compound deviates from this line.

(5) **Nitrates.**—A linear correlation can be obtained for the nitrates of sodium, potassium and rubidium. In this case, the linear correlation is held for the values both of Fajans and of Goldschmidt. Both of the ionic radii given by Pauling and by Goldschmidt can also be adopted to obtain the linear correlation. And the following values of a and b are obtained for $M_2O \cdot N_2O_5$,

$$a=0.113,\ b=1.57,\ \begin{bmatrix}\alpha_+\text{(Fajans)}\\ r_+\text{(Pauling)}\end{bmatrix} \qquad (5\text{-}1)$$

and

$$a=0.097,\ b=0.440,\ \begin{bmatrix}\alpha_+\text{(Goldschmidt)}\\ r_+\text{(Goldschmidt)}\end{bmatrix} \qquad (5\text{-}2)$$

Cesium nitrate deviates from this correlation. Linearity is better when the Pauling's value is adopted for the ionic radius of sodium than when the Goldschmidt's value is adopted.

Magnesium, strontium and barium give a linear correlation when Fajans' values are adopted for α_+ and Pauling's values for r_+, and in this case.

$$a=0.175 \text{ and } b=0.88 \text{ for } MO\cdot N_2O_5. \quad (5\text{-}3)$$

Goldschmidt's values for α_+ and r_+ are not so satisfying in this case.

(6) **Phosphates.**—The linearity does not sufficiently stand when the values of Fajans are adopted for α_+ and those of Pauling for r_+. The results are also not so satisfying when Goldschmidt's data are utilised. It may be due to the assumption that α_- is set as $(r_-)^3$ and this value is not close to the fact.

(7) **Sulphates.**—Sulphates of monovalent metals give very satisfying results. Especially four compounds of sodium, potassium, rubidium and cesium show a completely linear correlation when Goldschmidt's values are adopted for α_+ and r_+. Cesium salt deviates from the linear correlation slightly when Pauling's value is adopted for the ionic radius. When the polarizability of S^{6+} is set as $(r_-)^3$, following values are obtained for $M_2O\cdot SO_3$,

$$a=0.250,\ b=0.480,\ \begin{bmatrix}r_+\text{(Pauling)}\\ \alpha_+\text{(Fajans)}\end{bmatrix}, \qquad (7\text{-}1)$$

$$a=0.255,\ b=0.495,\ \begin{bmatrix}r_+\text{Golds.)}\\ \alpha_+\text{(Fajans)}\end{bmatrix}, \qquad (7\text{-}2)$$

$$a=0.263,\ b=0.666,\ \begin{bmatrix}r_+\text{(Golds.)}\\ \alpha_+\text{(Golds.)}\end{bmatrix}. \qquad (7\text{-}3)$$

The bivalent metal compounds show satisfying regularity when Goldschmidt's values are adopted for α_+ and r_+, and

$$a=0.36,\ b=0.62 \text{ for } MO\cdot SO_3.$$

The results are not satisfying when the values of α_+ and r_+ given by Fajans and by Pauling are adopted.

Summary

(1) An expression for the melting points of the inorganic compounds of type MXO_n has been obtained as,

$$T\cdot(\alpha_+-\alpha_-)^{1/6}=a-b\cdot(r_-/r_+),$$

and the values of a and b have been given, where T is the melting point in absolute temperature, α_+ and r_+ are the polarizability and the ionic radius of the cation M^+, respectively, and α_-, r_- are the polarizability and the ionic radius of the ion $X^{(2n-1)+}$ respectively.

(2) Considering the results of the practical calculation, the values given by Goldschmidt are to be adopted for the formula as the polarizabilities and ionic radii, and those given by Fajans and by Pauling are less satisfying in some cases. It is probably due to the fact that the Goldschmidt's values correspond to the ions in the solid and those of Fajans and of Pauling to the free ions.

(3) This formula will be useful for the examination of the known values of the melting points and for the estimation of the unknown data.

(4) It is very important that 'melting point' is presented as a function of the variables characteristic for atoms, such as ionic radius and polarizability of atoms.

The author wishes to express his sincere thanks to Prof. Kenjiro Kimura of Tokyo University of Tokyo for his guidance throughout L. this study. Many thanks are also due to Prof. Pauling of California Institute of Technology and Prof. G. T. Seaborg of the University of California, who have taken an interest in the advanced copy of this article and given valuable suggestions.

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