Session #19: Homework Solutions

Problem #1

Calculate the vacancy fraction in copper (Cu) at (a) 20°C and (b) the melting point, 1085°C. Measurements have determined the values of the enthalpy of vacancy formation, ΔH_V, to be 1.03 eV and the entropic prefactor, A, to be 1.1.

Solution

number of sites / unit volume (also known as site density) is given by:

$\frac{N_A}{V_{molar}}$ $\therefore$ site density = 6.02×10^{23} / 7.11 cm^3 = 8.47×10^{22}

$\rightarrow$ vacancy density = f_v x site density

$$\text{(a) } f_V = Ae^{-\frac{\Delta H_V}{k_B T}} = 1.1 \times e^{-\frac{1.03 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-22} \times (20+273)}} = 2.19 \times 10^{-18}$$

vacancy density at 20°C = 1.85×10^5 cm^{-3}

$$\text{(b) } f_v = Ae^{-\frac{\Delta H_V}{k_B T}} = 1.1 \times e^{-\frac{1.03 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-22} \times (20+1085)}} = 1.67 \times 10^{-4}$$

vacancy density at 1085°C = 1.41×10^{19} cm^{-3}

Note that the ratio of f_v(1085°C) / f_v(20°C) = 7.62×10^{13} !

Problem #2

In iridium (Ir), the vacancy fraction, n_v/N, is 3.091×10^{-5} at 1234ºC and 5.26×10^{-3} at the melting point. Calculate the enthalpy of vacancy formation, ΔH_V.

Solution

All we need to know is the temperature dependence of the vacancy density:

$\frac{n_v}{N} = Ae^{-\frac{\Delta H_V}{RT}}$, where T is in Kelvins and the melting point of Ir is 2446°C

$3.091 \times 10^{-5} = Ae^{-\frac{\Delta H_V}{RT_1}}$, where T_1 = 1234ºC = 1507 K

$5.26 \times 10^{-3} = Ae^{-\frac{\Delta H_V}{RT_2}}$, where T_2 = 2446ºC = 2719 K

Taking the ratio:

$$\frac{5.26\times10^{-3}}{3.091\times10^{-5}}=\frac{Ae^{-\frac{\Delta H_V}{RT_1}}}{Ae^{-\frac{\Delta H_V}{RT_2}}}=e^{-\frac{\Delta H_V}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$\therefore\ \ln 170.2 = -\frac{\Delta H_v}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\therefore\ \Delta H_v = -\frac{R\times\ln 170.2}{\frac{1}{1507}-\frac{1}{2719}}=-\frac{8.314\times\ln 170.2}{\frac{1}{1507}-\frac{1}{2719}}=1.44\times10^{5}\ \text{J/mole}\cdot\text{vac}$$

$$\therefore\ \Delta H_v = \frac{1.44\times10^{5}}{6.02\times10^{23}}=2.40\times10^{-19}\ \text{J/vac} = 1.5\ \text{eV/vac}$$

Problem #3

A formation energy of 2.0 eV is required to create a vacancy in a particular metal. At 800ºC there is one vacancy for every 10,000 atoms.

(a) At what temperature will there be one vacancy for every 1,000 atoms?

(b) Repeat the calculation, but this time with an activation energy of 1.0 eV. Note the big change in the temperature interval necessary to obtain the same change in vacancy concentration as was the case with an activation energy of 2.0 eV.

Solution

(a) We need to know the temperature dependence of the vacancy density:

$$\frac{1}{10^4}=Ae^{-\frac{\Delta H_V}{kT_1}}\quad\text{and}\quad\frac{1}{10^3}=Ae^{-\frac{\Delta H_V}{kT_X}}$$

From the ratio: $\dfrac{\frac{1}{10^4}}{\frac{1}{10^3}}=\dfrac{10^3}{10^4}=\dfrac{Ae^{-\Delta H_V/kT_1}}{Ae^{-\Delta H_V/kT_X}}$ we get $-\ln 10 = -\dfrac{\Delta H_v}{k}\left(\dfrac{1}{T_1}-\dfrac{1}{T_x}\right)$

$$\therefore\ \left(\frac{1}{T_1}-\frac{1}{T_x}\right)=\frac{k\ \ln 10}{\Delta H_v}$$

$$\frac{1}{T_x}=\frac{1}{T_1}-\frac{k\ \ln 10}{\Delta H_v}=\frac{1}{1073}-\frac{1.38\times10^{-23}\times\ln 10}{2\times1.6\times10^{-19}}=8.33\times10^{-4}$$

$$T_x = 1200\ \text{K} = 928^{\text{o}}\text{C}$$

(b) Repeat the calculation following the method given above but with $\Delta H_v = 1.0$ eV to find that T_x = 1364 K = 1091^{o}C

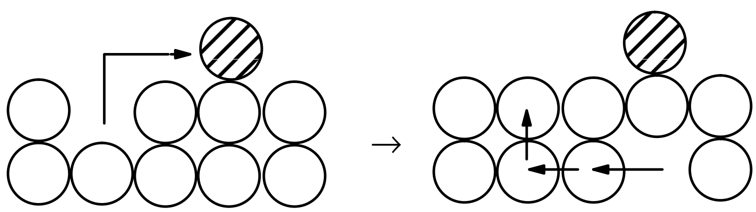
Note: the change in ΔH_v from 2.0 eV to 1.0 eV resulted in a change from 128 K to 291 K in ΔT.

Problem #4

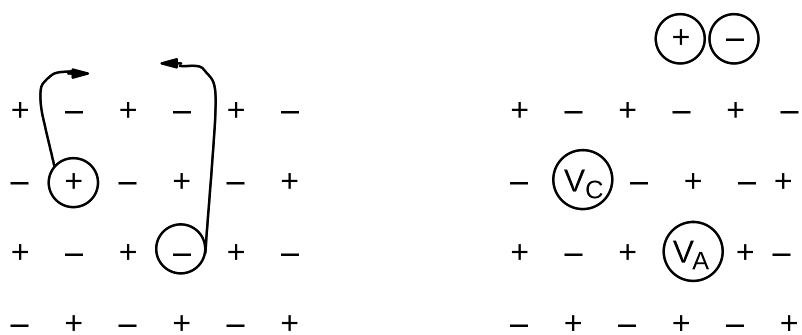
On appropriate schematic drawings show the generation and characteristics of Schottky defects in (a) a closed-packed metal, (b) an ionic crystal and (c) a semiconductor.

Solution

(a)



(b)



(c)