VII. Order-Disorder in Silicates

Long range order-disorder phenomena in silicates differ from those in alloys in several important respects. First, as opposed to alloys, silicates contain structural sites with definite polyhedral geometries and order-disorder is noticed whenever an ion occupies two or more sites which differ in their polyhedral shape and size. Second, usually only the ions which occupy the nonequivalent sites, take part in the order-disorder and the remaining silicate framework remains more or less inert. Third, when the ions are sufficiently alike in their charge and size, the site preference energies (corresponding to the difference in binding energy of the ion between the nonequivalent sites) are not strongly dependent on the degree of order as is usual in many binary alloys. Fourth, complete order or disorder in silicates is generally not possible because the variation in composition in binary solution would require that some of the ions of one species must inevitable occupy some of the sites belonging to the other species and also because there may be potential barrier for the ordering process to continue below a certain temperature. At the high temperature side there is usually a phase transformation or melting before complete disorder can be attained.

Order-disorder or the intracrystalline cation distribution in silicates is measurable by X-ray (see GHOSE, 1961) and other spectroscopic techniques. The energy of the intracrystalline ion exchange is part of the Gibbs free energy of the crystal and is, therefore, a very useful thermodynamic quantity (see MUELLER, 1969; THOMPSON, 1969).

Before considering order-disorder in crystalline solutions with two or more nonequivalent crystal structural sites, let us consider order-disorder in solutions with all sites structurally similar to each other. For such solutions the thermodynamic relations are simple and well understood.

1. Order-Disorder and the Crystalline Solution Models

As mentioned before the entropy of mixing in the regular solution model with the zeroth approximation is the same as that of the ideal solution. In other words it is assumed that there is complete disorder in the crystalline solution. Following GUGGENHEIM (1952) let a binary mixture contain \( N_A = N(1 - x) \) atoms of A and \( N_B = Nx \) atoms of B on a lattice of \( N \) sites with a coordination number \( z \). There are in all
The assumption of complete randomness implies the conversion of all $A A$ and $B B$ pairs to $A B$ pairs whose number is proportional to $\bar{x}$ given by

$$\bar{x} = \frac{N_A N_B}{N_A + N_B}.$$  \hspace{1cm} (VII.1)

The interaction energy $w$ (see Chapter II) is given by

$$2w = 2w_{AB} - w_{AA} - w_{BB}$$ \hspace{1cm} (II.2)

The presence of interaction energy implies that the mixing of A and B cannot be really random. In the quasi-chemical approximation the average value $\bar{x}$ is given by

$$\bar{x}^2 = (N_A - \bar{x})(N_B - \bar{x}) \exp(-2w/zK)$$ \hspace{1cm} (VII.2)

Multiplying $w$ by $N$ (Avogadro's number) and using the symbol $W$ for $Nw$ and the symbol $\eta$ for $\exp(W/zRT)$, we may write

$$(N_A - \bar{x})(N_B - \bar{x}) - \eta^2 \bar{x} = 0.$$ \hspace{1cm} (VII.3)

If $\bar{x}$ is expressed as

$$\bar{x} = \frac{N_A N_B}{N_A + N_B} \frac{2}{\beta + 1}$$ \hspace{1cm} (VII.4)

it is possible to write for the quantity $\beta$ from Eqs. (VII.3) and (VII.4)

$$\beta = \{1 + 4x(1-x)(\eta^2-1)\}^{1/2}$$ \hspace{1cm} (II.11)

where $x$ is the mole fraction $N_A/N_A + N_B$. Multiplying both sides of Eq. (VII.4) by the total number of atoms, we have,

$$\bar{x}' = x(1-x)(2/\beta + 1)$$ \hspace{1cm} (VII.5)

where $\bar{x}' = \bar{x}(N_A + N_B)$. $\beta = 1$ corresponds to complete disorder since we now have $\bar{x}' = x(1-x)$. Substituting $\beta = 1$ in (II.2) gives $\eta$ or $\exp(W/zRT) = 1$. In such a case the ideal solution model is obtained for which $W = 0$, $\beta$ or $\eta = 1$.

Positive deviations from ideal solution occur if $W > 0$, which would mean $\eta < 1$, $\beta > 1$, and, therefore $\bar{x}' < x(1-x)$. The number of AB pairs is less than that of the completely random configuration. This leads to a positive excess entropy of mixing besides the positive enthalpy. $W > 0$ therefore indicates a trend towards clustering and eventual unmixing into two phases.

Negative deviations from ideal solution occur when $W < 0$ and therefore $\eta > 1$, $\beta < 1$ and $\bar{x}' > x(1-x)$. In such solutions there is a trend towards compound formation and the free energy of mixing is more nega-