ChE 141 Midterm 2
Fall 2006

1) Note: For this problem the sign convention used is for quantities into a system are positive and quantities leaving the system are negative.

a) (15 points)

H_4 is given so H_1 can be found from adding the work for the pump or

$H_1 = H_4 + W_{41}$ = 188.4 kJ/kg + 8.676 kJ/kg = **197.1 kJ/kg = H_1** (3 points)

H_3 can be found on page 722 of your book (since it is saturated vapor).

H_3 = 2584.8 kJ/kg (3 points)

$W_{23} = H_3 - H_2$ = 2584.8 kJ/kg – 3391.6 kJ/kg = **-806.8 kJ/kg = W_{23}** (3 points)

To find H_3', we need to know the steam quality, x'.

$S_2 = S_3$' because we are looking at the isentropic case.

S_2 = 6.6858 kJ/(kg*K) = $S_3^{satvap}x' + S_3^{satliq}(1-x')$ (1 point)

= 8.1511 kJ/(kg*K) * x' + 0.6493 kJ/(kg*K) * (1-x')

x' = 0.805 (1 point)

Now, we can get H_3'.

$H_3' = H^{satvap}x' + H^{satliq}(1-x')$ = 2584.8 kJ/kg * 0.804 + 191.832 kJ/kg * (1 – 0.804)

H_3' = 2117.8 kJ/kg (1 point)

$W_{23}' = H_3' - H_2$ = 2115.8 kJ/kg – 3391.6 kJ/kg = **-1275.8 kJ/kg = W_{23}'** (3 points)

b) (9 points)

$Q_{12} = H_2 - H_1$ = 3391.6 kJ/kg – 197.1 kJ/kg = **3194.5 kJ/kg = Q_{12}** (3 points)

$Q_{34} = H_4 - H_3$ = 188.4 kJ/kg – 2584.8 kJ/kg = **-2396.4 kJ/kg = Q_{34}** (3 points)

$Q_{34}' = H_4 - H_3'$ = 188.4 kJ/kg – 2115.8 kJ/kg = **-1927.4 kJ/kg = Q_{34}'** (3 points)

c) (10 points) $0.632 = \eta_{turbine}$

$$\eta_{turbine} = \frac{W_{turbine}}{W'_{turbine}} = \frac{W_{23}}{W'_{23}} = \frac{-806.8kJ/kg}{-1275.6kJ/kg} = \mathbf{0.632 = \eta_{turbine}}$$

$$\eta_{cycle} = \frac{|W_{net}|}{Q_H} = \frac{|W_{23} + W_{41}|}{Q_{12}} = \frac{|-806.8 + 8.676|}{3194.5} = \mathbf{0.250 = \eta_{cycle}}$$

For each efficiency:
2 points for correct fraction
3 points for final answer

d) (10 points)

Note: for this section a subscript S refers to the isentropic case to avoid any confusion.

First, we need to realize what has been affected by the leak. Since the boiler has the leak, Q_{12} and H_2 will be affected. Since H_2 will be different, W_{23} and the isentropic work, W'_{23}, will also be affected.

Using the conditions given for state 2'', we can find H_2'' on page 739 with some interpolation using the entries for 3400 kPa at 375°C and 350°C.

$$H_2'' = \frac{3168 - 3108.7}{375 - 350} * (351.9 - 350) + 3108.7 = \text{ 3113.2 kJ/kg} \quad \text{(1 point)}$$

The entropy at 2'' can also be found in the same manner.

$$S_2'' = \frac{6.7719 - 6.6787}{375 - 350} * (351.9 - 350) + 6.6787 = \text{ 6.686 kJ/(kg*K) (1 point)}$$

$Q_{12}'' = H_2'' - H_1 = 3113.2$ kJ/kg – 197.1 kJ/kg = 2916.1 kJ/kg (1 point)

$W_{2''3} = H_3 - H_2'' = 2584.4$ kJ/kg – 3113.2 kJ/kg = -528.8 kJ/kg (1 point)

Since the entropy is the same as before,

$(H_3)_S = 2117.8$ kJ/kg (1 point)

$(W_{23})_S = 2117.8$ kJ/kg – 3113.2 kJ/kg = -995.4 kJ/kg (1 point)

Now for the efficiencies:

$\eta_{turbine} = \frac{W_{23}''}{W'_{23}} = \frac{-528.8}{-995.4} =$ **0.531 = η**

Midterm 2

November 17, 2006

Problem 2 (32 pts)

Consider a system at fixed T and P with two components and two phases.

(a) (4 pts)

What is the number of degrees of freedom for the intensive variables of such a system? Can all the intensive variables be determined by the conditions given above?

Phase rule for intensive variables:

$$F = 2 - \pi + N \quad \textbf{(1 pt)}$$

$$N = 2 \quad \textbf{(1/2 pt)}$$

$$\pi = 2 \quad \textbf{(1/2 pt)}$$

Thus,

$$\boxed{F = 2} \quad \textbf{(1 pt)}$$

So 2 degrees of freedom, thus fixing T and P determines all intensive variables. **(1 pt)**
The most common error was to subtract an additional 2 from the phase rule equation because of fixed T,P to get F=0. This is not correct because the phase rule specifies how many potential degrees of freedom there are given the number of components and the number of phases, not whether those degrees of freedom have been fixed and therefore the system is entirely specified (which is the case here).

(b) (12 pts)

In the liquid phase, the molar Gibbs free energy of the binary solution, G^l, is related to the mole fraction of component 1, x_1, in the liquid phase as: $G^l = 400x_1^2 - 200x_1 + 200$ (cal/mol). Please determine the partial molar Gibbs free energy of components 1 and 2 as a function of x_1.

$$\begin{aligned}
\bar{G}_i^l &= \left[\frac{\partial(nG^l)}{\partial n_i}\right]_{P,T,n_{j\neq i}} \qquad \textbf{(4 pts)} \\
\bar{G}_1^l &= \left[\frac{\partial(nG^l)}{\partial n_1}\right]_{P,T,n_2} = \left[\frac{\partial(400\frac{n_1^2}{n} - 200n_1 + 200n)}{\partial n_1}\right]_{P,T,n_2} \\
&= \frac{800nn_1 - 400n_1^2}{n^2} - 200 + 200 = \boxed{800x_1 - 400x_1^2} \quad \textbf{(4 pts)} \\
\bar{G}_2^l &= \left[\frac{\partial(nG^l)}{\partial n_2}\right]_{P,T,n_1} = -400\frac{n_1^2}{n^2} + 200 = \boxed{200 - 400x_1^2} \quad \textbf{(4 pts)}
\end{aligned}$$

Alternatively (and more easily), work directly from derived equations (11.15) and (11.16):

$$\begin{aligned}
\bar{G}_1^l &= G + x_2\frac{\mathrm{d}G}{\mathrm{d}x_1} \quad \textbf{(2 pts)} = \cdots = \boxed{800x_1 - 400x_1^2} \quad \textbf{(4 pts)} \\
\bar{G}_2^l &= G - x_1\frac{\mathrm{d}G}{\mathrm{d}x_1} \quad \textbf{(2 pts)} = \cdots = \boxed{200 - 400x_1^2} \quad \textbf{(4 pts)}
\end{aligned}$$

The most common error was to make an algebra error (several times due to misreading one's own sloppy handwriting) in the calculation of the final quantities, or to not simplify one's solutions to a function of x_1.

(c) (8 pts)

In the gas phase, the molar Gibbs free energy of the binary mixture, G^v, is a constant and is independent of the mole fraction of component 1, y_1, in the gas phase, i.e., $G^v = C$. Please determine the partial molar Gibbs free energy of components 1 and 2 as a function of C.

$$\begin{aligned}
\bar{G}_1^v &= = \left[\frac{\partial(nG^v)}{\partial n_1}\right]_{T,P,n_2} = \left[\frac{\partial(nC)}{\partial n_1}\right]_{T,P,n_2} = \boxed{C} \quad \textbf{(4 pts)} \\
\bar{G}_2^v &= \left[\frac{\partial(nG^v)}{\partial n_2}\right]_{T,P,n_1} = \left[\frac{\partial(nC)}{\partial n_2}\right]_{T,P,n_1} = \boxed{C} \quad \textbf{(4 pts)}
\end{aligned}$$

Equivalently, work through derived equations (11.15) and (11.16), as in (b).

(d) (8 pts)

At equilibrium, one observes that there are two phases in the system. What is the mole fraction of component 1 in the liquid phase? What is the value of the

constant C for the molar Gibbs free energy in the gas phase?
Equilibrium implies that:

$$\begin{aligned} 800x_1 - 400x_1^2 = \bar{G}_1^v &= \bar{G}_1^l = C \quad \textbf{(2 pts)} \\ 200 - 400x_1^2 = \bar{G}_2^v &= \bar{G}_2^l = C \quad \textbf{(2 pts)} \end{aligned}$$

Combining these two equations gives:

$$\boxed{x_1 = \frac{1}{4}} \quad \textbf{(2 pts)}$$

$$\boxed{C = 175} \quad \textbf{(2 pts)}$$

The most common error was to assert that $\bar{G}_1^v = \bar{G}_2^v$ and the same for liquids, or to assert that $G^l = G^v$.

Problem 3 (24 pts)

(a) (4 pts)

Prove that at constant Temperature, the difference of molar Gibbs free energy at two different pressures is: $G_2 - G_1 = \int_{P_1}^{P_2} V\mathrm{d}P$. Please start the proof by writing down the differential change of Gibbs free energy as a function of T and P.

$$\begin{aligned} G &= U - TS + PV \\ \mathrm{d}G &= dU - \mathrm{d}(TS) + \mathrm{d}(PV) \\ &= T\mathrm{d}S - P\mathrm{d}V - T\mathrm{d}S - S\mathrm{d}T + P\mathrm{d}V + V\mathrm{d}P \\ &= -S\mathrm{d}T + V\mathrm{d}P \quad \textbf{(1 pt)} \\ &= V\mathrm{d}P \quad \text{(const T)} \quad \textbf{(1 pt)} \\ \int \mathrm{d}G &= \int_{P_1}^{P_2} V\mathrm{d}P \quad \textbf{(1 pt)} \end{aligned}$$

$$\boxed{G_2 - G_1 = \int_{P_1}^{P_2} V\mathrm{d}P} \quad \textbf{(1 pt)}$$

The most common error was to leave in a $\sum \mu_i \mathrm{d}n_i$ term even though the system makes no mention of any composition changes.

(b) (8 pts)

Consider a mixture composed of methanol (1) and ethanol (2) at 300 K and 1 bar with the presence of both gas and liquid phases. The mole fraction of methanol in the gas phase is $y_1 = 0.3$. The fugacity coefficients of methanol and ethanol at this condition are 0.8 and 0.75, respectively. Please determine the fugacity of methanol and ethanol in the gas phase.

$$\begin{aligned}
\hat{f}_i &= y_i P \hat{\phi}_i \quad \textbf{(3 pts)} \\
\hat{f}_1^v &= y_1 P \hat{\phi}_1 = (0.3)(1bar)(0.8) = \boxed{0.24bar} \quad \textbf{(2.5 pts)} \\
\hat{f}_2^v &= y_2 P \hat{\phi}_2 = (0.7)(1bar)(0.75) = \boxed{0.525bar} \quad \textbf{(2.5 pts)}
\end{aligned}$$

The most common error was to work with f_i's even though this is a mixture, not a pure component.

(c) (12 pts)

In the liquid phase of the mixture, the solution can be considered as an ideal solution. In the case of $y_1 = 0.3$ at 300 K and 1 bar, the mole fraction of methanol in the solution is: $x_1 = 0.2$. Please determine the specific volume of the solution of methanol and ethanol.

Data:

The saturated vapor pressure for methanol and ethanol at 300 K are 0.6 bar and 0.75 bar, respectively. The fugacity coefficients of the saturated vapor of methanol and ethanol at 300 K are 0.8 and 0.9, respectively. $G_2 - G_1 = \int_{P_1}^{P_2} V \mathrm{d}P$ can be approximately equated to $G_2 - G_1 = V(P_2 - P_1)$ for both methanol and ethanol.

Translation:

$$
\begin{aligned}
x_1 &= 0.2 \\
x_2 &= 0.8 \\
y_1 &= 0.3 \\
y_2 &= 0.7 \\
P &= 1bar \\
P_1^{sat} &= 0.6bar \\
P_2^{sat} &= 0.75bar \\
\phi_1^{v,sat} &= 0.8 \\
\phi_2^{v,sat} &= 0.9
\end{aligned}
$$

From part (b):

$$
\begin{aligned}
\hat{\phi}_1^v &= 0.8 \\
\hat{\phi}_2^v &= 0.75
\end{aligned}
$$

At equilibrium:

$$y_i\hat{\phi}_i^v P = \hat{f}_i^v = \hat{f}_i^l = x_i\gamma_i f_i^l = x_i\gamma_i P_i^{sat}\phi_i^{v,sat}\exp\left[\frac{V_i^l(P-P_i^{sat})}{RT}\right]$$

Rearranging, and noting that $\gamma_i = 1$ for an ideal solution:

$$
\begin{aligned}
V_i^l &= \frac{RT}{P-P_i^{sat}}\ln\frac{y_i\hat{\phi}_i^v P}{x_i P_i^{sat}\phi_i^{v,sat}} \\
V_1^l &= \frac{(83.14cm^3barmol^{-1}K^{-1})(300K)}{1bar-0.6bar}\ln\frac{(0.3)(0.8)(1bar)}{(0.2)(0.6bar)(0.8)} \\
&= 57,140cm^3/mol \\
V_2^l &= \frac{(83.14cm^3barmol^{-1}K^{-1})(300K)}{1bar-0.75bar}\ln\frac{(0.7)(0.9)(1bar)}{(0.8)(0.75bar)(0.9)} \\
&= 15,380cm^3/mol
\end{aligned}
$$

$$V = x_1\bar{V}_1 + x_2\bar{V}_2 = x_1V_1 + x_2V_2 \quad \text{(ideal solution)} = \boxed{23,732cm^3/mol}$$