Q1. (40 Points)

This question has 5 parts, and the numerical results for later parts depend on your answers to the earlier parts. Show your reasoning clearly, to ensure partial credit if your numerical calculations end up being incorrect.

Consider molecules of type A, with chemical potential of 1.0 kJ/mole, under standard conditions.

Type A molecules can convert to molecules of type B, with a chemical potential of 0.5 kJ/mole, under standard conditions:

A <-> B

(A) What is the standard free energy of the reaction, $\Delta_r G^o$? Hint: $\Delta_r G^o$ is the molar free energy change in converting pure A to pure B. – 3 points

The standard free energy of the reaction is $\mu_B - \mu_A = 0.5 - 1.0 = -0.5$ kJ/mole

$= -500$ Joules/mole

(B) If we start with 10,000 molecules of A and zero molecules of B at 300K, how many molecules of A and B will be found at equilibrium? – 7 points

[Assume that volume is constant in 1B]

At equilibrium, $\Delta G_r^0 = -RT \ln K$

and $K = e^{-\Delta G^0/RT} = e^{+(0.5\times10^3)J / 8.314 J K^{-1} mol^{-1} \times 300K}$

$K = 1.22$

$\Rightarrow \frac{[B]}{[A]} = 1.22$ Because volume is constant $\frac{[B]}{[A]} = \frac{N_B}{N_A}$

where N_B and N_A are the number of A and B molecules

So $\frac{N_B}{N_A} = 1.22$ $N_B = 1.22\ N_A$ But $N_B + N_A = 10000$

$1.22 N_A + N_A = 10000$

$2.22\ N_A = 10000$

$N_A = 4504$

$N_B = 5496$

Note $x_A = \frac{4504}{10000} = 0.45$

$x_B = 1 - x_A = 0.55$

needed for later questions.

(C) Calculate the molar change in entropy, ΔS_{mix}, that arises from mixing reactions and products when the system reaches equilibrium. To do this use the following relationship between mole fractions and the molar entropy change:
$\Delta S_{mix} = -R\,(x_1 \ln x_1 + x_2 \ln x_2)$ - 5 points

$$\Delta S_{mix} = -R\,(0.45 \ln 0.45 + 0.55 \ln 0.55)$$
$$= -8.314\ \mathrm{J K^{-1} mole^{-1}}\,(-0.359 + (-0.329))$$
$$= +5.72\ \mathrm{J K^{-1} mole^{-1}}$$

(D) Compare your result to the molar entropy change calculated using a simple lattice model with 10,000 grid points. Assume that every grid point is occupied only by A molecules at the start of the reaction (i.e., the system starts off as pure A). Calculate the entropy for this situation. Then calculate the entropy for the equilibrium situation, where the number of A and B molecules are given by your answer to part (B). Show all steps in the calculation. – 15 points
Hint:
$S = k_b \ln W$, where W is the multiplicity and k_b is Boltzmann's constant.
Use the simplest form of Stirling's approximation: $\ln N! = N \ln N$

For initial condition, $S = 0$
because $W = \dfrac{N!}{N_A!\,0!} = 1$ and $\ln 1 = 0$

For final condition
$$S = k_B \ln W = k_B \ln\left[\frac{N!}{N_A!\,N_B!}\right]$$
$$= k_B\{10000 \ln 10000 - 4504 \ln 4504 - 5496 \ln 5496\}$$
$$= k_B\{92103 - 37891 - 47330\}$$

(BLANK SPACE FOR QUESTION 1, D)

$$= k_B \{ 6882 \} = 1.381 \times 10^{-23}\ JK^{-1} \times 6882$$

$$\Rightarrow \Delta S = 9504 \times 10^{-23}\ JK^{-1}$$

This is the entropy change for 10000 atoms

To get the molar entropy change

$$(\Delta S)_{molar} = \frac{9504 \times 10^{-23}}{10,000} \times \underset{\substack{\uparrow \\ \text{Avogadro's \#}}}{N_a}$$

$$= \frac{9504 \times 10^{-23}}{10000} \times 6.02 \times 10^{+23}\ JK^{-1}$$

$$= 5.72\ J K^{-1} mol^{-1}$$

Same as previous answer !

(E) Calculate the molar free energy change at 300K in going from an initial state consisting of pure A type molecules, to a final state consisting of A and B type molecules in equilibrium at 300K. – 10 points
Hint: There are two components to the free energy change. One is given by the chemical potentials of type A molecules and type B molecules. The second component is given by the free energy of mixing. Assume that the enthalpy of mixing is zero.

The molar free energy change is

Initially,

$$\text{free energy} = \underbrace{\boxed{1.0\ kJ/moles}}_{G_{INITIAL}}$$

finally:

free energy from chemical potential

$$+ \text{free energy of mixing} = X_A \mu_A + X_B \mu_B \underbrace{- T \Delta S_{MIX}}_{\text{free energy of mixing}}$$

mole fractions
see part B

$$= 0.45 \times \underbrace{1.0}_{kJ} + 0.55 \times \underbrace{0.5}_{kJ} - \overset{K}{\widetilde{300}} \times \underbrace{5.72 \times 10^{-3}}_{kJ\ K^{-1}}$$

Note: be careful to use only kJ, or only J!

$$= 0.725 - 1.716 = \underbrace{\boxed{-0.991\ kJ/mole}}_{G_{FINAL}}$$

$$\Delta G = G_{FINAL} - G_{INITIAL} = -0.991 - 1.0$$

$$= -1.991\ kJ/mole$$

Q2. (20 Points)
Consider a solution of two components, A and B, which behaves ideally. Initially, there are 2.0 moles of A and 2.5 moles of B in the liquid phase, and the total vapor pressure is 1.35 atmosphere. When the number of moles of A in the liquid phase is increased to 3.0 moles (keeping the number of moles of B constant), the vapor pressure increases to 1.5 atmospheres. What are the vapor pressures, in atmospheres, of pure A and of pure B? Assume that the temperature is constant.

Let vapor pressure of pure A $= p_A^*$

" " " " " B $= p_B^*$

Initially, $X_A = \frac{2.0}{2.0+2.5} = 0.44$ $\quad X_B = 1 - X_A = 0.56$

Total pressure $= X_A p_A^* + X_B p_B^*$

$= 0.44 p_A^* + 0.56 p_B^* = \underbrace{1.35}_{\text{INITIAL TOTAL PRESSURE}}$ atm

$\Rightarrow p_A^* = \frac{1.35 - 0.56 p_B^*}{0.44}$

$\Rightarrow p_A^* = 3.07 - 1.27 p_B^*$

Finally, $X_A = \frac{3.0}{5.5} = 0.55$ $\quad X_B = 1 - X_A = 0.45$

Total Pressure $= X_A p_A^* + X_B p_B^* = 0.55 p_A^* + 0.45 p_B^*$

$= 0.55(3.07 - 1.27 p_B^*) + 0.45 p_B^* = 1.5$ atm

$\Rightarrow 1.69 - 0.70 p_B^* + 0.45 p_B^* = 1.5 \Rightarrow 0.19 = 0.25 p_B^*$

$\Rightarrow p_B^* = 0.76$ atm $\quad p_A^* = 3.07 - 1.27 p_B^* = 2{,}1048$ Atm

Check Initially $X_A p_A^* + X_B p_B^* = 1.35$ Atm. Correct!

Q 3. (20 points)
A cell membrane at 300 K is permeable to Ca^{2+} but not to anions. The concentration of Ca^{2+} inside the cell is 0.1 M, and the concentration of Ca^{2+} outside the cell is 0.001 M.
(A) What is the molar Gibbs energy change in transporting Ca^{2+} ions from outside the cell to inside? The chemical potential of a component X is given by: $\mu_X = \mu_X^O + RT \ln[X]$. Assume that there is no potential across the membrane.
- 10 points

The free energy difference is

$$\mu_{inside} - \mu_{outside} = RT \ln \frac{[X]_{IN}}{[X]_{OUT}}$$

$$= 8.314\ JK^{-1}mol^{-1} \times 300K \times \ln\left[\frac{0.1}{0.001}\right]$$

$$= 2494.2 \times \ln(100)\ J/mole$$

$$= 2494.2 \times 4.605\ J/mole$$

$$= +11.49\ kJ/mole$$

[Note that the free energy difference is positive, which means that moving ions from OUT to IN is not spontaneous]

(B) What potential difference would have to exist across the membrane for Ca^{2+} to be in equilibrium at the concentrations given in part A? Give the sign of the potential inside with respect to outside. - 10 points

Hint: The molar free energy (in units of Joules/mole) of moving a charge against an electric potential difference across the membrane is:
$zF\Delta V$, where z is the charge, F is the Faraday constant (96,500 C/mol) and ΔV is the potential difference in volts.

At equilibrium

$$\Delta G = 0$$

$$\Delta G = \underbrace{\Delta G_1}_{\text{conc. gradient}} + \underbrace{\Delta G_2}_{\text{electrostatic}}$$

$$\Delta G_1 = +11.49 \text{ kJ/mole}$$

$$\text{So } \Delta G_2 = -11.49 \text{ kJ/mole}$$

$$= \underbrace{zF\Delta V}_{\text{This is in units of J/mole}} \times 10^{-3} \text{ kJ/mole}$$

$$\Rightarrow \quad z = 2\ (Ca^{2+}) \quad F = 96500 \quad \Delta V = ?$$

$$2 \times 96500 \times 10^{-3}\ \Delta V = -11.49$$

$$\Rightarrow \quad \Delta V = \frac{-11.49}{2 \times 96500 \times 10^{-3}} = -0.0595 \text{ V}$$

$$= -59.V \text{ mV}$$

The sign of the potential is such that it is negative <u>inside</u> the cell.

Q4. (20 points)
Consider a chemical reaction involving the conversion of molecules of type A into molecules of type B:

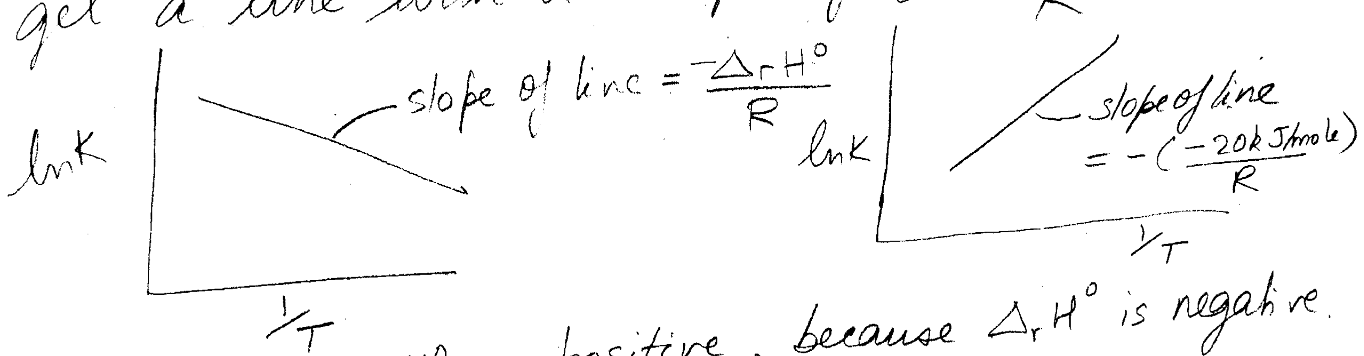
A <-> B

The standard enthalpy of the reaction, $\Delta_r H^\circ$ is –20 kJ/mole. A scientist wishing to produce more B from A increases the temperature of the reaction, without adding more A. Will she be successful at producing more B at equilibrium at the higher temperature? Explain your answer in terms of the van't Hoff equation.

The van't Hoff equation gives the dependence of the equilibrium constant with temperature.

$$\ln K = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

If we plot ln K as a function of $\left(\frac{1}{T}\right)$, we get a line with a slope of $\left\{-\frac{\Delta_r H^\circ}{R}\right\}$.



In this case, $\frac{-\Delta_r H^\circ}{R}$ is positive, because $\Delta_r H^\circ$ is negative. So, ln K increases with increase in $\frac{1}{T}$ ⇒ ln K decreases with ~~the~~ temperature. So K decreases with temperature. Since $K = [B]/[A]$, [B] decreases at higher temperature, So the scientist will fail. This phenomenon can also be explained by Le Chatelier's principle. Since the reaction is exothermic, it is disfavored at higher temperature.

-END OF EXAM-