Course MP4, Thermodynamics and Phase Diagrams, H. K. D. H. Bhadeshia

## Answer Sheet 1

The terminology used here is as in the lecture notes.

- 1. Consider equilibrium between two phases  $\alpha$  and  $\gamma$  in a binary alloy. Since the compositions of these phases are not identical,  $x^{\alpha\gamma} \neq x^{\gamma\alpha}$ , it follows that concentration gradients exist and yet there will be no diffusion since the phases are at equilibrium.
- Given that G = μ<sub>A</sub>(1 x) + μ<sub>B</sub>x, it follows that ∂G/∂x = μ<sub>B</sub> μ<sub>A</sub>.
  Coiling and uncoiling of molecular chains, vibration of side groups, rotation about covalent bonds.
- 4. In ordered crystals, A atoms prefer to be next to B atoms: the enthalpy of ordering  $\Delta H_{\Omega}$ is negative. However, there is a decrease in entropy on ordering so  $-T\Delta S_O$  is positive. The latter term dominates at high temperatures, making  $\Delta G_O$  positive and hence favouring disorder (random distribution of atoms).
- 5. An ideal solution is one in which the atoms are randomly mixed at all temperatures. The probability of finding an A atom next to a B atom (or vice versa) in an equiatomic ideal solution is  $p_{AB} = 2x(1-x) = 0.5$  since x is the probability of finding a B atom and x(1-x) is that of finding an A atom next to a B atom.
- The task is to calculate the equilibrium carbon concentration at any point given a fixed 6. manganese concentration gradient in austenite. The activity (a) of carbon will tend to become uniform:

$$\ln\{a_C^0\} = \ln\{a_C^{Mn}\}$$
$$\ln\{\Gamma_C^0\} + \ln\{x_C^0\} = \ln\{\Gamma_C^{Mn}\} + \ln\{x_C^{Mn}\}$$

where  $a_C^0$  is the activity of carbon at zero Mn,  $a_C^{Mn}$  is the activity of carbon at a finite Mn concentration,  $x_C^0$  and  $x_C^{Mn}$  are the corresponding mole fractions of carbon,  $\Gamma_C^0$  and  $\Gamma_C^{Mn}$  are the corresponding activity coefficients. The activity coefficients can be expanded as follows (Kirkaldy and Baganis, Metall. Trans. 9A, 1978, 495):

$$\ln\{\Gamma_C\} = 8.1 \times x_C - 5 \times x_{Mn}$$

where  $x_{Mn}$  is the concentration of manganese. It follows that

$$(8.1 \times x_C^0) + \ln\{x_C^0\} = (8.1 \times x_C^{Mn} - 5 \times x_{Mn}) + \ln\{x_C^{Mn}\}$$
  
 
$$\ln\{x_C^0\} - \ln\{x_C^{Mn}\} = (8.1 \times [x_C^{Mn} - x_C^0] - 5 \times x_{Mn})$$

Writing  $[x_C^0 - x_C^{Mn}] = \Delta x$ , we get

$$\ln\left\{1 + \frac{\Delta x}{x_C^{Mn}}\right\} = -8.1 \times \Delta x - 5 \times x_{Mn}$$

which for small  $\Delta x$  becomes

$$x_C^0 - x_C^{Mn} \equiv \Delta x = \frac{-5x_{Mn}}{8.1 + \frac{1}{x_C^{Mn}}}$$

Suppose we have 1 wt% C and the manganese concentration ranges from 0-5 wt%. 1 wt% C is about 0.05 mole fraction of carbon. Setting  $x_C^{Mn} \simeq 0.05$ ,  $x_{Mn} \simeq 0.05$  (since we have 5 wt% Mn), we see that  $\Delta x = 0.0089$  or 0.18 wt%. The carbon concentration in the Mn-rich region will therefore be higher by about 0.18 wt%.