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Scales of Acidity and Basicity of Slag Constituents in Steelmaking

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Abstract

Acidity is defined as the tendency to accept an electron-pair from a base. Basicity is defined as the tendency to donate an electron-pair to an acid. The authors took O^- in place of electron-pair and made two scales of acidity and basicity of the constituent oxides of slag by using thermodynamic cycles discussing the validity of those scales.

The basicity scale was not sufficiently explicit in case of comparing each group of different valence types, and the result obtained by our acidity scale was not so sufficient because of the difficulties in determining the radii of negative polyatomic ions.

I Introduction

Although basicity or acidity of molten salts has an important meaning at the high temperature reaction both in ceramic industry and in steelmaking processes, the relative strength of acidity or basicity of oxide has not been determined except empirical one, i. e. $CaO \equiv 1$, $SiO_2 \equiv 1$.

As the definition of acid and base, the $H^+ - OH^-$ theory of Arrhenius¹⁾, the H^+ theory of Brönsted²⁾ and the theory of Wickert³⁾ have been adopted.

Recently H. Luder⁵⁾ enlarged the electron-pair theory of Lewis⁴⁾ and showed its excellent validity in explaining the acid-base reactions. According to his theory, base is a donor of electron-pair and acid is its acceptor, therefore the tendency to accept an electron-pair from base means basicity and donate it to acid becomes acidity. Lux⁶⁾ defined base and acid of molten salts as follows:



He also discussed the concentration of O^- represented by P_o corresponding to P_H in aqueous solution.

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- 1) S. Arrhenius, Z. physik. Chem., 1(1887),631.
- 2) J. N. Brönsted, Rec. trav. chim., 42(1923),718.
- 3) K. Wickert, Z. physik. Chem., A178(1937),361.
- 4) G. N. Lewis, Valence and the Structure of Atoms and Molecules (1923). J. Am. Chem. Soc., 38(1916), 762.
- 5) H. Luder, Chem. Rev., 27(1940),547.
- 6) H. Lux, Z. Elektrochem., 45(1939),303.

It is easy to understand that the above-mentioned $O^=$ is the carrier of electron-pair and that the Lux's theory is the same as the Luder's in its essence. The concentration of $O^=$ in molten borates was also studied by Dietzel⁷⁾ by measuring E.M.F.

However, in these experiments they measured only the concentration of $O^=$ and did not present any scale of basicity which we can use in comparing each substance quantitatively.⁸⁾ We are measuring such a scale of oxides in our experiments but here we will show the possibility and the results of our calculation of the scales of basicity and acidity of the slag constituent oxides by the theoretical methods.

II Theories of Basicity and Acidity

According to Luder's theory, the tendency of donating an electron-pair to acid can be used as a scale of basicity and the tendency of accepting an electron-pair from a base as a scale of acidity, if we shall be able to express these tendencies quantitatively. As to oxides, however, it is sufficient to know the tendencies of $O^=$ in place of electron-pair. The authors here decide that the basicity and the acidity of oxides correspond to the energy changes when the substances donate and accept $O^=$ respectively. Therefore, the value of basicity is determined by dissociation energy U in the formula



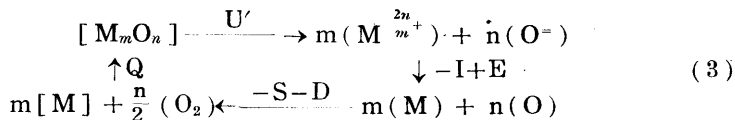
and the value of acidity is determined by the reaction energy E in the formula



The smaller the energy U is — the easier the dissociation of MO into M^{++} and $O^=$ is. — the stronger is its basicity. Similarly, in equation (2), the greater the energy E is the stronger is its acidity. The methods and the results of calculation of these energies U and E will be shown in the following sections.

III Calculation of Basicity

Considering a cycle



the energy U' is to be calculated by the relation

$$U' = Q + S + I + D - E, \quad (4)$$

where the oxide is represented by $M_m O_n$, parentheses and square brackets show the gaseous and solid states respectively. U' denotes the energy which dissociates $[M_m O_n]$ into

7) A. Dietzel, W. Stegmaier, *Glastechn. Ber.*, 18(1940),353.

8) Kuan-Han-Sun reported about the semi-quantitative scale of basicity but the authors have not got his paper yet. c.f. *Chem. Abst.* 42.

gaseous ions at 298°K; Q, the heat of formation of $[M_mO_n]$; S, the heat of sublimation of metal; D, the dissociation energy of oxygen molecule to atoms; I, the ionization potential of (M); and E, the electron affinity of oxygen. Now, assuming that specific heat of (M^{2n+}) equals to that of (M), the change of I by temperature is only due to the change of specific heat of electron gas. Similarly, assuming that the specific heat of (O^-) is equal to that of (O), the change of E by temperature is only due to the change of specific heat of electron gas. As I and E enter in the relation (4), the changes of E and I by the specific heat of electron gas cancel out each other. Therefore, the data of I and E at 0°K are also valid in the formula (4) even at 298°K⁹⁾. U in the formula (1) and U' have the relation

$$U = U' - (m+n)RT.$$

Here $(m+n)RT$ is the energy of work corresponding to the volume change of $(m+n)$ moles. Data in calculating U are shown on Table 1. The value of U does not change so much if the temperature becomes high and M_mO_n changes into the molten state.

Table 1. Thermal Data of Constituents (k cal/mol) at 25°C

	Q ¹⁰⁾	S ¹⁰⁾	I ¹⁰⁾ (0°K)	D ¹⁰⁾	-E (0°K)	U'	U
K ₂ O	86.8	21.5 × 2	199.2	58.6	168	556	554
Na ₂ O	100.7	26.0 × 2	235.6	"	"	615	613
CaO	152.1	42.5	412.9	"	"	834	833
MnO	96.7	69.7	532.3	"	"	925	924
MgO	145.8	35.9	520.3	"	"	929	928
FeO	64.5	96.7	553.1	"	"	941	940
H ₂ O	68.3	103.6	623.8	"	"	1022	1021
Fe ₂ O ₃	195.2	96.7 × 2	2582	58.6 × 3	168 × 3	3650	3647
Al ₂ O ₃	393.3	67.5 × 2	2441	"	"	3650	3647
Cr ₂ O ₃	288.9	89.4 × 2	2506	"	"	3653	3650
SiO ₂	200.5	85.0	2365	58.6 × 2	168 × 2	3109	3107
B ₂ O ₃	340.6	115 × 2 ¹¹⁾	3273	58.6 × 3	168 × 3	4524	4521
P ₂ O ₅	369.4	31.6 × 2	3149	58.6 × 5	168 × 5	9714	9710

To obtain the general scale independent of the valence types, i. e. M_2O , MO, M_2O_3 , etc., the following consideration is necessary. The tendency of donating O⁻ depends on the strength of a bond when we consider that positive and negative ions are mutually surrounded in accordance with their coordination numbers. The larger the coordination number P¹²⁾ in Table 2 is, the more bonds exist.

9) J. Shermann, Chem. Rev., 11 (1932), 93.

10) Landoit, Börnstein, Phys. chem. Tabellen

11) Harashima, Kotaino-Gyōshu-Kikō (Mechanisms of Binding of Solid), published in Japan, by Asakura pub. Co. (1948) P.3

12) Shibata, Muki-Kagaku-Genron (Fundamentals of Inorg. Chem.), published in Japan by Yōken-dō pub. Co. (1914) PP. 97, 396, 398

To calculate the strength of a bond, U is divided by m and the coordination number P which is the number of oxygen atoms surrounding one positive atom. If we consider more precisely, P must take a certain value in molten state but it is almost unknown to us. So we took the value in crystal state.

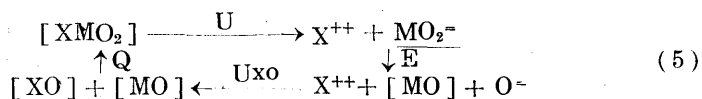
Table 2. Basicities of Oxides (U/Pm)

	U	$\frac{U}{m}$	P	$\frac{U}{Pm}$
K_2O	554	227	9	31
Na_2O	613	307	6	51
CaO	833	833	6	139
MnO	924	924	6	154
MgO	928	928	6	155
FeO	940	940	6	157
H_2O	1021	511	2	256
Fe_2O_3	3647	1824	4	456
Al_2O_3	3647	1824	4	456
Cr_2O_3	3650	1825	4	456
B_2O_3	4521	2261	3	754
SiO_2	3107	3107	4	777
P_2O_5	9710	4855	4	1214

This value $\frac{U}{Pm}$ is to be used as a scale of basicity. However, for the so-called acidic oxides which tend to take O^- into themselves, i. e. B_2O_3 , SiO_2 or P_2O_5 , this value indicates the weakness of basicity when they behave as base. Therefore, in the treatment of these oxides, it seems more natural to measure their tendencies of accepting O^- from the base. The following section shows this method of calculation.

IV Calculation of Acidity

The energy E in formula (2) corresponds to the acidity of MO . To evaluate E the following cycle was considered for the double salt XMO_2 was adopted.



Q : the reaction energy for $[MO] + [XO] \rightarrow [XMO_2]$

U : the dissociation energy for $[XMO_2] \rightarrow X^{++} + MO_2^-$

U_{xo} : the dissociation energy for $[XO] \rightarrow X^{++} + O^-$

E : the energy for $[MO] + O^- \rightarrow MO_2^-$

From the cycle (5), we have the relation

$$E = Q + U_{xo} - U.$$

To obtain the energy E , we must know the values of Q , U_{xo} , and U , but U is difficult to be determined directly.

In calculating the value of U indirectly, there are two methods, (A) and (B). (A) One is the method of calculating U as lattice energy of $[XMO_2]$. Assuming that crystal $[XMO_2]$ consisted of two kinds of ions, X^{++} and spherical MO_2^- , the following relation exists.

$$U = -\frac{Mz^2e^2}{r}\left(1 - \frac{1}{n}\right) \quad (6)$$

M ; the Madelung constant

n ; the repulsion exponent

z ; the number of electron charge of ion

e ; the charge of an electron

r ; the lattice constant

(B) The other is the method of calculating from the data of the heat of solution.

The energy U and the heat of solution have the relation,

$$U = H_{X^{++}} + H_{MO_2^-} - H_{XMO_2} \quad (7)$$

Here $H_{X^{++}}$, $H_{MO_2^-}$ and H_{XMO_2} respectively denote the heat of solution of gaseous X^{++} , of gaseous MO_2^- and of crystalline XMO_2 . Among the above three heats of solution only the value of $H_{MO_2^-}$ has not yet been reported. For the heat of solution of monatomic ion, however, Bernal and Fowler¹³⁾ presented the formulae (8) and (9), whose results are almost coincide with the observed values. The heat of solution of monatomic gaseous ion, H , is given by

$$H = \frac{\eta-1}{2\eta} \frac{z^2e^3}{Rz} + nP(z)P(r) - U_w \quad (8)$$

η : the dielectric constant of H_2O

z : the number of ionic charge

e : the charge of an electron

Rz : the critical radius of ion

n : the coordination number of ion

$P(r)$: the potential energy between an ion and a water molecule

$P(z)$: the correction term for $P(r)$

U_w : the correlation energy between water molecules.

The formula (8) is reduced to

$$H = \frac{163}{Rz} z^2 + nP(z)P(r) - 31 \text{ kcal.} \quad (9)$$

There is a possibility to calculate the heat of solution even for complex ion by the above formula. The authors tried to examine the validity of the formula (9) for the complex ion CO_3^- in calcite by comparing the value U obtained by the method (B) with the value obtained by the method (A).

13) J. D. Bernal, R. H. Fowler, J. Chem. Phys., 1 (1933), 515

a) U for CaCO_3 obtained by the method (A)

Madelung constant of calcite was calculated by Evjen's method¹⁴⁾ and was determined as 1.77. Suppose n is 9,¹⁵⁾ U becomes by the formula (6) 646 kcal.

b) U for CaCO_3 obtained by the method (B)

When the constants and the heats of solution in formula (9) take the values on Table 3. U becomes 609 kcal.

Table 3. Calculation of U_{CaCO_3}

(1) Values of constants in formula (.A) for CO_3^{2-}

r(Å)	z	n	P(z)	Rz(Å)	P(r)(kcal)	Hco ₃ ⁼ (kcal)
2.09	2	6	0.92	3.6	18.0	247

(2) Heats of solution for U_{CaCO_3} kcal / mole

Hca ⁺⁺	Hco ₃ ⁼	HcaCO ₃	UcaCO ₃
410	247	47.8	609

Since these two values of U almost coincide, the formula (9) can be regarded applicable to polyatomic ions. This formula will be used in the following calculation for acidity. The radius of CO_3^{2-} on Table 3 is adopted by the following reason. The radius of CO_3^{2-} is determined as the value subtracted the radius of cation from the carbon-metal distance. Table 4 shows the values for three carbonates.

Table 4. Radius of CO_3^{2-} in Å

Carbonates of calcite type	C-Metal ¹⁶⁾ distance	Radius of cation ¹⁷⁾ CO_3^{2-}	
CaCO_3	3.21	1.06	2.15
ZnCO_3	2.93	0.83	2.10
MnCO_3	3.00	0.91	2.09

The result of Table 4 indicates that the radius of CO_3^{2-} becomes larger by the strong contra-polarisation caused by cation. The true, not contra-polarized, radius of CO_3^{2-} will be smaller than the radii listed on Table 3, at least smaller than 2.09 obtained from MnCO_3 . We obtained the U as 609 kcal by taking $r=2.09\text{Å}$, but if we take the smaller value than 2.09Å , U becomes larger and approaches 646 kcal which has been calculated by the method (A).

14) H. M. Evjen, Phys. Rev., 39 (1932), 675.

15) Shermann, op. cit. A change of n by unity affects E by only 1 or 2 per cent from the equation (6).

16) L. W. L. Bragg, Atomic Structure of Minerals (Cornell Univ. Press 1937) P.116

17) Goldschmidt's value

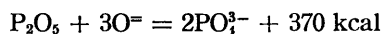
Acidities of B_2O_3 and P_2O_5 cannot be obtained by the application of the formula (6) to the double salts, e.g. $Na_6P_2O_8$, $Ca_3P_2O_8$, $Na_6B_2O_6$ and $Ca_3B_2O_6$, because the delung constants of these double salts have not been determined. But those acidities can be calculated from the formula (8) or (9). Radii of BO_3^{3-} and PO_4^{3-} were listed on Table 5 calculated by the same method as Table 4.

Table 5. Radii of PO_4^{3-} and BO_3^{3-} in Å

Substance	Structure type ¹⁸⁾	P or B-Metal distance	Radius of	
			cation ²⁰⁾	PO_4^{3-} , BO_3^{3-}
YPO ₄	tetragonal	3.02	0.95	2.07
Ag ₃ PO ₄	cubic	3.35	1.26	2.09
InBO ₃	rhombohedral	3.03 ¹⁹⁾	0.92	2.11
YBO ₃	"	3.25 ¹⁹⁾	1.06	2.19
ScBO ₃	"	3.02 ¹⁹⁾	0.83	2.19

Table 6 shows the E values of the above-mentioned double salts. Here, the radii of anion involved in double salts were calculated from the yttrium compounds.

From the results of Table 6



Then it is clear that the acidity of B_2O_3 is stronger than that of P_2O_5 .

Further research in calculating each value of E by the use of ionic radii in compounds which have the same crystal type and the same positive element was possible for us except the results of Table 6 because of the lack of data concerning those compounds.

V Discussion

In defining the scale of basicity as U/Pm there still remain uncertainties. However, the results in Table 2 will be summarized as follows:—

- 1) K_2O and Na_2O are the strongest bases and K_2O is stronger than Na_2O .
- 2) CaO is the next strong base and considerably stronger than MnO , MgO and FeO .
- 3) MnO and MgO are almost the same degree and may be stronger than FeO .
- 4) H_2O is stronger acids than the above compounds.
- 5) Al_2O_3 , Fe_2O_3 and Cr_2O_3 are almost the same.
- 6) SiO_2 , B_2O_3 , P_2O_5 are considerably stronger acid than the above oxides.

18) R. W. G. Wyckoff, The Structure of Crystals I, II (New York, 1931, 1935)

19) This value, the nearest distance for rhombohedral, can be converted from the distance a_0 and the angle α of the rhombohedral unit cell by

$$\sqrt{\frac{11-10\cos\alpha}{4}} a_0.$$

20) Goldschmidt's value

Table 6. Intensity of Acidity (kcal/mol)

Substance XMO ₂ (XO-MO)	Heat of formation Q ^{e)}	Heat of solution of			Na ⁺ or Ca ⁺⁺ HX ^{++c)}	Radius of PO ₄ ³⁻ or BO ₃ ³⁻ in Å ^{d)}	Heat of solution of		U U _{N₂O} or U ₂ O	E
		Na ₂ O or CaO HXO ^{a)}	P ₂ O ₅ or B ₂ O ₃ HMO ^{a)}	the substance HXMO ₂ ^{b)}			PO ₄ ³⁻ or BO ₃ ³⁻ HMO ₂ ^{e)}			
Na ₆ P ₂ O ₈ (3Na ₂ O P ₂ O ₅)	233.8	56.7 × 3	35.55	-28.2	114 × 6	2.07	495 × 2	1072	6133 ×	371
Ca ₃ P ₂ O ₈ (3CaO P ₂ O ₅)	149.1	18.33 × 3	"	-58.6	410 × 3	"	"	2279	833 × 3	369
Na ₆ B ₂ O ₆ (3Na ₂ O B ₂ O ₃)	104.1	56.7 × 3	7.2	75.2	114 × 6	2.19	463 × 2	1537	613 × 3	406
Ca ₃ B ₂ O ₆ (3CaO B ₂ O ₃)	60.0	18.33 × 3	"	2.2	410 × 3	"	"	2154	833 × 3	405

(8)

Symbols; Q, H_{XO}, H_{XMO₂}, U, E, etc., correspond with those of cycle (5) and Eqs. (7), (8) and (9).

a) Landolt-Börnstein Phys. chem. Tabellen

b) H_{XMO₂} was obtained from H_{XMO₂} = H_{XO} + H_{MO} + Q.

c) Fowler and Bernal, op. cit.

d) the value obtained from ytterium compound

e) HMO₂⁻ was calculated from Eq. (9) by the use of the values of radii in preceding column.

f) the value on Table 2

in it is said that when two oxides react, neutralization occurs: the above oxide in the Table 2 behaves as base and the below behaves as acid.

Therefore, two oxides indicated further apart in the table the easier cause a neutralization reaction. For example, SiO_2 , B_2O_3 or P_2O_5 neutralizes Na_2O , K_2O or CaO makes stable salt. H_2O will react as base for the acids shown below in the table and combine with the upper bases as acid. The same will be said about the tendency of H_2O to CaO in molten slag. This scale may be considered to show a more reasonable measure for basic oxides than for acidic oxides.

To compare each acidity of acidic oxide, i. e. SiO_2 , B_2O_3 or P_2O_5 , the second method defined as the tendency of accepting O^- will be more desirable. The second method is more accurate because there is no error of dividing U by P_m , but the second method is difficult in determining the radii of negative polyatomic ions.

VI Conclusions

These scales were calculated to set up the semi-quantitative standard of basicity for the benefit of slag control in steelmaking processes. However, these scales are not precise in the actual processes, i. e. the molten state and the coexistence of various oxides; but the order of these scales is in accordance with the tendency obtained from the experiences.

The authors are studying another scale to be applicable to all oxides by the experimental measurements at high temperature. The results will be reported later.