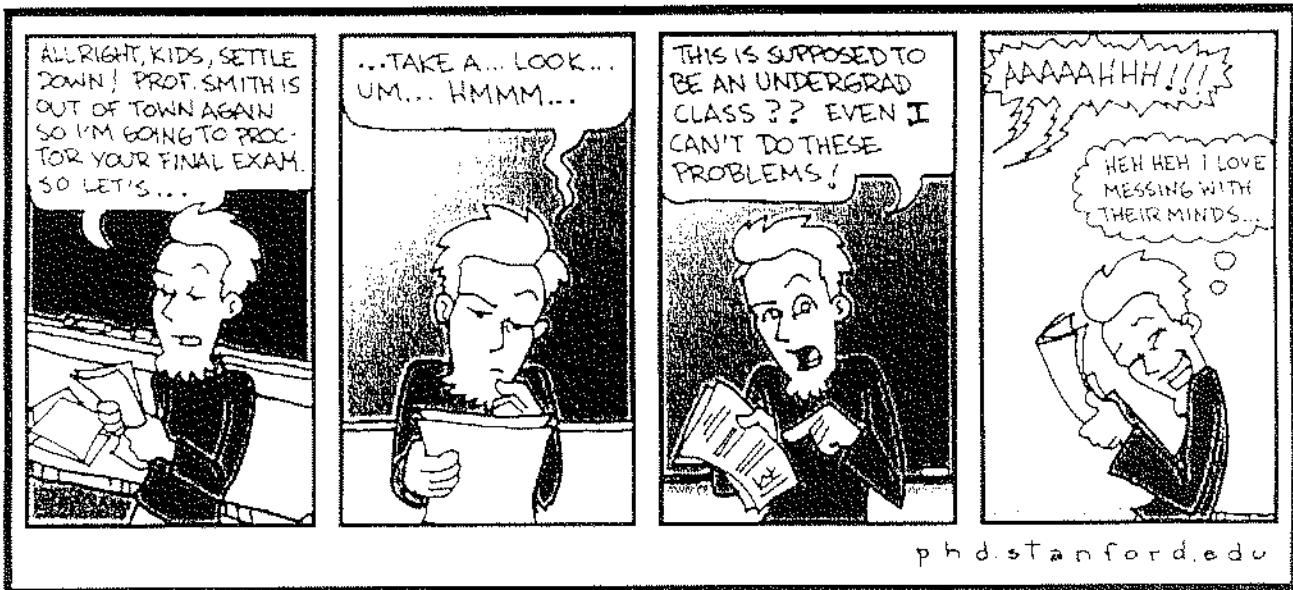


10.213 Final Exam
Friday, December 22, 2000
9 am - 12 pm

There are four (4) questions on this exam. You will have 3 hours to complete it.
Please put each problem in a SEPARATE blue book, for a total of 4.

Good Luck

3/16/2000



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Problem 1 (50 points total)

A steady-state mixing process combines three inlet streams. The flowrates, composition, and temperatures of each of these three streams is shown in the table below.

stream	Temperature (°F)	Wt.% H ₂ SO ₄ acid	Wt.% H ₂ O	Flowrate (lb _m /s)
Inlet A	40	30	70	0.2
Inlet B	80	10	90	0.3
Inlet C	60	75	25	0.5

Thermodynamic data for H₂SO₄ / H₂O mixtures can be found on page 404 of the Smith & Van Ness text.

For the sole outlet stream, determine the

- flow rate in units of kg/s,
- weight % acid
- temperature if the mixing process is adiabatic
- temperature if the mixing process has a heat removal rate of -30 Btu/s.

Problem 2 (50 points total)

A process is proposed where graphite would be heated to high temperature, T_H , at a high pressure, P_H , for a sufficient time for diamond to form. Once formed, the diamond would be quickly cooled and depressured so that it does not revert to graphite.

- Find the equation which describes/gives P_H as a function of T_H when equilibrium exists between diamond and graphite.
- Draw a PT diagram showing the equation found in part a. Indicate the equilibrium pressure at 0K and 1250 K. Also, show the conditions where diamond is formed by the earth's geology, which is typically around 1250 K and 6.5×10^9 Pa.

Thermodynamic data for both phases of solid carbon appear below. You can assume the entropy and density of both phases are approximately independent of temperature and pressure.

Properties at 298 K and 1 bar	Units	Graphite	Diamond
G	J/mol	0	2900
S	J/mol K	5.740	2.377
Density	kg/m ³	2220	3510

Problem 3 (50 points total) Consider the following mixture of two liquids at a total of 1 Bar (that is in contact with air at 1 Bar). The following information is available:

$$P_A^{sat}(298K) = 0.8 \text{ Bar}$$

$$P_B^{sat}(298K) = 0.5 \text{ Bar}$$

Enthalpy of mixing at 298K = -10 KJ/mol for a 50/50 mixture by mol fraction

Excess entropy of mixing at 298K = -1 J/mol-K for a 50/50 mixture by mol fraction

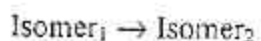
The solubility of air in A, B, or mixtures of A and B is small and can be ignored.

Assume that the excess Gibbs free energy has the following form

$$G^E = (\text{Constant})x_Ax_B$$

- (10 pts) What is the excess Gibbs energy for a 50/50 mol percent mixture?
- (10 pts) What is the total entropy change associated with mixing one mole of pure liquid A with one mol of pure liquid B at 298K?
- (10 pts) Is the equilibrium vapor pressure higher or lower than that of an ideal solution? Give the molecular reasoning behind the variation in vapor pressure based on this data.
- (10 pts) Determine the value of the activity coefficients for both A and B for this 50/50 mol % mixture.
- (10 pts) If this mixture is at 298K, what is the composition of the air in equilibrium with the liquid mixture that is 50 mol % A and 50 mol % B?

Problem 4 (50 points total) A gaseous isomerization reaction at 1 bar occurs as shown below.



The heat of reaction (change in enthalpy) for this system is small and equals 1 KJ/mol for this reaction as written above at 298K. The entropies of both pure isomers are the same at 298K.

The following data is also available:

$$S^E = 0 \text{ J/mol-K}$$

$$C_{p,1} = 20 \text{ J/mol-K}$$

$$C_{p,2} = 25 \text{ J/mol-K}$$

- (15 pts) What is the expected heat of reaction for this isomerization at 398K?
- (15 pts) What is the equilibrium mole fraction at 298K?
- (20 pts) What is the equilibrium mole fraction at 398K?

#1



find
 wt % acid
 flow rate
 temperature $\left\{ \begin{array}{l} \dot{Q} = 0 \\ \dot{Q} = 30 \text{ BTU/s} \end{array} \right.$

MASS BALANCES IN = OUT (SS, NO RXN)

TOTAL $\dot{m}_A + \dot{m}_B + \dot{m}_C = \dot{m}_D \leftarrow 5 \text{ pts}$
 $.2 + .3 + .5 = 1.0 \text{ lbm/s} \leftarrow 5 \text{ pts}$

ACID $w_A \dot{m}_A + w_B \dot{m}_B + w_C \dot{m}_C = w_D \dot{m}_D \leftarrow 5 \text{ pts}$
 $(.3)(.2) + (.1)(.3) + (.75)(.5) = w_D (1.0)$
 $.465 = w_D$
46.5% acid $\leftarrow 5 \text{ pts}$

ENERGY BALANCE (SS, $W_s = W_b = 0$) \leftarrow values +5
 $\dot{m}_A H_A + \dot{m}_B H_B + \dot{m}_C H_C - \dot{m}_D H_D + \dot{Q} = 0 \leftarrow +10$
 $\frac{\text{lbm}}{\text{s}} \quad \frac{\text{BTU}}{\text{lbm}}$ from page 404 SSUN
 BTU/s

for $\dot{Q} = 0$
 $(.2)(-85) + (.3)(+10) + (.5)(-128) - (1)H_D = 0$
 $-78 \frac{\text{BTU}}{\text{lbm}} = H_D \leftarrow +5$

for 46.5% acid & $-78 \frac{\text{BTU}}{\text{lbm}}$; $T \approx 105^\circ \text{F}$
 $\leftarrow +5$

for $\dot{Q} = -30 \text{ BTU/s}$
 $-78 \frac{\text{BTU}}{\text{s}} - 30 \frac{\text{BTU}}{\text{s}} = (1 \frac{\text{lbm}}{\text{s}})(H_D)$
 $-108 \frac{\text{BTU}}{\text{lbm}} = H_D \leftarrow +10$

for 46.5% acid & $-108 \frac{\text{BTU}}{\text{lbm}}$; $T \approx 60^\circ \text{F}$
 \leftarrow

#2

Pure substance

$$\mu = G \quad (5 \text{ pts})$$

$$d\mu = dG = VdP - SdT \quad (5 \text{ pts})$$

$$\text{for } V \text{ \& } S \text{ constant} \quad \Delta\mu = V\Delta P - S\Delta T \quad (5 \text{ pts})$$

$$\text{equilibrium} \quad \mu_G = \mu_D \quad (5 \text{ pts})$$

$$\mu_G^0 + V_G(P_H - 1) - S_G(T_H - 298) = \mu_D^0 + V_D(P_H - 1) - S_D(T_H - 298)$$

$$(5 \text{ pts}) \quad (S_D - S_G)(T_H - 298) = (\mu_D^0 - \mu_G^0) + (V_D - V_G)(P_H - 1)$$

$$\text{Let } \Delta X = X_D - X_G$$

$$T_H - 298 = \frac{\Delta\mu^0 + \Delta V(P_H - 1)}{\Delta S}$$

$$\Delta\mu^0 = 2900 - 0 = 2900 \text{ J/mol}$$

$$\Delta S = 2.377 - 5.740 = -3.363 \text{ J/mol K}$$

$$V_D = \frac{mW_D}{\rho_D} = \frac{129}{\text{mol}} \times \frac{\text{m}^3}{3510 \text{ kg}} \times \frac{10^6 \text{ cm}^3}{\text{m}^3} \times \frac{\text{kg}}{10^3 \text{ g}} = 3.41 \frac{\text{cm}^3}{\text{mol}}$$

$$V_G = \frac{12}{2220} \times 10^6 = 5.40 \text{ cm}^3/\text{mol}$$

$$\Delta V \cdot \text{bar} = (3.41 - 5.40) \frac{\text{cm}^3}{\text{mol}} \text{ bar} \left(\frac{1 \text{ J}}{10 \text{ cm}^3 \text{ bar}} \right)$$

$$= -0.2 \text{ J/mol}$$

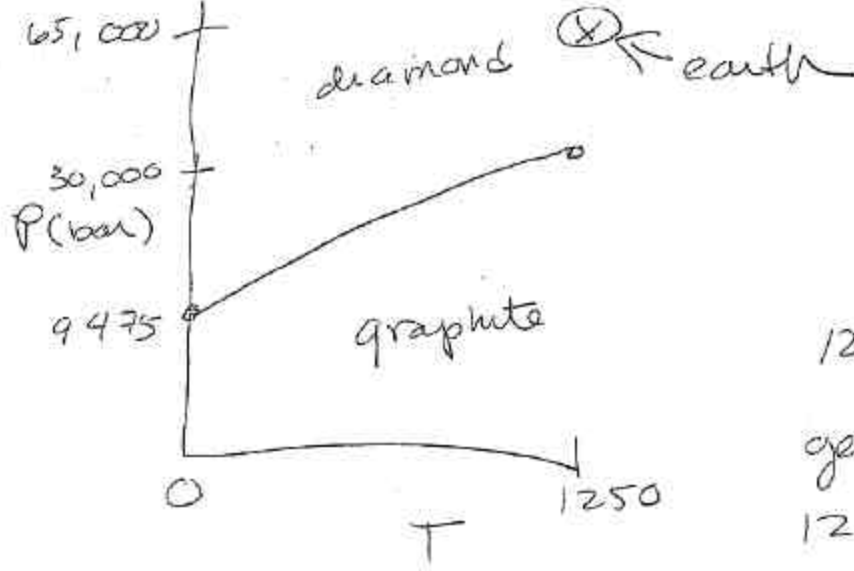
$$T_H = 298 \text{ K} + \frac{2900 \frac{\text{J}}{\text{mol}} - 0.2 \frac{\text{J}}{\text{mol}} (P_H - 1)}{-3.363 \text{ J/mol K}}$$

$$T_H = .059(P_H - 1) - 564$$

$$T_H = .059 P_H - 564$$

$$1/.059 = 16.8$$

$$16.8(T_H + 564) = P_H \text{ K}$$



$T_{\#}$	$P_{\#}$
0 K	9,475 bar
1250 K	30,475 bar
geo	6.5×10^9 Pa
1250 K	$\approx 6.5 \times 10^4$ bar
	65,000 bar

10 pts

Problem 3 solution:

$$\begin{aligned} \text{a.) } \Delta G^E &= \Delta H^E - T\Delta S^E \\ &= 10,000 \frac{\text{J}}{\text{mol}} - 298(-1 \frac{\text{J}}{\text{mol K}}) \\ &= -9,702 \frac{\text{J}}{\text{mol}} \end{aligned}$$

$$\begin{aligned} \text{b.) } \Delta S^{\text{Total}} &= 2 \text{ mol } (\Delta S^{\text{ID}} + S^E) \\ &= 2 (-R \cdot (\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2}) - 1 \frac{\text{J}}{\text{mol K}}) \\ &= 9.526 \frac{\text{J}}{\text{K}} \end{aligned}$$

c.) $\Delta H^E = \text{negative} \Rightarrow$ exothermic = stronger interaction
- lower vapor pressure
 $\Delta S^E = \text{negative} \Rightarrow$ more ordered = less entropy of mixing than ideal \Rightarrow increase vapor pressure
 ΔG^E - combined effect, best metric:
- negative \Rightarrow lowered vapor pressure.

$$\begin{aligned} \text{d.) } -9,702 \frac{\text{J}}{\text{mol}} &= K x_A x_B - K(0.5)(0.5) \\ K &= -38808 \frac{\text{J}}{\text{mol}} \end{aligned}$$

$$\ln \gamma_i = \frac{\partial (m G^E)}{\partial m_i} / RT$$

$$\text{Thus: } \frac{m G^E}{RT} = \frac{-38808 m_A m_B}{RT(m_A + m_B)}$$

$$\gamma_A = \exp\left(\frac{-38808}{RT} \cdot X_B^2\right)$$

$$= \underline{0.02}$$

$$\gamma_B = \exp\left(\frac{-38808}{RT} \cdot X_A^2\right)$$

$$= \underline{0.02}$$

e.) 50% A+B \Rightarrow air not soluble in liquid.

$$\text{V.P.} \cdot P_A = \gamma_A X_A P_A^{\text{SAT}} = (0.02)(0.5)(0.8 \text{ bar})$$

$$P_B = \gamma_B X_B P_B^{\text{SAT}} = (0.02)(0.5)(0.5 \text{ bar})$$

$$P_A = 0.008$$

$$P_B = 0.005$$

$$P_T = 1 \text{ bar}$$

98.7% air

.8% A

.5% B.

Problem 4 solution:

$$a) \Delta H^{398} = \Delta H^{298} + R \int_{298}^{398} \frac{\Delta C_p}{R} dT$$

$$= 1000 \frac{\text{J}}{\text{mol}} + (25-20) \frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot (398-298)\text{K}$$

$$= 1,500 \frac{\text{J}}{\text{mol}}$$

$$b) -\ln K^{298} = \frac{\Delta G^{298}}{RT} = \frac{\Delta H^\circ - T\Delta S^\circ}{RT^\circ}$$

$$= 0.404$$

$$K^{298} = 0.668$$

$$K^{298} = \prod_i y_i^{v_i} = \frac{y_{I2}}{y_{I1}} = \frac{y_{I2}}{1-y_{I2}} \quad (\text{Ideal gas } \phi_i=1)$$

$$\text{Thus: } y_{I1} = 0.600$$

$$y_{I2} = 0.400$$

$$c) -\ln K^{398} = \frac{\Delta G^{398}}{RT}$$

$$= \frac{\Delta G_0^\circ - \cancel{\Delta H_0^\circ}}{RT_0} + \frac{\Delta H_0^\circ}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p}{R} dT - \int_{T_0}^T \frac{\Delta C_p}{R} \frac{dT}{T}$$

$$= \cancel{\phi} + \frac{(1000 \frac{\text{J}}{\text{mol}})}{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(398\text{K})} + \frac{1}{398\text{K}} \cdot \frac{(5 \frac{\text{J}}{\text{mol}\cdot\text{K}})(100\text{K})}{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})} - \frac{5 \frac{\text{J}}{\text{mol}\cdot\text{K}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \cdot \ln \frac{398}{298}$$

$$= \phi + 0.3022 + 0.1511 - 0.1740$$

$$-\ln K^{398} = 0.2793$$

$$K^{398} = 0.7563 = \prod_i y_i^{v_i} \quad (\text{Ideal gas, } \phi_i = 1)$$

Thus: $\frac{y_2}{y_1} = 0.7563 = \frac{y_2}{1 - y_2}$

$$y_2 = 0.431$$

$$y_1 = 0.569$$