

Therefore the assumption i) is reasonable for the liquid such as the valence electrons can be looked upon as free electrons and Born approximation is held.

Now we verify the quasichemical approach by using the eq.'s (1) and (2). The internal energy of the liquid is

$$E = \frac{N^2}{2V} \int \phi(r) \cdot g(r) 4\pi r^2 dr. \quad (8)$$

Here, the kinetic term is omitted, because this term is not affected by "species". Substituting the eq.'s(1) and (2) into the eq.(8), we have

$$E = \alpha^2 U_A + \beta^2 U_B + \alpha \cdot \beta \omega_{AB}, \quad (9)$$

where

$$\begin{aligned} U_A &= \frac{N^2}{2V} \int \phi_{AA} \cdot g_{AA} \cdot 4\pi r^2 dr, \\ U_B &= \frac{N^2}{2V} \int \phi_{BB} \cdot g_{BB} \cdot 4\pi r^2 dr, \\ \omega_{AB} &= \frac{N^2}{2V} \int (\phi_{AA} \cdot g_{BB} + \phi_{BB} \cdot g_{AA}) \cdot 4\pi r^2 dr. \end{aligned} \quad (10)$$

The internal energy E is the averaged value of those for all configurations of the whole ions. We have defined a species anew by using the corresponding radial distribution function in the last section, that is, the radial distribution function g_{AA} , g_{BB} are looked upon as the species A and B respectively. If we choose the coefficients α , β such as to satisfy $\alpha + \beta = 1$, α and β must show the mole fractions of the species A and B respectively.

Otherwise this means that the numbers of ions constituting the species A and B are αN and βN respectively. Moreover the eq.(1) must hold independently of an arbitrarily chosen origin ion. Hence the number of different configurations of the whole ions must be $N! / ((\alpha N)! \cdot (\beta N)!)$. The energy E is the averaged value for all configurations of $N! / ((\alpha N)! \cdot (\beta N)!)$. Therefore the partition function is given approximately by and the Helmholtz free energy is

$$Z_N = \frac{N!}{(\alpha N)! (\beta N)!} e^{-E/kT}, \quad (\alpha + \beta = 1)$$

$$F = E + N k T \{ \alpha \ln \alpha + \beta \ln \beta \}. \quad (11)$$

Substituting the eq.(9) into (11), we obtain the equilibrium condition

$$\Delta \mu^\circ = k T \ln \frac{\beta}{\alpha} + (\alpha - \beta) \omega = k T \ln \frac{x}{1-x} + (1-2x) \omega \quad (12)$$

where

$$\begin{aligned} \Delta \mu^\circ &= \mu_A^\circ - \mu_B^\circ, \\ \mu_A^\circ &= U_A/N, \quad \mu_B^\circ = U_B/N \\ \omega &= (\omega_{AB} - U_A - U_B)/N, \end{aligned}$$

and x is the mole fraction of the species B. The eq.(12) has the same form that Rapoport derive, and the assumption ii) is verified.

General Treatment of Species

The intensity of the diffracted x-ray or neutron-ray for the liquid described until in the last section is given by

$$a(k) = 1 + \frac{N}{V} \alpha \int (g_{AA} - 1) \cdot \frac{\sin kr}{kr} 4\pi r^2 dr + \frac{N}{V} \beta \int (g_{BB} - 1) \cdot \frac{\sin kr}{kr} 4\pi r^2 dr \quad (\alpha + \beta = 1) \quad (13)$$

There, we have treated the liquid as the species A and B are clearly distinguishable. In the present section, we treat such a liquid in which a difference between the species A and B is not so clear, that is, some ions belong to the species A and B simultaneously. If there are N_C ions belonging to the species A and B simultaneously, the numbers of ions constituting the species A and B clearly become $\alpha N - N_C/2$ and $\beta N - N_C/2$ respectively. The eq.(13) then becomes

$$N a(k) = \left[N + \frac{N}{V} N_A a_{AA}(k) + \frac{N}{V} N_B a_{BB}(k) + \frac{1}{V} \left(N_C + N_A \cdot \frac{a_{AA}(k)}{a_{CC}(k)} + N_B \cdot \frac{a_{BB}(k)}{a_{CC}(k)} \right) \cdot N_C \cdot a_{CC}(k) \right] \quad (14)$$

where

$$N_A = \alpha N - \frac{N_C}{2}, \quad N_B = \beta N - \frac{N_C}{2}$$

and $a_{AA}(k)$ is defined as same as in the last section. Others defined similarly. The configurational entropy becomes approximately

$$S = k \ln \frac{N!}{N_A! N_B! N_C!} = -k \left(N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} + N_C \ln \frac{N_C}{N} \right) \quad (15)$$

for the same reason that has been said in the last section. As the number of the ions belonging to the species A and B simultaneously (i.e. N_C) increases, the eq.(14) becomes

$$a(k) \longrightarrow 1 + \frac{N}{V} a_{CC}(k)$$

and the eq.(15) becomes

$$S \longrightarrow 0$$

On the other hand, as the number of the ions decreases, $a(k)$ of the eq.(14) becomes that of the eq.(13) and the liquid in the present section becomes that in the last section.

Discussion

We have restricted the number of species to two, but the same treatment can be applied to a liquid consisting of more than two species. The forms of the radial distribution function and the pair-potential in this case become

$$g = \sum C_i g_{ii}$$

and

$$\phi = \sum C_i \phi_{ii}$$

C_i is the mole fraction of the species i and the sum is taken over all species which have influences to the properties of the liquid.

A species has a certain relation with the corresponding solid phase, but species corresponding to different solid phases are not always distinguishable. If distinguishable species exist in a molten metal, the influences must appear