ITESM
Q4001 Thermodynamics of materials **May, 2019**
Final Exam

By signing below, I certify all the contents of this exam come from my individual work and that all information used or assumptions made are fully cited and explained.

Name: ____________________________ Signature: ____________________

1. Demonstrate that:

   a) $\left(\frac{\partial P}{\partial V}\right)_S = -\frac{C_P}{\kappa_T C_V V}$

   b) $\left(\frac{\partial S}{\partial P}\right)_V = \frac{\kappa_T C_P}{\alpha T} - \alpha V$

2. The change in enthalpy when 1 mol of ice is melted at 273 K is 6008 J.

   a) Calculate the standard enthalpy of fusion for ice, $\Delta_\mathrm{m} H^{\ominus}$.

   b) Calculate the heat released when 100 g of water supercooled at 250 K solidify.

   c) Calculate the change in entropy for the fusion of ice $\Delta_\mathrm{m} S$ at 273 K.

   d) Calculate the change in entropy for the fusion of ice $\Delta_\mathrm{m} S$ at 250 K.

3. Produce a phase diagram for CaF_2 that includes the phases $CaF_2\,(\alpha)$, $CaF_2\,(\beta)$, $CaF_2\,(l)$ and $CaF_2\,(g)$. The diagram should clearly show the temperatures for the triple points and the boling temperature.

   Calculate also, the enthalpies for the transformation $CaF_2\,(\alpha) \to CaF_2\,(\beta)$ and for the melting of $CaF_2\,(\beta)$.

   Use the following for the vapor pressures of the species above expressed as

$$\ln(P/\mathrm{atm}) = -\frac{A}{T} + B \ln T + C$$

	A	B	C
$CaF_2\,(\alpha)$	54,350	−4.525	56.57
$CaF_2\,(\beta)$	53,780	−4.525	56.08
$CaF_2\,(l)$	50,200	−4.525	53.96

4. The excess free energy for the liquid mixture Fe–Mn at 1863 K is given as a function of composition in the following table.

x_Mn	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\Delta_\mathrm{mix} G^\mathrm{xcs}/\mathrm{J}$	395	703	925	1054	1100	1054	925	703	395

   a) Does this behavior fit that of a regular solution? Plot and explain.

   b) If it does, find Ω. Otherwise, try to use other model to fit the data.

   c) Calculate $\Delta_\mathrm{mix} G$ at $x_\mathrm{Mn} = 0.4$.

   d) Find $G^\mathrm{xcs}_\mathrm{Fe}$ and $G^\mathrm{xcs}_\mathrm{Mn}$ at $x_\mathrm{Mn} = 0.6$.

5. Copper, present as an impurity in liquid Pb, can me removed by adding PbS to the Cu–Pb alloy, allowing for the exchange reaction

$$\mathrm{Cu}_{\,(\mathrm{sln})} + \mathrm{PbS}_{\,(\mathrm{s})} \rightleftharpoons \mathrm{CuS}_{\,(\mathrm{s})} + \mathrm{Pb}_{\,(\mathrm{l})}$$

to come to equilibrium.

The solid sulfides are mutually immiscible, Pb is insoluble in solid Cu and the Cu liquidus below 850 °C, can be represented by

$$\log x_{\mathrm{Cu}} = -\frac{3500}{T} + 2,261$$

where x_{Cu} is the solubility of Cu in liquid lead. If Cu obeys Henry's law in the liquid Pb, calculate the extent to which Cu can be removed from liquid Pb by this process at 800 °C. Would the extent of purification of lead be increased or decreased by temperature?

The free energies of formation for PbS and CuS are respectively:

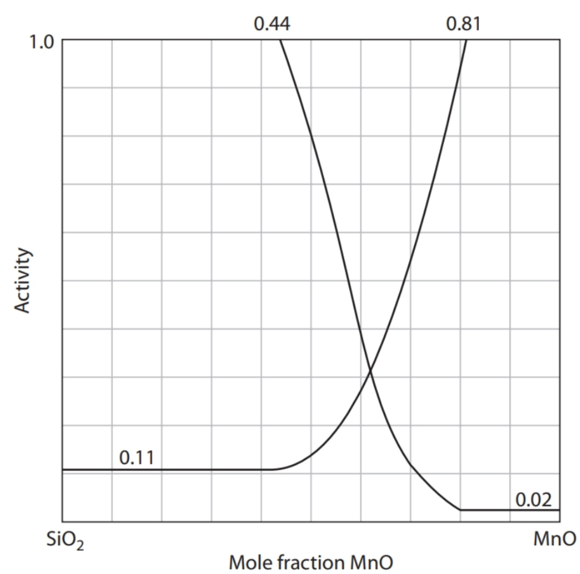
$$\begin{aligned} \Delta G^{\circ} &= -163,200 + 88.03T \quad \mathrm{J} \\ \Delta G^{\circ} &= -131,800 + 30.79T \quad \mathrm{J} \end{aligned}$$

6. Silicon and manganese are commonly used together as deoxidizers for liquid steel. At 1600 °C,

$$\begin{aligned} [\mathrm{Mn}]_{(\mathrm{l,wt}\,\%\mathrm{in\ Fe})} + [\mathrm{O}]_{(\mathrm{l,wt}\,\%\mathrm{in\ Fe})} &= \mathrm{MnO}_{\,(\mathrm{s})} \qquad K = 23.5 \\ [\mathrm{Si}]_{(\mathrm{l,wt}\,\%\mathrm{in\ Fe})} + 2\,[\mathrm{O}]_{(\mathrm{l,wt}\,\%\mathrm{in\ Fe})} &= \mathrm{SiO}_{2\,(\mathrm{s})} \qquad K = 27,840 \end{aligned}$$

a) Which of the two elements is more effective in the removal of oxygen?

b) It turns out that the mixture of Mn and Si is more effective as deoxidizing agent than either of the two elements by themselves. Explain why this is using the following figure



of the activities of MnO and SiO_2, with respect to solids as the standard states in MnO–SiO_2 melts at 1600°C.

Due date: Thursday, may 16th no later than 6:00pm.