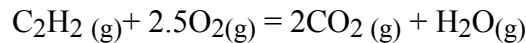# South Dakota School of Mines and Technology
Department of Metallurgical Engineering

2001

1. Find the adiabatic flame temperature for the combustion of C_2H_2. Use the data below. DRAW CALCULATION SCHEMATICS.
   a. With an oxygen-nitrogen mixture which is 50% O2 and 50% N_2. The mixture starts at a temperature of 1000 K and the C_2H_2 starts at <u>minus 23 °C</u>.

   b. Find the adiabatic flame temperature for the combustion of C_2H_2. With air (21% O2 and 70% N_2). The air and the C_2H_2 start at 298°K.

$$C_2H_2{}_{(g)} + 2.5O_2{}_{(g)} = 2CO_2{}_{(g)} + H_2O_{(g)}$$

Species	Heats of Formation (Calories/g mole at 298°K)	C_p (cal/ gmole °K)
$C_2H_2{}_{(g)}$	54,190	19.0
$H_2O_{(g)}$	-57,800	10.5
$CO_2{}_{(g)}$	-94,000	13.6
$O_2{}_{(g)}$		8.6
$N_2{}_{(g)}$		7.0

2. Using the attached JANAF Tables determine $\Delta H°$ K for the reaction below at 1300 K.

$$Cu_{(sol)} + F_2{}_{(gas)} = CuF_2{}_{(liq)}.$$
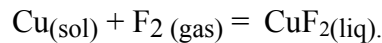
3. a) Use the JANAF Tables to determine the amount of heat it would take to raise one gram mole of pure solid Cu at 500 K to gaseous Cu at 3000 K.

   b)   Draw a calculation schematic for the above computation assuming the only data available are heat capacities and heats of transformations.

4. The atmospheric pressure on Pikes Peak on a particular day is 0.70 atm. What is the temperature of boiling water under this pressure? The heat of vaporization of water is 40,680 J/gmole.

5. At what pressure would the melting temperature of Pb be reduced by 1 one Kelvin degree to 599 K. The densities of $Pb_{(s)}$ and $Pb_{(l)}$ are 10.5 and 10.3 g/cm^3, respectively. The heat of fusion for Pb is 4794 J/gmole and its molecular weight is 207.

6. At Base Camp on your ascent of Mt. Everest you note that the water for your tea boils at boils at 90 °C. What is the barometric pressure? The heat of vaporization of water is 40,680 J/gmole.

1. Write the first four of the "Big Six Equations" relating pressure, fugacity, mole fraction, and activity to Gibbs energy.

2. Ellingham Diagram: find

a) The pressure of O_2 in equilibrium with V and V_2O_3 at 1400°C. (Show work.)
   Ans:

b) The H2/H_2O ratio in equilibrium with V and V_2O_3 at 1400°C. (Show work.)
   Ans:

c) Which of the following pure oxides could be reduced to pure metal by C at 1400°C?
   Cr_2O_3, MnO, SiO_2, TiO_2.
   Ans:

d) What is the melting point of Ca? (Circle the location on the diagram.).

e) Estimate the $\Delta H^o_{Vaporization}$ of one mole of $Mg_{(l)}$. (Show construction lines.)
   Ans:

3. What is the volume of one mole of O_2 at its two times its critical pressure and 1.2 times its critical temperature?

4. Set up a reaction extent problem for

$$SO_2 + 0.5\ O_2 = SO_3$$
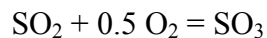
   if there are initially 10 moles of SO_2, 5 moles of O_2, and one mole of SO_3. The K_{EQ} is 1.19 and the total pressure is 2 atm.

5. Use the data given below for the liquid Cu-Sn system at 1400 K to determine the enthalpy change when (assume all components start in the liquid state at 1400 K)
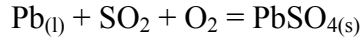
Heats of Mixing for Liquid Cu-Sn Alloys at 1400 K

X_{Sn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
H^M (cal/mole)	-666	-979	-934	-715	-475	-264	-97	13	52

a) 10 moles of Cu are dissolved in a large quantity of Cu-Sn alloy having a mole fraction of Sn of 0.8.

b) 2 moles of Sn and 8 moles of Cu are mixed at 1400 K

6. Show how to find the Gibb's Energy change and direction of the reaction

$$Pb_{(l)} + SO_2 + O_2 = PbSO_{4(s)}$$

when the pressure of SO_2 is 0.1 atm, the pressure of O_2 is 2 atm, the activity of Pb is 0.1 relative to pure liquid Pb, and the $PbSO_4$ is pure solid.

South Dakota School of Mines and Technology
Department of Materials and Metallurgical Engineering

$R = 1.987$ cal/K•gmole $= 8.31$ J/K•gmole
$\mathcal{F} = 23,060$ cal/volt•gram equivalent $= 96,259$ cal/volt•gram equivalent

1. Set up a reaction extent problem for
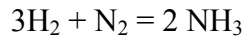
$$3H_2 + N_2 = 2\ NH_3 \qquad K_{EQ} = 1.2 \qquad P_T = 5\ atm$$

The table below shows the number of moles of each component initially.

Species	Moles initially		
NH_3	2		
H_2	1		
N_2	1		
total	4		

Use the attached Ellingham Diagram for the problems below.
(Show your work and submit the Ellingham Diagram.)
2. Show on the attached Ellingham Diagram
3. The pressure of O_2 in equilibrium with Ca and CaO at 1000°C
   a) The H_2/H_2O ratio in equilibrium with Si and SiO_2 at 1000°C
   b) The value for Standard Gibbs Energy change for the formation of one mole of TiO_2 at 1000 °C.

Refer to the data for the Al-Au system at the end of the exam for Problems 3 and 4

4. Calculate the Gibbs energy change for the oxidation of liquid Al in a liquid Al-Au alloy at a mole fraction of 0.1 with O_2 at a pressure of 1×10^{-12} ATM to form pure, solid Al_2O_3 oxide. The temperature is 1338 K (1611 ºC).

$$2/3 \ Al_{(l)} + O_{2(g)} = 4/3 \ Al_2O_{3 \ (s)} \qquad \Delta G^° = -711,620 \ \text{Joules/gmole } O_2$$

5. How much heat would be expected from mixing
   a) 2 moles of liquid Al at 1338 K and 8 moles of liquid Au at 1338 K?

   b) 1 mole of liquid Al at 1338 K and 1,000,000 moles of liquid Al-Au alloy of $X_{Al} = 0.7$ at 1338 K?

6. What voltage would be needed to form pure, liquid Mg from a cell at 800 K from pure, liquid $MgCl_2$ The pressure of Cl_2 is 0.1 atm?

$$MgCl_{2(l)} = Cl_{2(g)} + Mg_{(l)} \quad \Delta G^° = 605,000 - 125.4T \ \text{J/gmole}$$
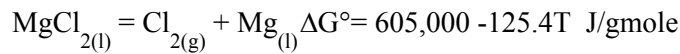
7. Fill in the blank.

To obtain in a binary alloy	Given	Use Method or Equation
The Integral Molar Quantity	The Partial Molar Quantities	
The Partial Molar Quantity #1	The Partial Molar Quantity #2	
Both Partial Molar Quantities	The Integral Molar Quantity	

DATA from Hultgren, et al. All G and H data are in calories. All S data are in calories/K

TABLE 3

Integral Quantities for Liquid Alloys at 1338°K

$$(1-x)\,Al_{(\ell)} + x\,Au_{(\ell)} = Al_{1-x}Au_{x\,(\ell)}$$
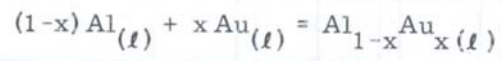
x_{Au}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-3145	-1845	0.972	-2281	0.326
0.2	-5605	-3869	1.297	-4274	0.303
0.3	-7586	-5795	1.339	-5962	0.124
0.4	-9066	-7264	1.347	-7277	0.010
0.5	-9875	-8070	1.350	-8032	-0.028
	(±200)	(±600)	(±.5)	(±200)	(±.5)
0.6	-9817	-8040	1.328	-8027	-0.010
0.7	-8830	-7147	1.258	-7205	0.044
0.8	-6878	-5410	1.097	-5547	0.103
0.9	-3950	-2916	0.773	-3085	0.127

Partial Molar Quantities for Liquid Alloys at 1338°K

Al Component $\qquad$ $Al_{(\ell)} = Al\ (in\ alloy)_{(\ell)}$

x_{Al}	a_{Al}	γ_{Al}	$\Delta\bar{G}_{Al}$	$\Delta\bar{G}^{xs}_{Al}$	$\Delta\bar{H}_{Al}$	$\Delta\bar{S}_{Al}$	$\Delta\bar{S}^{xs}_{Al}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.853	0.948	− 422	− 142	130	0.412	0.203
0.8	0.642	0.803	− 1177	− 584	197	1.027	0.584
0.7	0.413	0.590	− 2352	− 1404	− 597	1.312	0.603
0.6	0.195	0.325	− 4347	− 2989	− 2603	1.303	0.288
0.5	0.051	0.103	− 7893	− 6050	− 6047	1.379	0.002
	(±.002)	(±.004)	(±150)	(±150)	(±500)	(±.5)	(±.5)
0.4	0.0077	0.019	−12937	−10501	−10838	1.569	−0.252
0.3	0.00077	0.0026	−19048	−15847	−16371	2.001	−0.392
0.2	0.00005	0.00023	−26519	−22240	−22583	2.942	−0.256
0.1	0.000002	0.00002	−34456	−28334	−27304	5.346	0.770
0.0	0.00000	0.0000035	− ∞	−33400	−30724	∞	2.000

Au Component $\qquad$ $Au_{(\ell)} = Au\ (in\ alloy)_{(\ell)}$

x_{Au}	a_{Au}	γ_{Au}	$\Delta\bar{G}_{Au}$	$\Delta\bar{G}^{xs}_{Au}$	$\Delta\bar{H}_{Au}$	$\Delta\bar{S}_{Au}$	$\Delta\bar{S}^{xs}_{Au}$
0.0	0.00000	0.00011	− ∞	−24205	−16665	∞	5.635
0.1	0.00003	0.00030	−27657	−21535	−19624	6.004	1.28
0.2	0.00016	0.00078	−23314	−19035	−20135	2.376	−0.822
0.3	0.00058	0.0019	−19799	−16598	−17924	1.402	−0.991
0.4	0.0023	0.0058	−16146	−13709	−14255	1.413	−0.408
0.5	0.0116	0.0231	−11858	−10015	−10092	1.320	−0.058
	(±.001)	(±.002)	(±250)	(±250)	(±700)	(±.5)	(±.5)
0.6	0.0545	0.0908	− 7736	− 6378	− 6174	1.167	0.152
0.7	0.188	0.268	− 4450	− 3502	− 3194	0.939	0.230
0.8	0.477	0.596	− 1967	− 1374	− 1116	0.636	0.192
0.9	0.810	0.900	− 560	− 280	− 205	0.265	0.056
1.0	1.000	1.000	0	0	0	0.000	0.000

SEE DATA SHEET AT END OF EXAM   - NO CALCULATORS – CLOSED BOOK AND NOTES
If a problem seems to be in error, state the trouble, state an assumed correction, and proceed.

1. Refer to the attached MgO-Al_2O_3-SiO_2 ternary phase diagram.
    a) Characterize the bulk composition marked with an "A" at 2100 ºC
    b) What is the 1st crystal to appear upon cooling for the bulk composition marked with a "B"?
    c) What are the final 3 crystals for the bulk composition marked with a "B"?
2. Show on the attached Ellingham Diagram and write your answers below
    a) The pressure of O_2 in equilibrium with Si and SiO_2 at 1200°C.
    b) The H_2/H_2O ratio in equilibrium with Si and SiO_2 at 1200°C.
    c) The CO/CO_2 ratio in equilibrium with Si and SiO_2 at 1200°C.
3. Use the JANAF Thermochemical Tables provided to determine the
    a) Heat required at constant pressure to raise two gram moles of pure, solid Cu from 298 K to gaseous Cu at 3000 K.
    b) The heat of reaction at 1500 K for
       $4Cu_{(S)} + TiO_{2\ (S,\ Rutile)} = 2Cu_2O_{\ (L)} + Ti_{(S,\ Beta)}$
    c) The Standard Gibbs energy at 1000 K for the reaction
       $Cu_{(S)} = Cu_{\ (L)}$
4. Write the Big 6 equations and describe the standard state for each.
5. Find the adiabatic flame temperature for the combustion of C_2H_2 with air. The air and the C_2H_2 start at 298°K. Use the data provided below only.

$$C_2H_2\ (g) + 2.5O_2(g) = 2CO_2\ (g) + H_2O(g)$$

| Species	Heats of Formation (calories/g mole at 298°K)	C_p (cal/ gmole °K)
$C_2H_2(g)$	54,190	19.0
$H_2O(g)$	-57,800	10.5
$CO_2(g)$	-94,000	13.6
$O_2(g)$		8.6
$N_2(g)$		7.0

6. What voltage would be required to produce $W_{(S)}$ from $WCl_{5\ (L)}$ at 600 K? (Use JANAF Thermochemical Table for data.)
7. What would be the equilibrium pressure of SO_3 gas in a system at 1000 K and total pressure od 10 atm if the system initially contained 3 moles of SO_2 gas and 1 mole of O_2 gas. The predominant reaction is

$$SO_{2\ (G)} + 0.5\ O_{2\ (G)} = SO_{3\ (G)} \quad K_{EQ} = 1.88$$
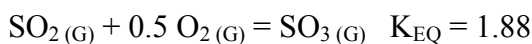
8. Show how to find the activity and the activity coefficient of Cu in a liquid Au-Cu alloy at 1550 K that is 30 atomic percent Cu from the following data:

Gibbs energy of Mixing for the Liquid Au-Cu System at 1550 K

X_{Cu}	G^M
0	0
0.1	-1519
0.2	-2461
0.3	-3089
0.4	-3453
0.5	-3572
0.6	-3453
0.7	-3089
0.8	-2461
0.9	-1519
1	0

Gibbs Energy of Mixing for theLiquid Au-Cu System at 1550 K
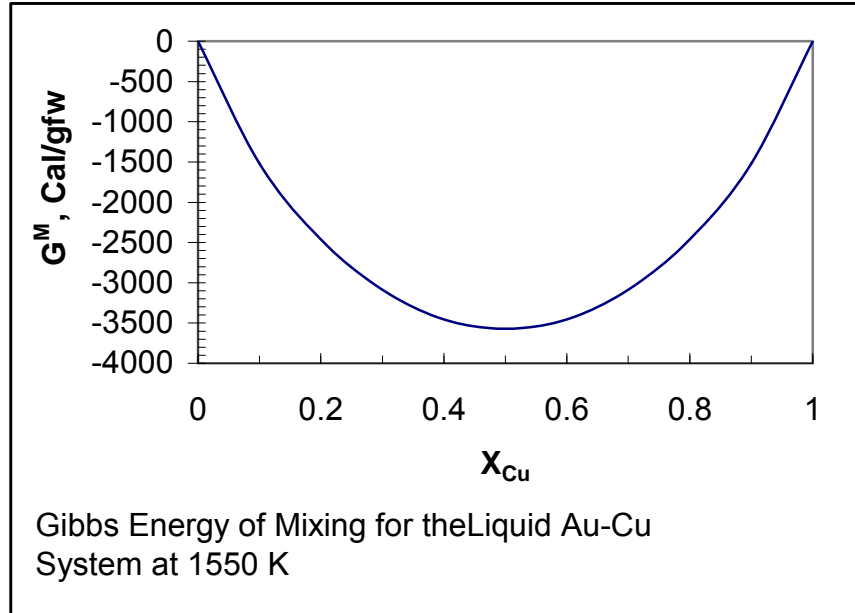
South Dakota School of Mines and Technology
Department of Materials Metallurgical Engineering

MET 320   HQ 3   Dec. 1, 2005

SEE DATA SHEET AT END OF EXAM - NO CALCULATORS – CLOSED BOOK AND NOTES
If a problem seems to be in error, state the trouble, state an assumed correction, and proceed.

1. Write the Big 6 Equations.

$$\mu_i = \mu_i^o + RT \ln p_i$$

$$\mu_i = \mu_i^o + RT \ln(p_i \gamma_i) - - or \ln(f_i)$$

$$\mu_i = \mu_i^o + RT \ln x_i$$

$$\mu_i = \mu_i^o + RT \ln(x_i \gamma_i) - - or \ln(a_i)$$

$$\mu_i = \mu_i^o + RT \ln[i]_i$$

$$\mu_i = \mu_i^o + RT \ln([i]_i \gamma_i) - - or \ln(a_i)$$

2. Short answer:
   a) What is the difference between ΔG and ΔG^o?

The super script "o" means "when every reactant and product is in its standard state"

b) What is the relative partial molar heat of mixing for an Ideal solution?
   Zero

c) What is the name of the ThermoCalc program module that lists values of ΔS°, ΔH°, and ΔG° for an entered reaction at user-defined temperature intervals?
   TAB

3. Estimate the volume of 100 moles of NH_3 at 445 K (1.1*Tcritical) and 223 atm (2*Pcritical)?
   See Figure 8.4 Law of Corresponding States: z = 0.4

$$V = \frac{znRT}{P} = \frac{0.4*100*0.08205*445}{223} Liters \qquad \textbf{Actual Solution: } 6.41 \mathscr{L}$$

4. Estimate the temperature required to raise the vapor pressure of water to 100 mmHg if it is known that the vapor pressure of water vapor above water at 22 °C is 20 mmHg.

   Clasius-Clapeyron Eq.

$$\ln\left[\frac{p_2}{p_1}\right] = -\frac{\Delta H^o_{Vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln\left[\frac{100}{20}\right] = -\frac{4320}{8.31}\left[\frac{1}{(273+T_2)} - \frac{1}{(273+22)}\right]$$

T_2 is in °C   **Actual Solution: 51.6 °C**

5. Cu in a liquid Ag-Cu solution having a composition of $x_{Cu} = 0.1$ at a temperature of 1423 K reacts with half a mole of O_2 at 12 atm to form pure, solid Cu_2O. Show how to calculate the Gibbs energy change for this process.
   Data: $2Cu_{(l)} + 0.5\ O_{2(g)} = Cu_2O_{(s)}$ $\Delta G^\circ = $ -195,000 -7.12TlnT +143T J/gmole

$$\Delta G = \Delta G^\circ + RT \ln(Q),$$

$$Q = \frac{a_{Cu_2O}}{a^2_{Cu}\, p^{0.5}_{O_2}} = \frac{1}{0.26^2_{Cu}12^{0.5}_{O_2}} \qquad \textbf{Actual Solution: } \Delta G = \Delta G^\circ + RT \ln Q$$

T, K	ΔG°, J/gfw	Q	ΔG, J/gfw
1423	-65,073	4.27	-47,906

6. Initially there are 5 moles of SO_2, 3 moles of O_2, and 1 mole of SO_3 in a reactor kept at a constant pressure or 2 atm and constant temperature. Setup the calculation to determine the equilibrium number of moles of each gas. All the species are gaseous.

1. $2SO_2 + O_2 = 2SO_3$ $\quad$ $K_{EQ} = 1.8$
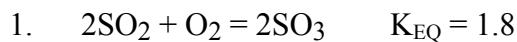
2. Let x = moles of O_2 reacted

3. Mole balance to Equilibrium

i	Moles		
i	N_{init}	N_{Final}	p_i
SO_2	5	5-2x	$\frac{5-2x}{9-x}2$
O_2	3	3-x	$\frac{3-x}{9-x}2$
SO_3	1	1+2x	$\frac{1+2x}{9-x}2$
Total	9	9-x	2

4. $K_{EQ} = \dfrac{\left[\frac{1+2x}{9-x}2\right]^2}{\left[\frac{5-2x}{9-x}2\right]^2\left[\frac{3-x}{9-x}2\right]} = \dfrac{[1+2x]^2}{[5-2x]^2\left[\frac{3-x}{9-x}2\right]}$
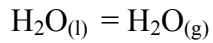
5. Solve for x. Note $-0.5 \le x \le 2.5$. Otherwise a mole value becomes negative.

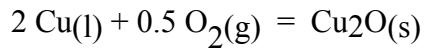**Actual Solution:** by Microsoft Excel Goal Seek$^{®}$

	x	Q
	0.965	1.800
i	Final	p_i
SO_2	3.069	0.764
O_2	2.035	0.506
SO_3	2.931	0.730
Total	8.035	2.000

DATA:

$H_2O_{(s)} = H_2O_{(l)}$ $\qquad\qquad\qquad$ $\Delta H° = $ 6,028 J/gmole

$H_2O_{(l)} = H_2O_{(g)}$ $\qquad\qquad\qquad$ $\Delta H° = $ 43,267 J/gmole

$2\ Cu_{(l)} + 0.5\ O_{2(g)} = Cu2O_{(s)}$ $\qquad$ $\Delta G° = $ -195,000 -7.12TlnT +143T J/gmole
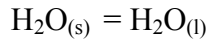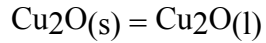
$Cu2O_{(s)} = Cu2O_{(l)}$ $\qquad\qquad\qquad$ $\Delta G° = $ 13,580 – 9.0 T J/gmole

Activity data for liquid
Ag-Cu Alloys at 1423 K

X_{Cu}	a_{Cu}
0.0	0.000
0.1	0.260
0.2	0.422
0.3	0.535
0.4	0.616
0.5	0.679
0.6	0.731
0.7	0.782
0.8	0.841
0.9	0.912
1.0	1.000

Table 8.1 The critical states, van der Waals constants, and values of Z at the critical points for several gases

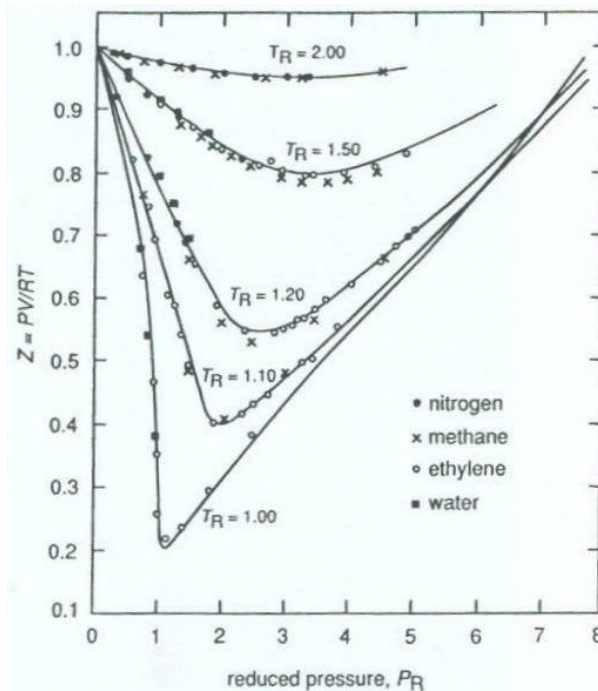| Gas	T_{cr}, K	P_{cr}, atm	V_{cr}, cm³/mole	$a, \dfrac{l^2 \cdot atm}{mole^2}$	b, liters/mole	Z_{cr}
He	5.3	2.26	57.6	0.0341	0.0237	0.299
H_2	33.3	12.8	65.0	0.2461	0.0267	0.304
N_2	126.1	33.5	90.0	1.39	0.0391	0.292
CO	134.0	35.0	90.0	1.49	0.0399	0.295
O_2	153.4	49.7	74.4	1.36	0.0318	0.293
CO_2	304.2	73.0	95.7	3.59	0.0427	0.280
NH_3	405.6	111.5	72.4	4.17	0.0371	0.243
H_2O	647.2	217.7	45.0	5.46	0.0305	0.184

Figure 8.4 The variations of the compressibility factors of several gases with reduced pressure at several reduced temperatures

South Dakota School of Mines and Technology
Department of Materials and Metallurgical Engineering

Closed Book and Notes   No Calculators   Data Sheet Provided MET 320

$R = 1.987$ cal/K•gmole $= 8.31$ J/K•gmole
$\mathcal{F} = 23{,}060$ cal/volt•gram equivalent $= 96{,}259$ cal/volt•gram equivalent

5. *Dry ice* (solid CO_2) is so named because it never melts at atmospheric pressure. Its vapor pressure is above 1 atm at its melting point so it is long sublimated before melting. The vapor pressure of *dry ice* is 5.11 atm at its melting point (-56.6 ºC, 216.4 K) and drops to 1 atm at (-78.5 ºC, 194.5 K). Determine the heat of sublimation for *dry ice* from these data.

<u>**Use the attached Ellingham Diagram for the problems below.**</u>
<u>(Show your work and submit the Ellingham Diagram.)</u>
6. Show on the attached Ellingham Diagram
    f) The pressure of O_2 in equilibrium with Ti and TiO_2 at 800°C
    g) The H_2/H_2O ratio in equilibrium with Ti and TiO_2 at 800°C
    h) The CO/CO_2 ratio in equilibrium with Ti and TiO_2 at 800°C
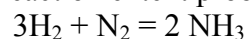
7. Set up a reaction extent problem for
    $$3H_2 + N_2 = 2\,NH_3 \qquad K_{EQ} = 1.2 \qquad P_T = 5 \text{ atm}$$

South Dakota School of Mines and Technology
Department of Materials and Metallurgical Engineering

MET 320   HQ 3   Dec 6, 2007
(Data from the text and Hultgren were provided)   The table below shows the number of moles

1. a) Referring to Table 8.1, cite the gases that exhibit a two phase gas-liquid behavior at room
        temperature (298 K).
           of each component initially.

Species	Initial Moles		

b) Telemetry from the Space Shuttle oxygen tank shows T= 184 K and P = 149
   atm. How many gram moles of oxygen remain in the 30-Liter tank?

NH_3	0		
H_2	10		
N_2	4		
total	2		

2. Show on the attached Ellingham Diagram
    The pressure of O_2 in equilibrium with Si   **Refer to the data for**
    and SiO_2 at 1300°C   **the Al-Au system at the end of the exam for**
                                                         Problems 3 and 4

    a) The H_2/H_2O ratio in equilibrium with Si and SiO_2 at 1300°C   8. What is the
                                                                                   volume of one
        gmole of CO_2 at 304 K and 219 atm, which is three times its critical pressure of 73 atm?

    9. a) Calculate the Gibbs energy change for the oxidation of pure, liquid Al with O_2 at a
            pressure of
            $1x10^{-12}$ atm to form pure, solid Al_2O_3 oxide.   The temperature is 1338 K (1611 ºC).

            $2/3\ Al_{(l)}\ +\ O_{2(g)} =\ 4/3\ Al_2O_3\ _{(s)}$ $\Delta G°_{1338\ K} = -711,620$ Joules/gmole O_2

    b) Which direction does the reaction proceed if the Gibbs energy change is less than 0?

b)   The CO/CO$_2$ ratio in equilibrium with Si and SiO$_2$ at 1300°C

c) Estimate the for one gram mole of Mg
    i) Heat of Fusion

    ii) Heat of Vaporization.

3. Solve for the equilibrium moles of HI at 500 K and total pressure of 5 atm.

$$H_{2\ (g)} + I_{2\ (g)} = 2\ HI_{(g)} \qquad \Delta G^o = \text{-RT ln K} = \text{(see text)}$$

The table below shows the number of moles of each component initially.

Species	Initial Moles		
HI	3		
H_2	10		
I_2	4		
total			

4. Calculate the Gibbs energy change for the oxidation of pure, liquid Mg with Cl_2 at a pressure of $1x10^{-8}$ atm to form pure, solid $MgCl_2$ oxide at 1200 K. Use the data from Table A-1 in the text.

5. What is the ΔH of for the following scenarios? (Use the handouts from class for data.)
   a) Three moles of liquid Al at 1273 K mix with 7 moles of liquid Ag at 1273 K.

   b) Two moles of liquid Al at 1273 mix with a million moles of Ag-Al alloy at 1273 K with a mole fraction of 0.3 Al.