1   315 Problems

1)   Use the Ellingham Diagram (reproduced here as Figure 1.1) to answer the following.

1. Find the temperature and partial pressure of O_2 where Ni(s), Ni(l), and NiO(s) are in equilibrium.

2. Can the same equilibrium be achieved with H_2 and H_2O instead of oxygen? If so, what is the ratio of H_2/H_2O?

3. At 1245ºC, H_2, and H_2O with a ratio of partial pressures of 10:1 is flowed through a tube furnace containing a crucible filled with MnO powder. Determine the driving force for the reaction

4. Can you safely melt aluminum in a magnesia (MgO) container? Why or why not? What is the resulting reaction and its driving force?

5. Establish the T-log P_{O_2} phase diagram between 1000ºC and 1500ºC fort he Mn-O system at 1 atm total pressure.

2)   In the days before the industrial revolution the P_{CO_2} in the earth's atmosphere was 275 ppm. Use the data in Figure 1.2 to calculate how high one would need to heat $CaCO_3$ to decompose it at a P_{CO_2} for the preindustrial concentration of 275 ppm and for present day P_{CO_2} (You will have to look this up, please give your source). Also calculate how high one would need to heat $CaCO_3$ to decompose it if the CO_2 level in the atmosphere reaches 500 ppm.

3)   Based on Raoultian liquid solution behavior, calculate the Sn-Bi eutectic phase diagram (using Excel, Mathematica, MATLAB, etc). Assume that there is negligible solid solubility of both Sn and Bi in the other component, and that $\Delta C_P \approx 0$ for both end members. Use the following melting points and enthalpies of fusion:

Material	Tm(K)	$\Delta H(s \rightarrow l)(J/mol)$
Sn	505.12	7030
Bi	544.59	11300

4)   Use MATLAB or a spreadsheet to calculate liquidus and solidus lines for a "lens-type" T-X diagram for the A-B system, using the data below. You may assume both the liquid and solid solutions behave ideally.

Type	Tm(ºC)	$\Delta H_m(J/mol)$
A	910	34700
B	1300	49800

1. Plot the T vs. X phase diagram. Label each region on the diagram with the phases present and the degrees of freedom.

2. For the temperatures 800ºC, 1100ºC, and 1500ºC, draw plots of the activity of component A vs. composition. Include two plots for each: One with respect to liquid as the reference state and one with respect to solid as the reference state.

5)   Based upon the temperature at the top of the miscibility gap in the Cr-W system (see Figure 1.3), do the following:

1. Predict the miscibility gap (solvus) and spinodals based upon the regular solution model. Use the spreadsheet and plot the results.

2. Compare your miscibility gap with the experimental one in the attached figure. Speculate about why there might be differences.
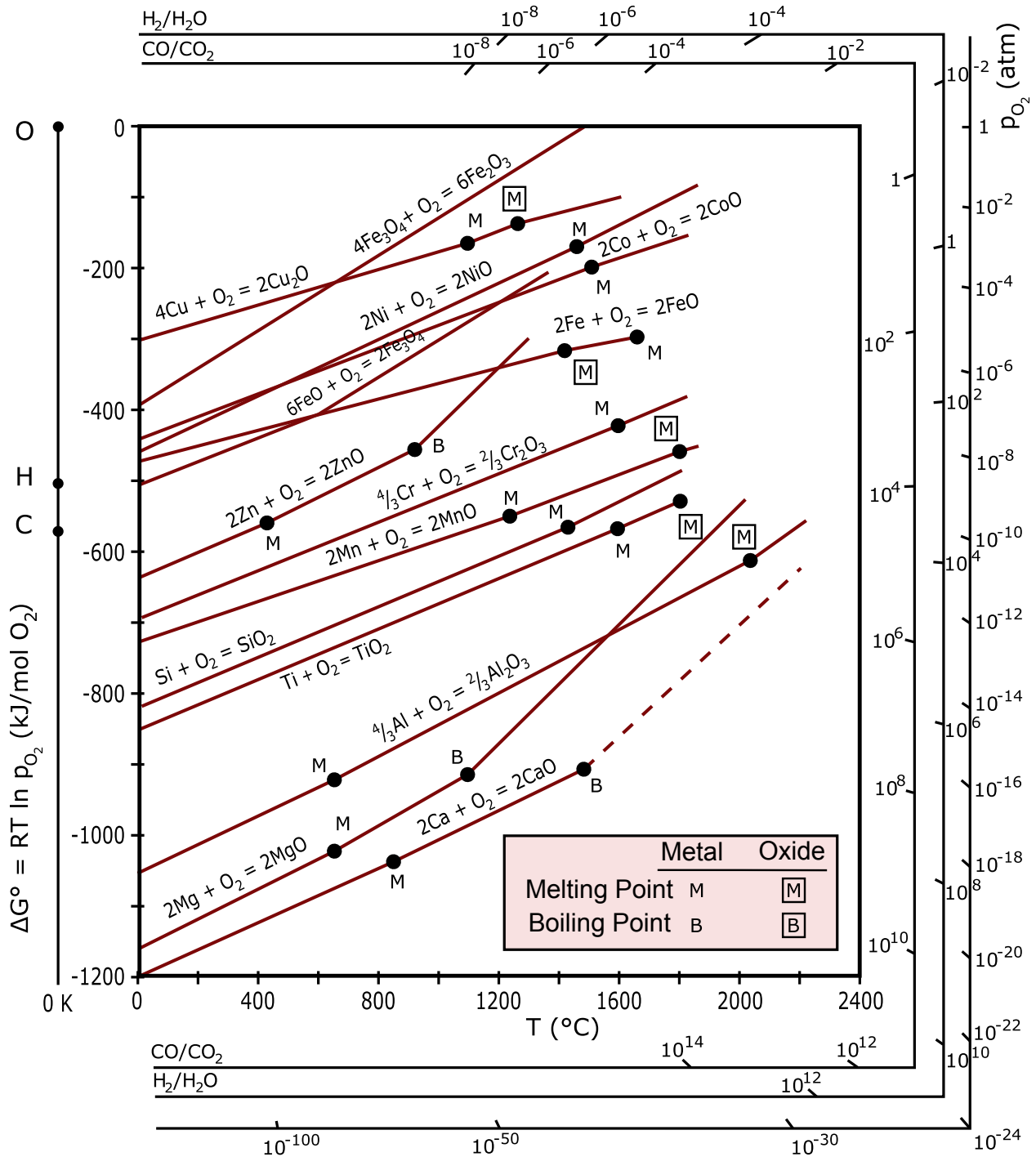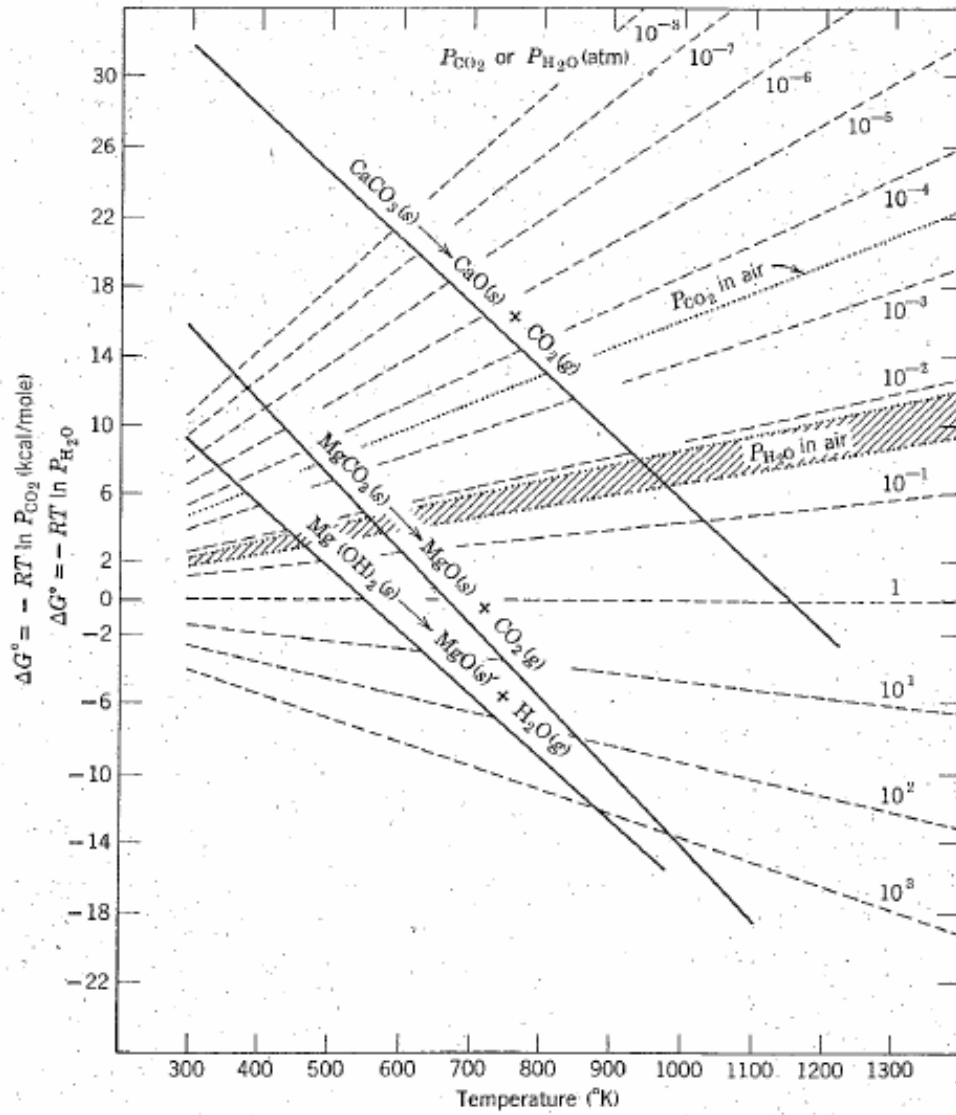
Figure 1.1: Ellingham diagram.

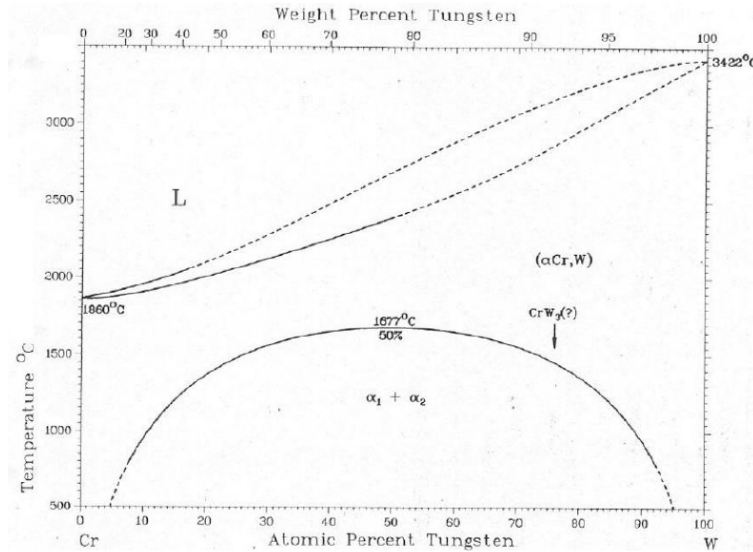**Figure 1.2:** Thermodynamic data for Mg and Ca oxides and carbonates.

Figure 1.3: Cr-W Phase diagram.

6)   Consider the Pb-Sn phase diagram (see Figure 1.4).

1. Label each region on the diagram with the degrees of freedom.

2. Sketch free energy vs. composition curves for all phases at 150°C, 200°C, 250°C, and the eutectic temperature.

3. For each temperature from part (b), draw plots of the activity of Sn vs. composition. Include two plots for each: One with respect to liquid as the reference state and one with respect to solid as the reference state. You may assume the liquid solution to be Raoultia. At 150°C, only plot activity of Sn vs. composition with respect to the solid reference state. At 250°C, only plot activity of Sn vs. composition with respect to the liquid reference state.

7)   Calculate and plot the liquidus projection of the ternary phase diagram for the NaF-NaCl-NaI system. The melting temperatures and heats of fusion are as follows: NaF (990°C, 29,300 J/mol), NaCl (801°C, 30,200 J/mol) and NaI (659.3°C, 22,300 J/mol). Assume and ideal liquid solution and negligible solid solubility. Compare your result with the experimental diagram shown in Figure 1.5. Why might they be different?

8)   On the liquidus projection diagram for the hypothetical system A-B-C shown in Figure 1.6), complete the following:

1. Label primary phase fields

2. Draw the subsolidus compatibility joins.

3. Label all the binary and ternary invariant points.

4. Indicate the directions of falling temperature (binaries and ternary).

5. Sketch all the binary phase diagrams (including those formed by subsolidus compatibility joins).
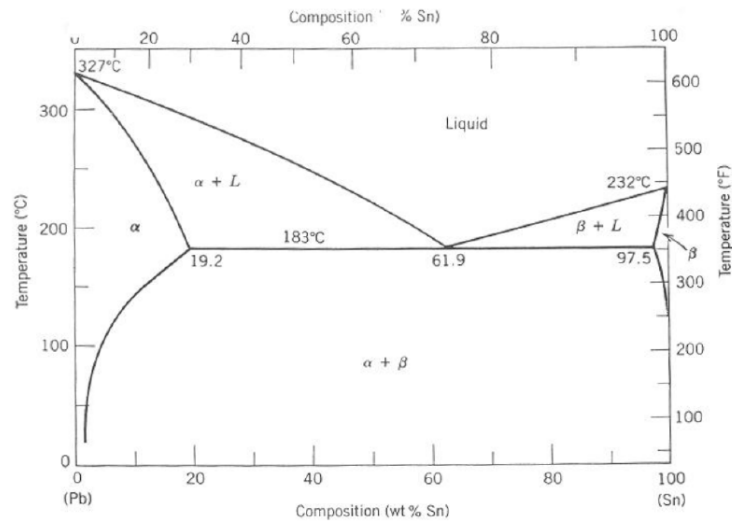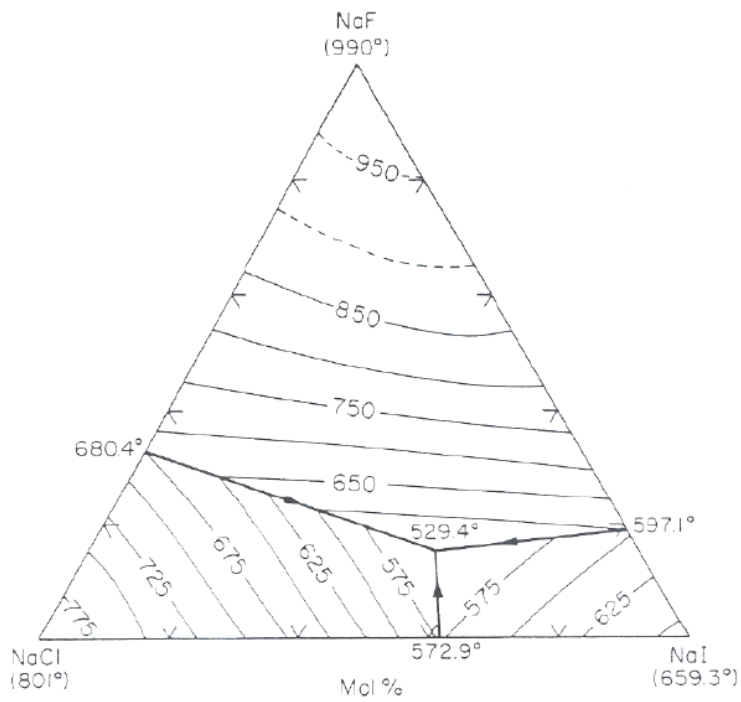
Figure 1.4: Pb-Sn phase diagram.

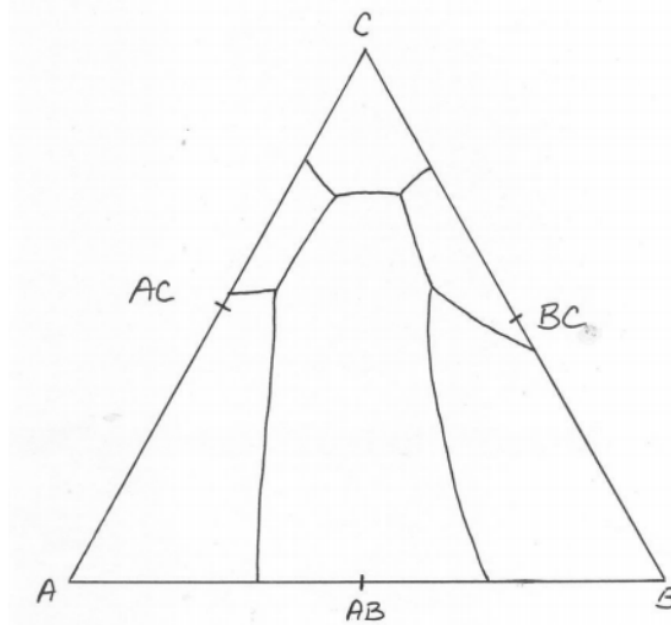**Figure 1.5:** NaF-NaCl-NaI phase diagram. From ref. [?].

5

Figure 1.6: Liquidus projection diagram.

9)   Using the attached liquidus projection diagram for the hypothetical system A-B-C shown in Figure 1.7, complete the following:

1. Determine the equilibrium crystallization path for the composition marked with the star.

2. Determine the microstructural constituents:

   (a) Just prior tot he liquid striking the phase boundary (liquid + solid 1 + solid 2).
   (b) At the eutectic but just prior to eutectic crystallization.
   (c) After crystallization is complete.

10)   On the $(LiCl)_2 - CaCl_2 - (KCl)_2$ phase diagram shown in Figure 1.8, draw isothermal sections at the following temperatures: (note- Ternary eutectic E_1 is at 332°C and ternary eutectic E_2 is at 412°C)

1. 600°C

2. 450°C

3. 400°C

4. 300°C

5. Also determine the precise (not schematic!) $(LiCl)_2 - KCaCl_3$ phase diagram.

11)   (Bonus question - 10% of problem set value) Starting with the regular solution model, prove that regardless of how positive the interaction parameter (or heat of mixing) might be, the inital slope on any free energy vs. composition curve must be infinitely negative on the left side ($X_B \rightarrow 0$) and infinitely positive on the right side ($X_B \rightarrow 1$).

12)   A steel tank contains hydrogen at 15 atm pressure. If the solubility of hydrogen in steel is $1x10^{-2}$ g/cm^3 under 15 atm pressure, the diffusion coefficient is $8x10^{-5}$cm^2/s at room temperature and the tank is placed in a vacuum, calculate the flux of hydrogen through a 3.5 mm thick wall.
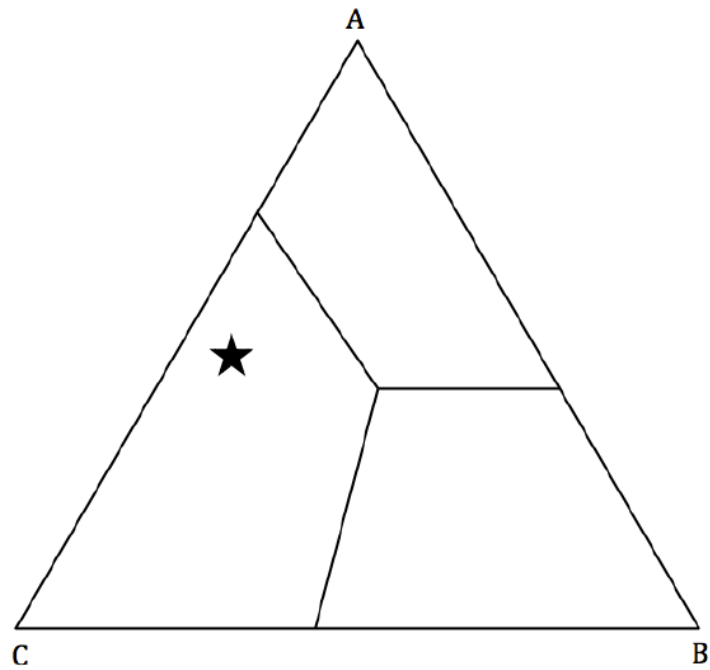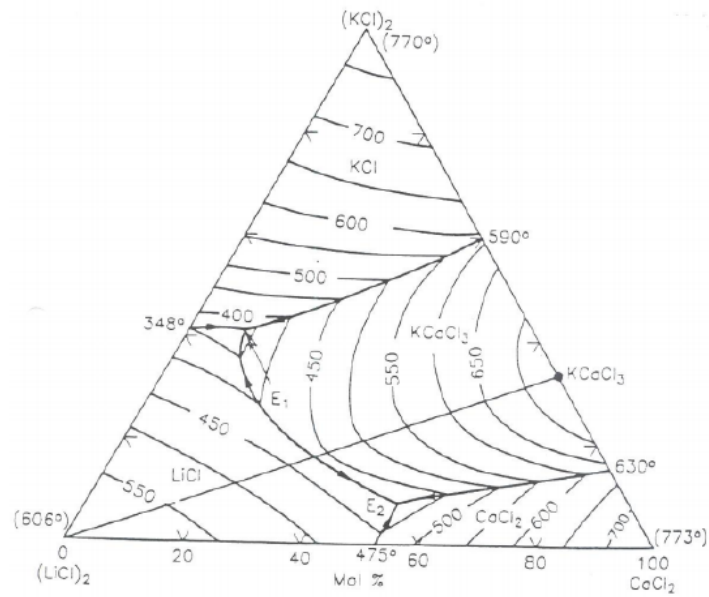
Figure 1.7: Liquidus projection diagram.

Note: Figure obtained from Ceramists diagram 7418

Figure 1.8: $(LiCl)_2 - CaCl_2 - (KCl)_2$ phase diagram.

13)   Austenite ($\gamma-$Fe) with .85 wt% carbon has a diffusion coefficient of $1.9 \times 10^{-11} \text{m}^2/\text{s}$ at 900°C.

1. Determine the jump distance in terms of the lattice parameter a_o and the coordination number for carbon diffusion in this structure.

2. How many jumps does a carbon interstitial make each second? Assuming a lattice vibration frequency of 10^{13}s^{-1}, what fraction of jumps is successful?

3. Calculate and compare the random walk distance with the total distance (back and forth) traveled by an interstitial carbon atom in one second.

14)   Ferrite ($\alpha-$Fe) (BCC structure) dissolves carbon to a lesser extent than austenite (FCC structure).

1. Determine the jump distance in terms of the lattice parameter a_o and the coordination number for carbon diffusion in this structure.

2. Given the data in Table 2.1 of Porter, Easterling & Sherif, make an Arrhenius plot of diffusion coefficients of carbon and nitrogen from room temperature to 800°C.

3. A different interstitial solute diffuses at a rate of $4.1 \times 10^{-2} \text{mm}^2/\text{s}$ at 300°C and $7.3 \times 10^{-2} \text{mm}^2/\text{s}$ at 600°C. Determine its activation energy and pre-exponential factor.

15)   Write a MATLAB code to evaluate the composition as a function of distance for the draining plate problem.

1. For $t/\tau = 0.05$ how many terms in the series is necessary to obtain a composition that is converged to within 1% of the exact answer. The percent error is the maximum value of $|c(x) - c_{exact}(x)|/c_{exact}(c) \times 100$. To determine the exact answer evaluate the summation to $j = 200$. L=100um, $C_o = 0.1$at. %

2. Plot the converged solution as a function of x for $t/\tau = 0.05, 0.5, 1.0, 2.0$.

3. For what approximate value of t/τ does a single term in the summation with $j = 0$ provide an approximation to the exact solution within 10%?

16)   (After Shewmon 2-13) We wish to consider the rate at which the vacancy concentration increases in a specimen after an increase in temperature. We assume that the vacancy concentration in the lattice near the free surface, grain boundaries and edge dislocations will rise to the new equilibrium value of the new temperature as soon as the temperature is raised. The vacancy concentration far from these vacancy sources rises only as fast as vacancies can diffuse to the region from the source.

1. Assume that vacancies come only from grain boundaries, and the grain diameter is approximately 1 mm. Calculate the relaxation time in two regimes, at high temperatures where the diffusion coefficient Dv is $10^{-5}\text{cm}^2/\text{s}$.

2. Calculate the relaxation time (τ) given a dislocation line length (dislocation density) of $10^7 \text{cm}/\text{cm}^3$. (Hint: First, calculate the distance between dislocations, i.e, the vacancy sources.)

17)   The diffusion coefficient of carbon in austenite can be approximated as:

$$D_c = 0.2 \exp\left(\frac{-136,000 \text{ J/mol}}{RT}\right) \text{ cm}^2/\text{s}$$

1. How long does it take for the composition $c_{0.5}$ during carburization to penetrate .45 mm at 900°C? How long for 5 mm?

2. What annealing temperature is required to double the penetration in a given time?

18)   Consider two blocks initially one pure A and the other pure B that are welded together and annealed at 1100°C. Plot the diffusion profile as a function of distance after half an hour. Assume that the diffusion coefficient of both specie is $D = 4.5 \times 10^{-11} \text{m}^2/\text{s}$ and that D is not a function of concentration.

19)   Calculate the enthalpy and entropy of vacancy formation ($\Delta H_v, \Delta S_v$) for a system given the equilibrium concentration of vacancies (X_v^β) is 1.7×10^{-8} at 440 K and 1.5×10^{-5} at 650 K.

20)   Given that $D = \frac{1}{6}\Gamma v \alpha^2$, consider the diffusion of vacancies in an FCC lattice:

1. Let $\frac{\Delta S_m}{R} = 2$ and $v = 10^{13}\text{s}^{-1}$. Calculate the pre-exponential factor D_o for vacancies (assume $a_o = 0.4$ nm.)

2. If $\Delta H_m = 6.5$ kJ/mol, calculate D_v for vacancies at 750°C

21)   Below are the linear thermal expansion ($\Delta L/L_o$) and X-ray lattice parameter ($\Delta a/a_o$) results at different temperatures for aluminum. Calculate and plot $\ln X_v$ from this data versus T^{-1} and determine the enthalpy and entropy of vacancy formation in aluminum. Show all equations used.

22)   Below is a table of linear thermal expansion ($\Delta L/L$) and lattice parameter expansion ($\Delta a/a$) vs. temperature for aluminum. Calculate and plot $\ln X_v$ form this data versus $1/T$ and determine the enthalpy and entropy of vacancy formation in this material. Show all equations used.

23)   A gold specimen is quenched from 700°C to room temperature (25°C). An identical specimen is air cooled from 700°C to room temperature. The difference in their resistances is $\Delta \rho_o$. The quenched specimen is annealed at 40°C for 120 hours and then annealed at 60°C. Resistivity measurements were taken periodically by quenching the sample to room temperature. From the two slopes shown in attached Figure 2-16, find ΔH_{motion}.

24)   Write balanced Kröger-Vink reactions for the following reactions, assuming full ionic charge for all ionic species.

1. Schottky defect formation in Li_2O

2. Anion Frenkel defect formation in Nb_2O_5

3. Oxidation of CdO to yield $Cd/O < 1/1$ (write both possible reactions)

4. Doping Al_2O_3 with ZnO to produce oxygen vacancies.

25)   Pure ZnO is an n-type semiconductor dominated by oxygen vacancies, but it can be further donor-doped by substituting Al^{3+} for Zn^{2+} sites.

1. Draw a schematic Brouwer diagram as a function of pO_2 at fixed Al content.

2. Draw a schematic Brouwer diagram at fixed pO_2 as a function of Al content. Include all relevant point defect reactions and mass-action relationships.

26)   Given the following oxygen ion diffusivities for calcia-stabilized zirconia (CSZ) of composition $(ZrO_2)_{0.85}(CaO)_{0.15}$ and density 5.5 g/cm^3, calculate a) the ionic conductivity at each temperature, and b) the enthalpy of motion. Assume oxygen vacancies are the dominant defect.