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
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.

<table>
<thead>
<tr>
<th>stream</th>
<th>Temperature (°F)</th>
<th>Wt.% H₂SO₄ acid</th>
<th>Wt.% H₂O</th>
<th>Flowrate (lbm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet A</td>
<td>40</td>
<td>30</td>
<td>70</td>
<td>0.2</td>
</tr>
<tr>
<td>Inlet B</td>
<td>80</td>
<td>10</td>
<td>90</td>
<td>0.3</td>
</tr>
<tr>
<td>Inlet C</td>
<td>60</td>
<td>75</td>
<td>25</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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:

a) flow rate in units of kg/s,
b) weight % acid
c) temperature if the mixing process is adiabatic
d) 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 depressurized so that it does not revert to graphite.

a) Find the equation which describes/gives P_H as a function of T_H when equilibrium exists between diamond and graphite.

b) 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 x 10⁹ 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.

<table>
<thead>
<tr>
<th>Properties at 298 K and 1 bar</th>
<th>Units</th>
<th>Graphite</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>J/mol</td>
<td>0</td>
<td>2900</td>
</tr>
<tr>
<td>S</td>
<td>J/mol K</td>
<td>5.740</td>
<td>2.377</td>
</tr>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>2220</td>
<td>3510</td>
</tr>
</tbody>
</table>
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:

\[ P_A^{\text{sat}}(298\text{K}) = 0.8 \text{ Bar} \]
\[ P_B^{\text{sat}}(298\text{K}) = 0.5 \text{ Bar} \]

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

\[ G^E = (\text{Constant})x_A x_B \]

a) (10 pts) What is the excess Gibbs energy for a 50/50 mol percent mixture?
b) (10 pts) What is the total entropy change associated with mixing one mole of pure liquid A with one mole of pure liquid B at 298K?
c) (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.
d) (10 pts) Determine the value of the activity coefficients for both A and B for this 50/50 mol % mixture.
e) (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.

\[ \text{Isomer}_1 \rightarrow \text{Isomer}_2 \]

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:

\[ S^F = 0 \text{ J/mol-K} \]
\[ C_{p,1} = 20 \text{ J/mol-K} \]
\[ C_{p,2} = 25 \text{ J/mol-K} \]

a) (15 pts) What is the expected heat of reaction for this isomerization at 398K?
b) (15 pts) What is the equilibrium mole fraction at 298K?
c) (20 pts) What is the equilibrium mole fraction at 398K?
MASS BALANCES \[ \text{IN} = \text{OUT} \] (SS, NOT R=kxW)

\[
\begin{align*}
\text{TOTAL:} & \quad m_A + m_B + m_C = m_D \quad \leftarrow \text{5 pts} \\
0.2 + 0.3 + 0.5 & = 1.0 \text{ lbm/s} \quad \leftarrow \text{5 pts} \\
\text{ACID:} & \quad w_A m_A + w_B m_B + w_C m_C = w_D m_D \quad \leftarrow \text{5 pts} \\
(0.3)(1.2) + (1.1)(1.3) + (1.75)(1.5) & = w_D (110) \\
46.5 & = w_D \\
\boxed{46.5\% \text{ acid}} & \quad \leftarrow \text{5 pts}
\end{align*}
\]

ENERGY BALANCE \[ \text{SS:} \quad W_S - W_B = 0 \] \[ \leftarrow \text{VALUES+5} \]

\[
\begin{align*}
16m & \quad \text{BTU from page 404-SUNU} \\
16m & \quad 46\text{ BTU/s} \\
\end{align*}
\]

\[ \text{for } Q = 0 \]
\[ (0.2)(-85) + (1.3)(+10) + (1.5)(-128) - (1) H_B = 0 \]
\[ -78 \text{ BTU/16m} = H_B \quad \leftarrow +5 \]

for \( 46.5\% \text{ acid } \)
\[ -78 \text{ BTU/16m} \]
\[ T = 105^\circ\text{F} \]

for \( Q = -30 \text{ BTU/15s} \)
\[ -38 \text{ BTU/15s} = (1 \text{ lbm/s})(-10^\circ\text{F}) \]
\[ -10^\circ\text{F} \text{ BTU/16m} = +10 \]

for \( 46.5\% \text{ acid } \)
\[ -10^\circ\text{F} \text{ BTU/16m} \]
\[ T = 60^\circ\text{F} \]
Pure substance: \( \mu = G \) (5pts)

\[ d\mu = dG = V_{Dp} - SAT \] (5pts)

for \( V_{Dp} \) constant: \( \Delta \mu = V_{Dp} - SAT \) (5pts)

Equilibrium: \( \mu_G = \mu_D \) (5pts)

\[ \mu^0_G + V_G (P_H - 1) - S_G (T_H - 298) = \mu^0_D + V_D (P_H - 1) - S_D (T_H - 298) \]

\[ (S_D - S_G) (T_H - 298) = (\mu^0_G - \mu^0_D) + (V_D - V_G) \]

Let \( \Delta X = X_D - X_G \)

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

\[ \Delta L = 2900 - 0 = 2900 \text{ J/mol} \]

\[ \Delta S = 3.377 - 5.740 = -3.363 \text{ J/mol K} \]

\[ V_D = \frac{m_D}{P_D} = \frac{12 \text{ g/mol} \times \frac{m^3}{3510 \text{ kg}}} {10^6 \text{ cm}^3 \times 10^3 \text{ g}} = 3.41 \text{ cm}^3 \text{ mol}^{-1} \]

\[ V_G = \frac{12 \text{ g/mol}}{3220} \times 10^6 \text{ cm}^3 = 5.40 \text{ cm}^3 \text{ mol}^{-1} \]

\[ \Delta V \cdot \text{bar} = (3.41 - 5.40) \text{ cm}^3 \text{ mol}^{-1} \times \frac{1 \text{ atm}}{10^5 \text{ cm}^3 \text{ bar}} = -0.2 \text{ J/mol} \]

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

\[ T_H = 0.059 (P_H - 1) - 564 \]

\[ T_H = 0.059 P_H - 564 \]

\[ 16.8 (T_H + 564) = P_H \]

\[ \mu = \mu_H \]
\[ \begin{align*}
\text{T} & \quad \text{P}\text{[bar]} \\
0 K & \quad 9,475 \text{ bar} \\
1250 K & \quad 30,475 \text{ bar} \\
65000 \text{ bar} & = 6.5 \times 10^9 \text{ Pa} \\
1250 K & = 6.5 \times 10^4 \text{ bar} \\
\end{align*} \]
Problem 3 solution:

a.) \( \Delta G^E = \Delta H^E - T\Delta S^E \)
    \[ -10,000 \text{ J/mol} - 298 (-1 \text{ J/mol K}) \]
    \[ = -9,702 \text{ J/mol} \]

b.) \( \Delta S^{\text{total}} = 2 \text{ mol} \left( \Delta S^{1D} + \Delta S^E \right) \)
    \[ = 2 \left( -8.31 \left( \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) - 1 \text{ J/mol K} \right) \]
    \[ = 9.534 \text{ J/K} \]

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

d.) \( -9,702 \text{ J/mol} = K \times A \times B - K(S)(S) \)
    \[ K = -38,808 \text{ J/mol} \]

\[ \ln \chi_i = \frac{\partial (\Delta G^E)}{\partial n_i} \]

Thus: \( \frac{\Delta G^E}{RT} = \frac{-38,808 m_A m_B}{RT(m_A + m_B)} \)
\[ \gamma_A = \exp \left( -\frac{38808 \cdot x_B^2}{RT} \right) \]
\[ = 0.02 \]
\[ \gamma_B = \exp \left( -\frac{38808 \cdot x_A^2}{RT} \right) \]
\[ = 0.02 \]

e) 50\% A + B \Rightarrow \text{Air not soluble in liquid.}

V.P.: \[ P_A = \gamma_A x_A P_A^{sat} = (0.02)(0.5)(0.8 \text{ bar}) \]
\[ P_B = \gamma_B x_B P_B^{sat} = (0.02)(0.5)(0.5 \text{ bar}) \]
\[ P_A = 0.008 \]
\[ P_B = 0.005 \]
\[ P_T = 1 \text{ bar} \]

\[ \{ \begin{align*}
98.7\% & \text{ air} \\
8\% & \text{ A} \\
.5\% & \text{ B}
\end{align*} \]
Problem 4 solution:

a) \( \Delta H^{\circ} = \Delta H^{\circ} + R \int_{T_0}^{T} \frac{\Delta C_P}{C} \, dT \)

\[ = 1000 \text{ J/mol} + (25-20) \frac{7}{\text{molK}} \cdot (398-298) \text{K} \]

\[ = 1500 \text{ J/mol} \]

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

\[ = 0.404 \]

\( K^{298} = 0.668 \)

\( K^{398} = \prod \frac{Y_i^{v_i}}{Y_{12}^{v_{12}}} = \frac{Y_{12}}{Y_{11}} \frac{Y_{12}}{1-Y_{12}} \)  (Ideal gas, \( a_i = 1 \))

Thus: \( Y_{11} = 0.6680 \)

\( Y_{21} = 0.400 \)

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

\[ = \frac{\Delta G^{\circ}}{RT} - \frac{\Delta H^{\circ}}{RT} + \frac{1}{T} \int_{T_0}^{T} \frac{\Delta C_P}{C} \, dT - \int_{T_0}^{T} \frac{\Delta C_P}{C} \, dT \]

\[ = \phi + \left( \frac{1000}{398 \text{JK}^{-1} \text{mol}^{-1}} \right) \left( \frac{7}{\text{molK}} \right) \left( 398 \text{K} \right) - \frac{1}{398 \text{JK}^{-1} \text{mol}^{-1}} \ln \left( \frac{398}{8314 \text{JK}^{-1} \text{mol}^{-1}} \right) \]

\[ = \phi + 0.3032 + 0.1511 - 0.1740 \]

\[ = 1.70 \]
\[
\ln K^\text{398} = 0.2793
\]

\[
K^\text{398} = 0.7563 = \prod_i \frac{y_i^{\varphi_i}}{\varphi_i} \quad \text{(Ideal gas, } \varphi_i = 1)\]

Thus:

\[
\frac{y_2}{y_1} = 0.7563 = \frac{y_2}{1-y_2}
\]

\[
y_2 = 0.431
\]

\[
y_1 = 0.569
\]