Exercises on Ch.14 *Partitionless transformations*

14.3 Quasi-adiabatic phase transformation. Exercises 1 and 2

14.5 Partial chemical equilibrium. Exercise 1

14.3 Quasi-adiabatic phase transformation

Exercise 14.3.1

To what temperature must a liquid metal be cooled before solidification starts, in order for the solidification to take place by a steady-state reaction controlled by heat conduction over short distances, i.e. quasi-adiabatic conditions? Use Richard's rule and suppose $C_P \cong 3R$ for the both phase.

Hint

Find inspiration from Fig. 14.3. The growing phase must form under local equilibrium if the conditions are quasi-adiabatic, i.e., at T^e. Richard's rule reads $H_m^L(T^e) - H_m^\alpha(T^e) = RT^e$, i.e., $S_m^L(T^e) - S_m^\alpha(T^e) = R$.

Solution

Under quasi-adiabatic conditions $H_m^L(T^L) - H_m^\alpha(T^e) = 0$. We can relate $H_m^L(T^L)$ to $H_m^L(T^e)$ by integration from T^L to T^e: $H_m^L(T^e) = H_m^L(T^L) + \int C_P dT$ $= H_m^L(T^L) + 3R(T^e - T^L)$. Insert $H_m^\alpha(T^e)$ and $H_m^L(T^L)$ in Richard's rule: $H_m^L(T^L) + 3R(T^e - T^L) - H_m^L(T^L) = RT^e$; $2T^e = 3T^L$; $T^L = (2/3)T^e$.

Exercise 14.3.2

Evaluate the entropy production for quasi-adiabatic solidification of 1 mole of a pure, liquid metal.

Hint

Compare with Exercise 14.3.1.

Solution

According to Exercise 14.3.1 we now have $T^{\alpha} = T^{e}$ and $T^{L} = (2/3)T^{e}$. Thus

$$\Delta S_{ip} = S_m^{\alpha}(T^e) - S_m^{L}(T^L) = S_m^{L}(T^e) - R - [S_m^{L}(T^e) - \int R(C_P/T)dT]$$

$$= -R + 3R\ln(3/2) = 0.216R$$

14.5 Partial chemical equilibrium

Exercise 14.5.1

The paraequilibrium condition $[(G_m - x_c\mu_c)/(1 - x_c)]^{\alpha} = [(G_m - x_c\mu_c)/(1 - x_c)]^{\gamma}$ is not valid if one has a measurable atomic mobility within the phase interface. Discuss the reason.

Hint

Examine under what conditions the equation was derived.

Solution

The equation was derived for $dN_{Fe} = dN_M = 0$ which is not true during the integration across the interface if there is an atomic mobility of M relative to Fe.