Free Energy of Solution in Binary Silicate Melts*

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A theoretical calculation of the free energy of solution of binary silicates is presented. Based on a random network model, a quasi-lattice treatment was applied to evaluate the partition function which has a parameter characteristic of the basic oxides. Calculated activities of the components and the free energy of solution as functions of composition fairly well reproduce experimental results. A basicity scale of oxides was defined in terms of the parameter.

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I. Introduction

The free energy of solution or activities of components of silicate melts are the most important factors which govern steelmaking processes, e.g. oxidation, desulfurization, dephosphorization, nonmetallic inclusions, etc. Besides, these thermodynamic quantities are closely related to the structure and other physicochemical properties of the silicates. It is, therefore, a quite interesting problem to make clear whether the activities of binary melts derived from a structural consideration can be extended to more complex silicate melts which are usually found in glasses and steelmaking slags.

Silicate melts are conveniently considered to consist of various ionic species which are in acid-base equilibrium with each other. However, a further theoretical development has been hampered because of the complex nature of the silicate network. Among various theoretical works carried out on the free energy relation from an ionic point of view, the following are to be noted. Flood and Knapp⁽¹⁾ analyzed the experimental results of Richardson and Webb on PbO-SiO_2 , assuming an equilibrium among silicate anions whose species varies in three ranges of composition. Masson⁽³⁾ assumed an equilibrium of chain ions of type $\text{Si}_n\text{O}_{3n-1}^{(2n-1)-}$ with various values of n , and concluded that the concentration of each anion depends on the composition and the parameter characteristic of each basic oxide. This is a treatment based on the polymer solution theory. He succeeded in this way in interpreting the general trend of the activity of the basic oxide in the composition range rich in the basic oxide. On the other hand, Toop and Samis⁽⁴⁾ assumed the following equilibrium:

where O^- , O° and O^{2-} are the oxygen ion bound to

silicon by one covalent bond, the oxygen bound to two silicon atoms and the free divalent oxygen anion, respectively. Thus any specific anion was not explicitly assumed, and O^- and O° were assumed to behave ideally, independent of anionic species to which they were bound. They found that the activity of the basic oxide is proportional to O^{2-} concentration in the melts, when the O^{2-} concentration is evaluated by Temkin's method from the number of various anions with a proper choice of the equilibrium constant in reaction (1).

The present paper deals with an approach to this problem from a viewpoint similar to that of Samis and Toop, based on the quasilattice treatment of the random network model on the silicate structure. Thus the derivation of the partial molar free energy or activities becomes much simpler and, unlike the case of Samis and Toop, particular anions and their ideal mixing need not be assumed.

II. Theory

A random network model on the silicate structure is employed. By addition of basic oxide (MO) to the silica network, its modification occurs at random and preferential production of any particular anion is neglected. Further the following are assumed for the way of atom's occupation on the lattice points when n molecules of MO and m molecules of SiO_2 are mixed in the liquid state. (1) Since silicon is always coordinated with four oxygen atoms, the number of lattice points which is potentially available to silicon is $m+1/2n$ or one half of the total of oxygen atoms. "Potentially available" implies that $2m+n$ oxygen can be so arranged in the space that m tetrahedrons which are accompanied by silicon are distributed among $m+1/2n$ lattice points. (2) When the neighboring two sites are occupied by silicon atoms, a Si-O-Si covalent bond is formed, while one vacant silicon site corresponds to the formation of four Si-O⁻ or end groups of anions. If the neighboring two sites are vacant, the oxygen atom between them is free O^{2-} ion. (3) After all silicon atoms are distributed, positions of M^{++} are assumed to be uniquely defined automatically, depending on the geometrical and charge distributional factors. (4) The energy of modification or the energy of Si-O⁻ relative to O^{2-} and

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(1) H. Flood and W. J. Knapp : J. Amer. Cer. Soc., **46** (1963), 61.

(2) F. D. Richardson and L. E. Webb : Bull. Inst. Min. Met., **583** (1955), 529.

(3) C. R. Masson : Proc. Roy. Soc., **A287** (1965), 201.

(4) G. W. Toop and C. S. Samis : Can. Met. Quart., **1** (1962), 129.

Si-O-Si is a constant w independent of composition: That is,

$$\Delta H = 2w \text{ (cal/bond)}. \quad (2)$$

In accordance with these assumptions, the distribution of silicon atoms are classified in terms of silicon to silicon pairs and summarized in Table 1. In Table 1 Vac means the vacant silicon site and r denotes the number of Si-O⁻ groups. The number of ways of configuration of these pairs is given by

$$\frac{(2m+n)!}{\left\{\frac{1}{2}(2n-r)\right\}! \left(\frac{r}{2}\right)! \left(\frac{r}{2}\right)! \left\{\frac{1}{2}(4m-r)\right\}!}.$$

Table 1 Pair distribution of silicon atoms

Pair	Number of pair	Energy
Vac-Vac	$\frac{1}{2}(2n-r)$	0
Vac-Si	r	rw
Si-Si	$\frac{1}{2}(4m-r)$	0
total	$2m+n$	rw

Noting that the total number of configurations of silicon atoms is $(m+n/2)!/m!(1/2n)!$ the normalized number of ways of configuration is⁽⁵⁾

$$\mathcal{Q}' = \frac{\left\{\frac{1}{2}(2n-r^\circ)\right\}! \left(\frac{r^\circ}{2}\right)! \left(\frac{r^\circ}{2}\right)!}{\left\{\frac{1}{2}(2n-r)\right\}! \left(\frac{r}{2}\right)! \left(\frac{r}{2}\right)!} \times \frac{\left\{\frac{1}{2}(4m-r^\circ)\right\}!}{\left\{\frac{1}{2}(4m-r)\right\}!} \cdot \frac{\left(m + \frac{n}{2}\right)!}{m! \left(\frac{1}{2}n\right)!}, \quad (3)$$

where r° is the value of r at random mixing, that is, $r^\circ/4 = m(1/2n)/(m+1/2n)$ or $r^\circ = 2nm/(m+n/2)$. The additional factor of the partition function of solution relative to the pure component melts can be expressed as

$$\mathcal{Q} = \mathcal{Q}' \exp\left(\frac{r \Delta S^\circ}{k}\right) \exp\left(-\frac{rw}{kT}\right), \quad (4)$$

where ΔS° is one half of the standard entropy of reaction (2). Arriving at eq. (4), it is assumed that the internal partition functions remain the same on mixing except energy increase w and extra entropy ΔS° . The ΔS° term is introduced to take into account the fact that there occurs a significant change of entropy when the SiO₂ network disintegrates into Si-O⁻ groups. Further, $\exp(\Delta S^\circ/k)$ is assumed to be factorized irrespective of anionic species on which the Si-O⁻ groups are bound. The value of r is determined by the condition that $\mathcal{Q}$ becomes maximum. Thus

$$\frac{\partial \ln \mathcal{Q}}{\partial r} = \ln \frac{\left\{\frac{1}{4}(2n-r)(4m-r)\right\}^{1/2}}{\frac{r}{2}} - \frac{w - T \Delta S^\circ}{kT} = 0. \quad (5)$$

Using a new set of units of concentration,

$$x = \frac{n}{n+m}, \quad r' = \frac{r}{n+m},$$

eq. (5) leads to

$$\ln \frac{(2x-r')(4-4x-r')}{r'^2} = \left\{ \frac{2(w - T \Delta S^\circ)}{kT} \right\} \quad (5')$$

or

$$(2x-r')(4-4x-r') = r'^2 \exp\left\{ \frac{2(w - T \Delta S^\circ)}{kT} \right\} = K r'^2, \quad (5'')$$

where

$$K \equiv \exp\left\{ \frac{2(w - T \Delta S^\circ)}{kT} \right\} \quad (6)$$

is a parameter specific to each basic oxide.

When the general relation $\Delta G \approx \Delta F = -RT \ln \mathcal{Q}$ is applied to eq. (4), the free energy change for one mole of solution is calculated to be

$$\begin{aligned} \frac{\Delta G}{RT} = & -\frac{3}{2}x \ln x - 3(1-x) \ln 2(1-x) \\ & + \frac{2-x}{2} \ln(2-x) + x \ln\left(x - \frac{r'}{2}\right) \\ & + 2(1-x) \ln\left\{2(1-x) - \frac{r'}{2}\right\} \end{aligned} \quad (7)$$

where r' is determined by eq. (5). Likewise equations are derived for activities of MO and SiO₂:

$$\begin{aligned} \ln a_{\text{MO}} = & -\frac{1}{RT} \frac{\partial \ln \mathcal{Q}}{\partial n} \\ = & \ln \left[\left(\frac{2-x}{x} \right)^{1/2} \left(1 - \frac{r'}{2x} \right) \right], \\ \ln a_{\text{SiO}_2} = & -\frac{1}{RT} \frac{\partial \ln \mathcal{Q}}{\partial m} \\ = & \ln \left[\frac{2-x}{2-2x} \left(1 - \frac{r'}{4-4x} \right)^2 \right]. \end{aligned} \quad (8)$$

Thus the free energy and activities can be derived as functions of the concentration with a parameter characteristic of the basic oxide.

We note that the free energy of solution of silicate melts consists of the free energy change of the modification reaction, which is in turn divided into the enthalpy term w and the entropy term ΔS° , and the entropy of configuration of the products. Calculation of the activities of the components does not need an assumption of Temkin's model.

III. Discussion on Various Assumptions

1. Random network model

A question might arise as to the validity of the random network model. The discrete anion model seems to give better pictures in some respects, especially in the range of low SiO₂ contents, while the former is

appropriate to the silicate structure of high SiO_2 composition. In a liquid silicate at high temperature the packing energy may not be so important as in the solid and the contribution of entropy term becomes significant in the free energy of the liquid solution compared with a small energy difference due to the way of modification, random or particularly stepwise. Thus the random network model will be a good starting point in treating the whole range of composition.

2. Quasi-lattice treatment

According to this theory, the number of sites available for silicon is assumed to be $m+1/2n$, since all O atoms can be so arranged that $m+1/2n$ of the tetrahedrons are appropriate to accommodate silicon atoms. An array of oxygen atoms of closest packing like a *fcc* lattice gives eight tetrahedrons per unit cell, while in a cristobalite one half of the oxygens are missing from a closest packing lattice site and the number of tetrahedrons is one half of the total number of oxygens. Since the partial molar volumes are found experimentally to be additive in silicate melts, it can be assumed that some part of the lattice is MO-like and the other part is SiO_2 -like. In the sense that pure MO and SiO_2 are different in structure, the quasi-lattice treatment will not be adequate at first sight. However, the packing of oxygen atoms is not so different from each other, if the composition dependent number of oxygen vacancy is taken into consideration. Further, calculation can be simplified and made chemically plausible since the coordination number of silicon atoms in the lattice is small and constant. As the MO content increases, the silicate network disintegrates to give various anions. The relative configuration of silicons and silicon vacancies is uniquely specified if they are in one anion (or intra-ionic case), while it is not necessary true across the anion boundary (inter-ionic case). The present treatment ignoring this difference will give some error, although a long range order is not a necessary condition for the quasi-lattice calculation.

3. w and ΔS°

w , the heat of modification of the network, is assumed independent of composition. The energy of breakdown of the Si-O-Si linkage will actually depend on the number of bonds which have already been modified as to silicon atoms concerned. Thus w will depend on composition. The extreme case leads to production of particular anions. Another source of composition dependence of w is the fact that M-O coordination depends on composition. In the SiO_2 -rich range, a sufficient number of oxygen atoms are not provided around every M^{++} cation and the energy of M^{++} becomes relatively high. The contribution of this energy to w will be a cause of two liquid separation which is actually found in binary silicates. These effects are neglected in the present derivation and it is rather intended to see how far this simplification can be true. The term ΔS° is introduced because the vibrational and rotational partition function will be

significantly modified as the end group Si-O^- is formed. It may be oversimplified to assign $2\Delta S^\circ$ to $\{\text{Si}\langle\text{O}^-\rangle$ as is done in the present calculation.

One should note that since r is not always equal to $2x$ the partial molar enthalpy of solution of the component oxides is not assumed constant. In Fig. 1 r is plotted as a function of composition at various values of K . In CaO-SiO_2 ($K=e^{-6}$) r nearly equals to $2x$ below $x=0.667$. This means that O^{2-} ions of CaO modifies the SiO_2 network almost quantitatively and the free O^{2-} ion is not left except the narrow region around $x=0.667$. Fig. 2 shows the partial molar enthalpy of solution of the basic oxide in the unit of w .

Fig. 1 Relative number of the modified Si-O⁻ bonds vs. composition at various values of K

Fig. 2 Partial molar enthalpy of solution of basic oxide with various K vs. composition

IV. Comparison with Experimental Results

In Fig. 3 the integral molar free energy of solution of four silicates are plotted as a function of composition. Pure liquid component oxides are taken as

the standard state*. The dotted lines are experimental values and the solid lines are theoretical curves, eq. (6), with K values noted along the curves. The sources of data are Darken's calculation⁽⁶⁾ for SiO_2 -CaO at 1600°C, Richardson and Webb's⁽²⁾ measurement for SiO_2 -PbO at 1000°C, Abraham, Davies and Richardson's⁽⁷⁾ measurement at 1650°C for SiO_2 -MnO, and Schuhman and Ensio's work⁽⁸⁾ for SiO_2 -FeO at 1350°C. Fig. 3 shows that the free energy composition relations are fairly well reproduced by the calculated curves except in the case of SiO_2 -FeO. The reason of this discrepancy will be found in the facts (1) that FeO is actually a mixture of FeO and Fe_2O_3 in experimental conditions, the relative contents of which is dependent on the concentration of

Fig. 3 Relation between integral molar free energy of solution of binary silicates and composition

SiO_2 , and (2) that FeO is not a strong base and especially Fe_2O_3 is neutral or even acidic. Therefore, the activity of "total FeO" may not be well treated in the present calculation. Nevertheless, the ex-

* This transfer of the standard state needs the knowledge of heat of fusion of SiO_2 . Its best known value is based on the freezing point depression of alkali silicates which has been determined by Kracek (J. Amer. Chem. Soc., 52 (1930), 1436). He assumed that the silicate was composed of molecular SiO_2 and alkaline oxide which is not the case as is understood at present. The present authors have the opinion that on addition of a basic oxide the giant molecule of SiO_2 disintegrates into quite different anionic species. Thus the use of freezing point depression for this end is questionable and any results can be accepted only with some structural assumption.

- (6) L. S. Darken and R. W. Gurry : *Physical Chemistry of Metals*, McGraw-Hill Book Co., (1953).
- (7) K. P. Abraham, M. W. Davies and F. E. Richardson : J. Iron and Steel Inst., 196 (1960), 82.
- (8) R. Schuhman, Jr. and P. J. Ensio : Trans. AIME, 191 (1951), 401.

perimental result that the temperature dependence of activity in this system is nearly zero is consistent with the present theory which concludes that the K value should be small ($w \approx 0$). Figs. 4~6 show

Fig. 4 Activities of CaO-SiO₂ and calculated curves with $K=e^{-6}$

Fig. 5 Activities of PbO-SiO₂ and calculated curves with $K=e^{-3}$

Fig. 6 Activities of FeO-SiO₂ and calculated curves with $K=e^0$ and $K=e^{-0.5}$

Table 2 Standard free energy change reaction (2)

MO (temp.)	FeO (1350°C)	MnO (1650°C)	PbO (1000°C)	MgO (1600°C)	CaO (1600°C)
ΔG° (kcal/mol)	0	-7.7	-7.6	-15	-22

activity-composition relation of the binary systems. One notes that activities of CaO and PbO are reproduced well by equations with K values of $\exp(-6)$ and $\exp(-3)$, respectively. Finer adjustment will give better agreement. However, with respect to the activity of SiO_2 in the SiO_2 rich range the agreement is only qualitative. Thus the Gibbs-Duhem relation implies that the activity of basic oxide as well as SiO_2 does not follow the simple theoretical relation over that range. It is not clear at present whether introduction of a concentration dependence of w will remedy this discrepancy.

As to the FeO- SiO_2 system, the activities of the components deviate from the theoretical curves as compared with those in the systems previously described. However, one should note that the rather complex nature of theoretical curves of $K=\exp(0)$ and $\exp(-0.5)$ are qualitatively followed by the experimental curve (see the deviation from ideality at concentration limits and its conversion in the intermediate range). This means that the way of analysis is promising although the theoretical approach is far from the actual observation.

V. Basicity of Oxides

As is described in the foregoing section, the free energy of solution consists in the two terms. The first term comes from the reaction of network modification. The second term corresponds to the entropy gain due to configuration of the modified bonds. While the both terms determine the activity-composition relation, the reference of the activity of the basic oxide or its basicity is characterized by the magnitude of K or the standard free energy of reaction (2), which is related to K :

$$\Delta G^\circ = RT \ln K = 2 N^\circ (w - T \Delta S^\circ). \quad (9)$$

This is a treatment similar to what Flood et al.⁽⁹⁾

applied to ionic melts. Table 2 summarizes approximate values of ΔG° of several oxides. It is proposed that K or this ΔG° is a measure of the basicity of any oxide in silicate melts. It will be much more interesting and fruitful if ΔG° can be divided into w and ΔS° terms. At present ΔS° cannot be evaluated and experimental data of ΔH , and ΔS are not so reliable to estimate w and ΔS° . Application of a high temperature calorimetry and reliable determination of the temperature coefficient of equilibrium are much desired.

VI. Summary

The free energy of solution of binary silicate melts and the activities of the component were derived by the application of a quasi-chemical treatment to the random network model of silicates. The free energy consists in the standard free energy change of reaction (eq. (2)) and the configurational entropy of the bonds modified by the reaction (2).

One parameter description reproduces successfully the experimental relations of thermodynamic function versus composition. The agreement is quantitative for silicates of strong basic oxides, while it is only qualitative in the silica-rich composition range and throughout the whole composition range in the FeO- SiO_2 system. The basicity of oxides in a silicate solvent was newly defined.

The application of the present treatment to the ternary silicate of given basicities, $\text{M}_1\text{O}-\text{M}_{11}\text{O}-\text{SiO}_2$, will be discussed elsewhere.

Note added in proof: * Recently Østvold and Kleppa⁽⁹⁾ measured heat of mixing of liquid PbO- Si_2 system. The partial molar heat of solution of PbO varies with the composition in the same way as Fig. 2 predicts, where the w is found to be -1.3 kcal/mol.

(9) T. Østvold and O. J. Kleppa : to appear in Inorg. Chem. 8 (1969).