

Thermodynamics: Quiz #1

April 4, 2008

1. (10%) What is heat capacity? Calculate the difference between C_p and C_v .
2. (20%) Find the ΔS_{total} and ΔU of a system when 1 mole of an ideal gas expands from V_A to V_B through the following ways.
 - i) isothermally and reversibly ($P=P_{\text{ext}}$)
 - ii) adiabatically and reversibly ($P=P_{\text{ext}}$)
 - iii) isothermally and irreversibly ($P_{\text{ext}}=0$)
 - iv) adiabatically and irreversibly. ($P_{\text{ext}}=0$)
3. (10%) In a Carnot cycle shown in Figure 1 as below, show that (a) $\frac{V_b}{V_a} = \frac{V_c}{V_d}$ and (b) the efficiency is equal to $\frac{T_2 - T_1}{T_2}$.
4. (10%) Show that $\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$ which is called chemical potential (μ_i). (10%)
5. (10%) Show that $S = k \ln \Omega$ through statistical approach.

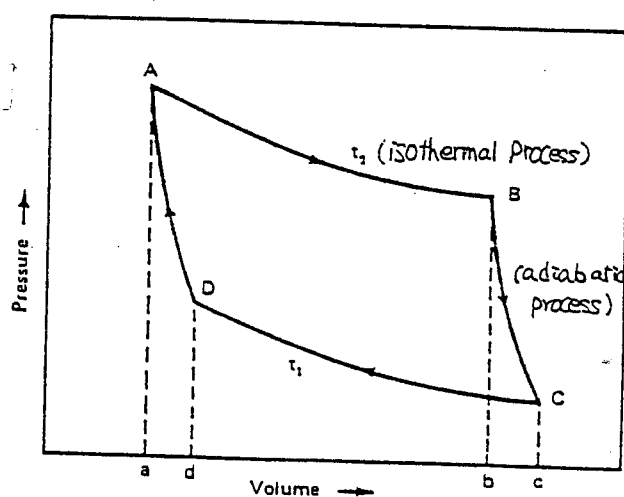


Fig. 1.

(over)

6. (15%) A rigid container at constant temperature is divided into three compartments of equal volume by two partitions. Each compartment contains 1 mole of ideal gas A, B, and B in series. All gases are at 1 atm pressure.
- Calculate the increase in entropy, by classical and statistical methods, which occurs when the partition between A and B is removed.
 - Calculate the increase in entropy, by classical and statistical methods, which occurs when all three partitions are removed.
 - If each compartment contains 1 mole of A, 2 moles of B, and 0 moles of B in series, respectively and the first partition between A and B gases is removed, calculate the increase in entropy and discuss the result with the result from (b).
7. (10%) Using the Second Law of Thermodynamics, show that $\Delta G=0$ and $\Delta G<0$ for the equilibrium and the spontaneous process of a reaction, respectively and state the conditions to use these.
8. (15%) A particular substance undergoes a reversible expansion from an initial pressure of 20 atm. to a final pressure of 8 atm. The path of the process is described by the equation

$$P = \frac{36}{V} - 4$$

where P is in (atm.) and V is in (liter/mole). If ΔU for this change in state is -1400 J/mol , determine (a) W, (B) Q, and (c) ΔH in (J/mol). Note: 1 (atm)(liter)=101.3 J

Please answer the following question.

I have missed () classes during the period of 3/3~4/4/08

Thermodynamics: Quiz #2

May 9, 2008

1. (20%) (a) One mole of supercooled liquid Ag is adiabatically contained at 1224K. Calculate (a) the fraction of the silver which spontaneously freezes and (b) the entropy produced by the freezing.

$$\Delta H^M = 11,090 \text{ J at } T_m = 1234\text{K}$$

$$C_{p,Ag(l)} = 30.5 \text{ J/mole K}$$

$$C_{p,Ag(s)} = 21.30 + 8.54 \times 10^{-3} T + 1.51 \times 10^{-5} T^{-2} \text{ J/mole K}$$

2. (20%) (a) Derive the Clausius-Clapeyron equation and (b) calculate the molar heat of evaporation, $\Delta H_{(l-v)}$, and (c) the molar heat of melting, $\Delta H_{(s-l)}$, of Zn at the triple point and with following information:

$$\ln P^*(\text{atm}) = -15,780/T - 0.755 \ln T + 19.25 \quad (\text{vapor pressure of solid Zn})$$

$$\ln P^*(\text{atm}) = -15,250/T - 1.255 \ln T + 21.79 \quad (\text{vapor pressure of liquid Zn})$$

3. (10%) Using Gibbs-Helmholtz equation, show that $\Delta H'^{\text{Mix}}$ of an ideal gas is equal to zero.

4. (10%) Show that $\Delta G^M = \Delta G^{M,\text{id}} + G^{\text{xs}}$

$$\text{using } G_i^o, \bar{G}_i \text{ and the facts that } G^M = \Delta G^{M,\text{id}} + G^{\text{xs}}.$$

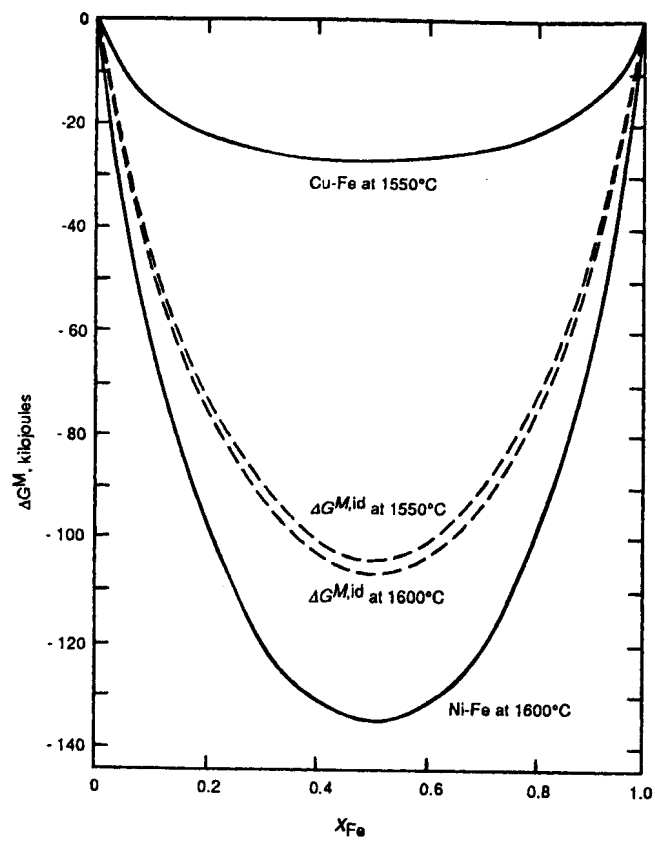
5. (20%) (a) Explain why we do not obtain a completely ordered or segregated solution when A-B bond energy is different from A-A and B-B bond energy, (b) What is the limiting conditions to use Q-C model for a solution? (c) Estimate ϵ_{AB} for the Au(fcc)-Cu(fcc) solid solution below if $\epsilon_{AB} = 1.1\epsilon_{AA} = 1.2\epsilon_{BB}$ and (d) calculate the ΔG^M at 1100K at $X_{Au} = 0.7$:

$$G^{\text{XS}} = -28,280 X_{Au} X_{Cu} \quad (\text{J})$$

6. (20%) (a) Using the free energy diagram for Ni-Fe (at 1600K) below, (a) find the G^M of the solution with $X_{Fe} = 0.2, 0.4, 0.6$, and 0.8 , respectively and (b) plot a_{Ni} and a_{Fe} vs X_{Fe} . Show your detailed calculations. Note: $G_{Ni}^0 = -90.33$ KJ/mol, and $G_{Fe}^0 = -89.34$ KJ/mol at 1600K.

Please answer the following question.

I have missed () classes during the period of 4/07~5/09/08



Thermodynamics: Quiz #3 (Final)

June 13, 2008

1. (a) Express the state functions U, H, A, and G in differential forms using thermodynamic first and second laws.
 (b) Show that the Raoult's law works for the solvent where the Henry's law works for the solute B.
2. (a) Derive the Clausius-Clapeyron equation and (b) calculate the molar heat of melting, $\Delta H_{(s-l)}$, of substance A at the triple point with following information:

$$\ln P^*(\text{atm}) = -\frac{44400}{T} - 1.01 \ln T + 21.88 \quad (\text{vapor pressure of solid A})$$

$$\ln P^*(\text{atm}) = -\frac{40350}{T} - 1.21 \ln T + 23.79 \quad (\text{vapor pressure of liquid A})$$

3. (10%) Demonstrate that if the activity coefficients of a binary solution can be expressed as

$$\ln \gamma_A = \alpha_1 X_B + \frac{1}{2} \alpha_2 X_B^2 + \frac{1}{3} \alpha_3 X_B^3 + \dots$$

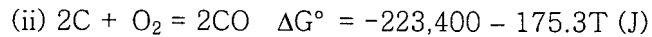
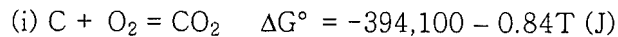
$$\text{and } \ln \gamma_B = \beta_1 X_A + \frac{1}{2} \beta_2 X_A^2 + \frac{1}{3} \beta_3 X_A^3 + \dots$$

over the entire composition range, then $\alpha_1 = \beta_1 = 0$, and that if the variation of the activity coefficients can be represented by the quadratic terms alone, then $\alpha_2 = \beta_2$.

4. (20%) A binary A-B system shows a regular solution behavior with $\Omega = 14,421.5 \text{ J}$.
 (a) Find out the compositions of the separated phases at 700K.
 (b) Estimate the activity of B when $X_B = 0.40$ at 700K.
 (c) Calculate the ratio of the separated phases at 700K. Note the molecular weights of A and B elements are 45 and 60, respectively.
5. (20%) Al_2O_3 , which melts at 2324K and Cr_2O_3 , which melts at 2538K form

complete ranges of solid and liquid solutions. Assuming that $\Delta S_{mCr_2O_3}^o = \Delta S_{mAl_2O_3}^o$ and that the solid and liquid solutions in the system $Al_2O_3 - Cr_2O_3$ behave ideally, calculate

- (a) The temperature at which equilibrium melting begins when an alloy $X_{Al_2O_3} = 0.5$ is heated
 - (b) The composition of the melt which first forms
 - (c) The temperature at which equilibrium melting is complete
 - (d) The composition of last-formed solid (Note: $\Delta H_{mAl_2O_3}^o = 107,500 \text{ J}$)
6. (20%) A CO_2 - CO - H_2 - H_2O gas mixture at a total pressure of 1 atm exerts an oxygen partial pressure of 10^{-7} atm at $1600^\circ C$. Use the data below
- i) In what ratio was CO_2 and H_2 mixed to produce this value of P_{O_2} ?
 - ii) What is the P_{CO} ?
 - iii) What oxygen partial pressure is exerted by the equilibrium gas mixture produced by mixing CO_2 and H_2 in the ratio 3:1?



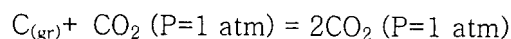
7. (10%)

Consider the partial decomposition of gaseous P_4 according to $P_{4(g)} = 2P_{2(g)}$.

- (a) Calculate the temperature at which X_{P_4} and X_{P_2} are 0.6 and 0.4, respectively at total pressure of 1 atm.
- (b) Find total pressure at which X_{P_4} and X_{P_2} are 0.6 and 0.4, respectively at 1800K.

For the decomposition reaction $\Delta G^\circ = 225,400 + 7.90 T \ln T - 209.4T \text{ (J)}$

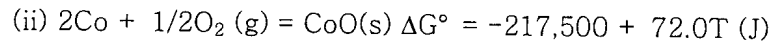
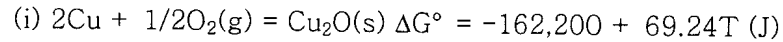
8. (30%) (a) (5%) Using the information provided in Prob. 6, find out the equilibrium temperature for each reaction below,



- (b) (10%) Find out the equilibrium P_{CO}/P_{CO_2} ratio at the same temperature numerically if total pressure is 1 atm.
- (c) (10%) Find out the oxygen partial pressure by calculation which is at

equilibrium with CO and CO₂ at the ratio.

(d) (5%) What are the ranges of the CO/CO₂ ratio and oxygen partial pressure to reduce Cu₂O selectively from the powder mixture of CoO and Cu₂O at 900°C. R=8.3144 J/K. Show the results graphically using the Diagram provided. Check with following information.

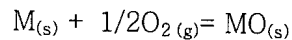


9. (10%) $\text{H}_2 + 1/2\text{O}_2 = \text{H}_2\text{O}$ $\Delta G^\circ = -247,500 + 55.85T \text{ (J)}$ for 298–2000°C. Use this information and Ellingham diagram provided,

(a) Find the range of pressure ratio of $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ to reduce MnO₂ at 900K.

(b) Find the same for $P_{\text{CO}}/P_{\text{CO}_2}$.

10. (10%) Using the definition of activity, P_i/P_i° , show that the reaction constant, K, can be expressed as $K = a_{\text{MO}}/a_{\text{M}} P_{\text{O}_2}^{1/2}$ for the reaction below. Note that M_(s) and MO_(s) are not pure in this system.



11. (Bonus 20%) see the problem in the back of the Ellingham diagram.

12. Please answer the following question.

I have missed () classes during the period of 5/12~6/15/08

Have a wonderful summer!!