Homework #1 - Solutions

Due Monday August 29 by noon

Reading

- Kasap, Chapter 1

Videos

- MSE Content Review Part 1 and Part 2

Problems

1. (Kasap 4th Ed. Problem 1.38) **Vacancies in Metals**

   a. The energy of formation of a vacancy in the copper crystal is about 1 eV. Calculate the concentration of vacancies at room temperature (300 K) and just below the melting temperature, 1084 °C. Neglect the change in the density, which is small.

   b. The table below shows the energies of vacancy formation in various metals with *close-packed* crystal structures and their melting temperatures T_m. Plot E_v (in eV) versus T_m (in Kelvins), and explore if there is a correlation between E_v and T_m. Some materials engineers take E_v to be very roughly $10k_BT_m$. Do you think that approximation is justified? (Explain.)

Table 1.12 Energy of formation of vacancies for selected metals

	Al	Ag	Au	Cu	Mg	Pt	Pb	Ni	Pd
Crystal	FCC	FCC	FCC	FCC	HCP	FCC	FCC	FCC	FCC
E_v (eV)	0.70–0.76	1.0–1.1	0.90–0.98	1–1.28	0.89	1.3–1.5	0.50	1.63–1.79	1.54–1.85
T_m (°C)	660	962	1064	1085	650	1768	328	1455	1555

Solution

a. Equilibrium concentration of vacancies is given by

$$n_v = N\exp\left(-\frac{E_v}{kT}\right)$$

where N is atomic concentrations. Vacancy formation energy $E_v = 1\text{ eV} \times (1.6\times10^{-19}\text{ J eV}^{-1}) = 1.6\times10^{-19}$ J. The atomic mass of Cu is $M_{\text{at}} = 63.54\text{ g mol}^{-1}$ and the density at 293 K is 8.96 g cm^{-3}.
Atomic concentration is calculated as

$$N = \frac{\rho N_A}{M_{\text{at}}} = \frac{(8.96\,\text{g cm}^{-3})(6.022\times10^{23}\,\text{mol}^{-1})}{63.54\,\text{g mol}^{-1}}$$

$$= 8.49\times10^{22}\text{ cm}^{-3}\text{ or }8.49\times10^{28}\text{ m}^{-3}$$

At $T = 300$ K

$$n_v = (8.49\times10^{28}\,\mathrm{m^{-3}})\exp\left(-\frac{1.6\times10^{-19}\,\mathrm{J}}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})(300\mathrm{K})}\right)$$

$$\boldsymbol{n_v = 1.42\times10^{12}\ \mathrm{m^{-3}}\ \text{or}\ n_v = 1.42\times10^{6}\ \mathrm{cm^{-3}}.}$$

This implies that there is a vacancy in every 5.97×10^{10} atoms (= N/n_v)

At $T = 1084$°C (1357 K)

$$n_v = (8.49\times10^{28}\,\mathrm{m^{-3}})\exp\left(-\frac{1.6\times10^{-19}\,\mathrm{J}}{(1.3806\times10^{-23}\,\mathrm{J\,K^{-1}})(1357\mathrm{K})}\right)$$

$$\boldsymbol{n_v = 1.66\times10^{25}\ \mathrm{m^{-3}}\ \text{or}\ n_v = 1.66\times10^{19}\ \mathrm{cm^{-3}}.}$$

This implies that 1 in 5115 atoms is a vacancy.

A better calculation would use the atomic concentration N at 1357 K by calculating the new density at 1357 K through the thermal coefficient of volume expansion. However, its effect on the result is small.

b. The vacancy formation E_v and the melting temperature T_m in K are plotted in Figures 1Q38-1 and 1Q38-2. Table 1Q38-1 provides the values that were used in these plots.

The $10kT_m$ line is also plotted on the same graph. It seems that this is a reasonable approximation to predicting E_v. Table 1.12 has range of values for most of the metals.

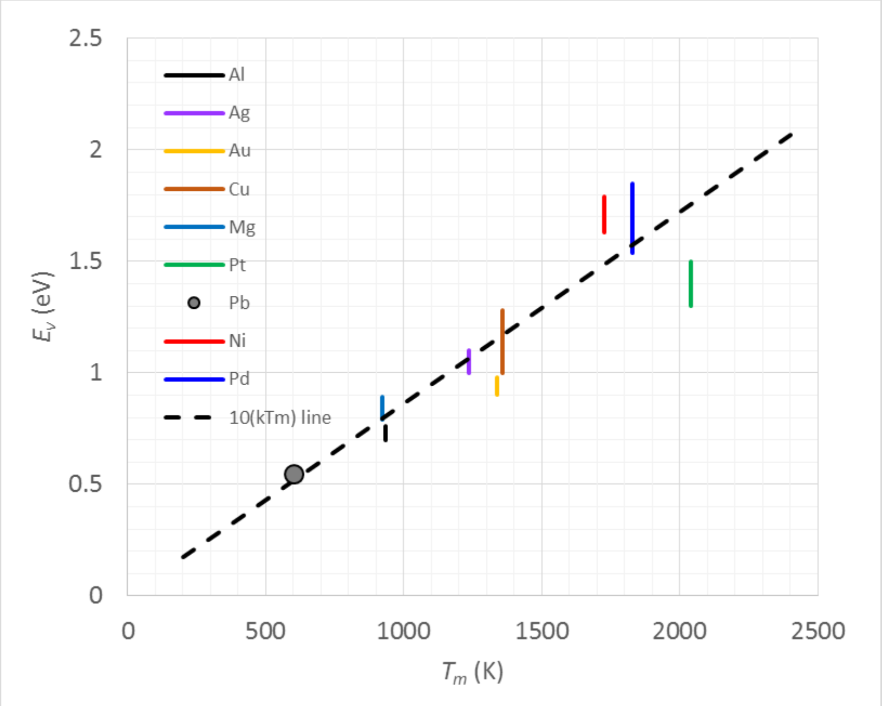

Figure 1Q38-1: Plot of vacancy formation energy versus melting temperature T_m. The $10kT_m$ line is also plotted on the same graph.

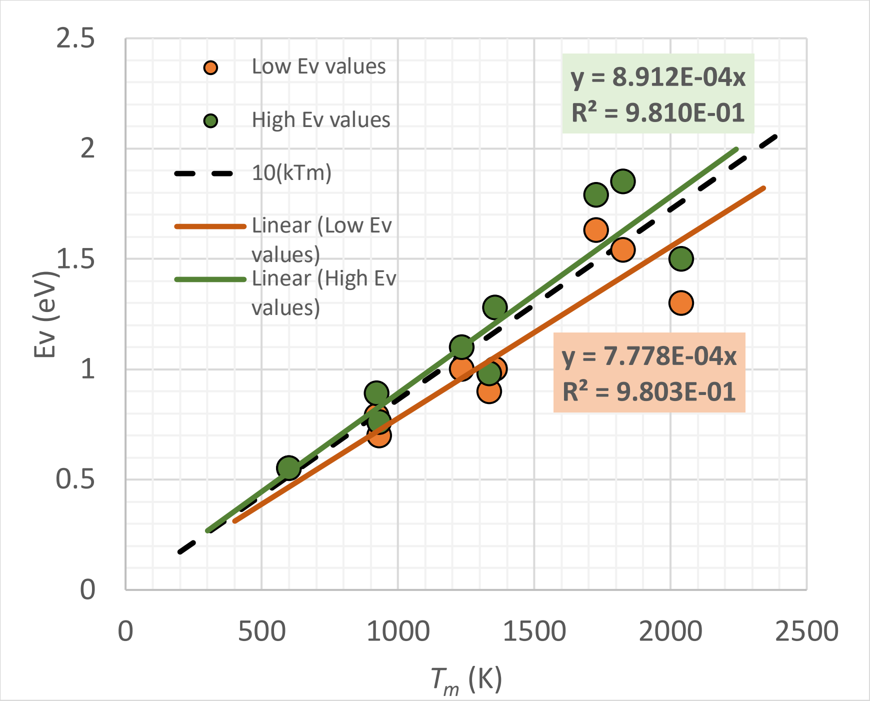

Figure 1Q38-2: Plot of vacancy formation energy versus melting temperature T_m. The $10kT_m$ line is also plotted on the same graph.

Table 1Q38-1 Values used in Figure 1Q38-2

Metal	**k (eV/K)**	**8.62E-05**	**m =**	**10**					
	Tm (C)	**Tm (K)**	**Ev (eV)**	**Tm (K)**	**Ev (eV)**	**Tm (K)**	**Ev (eV)**	**Tm (K)**	**10(kTm)**
Al	660	933	**0.7**	**933**	**0.7**	**933**		**200**	**1.72E-01**
Al	660	933	**0.76**	**933**		**933**	**0.76**	**400**	**3.45E-01**
Ag	962	1235	**1**	**1235**	**1**	**1235**		**1000**	**8.62E-01**
Ag	962	1235	**1.1**	**1235**		**1235**	**1.1**	**1500**	**1.29E+00**
Au	1064	1337	**0.9**	**1337**	**0.9**	**1337**		**2000**	**1.72E+00**
Au	1064	1337	**0.98**	**1337**		**1337**	**0.98**	**2400**	**2.07E+00**
Cu	1085	1358	**1**	**1358**	**1**	**1358**			
Cu	1085	1358	**1.28**	**1358**		**1358**	**1.28**		
Mg	650	923	**0.79**	**923**	**0.79**	**923**			
Mg	650	923	**0.89**	**923**		**923**	**0.89**		
Pt	1768	2041	**1.3**	**2041**	**1.3**	**2041**			
Pt	1768	2041	**1.5**	**2041**		**2041**	**1.5**		
Pb	328	601	**0.55**	**601**	**0.55**	**601**	**0.55**		
Ni	1455	1728	**1.63**	**1728**	**1.63**	**1728**			
Ni	1455	1728	**1.79**	**1728**		**1728**	**1.79**		
Pd	1555	1828	**1.54**	**1828**	**1.54**	**1828**			
Pd	1555	1828	**1.85**	**1828**		**1828**	**1.85**		

Comment: Usually the vacancy formation energy E_v is deduced indirectly from monitoring a property, such the resistivity of the metal, right after it has been quenched etc.

2. (1.40) **Pb-Sn solder**

Consider the soldering of two copper components using a Pb-Sn solder. When the solder melts, it wets the metal surfaces. If the surfaces are not clean or have an oxide layer, the molten solder cannot wet the surfaces and the soldering fails. Assume that soldering takes place at 250 ºC, and consider the diffusion of Sn atoms into the copper (the Sn atom is smaller than the Pb atom and hence diffuses more easily).

a. The diffusion coefficient of Sn in Cu at two temperatures is $D = 1.69 \times 10^{-9}$ cm^2 hr^{-1} at 400 ºC and $D = 2.48 \times 10^{-7}$ cm^2 hr^{-1} at 650 ºC. What is the activation energy (in eV/atom) for the diffusion of Sn in Cu?

b. What is the pre-exponential constant, D_o (in m^2/s)?

c. Calculate the rms distance diffused by an Sn atom into the copper at 250 ºC, assuming the process takes 10 seconds.

d. What should be the composition of the solder if it is to begin freezing at 250 ºC? (Consult Fig. 1Q40-1 below).

e. What are the components (phases) in this alloy at 200 ºC? What are the compositions of the phases and their relative weights in the alloy?

f. What is the microstructure of this alloy at 25 ºC?

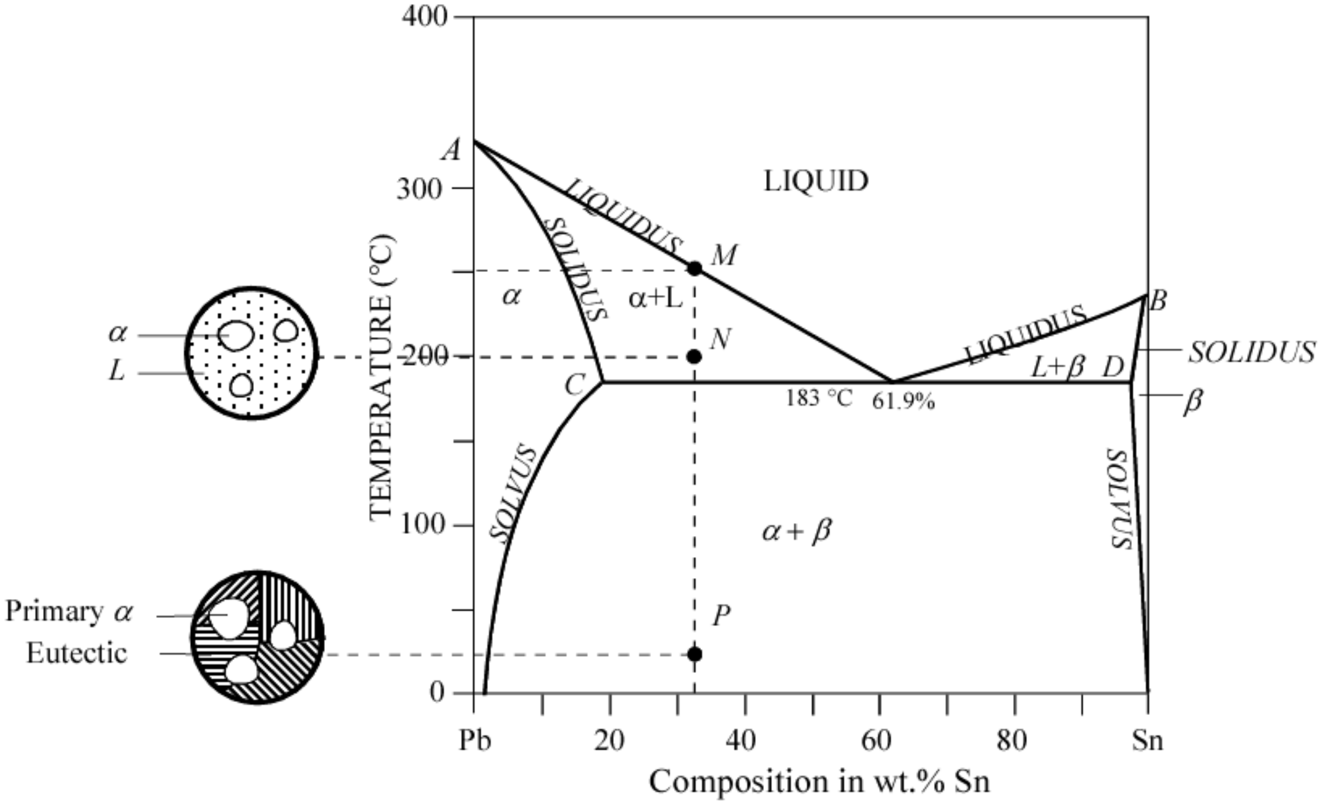

Figure 1Q40-1: The equilibrium phase diagram of the Pb-Sn alloy.

Solution

a. Given information:

Temperatures: $T_1 = 400\ °\text{C} + 273 = 673\ \text{K}$ $\qquad$ $T_2 = 650\ °\text{C} + 273 = 923\ \text{K}$

Diffusion coefficients: $D_1 = 1.69 \times 10^{-9}\ \text{cm}^2/\text{hr} = (1.69 \times 10^{-9}\ \text{cm}^2/\text{hr})(0.01\ \text{m/cm})^2 / (1\ \text{hr}) \times (3600\ \text{sec/hr})$

$D_1 = 4.694 \times 10^{-17}\ \text{m}^2/\text{s}$

$D_2 = 2.48 \times 10^{-7}\ \text{cm}^2/\text{hr} = (2.48 \times 10^{-7}\ \text{cm}^2/\text{hr})(0.01\ \text{m/cm})^2 / (1\ \text{hr}) \times (3600\ \text{sec/hr})$

$D_2 = 6.889 \times 10^{-15}\ \text{m}^2/\text{s}$

The diffusion coefficients D_1 and D_2 at T_1 and T_2 respectively are given by:

$$D_1 = D_o \exp\left(-\frac{qE_A}{kT_1}\right) \qquad\qquad D_2 = D_o \exp\left(-\frac{qE_A}{kT_2}\right)$$

where E_A is the activation energy in eV/atom and $q = 1.6\times10^{-19}$ J/eV (conversion factor from eV to J). Since

$$\frac{\exp(-x)}{\exp(-y)} = \exp(y - x)$$

we can take the ratio of the diffusion coefficients to express them in terms of E_A (eV):

$$\frac{D_1}{D_2} = \frac{D_o \exp\left(-\frac{qE_A}{kT_1}\right)}{D_o \exp\left(-\frac{qE_A}{kT_2}\right)} = \exp\left(\frac{qE_A}{kT_2} - \frac{qE_A}{kT_1}\right) = \exp\left(\frac{q[T_1 - T_2]E_A}{kT_1T_2}\right)$$

$$\therefore \qquad E_A = \frac{kT_1T_2 \ln\left(\frac{D_1}{D_2}\right)}{q(T_1 - T_2)} \qquad \text{(in eV)}$$

$$\therefore \qquad E_A = \frac{(1.381\times10^{-23}\ \text{J K}^{-1})(673\ \text{K})(923\ \text{K})\ln\left(\frac{4.694\times10^{-17}\ \text{m}^2/\text{s}}{6.889\times10^{-15}\ \text{m}^2/\text{s}}\right)}{(1.602\times10^{-19}\ \text{J/eV})(673\ \text{K} - 923\ \text{K})} \qquad \text{(in eV)}$$

$\therefore \qquad E_A = 1.068$ eV/atom

b. Now the diffusion coefficient D_o can be found as follows:

$$D_1 = D_o \exp\left(-\frac{qE_A}{kT_1}\right)$$

$$\therefore \qquad D_o = \frac{D_1}{\exp\left(-\frac{qE_A}{kT_1}\right)} = \frac{4.694\times10^{-17}\ \text{m}^2/\text{s}}{\exp\left(-\frac{(1.602\times10^{-19}\ \text{J/eV})(1.068\ \text{eV})}{(1.381\times10^{-23}\ \text{J K}^{-1})(673\ \text{K})}\right)} = 4.638 \times 10^{-9}\ \text{m}^2/\text{s}$$

To check our value for D_o, we can substitute it back into the equation for D_2 and compare values:

$$D_2 = D_o \exp\left(-\frac{qE_A}{kT_2}\right) = \left(4.638\times10^{-9}\ \text{m}^2/\text{s}\right)\exp\left(-\frac{\left(1.602\times10^{-19}\ \text{J/eV}\right)\left(1.068\ \text{eV}\right)}{\left(1.381\times10^{-23}\ \text{J K}^{-1}\right)\left(923\ \text{K}\right)}\right)$$

∴ $D_2 = 6.870 \times 10^{-15}\ \text{m}^2/\text{s}$

This agrees with the given value of $6.889 \times 10^{-15}\ \text{m}^2/\text{s}$ for D_2.

c. Now we must calculate the diffusion coefficient D_3 at $T_3 = 250\ °\text{C} + 273 = 523\ \text{K}$ (temperature at which soldering is taking place).

$$D_3 = D_o \exp\left(-\frac{qE_A}{kT_3}\right) = \left(4.638\times10^{-9}\ \text{m}^2/\text{s}\right)\exp\left(-\frac{\left(1.602\times10^{-19}\ \text{J/eV}\right)\left(1.068\ \text{eV}\right)}{\left(1.381\times10^{-23}\ \text{J K}^{-1}\right)\left(523\ \text{K}\right)}\right)$$

∴ $\text{D}_3 = 2.391 \times 10^{-19}\ \text{m}^2/\text{s}$

The rms distance diffused by the Sn atom in time $t = 10$ s (L_{rms}) is given by:

$$L_{rms} = \sqrt{2D_3 t} = \sqrt{2\left(2.391\times10^{-19}\ \text{m}^2/\text{s}\right)\left(10\ \text{s}\right)} = \mathbf{2.19 \times 10^{-9}\ m} \text{ or } \mathbf{2\ nm}$$

d. From Figure 1Q40-1, 250 °C cuts the liquidus line approximately at 33 wt.% Sn composition (C_o).

∴ $\boldsymbol{C_o = 0.33}$ (Sn)

e. For α-phase and liquid phase (L), the compositions as wt.% of Sn from Figure 1.69 or 1Q31-1 are:

$C_\alpha = 0.18$ and $C_L = 0.56$

The weight fraction of α and L phases are:

$$\boldsymbol{W_\alpha} = \frac{C_L - C_o}{C_L - C_\alpha} = \frac{0.56 - 0.33}{0.56 - 0.18} = \mathbf{0.605} \text{ or } \mathbf{60\ wt.\%\ \boldsymbol{\alpha}\text{-phase}}$$

$$\boldsymbol{W_L} = \frac{C_o - C_\alpha}{C_L - C_\alpha} = \frac{0.33 - 0.18}{0.56 - 0.18} = \mathbf{0.395} \text{ or } \mathbf{39.5\ wt.\%\ liquid\ phase}$$

f. The microstructure is a primary α-phase and a eutectic solid ($\alpha + \beta$) phase. There are two phases present, $\alpha + \beta$. (See Figure 1Q31-2)

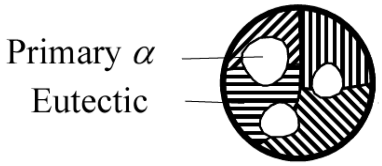

Figure 1Q40-2: Microstructure of Pb-Sn at temperatures less than 183°C.