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ACID AND BASE OF SLAGS

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Synopsis: Various attempts to determine the basicity of slags were reviewed. Acid and base concept has its origin in electronic interaction between the molecules or ions in condensed phase. The interaction is primarily important in free energy minimization of the solute-solvent reaction. The numerical evaluation, however, is quite difficult especially in ionic liquid in which supporting electrolytes are missing. The optical basicity with weak acid or basic indicator will be the most faithful to the concept. Thermodynamic alternatives of the optical basicity may be possible and well useful for understanding chemical reactions if used with cautions. NMR is a promising technique.

Key words: acid and base, basicity of slags, optical basicity, redox and basicity. thermodynamic activity, NMR and basicity.

I. Introduction

History of acid and base of slags is as old as that of metallurgical study. When the Brφnsted theory of donor-acceptor of H^+ gave the way to Lewis' theory of donor-acceptor of electron pair, the acid-base concept found the wide applicability beyond the aqueous solutions. Lux-Flood's definition

$$\text{base} = \text{acid} + O^{2-} \qquad (1)$$

was a natural extension. However, because we lack supporting electrolytes like KCl in aqueous solutions, the donability of O^{2-} brought out often the difficulty to maintain thermodynamic soundness, whenever we try to measure it at high temperatures.

Acid and base concept is so important in order to understand the reactions between solvents and solutes, that is, solvation, in any solvent system. This is so not simply because this is a convenient and broadminded concept but because the free energy of a solute is substantially given by the acid-base reaction with the solvent.

Many models and measures of the basicity of oxide systems have been proposed. These are usually consistent and agree each other quantitatively. However, because of very nature of electronic interaction, it cannot always be translated to the thermodynamic equilibrium quantities. We happen to have complete reverse sequence of basicity, depending on the way it is measured. There is another confusion that we discuss in terms of basicity of various single oxides on one hand and basicity of a mixture of acid and base oxides on the other hand. We are interested in the effect of mixing of different oxides. We must be cautious to differentiate the relative basicity of every oxide and the resultant basicity of mixtures of oxides of various basicity strengths.

In this article quantitative treatments of the basicity will be reviewed. Starting with room temperature solutions with well defined basicity, the relation between various definitions will be compared.

II. Acid and Base in Ambient Temperature

A Lewis basicity of a solvent is called donor number(DN) which was defined by Gutmann [1] to be given by the enthalpy of the reaction,

$$D + SbCl_5 = D \cdot SbCl_5, \quad DN = -\Delta H \qquad (2)$$

where $SbCl_5$ is dissolved in dichloroethylene at the concentration of 10^{-3} M and ΔH is expressed by kJ/mol.

It is to be noted that ^{23}Na NMR chemical shift of $NaClO_4$ in the sample is proportional to its DN [2]. In this case Na^+ is understood to be an acid and act as an indicator of Na^+ -solvent (base) interaction.

A Lewis acidity of a solvent is called acceptor number(AN) which is defined by the chemical shift of ^{31}P in $(Et)_2PO$ in the sample solvent,

$$AN = \frac{\delta - \delta(Et_2PO \cdot C_6H_{14})}{\delta(Et_2PO \cdot SbCl_5) - \delta(Et_2PO \cdot C_6H_{14})} \times 100 \qquad (3)$$

The chemical shift is influenced by the electron accepting tendency of the solvent molecule. AN of C_6H_{14} and $SbCl_5$ are set to be 0 and 100.

These examples at room temperature show that acid-base is a concept of electronic origin in condensed phases and it needs quantum mechanical calculation to evaluate it rigorously. It is only fortuitous if we could quantitatively measure it with thermodynamic activity like pH.

III. Acid-Base of Oxides

Oxide melts are the solution in which O^{2-} is the only one anion, if we ignore the polyatomic anions of acid oxide network for a while. One need not be worry about softness and hardness of negative ions. (O^{2-} is classified as a hard base.) An acid lack of electron pair is realized in the oxide networks like P_2O_5, SiO_2, while a base full of electron pairs is realized in ionic oxides like Na_2O, CaO etc. As a matter of fact, Ichise and Morooka [3] found that the linear relation between the lattice energy defined by the equation

$$M^{n+}(g) + n/2\ O^{2-}(g) = MO_{n/2}\ (s) \qquad (4)$$

and the basicity (sulfide capacity).

The lattice energy is stabilized by Madelung energy. Therefore, it is hard to tell whether donability of electron pair in ionic liquid is evaluated in the same level as in molecular liquid like ammonia, since there the lone pair electrons of O^{2-} play rather repulsive role and fixes the ionic radius. On the other hand, in acidic oxide like SiO_2, the chemical bond carries covalent nature. The content of lattice energy is not the same as in ionic crystal. Nevertheless, acid oxides show enormous lattice energy, reflecting stability of the outermost electron clouds of oxygen atoms.

IV. Acid-Base of Oxide Mixtures

When both acid and basic oxides mix, the salt is formed. The basic oxide BO dissociates into B^{2+} and O^{2-}

$$BO = B^{2+} + O^{2-} \qquad (5)$$

and the acid oxide AO accepts this O^{2-}

$$A\text{-}O\text{-}A + O^{2-} = 2A\text{-}O^- \qquad (6)$$

rather than dissociates into A^{2+} and O^{2-}. This is because O atoms of two oxides are so different and they tend to be equalized on mixing. Eq(6) means A^{2+} accepts lone pair of electrons of free O^{2-} instead of the O^{2-} which is already shared by another A^{2+} cation.

Next, we shall consider to dissolve Na_2O step by step into an acid oxide P_2O_5. P_2O_5 network is disintegrated into sheet, chain and finally discrete PO_4^{3-} ion. The representative formulae are $(PO_3^-)_n$(linear chain) and $P_2O_7^{2-}$(dimer). Every step of neutralization must be characterized by special range of O^{2-} concentration. This is theoretically conceivable at least, although big jump is not always observed.

Among the oxide melts, P_2O_5 is one of the strongest acid. However, the meaning of strength is not so simple. First, P_2O_5 is a polybasic acid and its capacity to be neutralized by a basic oxide is high. Secondly P_2O_5 lowers the activity of the basic oxide near pure P_2O_5. If the first of neutralization is assumed to be

$$P_2O_5 + O^{2-} = 2\ PO_3^- , \qquad (7)$$

the O^{2-} activity is buffered at a stational state until all P_2O_5 changes into PO_3^-. The fact that P_2O_5 is a strong acid means that PO_3^- is still strong acid.

V. Thermodynamic Activity of the Component as the Measure of Basicity

The hydrogen ion concentration is a thermodynamic measure in aqueous solutions. This success is brought out only by the presence of supporting strong electrolytes. Other reason may be the nature of water: highly polarizable yet molecular entity is kept without much discociation. On the other hand in oxide melts, oxygen atom (formally di-valent) changes the outermost electron of fully spherical to tetrahedral of sp^3 covalent character. Concentration loses its significance if the ionic long range force is considered, that is to say, the activity coefficient is dependent on the composition and the coexisting components, because we lack any supporting electrolytes.

Nevertheless, the thermodynamic activity of any neutral molecular constituent is definite and the activity of the basic component in binary melts will be the good measure of the basicity and that of the acidic component gives an acidity of the melts, although the choice is not unique and any other way of basicity scale is equally possible. Thus, we could measure the basicity of binary melts of Na_2O and one of P_2O_5, B_2O_3, MoO_3, GeO_2, and SiO_2, and compare the acidity strength from the activities of Na_2O [4]. We could also see the relative acidity strength of B_2O_3 and SiO_2 not simply by comparing Na_2O-B_2O_3 with Na_2O-SiO_2 but measuring the activity in the ternary melts. The results show SiO_2 is a weak acid compared with B_2O_3 [5].

Another thermodynamic scales of basicity have been proposed, CO_2 solubility and sulfide and phosphate capacities. Consider the following equilibrium [6].

$$CO_2(g) + O^{2-} = CO_3^{2-} , \quad (O^{2-}) = K(CO_3^{2-})/P_{CO_2} \qquad (8)$$

The solubility $(CO^{2-})/P_{CO_2}$ will be a measure of basicity [7], if the following conditions are fulfilled.

(1) The content of CO_3^{2-} is kept far below of the solubility limit of carbonate, say, $MgCO_3$, by reducing P_{CO_2}.

(2) CO_3^{2-} is the salt of acid CO_2 and base O^{2-} and the activity coefficient may not be composition dependent since the size and charge is big and small respectively.

(3) Activity of molecular species like CaO or Na_2O instead of (O^{2-}) is thermodynamically more sound. (O^{2-}) in eq(8) includes the effect of the cation and symbolically means the activity of the basic oxide.

These are not serious assumptions and satisfied in most of cases. Only one thing we must be careful is that CO_2 must be the weakest acid in the slag. Otherwise, CO_2 gets rid of the weaker component and occupies its site.

Next, sulfide capacity shall be considered,

$$O^{2-} + S = S^{2-} + O \qquad (O^{2-})=K(S^{2-})\times \frac{[O]}{[S]} \qquad (9)$$

where ( ) and [ ] mean the concentration in the oxide and metal phase respectively. Here the activity coefficient of S^{2-} must be included in K. However, because of similarity of S^{2-} to O^{2-}, the activity coefficient of S^{2-} will be highly dependent on O^{2-} activity. This leads to diminishing the basicity dependence. Nevertheless, the sulfide capacity is found to be proportional to other basicity scales. That means that the proportionality constant is appreciable even after reduced by the amount of the basicity dependence of S^{2-}.

Dephosphorization is another important role of slags. The term of phosphate capacity is also pointed out as a measure of the basicity. Thus, highly basic slag works better for dephosphorization. However, the phosphate capacity is not so simple as the sulfide capacity. Since P_2O_5 is neutralized into various phosphates depending on the basicity as described above.

Solubility of water vapor is also basicity dependent [8] and quite important to understand acid and basic magmas as well as slags.

VI. Redox Equilibria

Redox equilibria of multi-valent metal oxides depend not only on the oxygen pressure but also on the basicity of the solvent. Pourbaix diagram of aqueous solutions is the model of room temperature solutions.

In a redox reaction equilibrium

$$M^{m+} + (m-n)/2\ O^{2-} = M^{n+} + (m-n)/4\ O_2 \qquad (10)$$

M^{n+} and M^{m+} cations change their stability with solvent basicity. Thus, the equilibrium ratio at a given $P(O_2)$ depend on O^{2-} activity more than eq(10) suggests. As the case of aqueous solution the solute ions are coordinated with solvent molecule (O^{2-} ion). The number of O^{2-} of coordination was supposed to be determined from the redox equilibrium. Since the basicity is not given by (O^{2-}) but the activity of a neutral compound, usually we get a nonintegral slope in the type of relation

$$\log \frac{[Fe^{3+}]}{[Fe^{2+}]} = r \log a(Na_2O) \qquad (11)$$

from which the chemical formula of complexes may be derived.

We have measured the equilibria of several redox pairs [9]-[11]. Fe^{3+}/Fe^{2+} does not show much basicity dependence, while Cr^{6+}/Cr^{3+} shows enormous basicity dependence. This difference can be understood if Fe^{2+} and Fe^{3+}, and Cr^{3+} are weak acids and are located in the series of acidity between the two solvent cations Na^{+} and Si^{4+} or Na^{+} and B^{3+} etc., while Cr^{6+} is much stronger acid than Si^{4+}. Then, the redox reaction can be expressed by sum of reactions

$$\begin{array}{llll}
2\ Cr_2O_3 & +\ 3/2\ O_2 & =\ 2\ CrO_3 & (12) \\
Cr_2O_3 & +\ 3/2\ SiO_2 & =\ 2\ Cr^{3+} \quad +\ 2\ SiO_4{}^{4+} & (13) \\
2\ CrO_3 & +\ SiO_4{}^{4+} & =\ 2\ CrO_4{}^{2+} +\ SiO_2 & (14) \\
\hline
\end{array}$$

$$2\ Cr^{3+} + 5/2\ SiO_4{}^{4+} + 3/2\ O_2 = 2\ CrO_4{}^{2-} + 5/2\ SiO_2 \qquad (15)$$

Although the basicity dependence of stability of Cr^{3+} is not shown explicitly, the substantial part of the dependence is originated from the existence of $CrO_4{}^{2-}$ complex. Another interesting observation was noticed when Cr^{6+}/Cr^{3+} redox in various binary alkali silicates was compared [12].

VII. Structural Model of Acid and Base

There are many ways to construct the model of atomic arrangements of oxide melts. One of them will be to consider acid and basic character of components. Thus one may assume polymer anions of various sizes [13]. The ideal associated solution is another approach. In 1969, Yokokawa and Niwa [14], [15] employed the quasi-chemical treatment of Guggenheim to visualize acid and basic function of SiO_2 and a basic oxide MO(like CaO). In a quasi-lattice of O^{2-}, a part of tetrahedral interstitial site which is potentially available for Si^{+} is filled and the other part is vacant. There occur three kinds of site-site pair; Si^{4+}-Si^{4+}, Si^{4+}-vacant, and vacant-vacant, each corresponding to Si-O-Si, Si-O^{-}, and O^{2-} respectively. Further we assumed Si^{4+}-vacant site is associated with energy w(neutralization energy). Thus, the configuration lead to the equilibrium

$$O^{\circ} + O^{2-} = 2\ O^{-}\ , \quad \Delta H = 2w \qquad (16)$$

and the most probable configuration will be determined by w and the configuration entropy and a extra entropy associated with the reaction(16). The thermodynamic activity of O° ($=a(SiO_2)$) and activity-composition relation were well reproduced by the only one parameter ($w-T\Delta S$). Here, the acid and basic oxides were assumed to occupy the characteristic sites.

Later, Pelton and Blander applied quasi-chemical method in more abstract fashion, where sites for Si and the counter metal ion were not distinguished and two or more parameter were introduced [16], [17]. The number of the nearest neighbour of two is assumed although it is not likely to consider only chain like silicates. However this theory is quite successful in reproducing the free energy and phase diagrams of binary as well as multi- component systems. The acid base character is retained in highly negative interaction parameters.

VIII. Spectroscopic Methods

As was stated in earlier section, Lewis' definition is based on interionic or intermolecular interactions in condensed phase. One can not necessarily count basicity by number of species. pH in aqueous solution is a special case, where the continuous property can be measured by integral number density of H^{+} or OH^{-}. In ionic liquids the existence of a foreign species affects over a long distance and the activity coefficient will be concentration dependent except for the case of supporting electrolytes of constant concentration to retard the long range effect.

The optical basicity developed by Duffy and Ingram [18],[19] is a faithful device to tell the electronic level of indicator cation. Here Pb^{2+}, Tl^{+} and Bi^{3+} must be a weak acid and must respond to the most basic site which remains after other acids have eaten away.

On the other hand we have measured the chemical shift of X-ray fluorescence spectra of various cations in quenched glasses. Although the spectra are not always well defined because of short information of the excited states, the chemical shift of Si in silicates is quite interesting [20]. Especially SiKα-SiKβ relations were linear: with increase of the basicity Kα shifts negatively indicating decrease of effective charge on Si atom, while Kβ shifts positively indicating decrease of Si-O bond strength. It was also interesting observation that K$^+$ in K_2O-B_2O_3 [21] shows chemical shift of k'(satellite) with the composition although complete dissociation of potassium salts implies no appreciable change of its electronic level.

NMR is also becoming a potential strategy. As stated in the foregoing section, the chemical shifts of NMR signal reflect the outer electronic structure. ^{29}Si NMR of silicate minerals as well as glassy materials has been studied extensively [22]. The chemical shift is much dependent on the chemical bond: which is primarily characterized by the number n of oxygen atoms bound to another silicon atoms , i.e. the bonding oxygen. The other oxygens of 4-n are nonbonding oxygen atoms, when we call it Q$_n$. Thus, the distributions of Q$_n$ in a silicate mixture can be compared with the thermodynamic equilibrium

$$\text{Si-O-Si} + O^{2-} = 2\ \text{Si-O}^- \qquad (17)$$

which was found to be true. Furthermore, the equilibrium

$$Q_{n-1} + Q_{n+1} = 2\ Q_n$$

is also dependent on the temperature and alkali oxide species [23],[24]. This is a secondary effect rather than eq(17) governs, and these findings allow us to analyse finer details of equilibrium.

The theoretical optical basicity introduced by Duffy and Ingram [25] has been widely accepted. Since most of slag are not amenable to optical basicity measurement, it is quite valuable to estimate it. However, it is an average over component oxides and not the basicity of that mixture, that is, the remaining most basic site that responds to the indicator.

IX. Conclusion

At the end of this review, it will be interesting to see how the basicities look like when they are brought to common diagrams. In Fig.1 pO = -log a(Na_2O) in Na_2O-SiO_2 melts is plotted as functions of Na_2O content. Line a is a theoretical curve of reference 14 at the parameter $K = e^{-8}$. Line b is another calculated curve of reference 23 with adjustable parameter of equilibrium distribution of Q$_n$s to show the general tendency. The dotted line is an average experimental value quoted from the data book [26]. They are qualitatively consistent.

In Fig.2 pO [27] and the optical basicity [19] of Na-borates are plotted. The shift of Pb^{2+} goes along the thermodynamic result. The relative basicity of various alkali metal oxides is quite interesting if the results derived from the redox equilibria is true. NMR is also a promising technique.

References

1) Victor Gutmann "The donner-Acceptor Approach to Molecular Interactions", Plenum Press, New York, 1978.
2) R.H.Erlich and A.I.Popov, J.Am.Chem.Soc. 93(1971)5620.
3) E.Ichise and A.Morooka, The 19. Committee, The Japan Soc. Promotion of Science Rep. No11078 (1990).
4) T.Yokokawa and S.Kohsaka, J.Chem.Eng.Data, 24(1979)167.
5) T.Yokokawa, K.Kawamura and S.Denzumi, "Electrochemical Studies on MOlten Oxide Mixtures. "Trend in Electro Chemistry Council of Scientific Research Interaction, India (1992, in press)
6) M.L.Pearce, J.Am.Cerm.Soc., 47(1964)342.

7) C.Wagner, Metall.Trans., 613(1975)405.
8) T.Fukushima, Y.Iguchi, S.Ban-ya and T.Fuwa., Trans Iron Steel Inst. Japan, 6(1966)225.
9) A.Paul and R.W.Douglas, Phys. Chem.Glasses, 7(1966)1.
10) K.Takashi and Y.Miura, J.Non-Crys.Solids, 38439(1980)527, Yogyo-Kyokaishi, 89(1991)307.
11) K.Suzumura, K.Kawamura and T.Yokokawa, J.Chem.Soc.Faraday Trans. 87(1991)307.
12) S.Denzumi, K.Kawamura and T.Yokokawa (to be published)
13) C.R.Masson, Proc.Roy.Soc., a187(1965)1409.
14) T.Yokokawa and K.Niwa, Trans.JIM, 10(1969)3.
15) T.Yokokawa and K.Niwa, ibid, 10(1969)81.
16) A.D.Pelton and M.Blander, Proc. 2nd International Symposium on Metallurgical Slags and Fluxes, (1984)p281, M.Blander and A.D.Pelton. ibid. p295
17) A.D.Pelton and M.Blander, Metall.Trans., 1713(1986)805. M.Blander and A.D.Pelton Geochim. et. Cosmochim Acta, 51(1987)85.
18) J.A.Duffy and M.D.Ingram, J.Am.Chem.Soc., 93(1971)6448.
19) J.A.Duffy and M.D.Ingram, J.Non-Cryst.Solids, 21(1976)373.
20) N.Kikuchi, T. Maekawa and T.Yokokawa, B.Chem.Soc.Japan, 52(1979)1260.
21) T.Maekawa and T.Yokokawa, Spectrochimica Acta, 37b(1982)713.
22) G.Engelhardt and D.Michel, High-Resolution Solid-State NMR of Silicate and Zeolite, John-Wily and Sons, Chichester et al. (1986).
23) W.G.Dorfeld, Phys.Chem. Glasses, 29(1988)179.
24) H.Maekawa, T.Maekawa, K,Kawamura and T.Yokokawa, J.Non-Crys. Solids, 127(1991)53.
25) J.A.Duffy and M.D.Ingram, J.Inorg.nuclear Chem, 27(1975)1203.
26) S.Ban-ya and M.Hino, Chemical Properties of Molten Slags, Iron and Steel Institute of Japan(1991)
27) H.Ito, A.Sasahira, T.Maekawa and T.Yokokawa, J.Chem.Soc.Faraday Trans.1 80(1984)473.

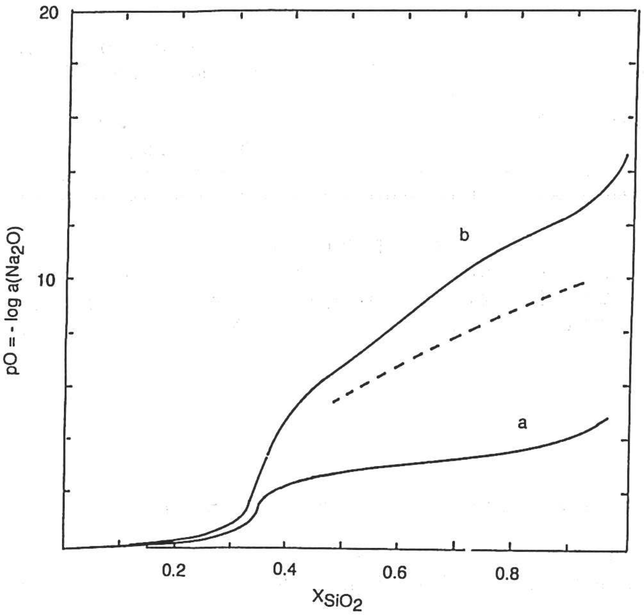

Fig. 1 pO versus X_{SiO_2} in NaO_2-SiO_2
a and b : theoretical curves (see text)
dotted line : experimental (averaged)

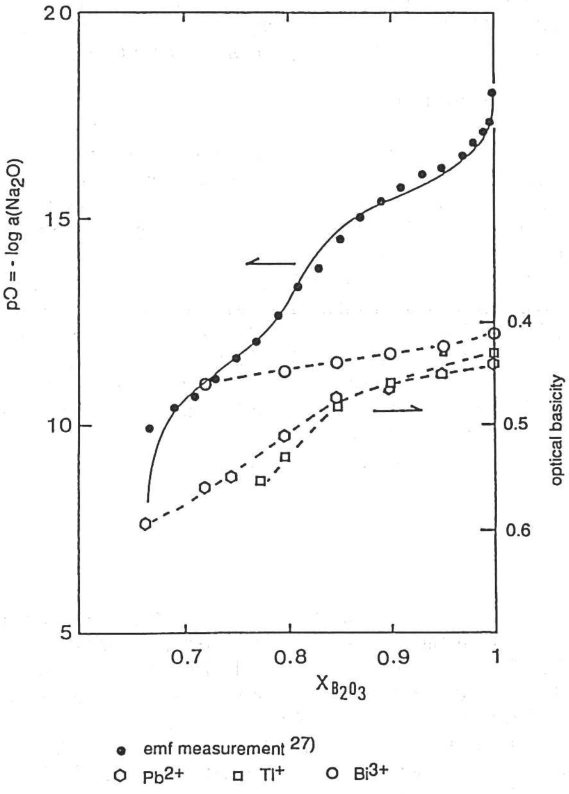

Fig. 2 pO versus $X_{B_2O_3}$ in Na_2O-B_2O_3