A Note on the Heat of Fusion of Cristobalite

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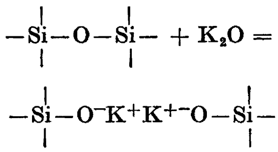
Despite several thermochemical studies of silica and its modifications carried out over a period of more than 50 years, there is as yet no general agreement about its enthalpy of fusion. The most accepted value for the enthalpy of fusion of cristobalite to now, has been the value 1.835 kcal/mole, calculated by Kracek [1] from his own freezing point depressions obtained by adding different alkali oxides to molten silica. This value was also derived by Førland [2] on the basis of recent reanalysis of the available cryoscopic data for silica rich solutions.

By adding an alkali oxide like K_2O to fused SiO_2 a reaction takes place as illustrated by



(1)

An oxygen bridge is broken and two non-bridging oxygens are formed. According to Førland [2] the structural units that can be assumed to be interchangeable in this melt will not be the cations, but a single bridging oxygen and a pair of non-bridging oxygen ions.

The partial molar entropy of SiO_2 then becomes

$$\Delta\bar{S}_{SiO_2} = -2R \ln X' \qquad (2)$$

where

$$X'_{-O-} = \frac{n_{-O-}}{n_{-O-} + 1/2\, n_{O-}} \qquad (3)$$

The heat of fusion, ΔH_f, can then be calculated from eqn. (3)

$$\Delta\bar{S}_{SiO_2} = \Delta H_f \left(\frac{1}{T} - \frac{1}{T_f}\right) \qquad (4)$$

where T_f is the melting point of pure cristobalite and T the melting temperature.

According to Førland [2] additions of Rb_2O and Cs_2O should give ideal freezing point depressions. On this basis he arrived at his value 1.85 kcal for the heat of fusion shown as a dashed line on Fig. 1.

Lumsden [3] later has argued that the alkali oxides will go into solution as $XO_{0.5}$. When he made this choice, he found that the freezing point for rubidium and cesium oxides was consistent with that for titania. According to Lumsden the heat of fusion of cristobalite should be 3.60 kcal/mole, twice the value obtained by Kracek [1] and Førland.[2]

Recently Holm, Kleppa and Westrum [4] measured the enthalpies of solution of quartz, cristobalite, and quartz glass in a lead-cadmium-boron-oxide solvent at 700°C. The enthalpies of transition were calculated from the enthalpies of solutions. The results are summarized in Table 1 and compared with other available calorimetric data.

Using the available enthalpy data for cristobalite and silica glass between 298°K

Table 1. Enthalpies of transition for different modifications of silica at 298°K.

	Holm, Kleppa and Westrum [a]	Mosesman and Pitzer [b]	Kracek [c]	Hummel and Schwiete [d]	Humphrey and King [e]
Quartz = Cristobalite	0.64 ± 0.15	0.35	0.63		0.93 ± 0.52
Quartz = Glass	2.15 ± 0.15		2.18	2.27 ± 0.2	
Cristobalite = Glass	1.51 ± 0.15		1.55		

[a] Holm, J. L., Kleppa, O. J. and Westrum, Jr., E. F. *Geochim. Cosmochim. Acta* **31** (1967) 2289.
[b] Mosesman, M. A. and Pitzer, K. S. *J. Am. Chem.* **63** (1941) 2348.
[c] Kracek, F. C. *Ann. Rept. Carnegie Inst. Wash.* **52** (1953) 72.
[d] Hummel, C. and Schwiete, H. E. *Glastech. Ber.* **32** (1959) 327.
[e] Humphrey, G. L. and King, E. G. *J. Am. Chem. Soc.* **74** (1952) 2041.

and the melting point of cristobalite, 1996°K (Kelley [5] and JANAF [6]), Holm, Kleppa and Westrum [4] obtained for the process

Cristobalite → Liquid,
$\Delta H_{f,1996} = 2.5 \pm 0.2$ kcal/mole

A line with a slope corresponding to this value is shown on Fig. 1. As can be seen, the new line divides the alkali oxides into two groups. K_2O, Rb_2O, and Cs_2O all give negative deviations from ideality increasing from potassium to cesium, while additions of Li_2O and Na_2O as before both give positive deviations from ideality.

It is obvious from the new heat of fusion given in Fig. 1, that the model suggested by Førland [2] (eqn. (2)) will give the best fit. The model suggested by Lumsden [3] seems more doubtful, since it will give rather large positive deviations for all of the alkali metal oxides added to the melt.

On the basis of available freezing point depressions of cristobalite on additions of titania, Førland [2] further assumed that titania went into solution as Ti_2O_4 molecules and that they occupied neighbouring tetrahedra. According to the new heat of fusion, this seems implausible. Titania seems instead to dissolve in the silica melt as separate TiO_2 molecules and give a positive deviation from ideality as shown on Fig. 1. Positive deviation from ideality in this system is further indicated by the phase diagram determined by De Vries, Roy and Osborn,[7] which shows a large region of liquid immiscibility. The partial molar entropy is given by

$$\Delta\overline{S}_{SiO_2} = -R \ln X_{SiO_2} \qquad (5)$$

where

$$X_{SiO_2} = \frac{n_{SiO_2}}{n_{SiO_2} + n_{TiO_2}} \qquad (6)$$

Two points are plotted on Fig. 1.

At last it should be mentioned that alumina seems to dissolve as molecules by replacement of SiO_2 by one Al_2O_3 as suggested by Førland.[2]

The partial molar entropy of mixing is given by

$$\Delta\overline{S}_{SiO_2} = -R \ln X'_{Si} \qquad (7)$$

$$X'_{Si} = \frac{n_{SiO_2}}{n_{SiO_2} + n_{Al_2O_3}} \qquad (8)$$

One point corresponding to the eutectic point in the system, is plotted on Fig. 1.

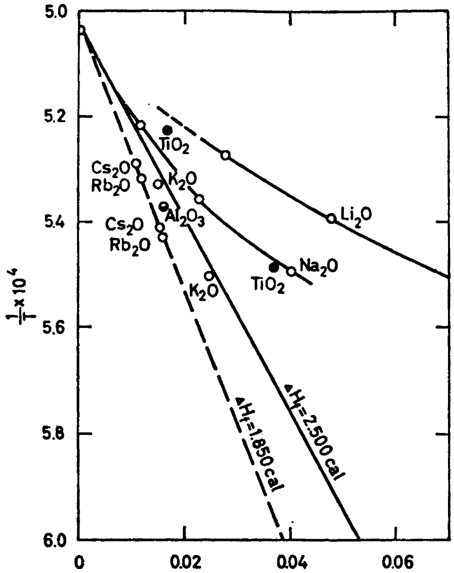


Fig. 1. Freezing point depressions of cristobalite caused by additions of various oxides. The figure is taken from Førland.[2]

○ $-2 \log X'_{-O-}$, ● $-\log X_{SiO_2}$, ◒ $-\log X'_{Si}$.

The results from the SiO_2-systems are not surprising when they are compared with thermodynamic properties of equivalent mixtures. It is well known that BeF_2-systems can serve as models for SiO_2-systems. Holm and Kleppa [8] found while measuring the enthalpies of mixing in the system $LiF-BeF_2$ rather strong positive deviations on the BeF_2-side, $\Delta\overline{H}_{BeF_2} > 0$. Mathews and Baes Jr.[9] have measured the activity of BeF_2 in $LiF-BeF_2$ mixtures and found positive deviations on the BeF_2-side. In the system $MgCl_2-CaCl_2$ which can serve as a model for the system SiO_2-TiO_2, Kleppa [10] found positive deviations of $MgCl_2$ for all compositions. Østvold [11] has calculated the activity of $MgCl_2$ and $CaCl_2$ in the same mixture from EMF measurements in the system $NaCl-MgCl_2-CaCl_2$, and found that both components show positive deviations from ideality. The phase diagram BeF_2-MgF_2 determined by Coints, Roy and Osborn [12] also indicates large positive deviations from ideality.

At least two contributions are believed to be important in these types of mixtures.

1) There is an endotermic term opposing the components to be mixed due to strong oxygen or halogen bridges (covalent forces) present in one of the components.

2) The other term is the exotermic coulombic repulsion term which arises from the reduction in second nearest neighbour coulombic repulsion between the cations. A small cation like Si^{4+}, Be^{2+} or Mg^{2+} strongly favours a large cation of low charge as next nearest neighbour.

The size of these two opposing terms will determine whether the energy of mixing shall be a) only positive, b) both positive and negative and c) only negative.

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Investigation into the Influence of Electric Charges on the Corrosion of Metals

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When the role of the electron exchange at phase boundary processes — self-evident *per se* — could be subjected to quantitative determinations, it was possible to submit an old theory of one of the authors to the verification of experimental testing.

If a metal rod is charged with electricity, by passing an electric current through it or by some other method, it will be surrounded by a non-homogeneous electric field. A dipole in this field will get a certain orientation and a certain acceleration in the direction towards the metal. It is consequently probable that a corrosive gas consisting of dipoles, *e.g.*, hydrochloric gas, hydrogen sulphide, or water vapour, will react in one fashion if the metal is electrically charged, in another fashion if it is uncharged.

In order to make some preliminary investigations into the question whether our assumptions were correct and whether measurable differences could be observed, silver and copper rods were caused to react with corrosive gases the molecules of which either were permanent dipoles, as

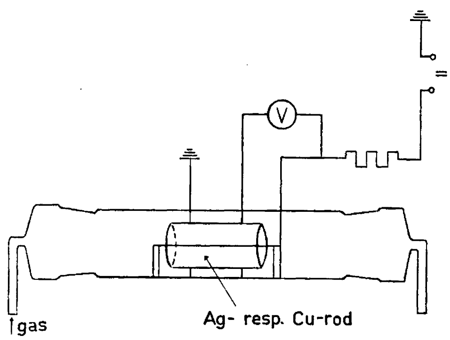

Fig. 1. Experimental apparatus.