1. (30 Points) ***Do 5 out of 6*** (If 6 are done only the first 5 will be graded)***

a). In the reaction $3O_2 \rightarrow 2O_3$ it is found that 0.6 mol of $O_2$ are consumed. Find the extent of reaction, $\xi$

$$n_i - n_i^0 = \nu_i \xi$$ and $$n_{O_2} - n_{O_2}^0 = 0.6 \cdot \left( n_{O_2} - n_{O_2}^0 \right)/\nu_{O_2} = \xi = (-0.6)/(-3) = 0.2 .$$

b) It is found that $K_P$ is independent of $T$ for a particular chemical reaction. What does this tell you about the reaction?

This is true if $\Delta H_{reaction} = 0$.

.

c). Define the term “triple point”. What conditions are satisfied?

At the triple point three phases are in equilibrium. This means that

$$p_a = p_b = p_c$$
$$T_a = T_b = T_c$$
$$\mu_a = \mu_b = \mu_c$$
d). Show that \( \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_j,n_k} = \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_j,n_k} \)

The Gibbsian differentials for \( U \) at fixed \( S \) and \( V \) and \( A \) at fixed \( T \) and \( V \) with the inclusion of the chemical potential terms are:

\[
dU = TdS - pdV + \sum_i \mu_i dn_i
\]

\[
dA = -SdT - pdV + \sum_i \mu_i dn_i
\]

The above definitions of the chemical potential for these independent variables show they are equal.

e). In setting up thermodynamic tables for the entropy, how is the third law of thermodynamics used, and what is the convention for the entropy?

The third law states that the entropy change approaches zero as \( T \to 0 \) as long as the substance is in internal equilibrium. This feature along with the convention that the entropy at \( T=0 \) of the elements is taken as 0 then sets the entropy to be zero for compounds at \( T=0 \) (and 1 atm pressure).

f). Define an ideal solution in terms of the chemical potential of its species. Explain the meaning of all symbols used and indicate what they depend on.

In an ideal solution the chemical potential is expressed as

\[
\mu_i = \mu_i^*(T,p) + RT \ln x_i
\]

where the standard state \( \mu_i^* \) corresponds to pure species \( i \) and depends on \( T \) and \( p \). The expression holds for all values of the mole fractions, \( x_i \).
2. (30 points).
A) Which of the following reactions are spontaneous at 25 C in the direction written? Which are exothermic or endothermic?

\[ \text{HCl(g)} + \text{NH}_3(g) = \text{NH}_4\text{Cl(s)} \]
\[ 2\text{Al}_2\text{O}_3(s) + 3\text{Si(s)} = 3\text{SiO}_2(s) + 4\text{Al(s)} \]

<table>
<thead>
<tr>
<th>(at 25 C)</th>
<th>( \Delta H_f ) (kJ/mole)</th>
<th>( \Delta G_f ) (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HCl(g)} )</td>
<td>−92.91</td>
<td>−95.26</td>
</tr>
<tr>
<td>( \text{NH}_3(g) )</td>
<td>−46.11</td>
<td>−16.63</td>
</tr>
<tr>
<td>( \text{NH}_4\text{Cl(s)} )</td>
<td>−314.0</td>
<td>−203.89</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3(s) )</td>
<td>−1669.8</td>
<td>−1564.4</td>
</tr>
<tr>
<td>( \text{SiO}_2(s) )</td>
<td>−859.4</td>
<td>−805.0</td>
</tr>
</tbody>
</table>

\[ \Delta G_{rxn}^0 = \sum \Delta G_{f,\text{prod}}^0 - \sum \Delta G_{f,\text{react}}^0 \]

For first reaction:
\[ \Delta G_{rxn}^0 = \left[ (−203.89) − (−95.26) − (−16.63) \right] \text{kJ/mol} = −92.00 \text{kJ/mol} \]
Spontaneous since \( \Delta G_{rxn} < 0 \).
\[ \Delta H_{rxn}^0 = \left[ (−314.0) − (−92.91) − (−46.11) \right] \text{kJ/mol} = −174.98 \text{kJ/mol} \]
Exothermic since \( \Delta H_{rxn} < 0 \).

For second reaction:
\[ \Delta G_{rxn}^0 = \left[ (4)(0) + 3(−805.0) − (2)(−1564.4) − (3)(0) \right] \text{kJ/mol} = 713.8 \text{kJ/mol} \]
Not spontaneous since \( \Delta G_{rxn} > 0 \)
\[ \Delta H_{rxn}^0 = \left[ (4)(0) + 3(−859.4) − (2)(−1669.8) − (3)(0) \right] \text{kJ/mol} = 761.4 \text{kJ/mol} \]
Endothermic since \( \Delta H_{rxn} > 0 \)
B) In which direction will the equilibrium shift if the temperature is increased? To answer this question, obtain the van’t Hoff equation by evaluating $\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p$ and relate to the equilibrium constant.

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{G}{T^2} + \frac{1}{T} \frac{\partial G}{\partial T}_p = -\frac{H - TS}{T^2} - \frac{S}{T} = -\frac{H}{T^2}$$

Since the equilibrium constant is related to $\Delta G_{\text{rxn}}^0$ by

$$\Delta G_{\text{rxn}}^0 = -RT \ln K_p^0$$

it then follows that

$$\frac{d \ln K_p^0}{dT} = \frac{\Delta H_{\text{rxn}}^0}{RT^2}$$

which is the van’t Hoff equation.

For $\Delta H_{\text{rxn}}^0 < 0$ the equilibrium constant decreases as $T$ increases and for $\Delta H_{\text{rxn}}^0 > 0$ the equilibrium constant increases as $T$ increases.
3. (20 points)

Using the phase rule, find the number of degrees of freedom, \( f = c_{ind} + 2 - p \), for:

A) \( \text{H}_3\text{PO}_4 \) in water in equilibrium with water vapor; disregard salt ionization.

Two phases \( p=2 \)

Two components \( c_{ind}=2 \)

No reaction or other restrictions so \( f=2+2-2=2 \)

B) The same as A) but take into account \( \text{H}_3\text{PO}_4 \) ionization into all possible ions (up to \( \text{PO}_4^{3-} \) ) for \( \text{H}_3\text{PO}_4 \):

\[
\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-
\]

\[
\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}
\]

\[
\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}
\]

Two phases \( p=2 \)

Six components \( c=6 \)

Three ionization equilibria \( r=3 \) listed above

One charge balance, to balance \( \text{H}^+ \) with all the cations, \( a=1 \).

\[
c_{ind} = c - r - a = 6 - 3 - 1 = 2
\]

\( f=2+2-2=2 \). Still 2.
4. (20 points)
A bartender who clearly has not studied thermodynamics attempts to prepare 100 cm$^3$ of some potable by mixing 30 cm$^3$ of ethanol with 70 cm$^3$ of water. Does she succeed? The figure will be of help. The density of ethanol is 0.785 g/cm$^3$ and that of water is 1.00 g/cm$^3$. The molecular weight of ethanol is 46.1 g/mol and that of water is 18 g/mol.

Need to first figure out the mols for the amounts of water and ethanol:

$$n_{\text{H}_2\text{O}} = \frac{(70 \text{ cm}^3)(1 \text{ g/cm}^3)}{(18 \text{ g/mol})} = 3.89 \text{ mol}$$

$$n_{\text{ETOH}} = \frac{(30 \text{ cm}^3)(0.785 \text{ g/cm}^3)}{(46.1 \text{ g/mol})} = 0.51 \text{ mol}$$

The mol fractions are:

$$x_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{tot}}} = \frac{3.89}{(0.51 + 3.89)} = 0.88$$

$$x_{\text{ETOH}} = \frac{n_{\text{ETOH}}}{n_{\text{tot}}} = \frac{0.51}{(0.51 + 3.89)} = 0.12$$
Estimate from the figure that at this composition

\[ \bar{V}_{\text{H}_2\text{O}} = 18.2 \text{ cm}^3/\text{mol} \]

\[ \bar{V}_{\text{ETOH}} = 52.5 \text{ cm}^3/\text{mol} \]

Construct total volume:

\[ V = n_{\text{ETOH}} \bar{V}_{\text{ETOH}} + n_{\text{H}_2\text{O}} \bar{V}_{\text{H}_2\text{O}} = (0.51)(52.5 \text{ cm}^3) + (3.89)(18.2 \text{ cm}^3) = 97.6 \text{ cm}^3. \]

She doesn’t succeed.
Mathematical expressions:

\[
\int x^n \, dx = x^{(n+1)} / (n + 1); \quad n = 0, 1, 2, \ldots
\]

\[
\int \frac{1}{x} \, dx = \ln x
\]

\[
\int x^{-n} \, dx = -x^{-(n-1)} / (n - 1); \quad n = 2, 3, \ldots
\]

Euler: \[\frac{\partial x}{\partial y} \bigg|_z \frac{\partial y}{\partial z} \bigg|_x \frac{\partial z}{\partial x} \bigg|_y = -1\]

Inverter: \[\frac{\partial x}{\partial y} \bigg|_z = \frac{1}{\frac{\partial y}{\partial x} \bigg|_z}\]

\[
dU = \delta q + \delta w \quad \delta w = -P_{ext}dV \quad \frac{N}{V} \left( \frac{h^4}{8mk_BT} \right)^{3/2} \ll 1
\]

\[
dU = C_v dT \quad \Delta U = q_v \quad C_v = (\partial U / \partial T)_V
\]

\[
H = U + PV \quad \Delta H = q_P \quad C_P = (\partial H / \partial T)_P
\]

\[
\mu / T = (\partial T / \partial P)_H = - (\partial H / \partial P)_T / C_P \quad H(T_2) = H(T_1) + \int_{T_1}^{T_2} (C_P) dT
\]

\[
dS = \delta_{qrev} / T \quad \Delta S_{univ} = \Delta S + \Delta S_{surr} \quad S = k_B \ln W
\]

\[
S = U / T + k_B \ln Q \quad S = k_B T \left( \delta \ln Q / \partial T \right)_{N,V} + k_B \ln Q
\]

\[
\ln N! \approx N \ln N - N \quad S(T_2) = S(T_1) + \int_{T_1}^{T_2} (C_v / T) dT
\]

\[
dH = dU + d(PV) \quad dU = TdS - PdV \quad dH = TdS + VdP
\]

\[
A = U - TS \quad dA = dU - TdS \quad dA = - PdV - SdT
\]

\[
G = H - TS \quad dG = dH - TdS \quad dG = VdP - SdT
\]

\[
(\partial U / \partial S)_V = T \quad (\partial U / \partial V)_S = -P \quad (\partial T / \partial V)_S = (\partial P / \partial S)_V
\]

\[
(\partial H / \partial S)_P = T \quad (\partial H / \partial P)_S = V \quad (\partial T / \partial P)_S = (\partial V / \partial S)_P
\]

\[
(\partial A / \partial V)_T = -P \quad (\partial A / \partial T)_V = -S \quad (\partial P / \partial T)_V = (\partial S / \partial V)_T
\]

\[
(\partial G / \partial T)_P = -S \quad (\partial G / \partial P)_T = V \quad (- \partial S / \partial P)_T = (\partial V / \partial T)_P
\]
\[
\begin{align*}
(\partial U / \partial V)_T &= T (\partial P / \partial T)_V - P \\
C_p - C_v &= \alpha^2 VT / \kappa \\
\kappa &= (-1 / V) (\partial V / \partial P)_T \\
\alpha &= (1 / V) (\partial V / \partial T)_P \\
\Delta G(V_1 \rightarrow V_2, \text{isothermal}) &= \int P dV \\
\Delta_r H &= \Delta_r H^0 + \int_{T_2}^{T_1} (\partial \Delta_r H / \partial T)_P dT \\
\eta_i d\mu_i + S dT - V dp &= 0 \quad \text{(Gibbs-Duhem)} \\
\sum \nu_i \mu_i &= 0 \quad \text{(reaction equilibrium)}.
\end{align*}
\]

\[
\begin{align*}
\mu_i &= \mu_i^0 + RT \ln a_i \\
\gamma_i &= \gamma \gamma_i.
\end{align*}
\]