Melting temperatures of some simple inorganic compounds: an approach by Lindemann's theory

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By introduction of ionicity into Lindemann's one-phase theory on melting temperature, a semi-empirical formula for melting temperature of simple compounds,

$$T_m \doteqdot f_i C_i / r_{AB} + f_c C_c / r_{AB}^{2.5}$$

has been given, where T_m, f_i, f_c and r_{AB} stand for melting temperature, ionicity, co-valency and bonding distance, respectively. C_i and C_c are numerical factors which are common to a group of compounds of similar character (crystal structure, valency, etc). Application of Sanderson's ionicity scale to the formula shows good agreement with the observed melting temperatures of alkali halides. A good agreement is also obtained for single oxides. From application of the formula to alkali halides, it is suggested that an anion plays an important role in melting. Similarity of C_i and C_c in alkali halides of NaCl structure and MO-type oxides of the same structure suggests that melting occurs at almost the same critical position in Lindemann's model for melting in both types of compound.

1. Introduction

The melting temperature of an inorganic substance is an important characteristic, which serves as an index for its refractoriness. Thus, its prediction is important in the synthesis of a new ceramic material. The object of this paper is to present a phenomenological theory for prediction of melting temperatures of some simple compounds.

At a melting temperature, a liquid phase has the same free energy as the corresponding solid phase. Thus, a formula for the prediction should involve some parameters characteristic of both the liquid and solid phases. Thus, the two-phase theory should be taken into consideration. Two-phase theory, however, is too complex and still involves some ambiguity because of uncertainty in determination of the structure of a liquid phase. However, the one-phase theory is generally unsatisfactory for accurate prediction. It is, however, simple and yet relatively accurate [1, 2] for some kinds of compounds. In particular, it will be useful for material groups in which the structure

and the material parameters of the liquid phase are similar to those of the corresponding solid one. Thus, the theory is applicable as a good approximation for some groups consisting of similar materials.

In the one-phase theory introduced by Lindemann [3], a melting temperature is given by equating the kinetic energy of an atom or ion with the critical potential energy in the crystal. In this theory, the potential energy is assumed to be of a harmonic type. In materials, however, it is evident that covalent as well as ionic interactions occur between ions or atoms. Thus, introduction of ionicity and covalency in the one-phase theory would increase the accuracy of the prediction.

2. Theory

In a crystal, the lth atom or ion has the potential energy, E_l, which can be expressed as

$$E_l = f_i E_{i,l} + f_c E_{c,l} - E_{d,l} \qquad (1)$$

where f_i and f_c are the ionicity and the covalency

of a bond, respectively. $E_{i,l}, E_{c,l}, E_{d,l}$ are the ionic, covalent and repulsive potential energies, respectively. $E_{i,l}, E_{c,l}$, and $E_{d,l}$ can be further expressed as follows:

$$E_{i,l} = \sum_{k \neq l} \frac{Z_l Z_k e^2}{|r_{l,k}|} \qquad (2)$$

$$E_{c,l} = \sum_{k \neq l} \frac{nC}{|r_{l,k}|^p} \qquad (3)$$

$$E_{d,l} = \sum_{k \neq l} \frac{D}{|r_{l,k}|^q} \qquad (4)$$

where Z_l and Z_k are the valences of the lth and kth atoms, respectively, $r_{l,k}$, n, C and D are the distances between lth and kth atoms or ions, the number of covalent bonds and the constants, respectively, and p and q are the exponents for the covalent and repulsive potentials, respectively.

The potential energy of covalent bonds is approximated by use of a simple exponent in Equation 3, instead of the Morse potential which is more exact but a little complicated.

As is well known, the potential energy due to the repulsive force introduced by Born, (Equation 4), is much smaller, in comparison with the ionic term [4], (Equation 1), in ionic crystals, such as KCl, NaCl, etc. The covalent potential energy is expected to be of the same order as that of the ionic one in many compounds. Thus, the repulsive term, (Equation 3), may be neglected in a rough estimation, and the total energy of a solid can be expressed as follows:

$$E_p \doteq \frac{1}{2} \sum_l E_l = \frac{1}{2} f_i \sum_{k \neq l} \frac{Z_l Z_k e^2}{|r_{l,k}|}$$
$$+ \frac{1}{2} f_c \sum_{k \neq l} \frac{nC}{|r_{l,k}|^p} \qquad (5)$$

For a given crystal structure, $|r_{l,k}|$ is represented by
$$|r_{l,k}| \doteq r_{AB} \alpha |x_{l,k}|$$

where r_{AB} is the sum of the negative and positive ionic radii or covalent radii, α is a constant, and $|x_{l,k}|$ is the separation between the lth and kth atoms or ions expressed by the position parameter in the unit cell. Then Equation 5 can be rewritten as

$$E_p = f_i \frac{1}{r_{AB}} C'_i + f_c \frac{1}{r_{AB}^p} C'_c, \qquad (6)$$
where
$$C'_i = \frac{1}{2\alpha} \sum_{l \neq k} \frac{Z_l Z_k e^2}{|x_{l,k}|} \qquad (7)$$

$$C'_c = \frac{1}{2\alpha^p} \sum_{l \neq k} \frac{nC}{|x_{l,k}|^p} \qquad (8)$$

The potential barrier for melting will be given as the difference between the potential energy at zero degrees on the Kelvin scale and that at the melting temperature, at which the atom or ion reaches the critical position. Thus,

$$\Delta E = f_i \frac{1}{r_{AB}} C''_i + f_c \frac{1}{r_{AB}^p} C''_c, \qquad (9)$$
where

$$C''_i = \frac{1}{2\alpha} \sum_{l \neq k} \left(\frac{Z_l Z_k e^2}{|x_{l,k}|_c} - \frac{Z_l Z_k e^2}{|x_{l,k}|_0} \right) \qquad (10)$$

$$C''_c = \frac{1}{2\alpha^p} \sum_{l \neq k} \left(\frac{nC}{|x_{l,k}|_c^p} - \frac{nC}{|x_{l,k}|_0^p} \right) \qquad (11)$$

where suffixes 0 and c relate to the separations at 0 K and at a melting temperature, respectively.

At a melting temperature, the thermal energy is equal to the potential barrier for melting ΔE (Equation 9), then the following equations are given

$$T_m \doteq \Delta E / N \kappa \qquad (12)$$

$$\doteq f_i \frac{1}{r_{AB}} C_i + f_c \frac{1}{r_{AB}^p} C_c \qquad (13)$$

$$C_i = \frac{1}{2N\kappa\alpha} \sum_{l \neq k} \left(\frac{Z_l Z_k e^2}{|x_{l,k}|_c} - \frac{Z_l Z_k e^2}{|x_{l,k}|_0} \right) \qquad (14)$$

$$C_c = \frac{1}{2N\kappa\alpha^p} \sum_{l \neq k} \left(\frac{nC}{|x_{l,k}|_c^p} - \frac{nC}{|x_{l,k}|_0^p} \right) \qquad (15)$$

where N and κ are the number of atoms or ions, and Boltzmann's constant, respectively. The C_i and C_c should be common to the crystals with the same crystal structure type, valence and the critical positions of the atoms or ions in melting. The values of C_i and C_c, however, cannot be given by calculation of each term because of the lack of knowledge of the position parameters of the atoms or ions at a melting temperature. However, they can be determined for a series of similar com-

TABLE I Electronegativities of several elements at high temperatures

Element	Temperature (K)		
	298	1000	2000
Al	1.4		1.7
Na	0.7	0.7	
Ba	1.6	1.6	

pounds by taking such values as to make the calculated value (Equation 12 or 13) fit best to the actual melting temperatures of the compounds. For the calculation, the values of f_i and f_c determined by L. Pauling [5] and R. T. Sanderson [6] were used.

3. Calculated melting temperatures and their comparison with those actually measured

3.1. f_i at high temperatures
The ionicities of various compounds are given by many authors, typically by L. Pauling [5] and R. T. Sanderson [6]. There is, however, a significant difference between those given by Pauling and those by Sanderson.

In this paper, both series of ionicity values were used for calculation of Equation 13.

In Pauling's system, the ionicity is related to the electronegativity of an element through the following equation

$$\Delta E_b = E_b(A-B) - \tfrac{1}{2}[E_b(A-A) + E_b(B-B)]$$

$$= 23(X_A - X_B)^2$$

where $E_b(A-A)$, $E_b(B-B)$ and $E_b(A-B)$ are the binding energies of the compounds AA, BB and AB, X_A and X_B are the Pauling electronegativities of elements A and B, and ΔE_b is the heat of formation of the compound AB.

The temperature dependence of ionicity, therefore, is given by the temperature dependence of ΔE_b or that of the heat capacity of the elements. Table I shows a few examples of the calculated electronegativities at high temperatures by use of Barin and Knacke's data [7].

As shown in Table I, the electronegativities are fairly constant over the range 298 to 2000 K. Thus, ionicity can be well approximated to be constant.

Because the electronegativity in Sanderson's system, (S), is closely related to that in Pauling's

system, (X), by $\sqrt{X} = 0.21S + 0.77$, the ionicity in Sanderson's system may also be approximated to be constant.

3.2. Determination of the exponent of potential energy of covalent bonding
As mentioned above, the exponent p and the constant C_c in Equation 13 should be determined for a group of completely covalent crystals of a common crystal structure and valence. As such, diamond (C), Si and Ge were chosen. Diamond, however, sublimes under ambient pressure. Therefore, the melting temperature, under a pressure of 10 katm was taken for the calculation on the assumption that the pressure dependence of the temperature is small.

The results obtained by the least squares method are shown in Table II. The interatomic distances were calculated from covalent radii of C, Si, and Ge. As shown in the table, p is found to be 2.30. Though the p value of 2.30 may be near the true value, it would not be exactly the true value because the melting temperature of diamond is an assumed value. Therefore, the true value is needed to be confirmed by other theories or experiments.

J. C. Phillips [11] and Van Vechten [12, 13] introduced the average energy gap E_g in dealing with bonding in $A^n B^{8-n}$ compounds. By separating E_g into the covalent part, E_h, and the ionic part, C, Phillips [11] succeeded in grouping 80 $A^n B^{8-n}$ compounds into four-fold structure type and six-fold structure type compounds with an accuracy of 1%. The covalent part, E_h, depends on the bond length, d, as shown below.

$$E_h(AB) = E_h(Si)(d_{Si}/d_{AB})^{2.5} \quad (16)$$

The exponent, 2.5, is defined in the formula which has the dimension of energy and is a function of the distance. Phillips' formula, Equation 16, suggests that the total energy of the covalent part can be expressed in terms of $r^{-2.5}$. According to

TABLE II p and C_c determined from the diamond series

Material	T_m (K)[*]	$r \pm$ (Å)[‡]	p	C_c(K Å$^{2.5}$)	T_m (K)[§]	ΔT_m (°C)[‖]
Diamond	3900[†]	1.54			4006	− 106
Si	1693	2.34	2.30	10817	1531	162
Ge	1232	2.44			1390	− 158

[*] Observed melting temperature taken from [8].
[†] Melting temperature at 10 katm taken from [9].
[‡] Inter-atomic or inter-ionic distances taken from [10].
[§] Calculated melting temperature.
[‖] ΔT_m (°C) = T_m (observed) − T_m (calculated).

TABLE III T_m for $p = 2.5$ and $C_c = 11\,749$ (KÅ$^{2.5}$)

Material	T_m (observed) (K)*	T_m (calculated) (K)	ΔT_m (°C)[‡]	C_c (KÅ$^{2.5}$)
Diamond	3900[†]	3932	−32	11749
Si	1693	1403	290	
Ge	1232	1301	−69	

* Taken from [8].
[†] Melting temperature at 10 katm taken from [9].
[‡] ΔT_m (°C) = T_m (observed) − T_m (calculated).

TABLE IV Observed and calculated melting temperatures of the alkali halides by use of Pauling's f_i for molecules

Material*	f_i[†]	T_m (K) Observed[‡]	T_m (K) Calculated	Deviation [ΔT_m (°C)][§]	C_i (KÅ)	C_c (KÅ$^{2.5}$)
NaF	0.91	1265	1276	−11	3074.7	15805.6
KF	0.92	1133	1099	34		
RbF	0.92	1033	1038	−5		
CsF	0.93	957	976	−19		
NaCl	0.67	1073	1091	−18	4562.5	265.4
KCl	0.70	1049	1018	31		
RbCl	0.70	990	972	18		
CsCl	0.73	918	949	−31		
NaBr	0.59	1028	1029	−1	5273.0	−576.5
KBr	0.63	1003	999	4		
RbBr	0.63	955	959	−4		
NaI	0.47	924	928	−4	7644.5	−6530.8
KI	0.51	996	968	28		
RbI	0.51	915	940	−25		

* Inter-atomic distances are taken from [10].
[†] Taken from [5].
[‡] Taken from [8].
[§] ΔT_m (°C) = T_m (observed) − T_m (calculated).

the virial theorem, the average kinetic energy is proportional to the average potential energy, on the assumption that the potential energy is expressed by r^n, where r stands for the interatomic distance. Thus, the potential energy of the covalent part may also be expressed in terms of $r^{-2.5}$. The value of 2.5 is very near to 2.30 determined from the melting temperatures for the diamond series. Thus, it seems more desirable to take 2.5 instead of 2.30 as p.

The constant, C_c in Equation 13, calculated by using $p = 2.5$ for the diamond series through the best fit, was $11\,749$ KÅ$^{2.5}$. These values of p and C_c give the calculated melting temperature for each member of the series as shown in Table III. The deviation of the calculated value from the observed one does not differ significantly from that obtained by using $p = 2.30$.

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3.3. The melting temperature (T_m) of some alkali halides

Alkali halides are very similar in character to one another, except for Li halides. For such a group of compounds, common C_i and C_c will be applicable. On this assumption, the melting temperature of the alkali halides was calculated by use of Pauling's system of ionicity as well as Sanderson's. Two systems of the Pauling ionicities, one for molecules [5] and the other for crystals [14], were tested.

The values of C_i and C_c shown in Tables IV to VI were chosen so as to minimize the sum of the squares of the deviation for respective groups of fluorides, chlorides, bromides and iodides.

Table IV shows the results of the calculation using Pauling's system for molecules. In this table, the values of C_c for the bromides and iodides are

TABLE V Observed and calculated melting temperatures of the alkali halides by use of Pauling's f_i for crystals

Material[*]	f_i [†]	T_m (K)		Deviation [ΔT_m (°C)] [§]	C_i (K Å)	C_c (K Å$^{2 \cdot 5}$)
		Observed [‡]	Calculated			
NaF	0.98	1265	1295	− 30	2786	46021
KF	0.99	1133	1072	61		
RbF	0.99	1033	1012	21		
CsF	0.99	957	946	11		
NaCl	0.95	1073	1105	− 32	3700	− 37703
KCl	0.95	1049	1008	40		
RbCl	0.95	990	970	20		
CsCl	0.96	918	944	− 26		
NaBr	0.93	1028	1029	− 1	3982	− 46764
KBr	0.94	1003	995	8		
RbBr	0.94	955	962	− 7		
NaI	0.92	924	935	− 11	6178	− 193168
KI	0.92	996	950	46		
RbI	0.92	915	950	− 35		

[*] Inter-atomic distances are taken from [10].
[†] Taken from [14].
[‡] Taken from [8].
[§] ΔT_m (°C) = T_m (observed) − T_m (calculated).

TABLE VI Observed and calculated melting temperatures of the alkali halides by use of Sanderson's f_i

Material[*]	f_i [†]	T_m (K)		Deviation [ΔT_m (°C)] [§]	C_i (K Å)	C_c (K Å$^{2 \cdot 5}$)
		Observed [‡]	Calculated			
NaF	0.75	1265	1274	− 9	3083.8	8838.9
KF	0.85	1133	1096	37		
RbF	0.88	1033	1042	− 9		
CsF	0.90	957	978	− 21		
NaCl	0.67	1073	1084	− 11	3801.5	7318.8
KCl	0.76	1049	1017	32		
RbCl	0.79	990	988	2		
CsCl	0.82	918	942	− 24		
NaBr	0.62	1028	1031	− 3	4069.6	7442.3
KBr	0.71	1003	988	15		
RbBr	0.74	955	967	− 12		
NaI	0.54	924	937	− 13	4833.8	5245.7
KI	0.63	996	946	50		
RbI	0.67	915	952	− 37		

[*] Inter-atomic distances taken from [10].
[†] Taken from [6].
[‡] Taken from [8].
[§] ΔT_m (°C) = T_m (observed) − T_m (calculated).

negative, which is unacceptable for C_c as well as C_i, because they represent the barrier height of the potential energy. Thus, Pauling's system for molecules is inadequate for calculation of the melting temperatures.

The results using Pauling's system for crystals are listed in Table V. The values of C_c for chlorides, bromides and iodides are also negative. Thus, the system for crystals is inadequate for the calculation also.

In Table VI, the results of the calculation using Sanderson's ionicity are listed. The values of C_i and C_c are fairly constant, and the value of C_i systematically increases from the fluoride to the iodide, and that of C_c systematically decreases.

The f_i values of Sanderson's system for the alkali halides seem not to differ so much from those of Pauling's system, especially for the chlorides. There is, however, a great deal of difference between C_c values calculated from the two sys-

TABLE VII Observed and calculated melting temperatures of the alkali halides grouped by the cation, using Sanderson's f_i

Material*	f_i[†]	T_m (K)		Deviation [ΔT_m (°C)] [§]	C_i (K Å)	C_c (K Å$^{2.5}$)
		Observed[‡]	Calculated			
NaF	0.75	1265	1301	−36	905	32670
NaCl	0.67	1073	1030	−43		
NaBr	0.62	1028	998	30		
NaI	0.54	924	953	−29		
KF	0.85	1133	1141	−8	1902	41543
KCl	0.76	1049	1025	24		
KBr	0.71	1003	1018	−15		
KI	0.63	996	996	0		
RbF	0.88	1033	1047	−14	2144	42099
RbCl	0.79	990	960	30		
RbBr	0.74	955	955	0		
RbI	0.67	915	930	−15		
CsF	0.90	957	957	0	1884	61867
CsCl	0.82	918	918	0		

* Inter-atomic distances taken from [10].
† Taken from [6].
‡ Taken from [8].
§ ΔT_m (°C) = T_m (observed) − T_m (calculated).

TABLE VIII Observed and calculated melting temperatures of the NaCl type MO compounds

Material*	f_i[†]	T_m (K)		Deviation [ΔT_m (°C)] [§]	C_i (K Å)	C_c (K Å$^{2.5}$)
		Observed[‡]	Calculated			
MgO	0.21	3140	3194	−54	12421	15952
CaO	0.29	2850	2778	72	(3104)	
SrO	0.31	2690	2522	168		
BaO	0.34	2170	2362	−192		

* Inter-atomic distances taken from [10].
† Taken from [6].
‡ Taken from [8].
§ ΔT_m (°C) = T_m (observed) − T_m (calculated).

tems. This difference is attributable to the fact that the ionicity in Sanderson's system reflects the individuality of the compounds in each group more explicitly than that in Pauling's system. (For example, f_i in iodides is a common value in Pauling's system, but is varied in Sanderson's).

In the calculation of the C_i and C_c mentioned above, the alkali halides are grouped with respect to the anion groups, such as fluorides, chlorides, etc. There is, however, another way of grouping with respect to the cation groups. The results from this grouping of the alkali halides are listed in Table VII. The value of C_c of each group is much larger than the corresponding C_i, especially in Na halides. The large value of C_c in Na halides yields a larger value of covalent potential than ionic, indicating that the contribution of covalent interaction exceeds the ionic one, which is contra-

dictory to the nature of the compounds. These results seem to suggest that the nature of the anions is important in the melting.

3.4. Melting temperature of the oxides
3.4.1. MO−type oxides
MO-type compounds would be further grouped into: MgO, CaO, SrO, BaO (NaCl type); MnO, FeO, CoO, NiO (NaCl type); and BeO, ZnO (wurtzite type). The last group contains only two compounds, and therefore application of the least squares method to this group is meaningless.

The results of the calculation and the actual melting temperatures are listed in Tables VIII and IX. In the column of C_i in the tables, the values in parenthesis are the ratio of C_i to a product of the valences for a cation, (Z_A) and an anion, (Z_B). This value corresponds to the barrier height due to

TABLE IX Observed and calculated melting temperatures of the NaCl-type and the wurtzite type MO compounds

Material[*]	f_i [§]	T_m (K)		Deviation [ΔT_m (° C)] [b]	C_i (K Å)	C_c (K Å$^{2 \cdot 5}$)
		Observed[‖]	Calculated			
MnO[†]	0.21	1923	1905	18	12024	7135
FeO[†]	0.20	~ 1643	1961	− 317	(3006)	
CoO[†]	0.20	~ 2073 (decomp.)	1991	82		
NiO[†]	0.20	2271	2038	233		
BeO[‡]	0.18	2843	3018	− 175		
ZnO[‡]	0.14	2223[a]	1981	242		

[*] Inter-atomic distances are taken from [10].
[†] NaCl type structure.
[‡] Wurtzite type structure.
[§] Taken from [6].
[‖] Taken from [8].
[a] Taken from [15].
[b] ΔT_m (° C) = T_m (observed) − T_m (calculated).

TABLE X Observed and calculated temperatures of the non-rare earth M_2O_3-type oxides

Material[*]	f_i [§]	T_m (K)		Deviation [ΔT_m (° C)]	C_i (K Å)	C_c (K Å$^{2 \cdot 5}$)
		Observed[‖]	Calculated			
α-Al$_2$O$_3$ [†]	0.16	2288	2197	91	9189.1	8564.3
α-Ga$_2$O$_3$ [†]	0.10	2013	1923	90	(2384)	
V$_2$O$_3$ [†]	0.21	2243	2161	80		
Cr$_2$O$_3$ [†]	0.19	2263	2181	82		
α-Fe$_2$O$_3$ [†]	0.17	1823 (decomp.)	2098	− 275		
Bi$_2$O$_3$	0.10	1133	1247	− 124		

[*] Inter-atomic distances taken from [10], [16].
[†] Corundum type.
[‡] Fluorite type.
[§] Taken from [6].
[‖] Taken from [8].

ionic potential in a compound of unit valence at the critical position for melting.

As shown in Table VIII, the calculated values of the melting temperatures agree rather well with observed values, although the agreement is worse than that for the alkali halides.

Calculation of melting temperatures of BeO and ZnO was tried by applying the values of C_i and C_c determined for NaCl-type oxides. The results are listed in Table IX. The calculated value agrees unexpectedly well with the observed one. The reason for the agreement is unknown.

The ratio of C_i to the product of valences of a cation and an anion in the MgO group is nearly equal to that in the fluoride group. Then it is considered that in the MgO group, with NaCl-type structure, melting occurs at a similar critical position as in the fluoride.

The deviation of the calculated melting temperature from the observed values of the CoO group is larger than that for the MgO group. This could be attributed to the fact that CoO does not melt under ambient pressure and that this group has two kinds of compounds having different crystal structures.

3.4.2. M_2O_3-type oxides

In M_2O_3-type oxides, there are corundum type, fluorite type, La$_2$O$_3$ type (A type), Sm$_2$O$_3$ type (B type) and Sc$_2$O$_3$ type (C type) structures. The number of members in each group is too small to apply the least squares method. Thus, they are classified into a non-rare earth metal oxide group and a rare earth metal oxide group, and calculation of melting temperatures was tried for each group.

The calculated and observed melting temperatures are listed in Tables X and XI. As shown in the tables, the agreement between the calculated and observed values is excellent except for α-Fe$_2$O$_3$ and Bi$_2$O$_3$. This good agreement cannot be ex-

TABLE XI Observed and calculated melting temperatures of the rare earth M_2O_3 oxides

Material*	f_i[†]	T_m (K)		Deviation $[\Delta T_m$ (°C)] [§]	C_i (K Å)	C_c (K Å$^{2.5}$)
		Observed[‡]	Calculated			
Yb_2O_3	0.27	2684	2752	− 68	18618	4903
Er_2O_3	0.27	2673	2705	− 32	(3103)	
Ho_2O_3	0.27	2669	2690	− 21		
Y_2O_3	0.26	2708	2599	108		
Dy_2O_3	0.27	2664	2675	− 11		
Tb_2O_3	0.27	2663	2646	17		
Gd_2O_3	0.27	2668	2632	36		
Eu_2O_3	0.27	2603	2603	0		
Sm_2O_3	0.27	2593	2603	10		
Nd_2O_3	0.28	2583	2649	− 66		
La_2O_3	0.28	2573	2516	− 57		

* Inter-atomic distances taken from [16], [17] for cubic lattice.
† Taken from [6].
‡ Taken from [18].
§ ΔT_m (°C) = T_m (observed) − T_m (calculated).

pected, and the reason is unknown. α-Fe_2O_3, which has non-stoichiometric composition, does not melt under ambient pressure. Bi_2O_3 is not of the corundum-type structure, but of the fluorite type. This would cause a comparatively large deviation of the calculated from the observed melting temperature for α-Fe_2O_3 and Bi_2O_3.

Recently, two new phases were found for M_2O_3-type rare earth oxides at high temperatures. They are classified as H [19] and X [20] types. H type has a hexagonal crystal structure. Each of the M_2O_3-type rare earth oxides transforms into H type at high temperatures, and at higher temperatures some of the oxides, La_2O_3 to Gd_2O_3, transform into X type, whose crystal structure is left undetermined. These findings seem to suggest a possible occurrence of a structure common to all M_2O_3 rare earth oxides just below their melting temperatures, which may be responsible for the unexpectedly good agreement of the calculated value with the observed one on the assumption of a common structure for rare earth oxides.

4. Conclusions

The following conclusions were reached:

(1) A semi-empirical formula for melting temperatures of simple compounds is proposed.

(2) By use of Sanderson's system for ionicity in the calculation, a good agreement was obtained between calculated and observed values for many halides and oxides.

(3) From application of the formula to halides grouped with respect to a common anion or a common cation, it is suggested that an anion plays an important role in melting.

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