Sample quiz and test questions – Chapter 3

I. Terms and short answers

1. The statement of the Second Law of Thermodynamics is

   The entropy of the universe tends to increase OR \( \Delta S_{\text{univ}} > 0 \) or = 0

2. The change in entropy of the system when the temperature is raised at constant volume is given by equation

   \[
   \Delta S = C_v \ln \left( \frac{T_f}{T_i} \right)
   \]

3. The Trouton’s rule states that

   The entropies of vaporization of all liquids, except those with H-bonds, are approximately the same.

4. Compound with negative Gibbs energies of formations are said to be thermodynamically stable

   with respect to their elements

5. The thermodynamic condition of equilibrium is given by equation

   \[
   \Delta G = 0 \text{ at } T=\text{const and } p=\text{const}
   \]

6. For the following reaction

   \[
   2\text{NOBr}(g) \rightleftharpoons 2\text{NO}(g) + \text{Br}_2(g) \quad \Delta H^\circ = -344 \text{ kJ}
   \]

   state which way the equilibrium will shift (left, right, or no change) when each of the following changes is made

   a) increase in the container volume \hspace{1cm} \text{right}

   b) decrease in temperature \hspace{1cm} \text{right}

   c) increase in pressure \hspace{1cm} \text{left}

II. Sketch the graph illustrating the estimation of the absolute entropy of a substance at 300 K from the measurement of the heat capacities
### III Problems

1. Calculate the entropy change when a sample of 30 g of Ne is expanded from 1 L to 10 L and simultaneously cooled from 350 K to 300 K. \(C_v,m = 3/2R\).

   \[
   \begin{align*}
   \text{30 g Ne} & \quad V_i = 1 \text{ L} \quad V_f = 10 \text{ L} \\
   & \quad T_i = 350 \text{ K} \quad T_f = 300 \text{ K} \\
   30 \text{ g}/20.18 \text{ g/mol} & = 1.49 \text{ moles} \\
   \text{Two reversible steps:} \\
   (i) & \quad \text{constant volume cooling} \quad \Delta S = nC_v \ln(T_f/T_i) = -2.86 \text{ J/K} \\
   (ii) & \quad \text{isothermal expansion} \quad \Delta S = nR \ln(V_f/V_i) = 28.52 \text{ J/K} \\
   \Delta S_{\text{tot}} & = 25.66 \text{ J/K} 
   \end{align*}
   \]

2. Calculate the change in entropy when 200 g of \(\text{H}_2\text{O}\) at 100°C is mixed with 300 g of \(\text{H}_2\text{O}\) at 20°C in an insulated vessel. \(C_{p,m} = 75.5 \text{ kJ/mol}\).

   \[
   \begin{align*}
   200 \text{ g } \text{H}_2\text{O} & = 11.1 \text{ moles at } T = 373 \text{ K} \quad 300 \text{ g } \text{H}_2\text{O} = 16.7 \text{ moles at } T = 293 \text{ K} \\
   \text{We need to set up the heat balance to find the final temperature of a mixture} \\
   \text{heat lost by hot water} & = \text{heat gained by cold water} \\
   q & = n \ C_p \Delta T \\
   -11.1 \times 75.5 \times (T_f - 373) & = 16.7 \times 75.5 \times (T_f - 293) \\
   T_f & = 325 \text{ K} \\
   \Delta S & = n(\text{hot water})C_p \ln(T_f/T_i) + n(\text{cold water})C_p \ln(T_f/T_i) \\
   & = 11.1 \times 75.5 \times \ln(325/373) + 16.7 \times 75.5 \times \ln(325/293) \\
   & = 15.3 \text{ J/K} 
   \end{align*}
   \]

3. Calculate the change in the entropies of the system and the surroundings, and the total entropy change when a sample of oxygen gas of mass 50 g at 300 K and 1 bar doubles its volume in:

   \[
   \begin{align*}
   50 \text{ g O}_2(\text{g}) & = 1.56 \text{ moles} \quad T = 300 \text{ K} = \text{const} \quad p = 1 \text{ bar} \quad V_f = 2 \times V_i \\
   \text{a) isothermal reversible expansion} \\
   \Delta S_{\text{sys}} & = nR \ln(V_f/V_i) = 1.56 \times 8.314 \times \ln2 = 9 \text{ J/K} \\
   \Delta S_{\text{surr}} & = -9 \text{ J/K} \quad (\text{see the example from the lecture})
   \end{align*}
   \]
b) isothermal irreversible expansion against \( p_{\text{ext}} = 0 \)
\[ \Delta S_{\text{sys}} = nR \ln \left( \frac{V_f}{V_i} \right) = 1.56 \times 8.314 \times \ln 2 = 9 \, \text{J/K} \]
\[ \Delta S_{\text{surr}} = 0 \text{ (see the example from the lecture)} \]

4. Calculate the non-expansion work, expansion work, and the total work that can be obtained when one mole butane is burned under standard conditions at 25°C.

\[ \text{C}_4\text{H}_{10}(g) + 13/2 \text{ O}_2(g) \rightarrow 4\text{CO}_2(g) + 5 \text{ H}_2\text{O}(l) \]
\[ \Delta G = \Delta H - T \Delta S \]
\[ \Delta H = \Delta_{\text{comb}} H^0 = -2878 \, \text{kJ/mol} \]
\[ \Delta S = \Delta_{\text{comb}} S^0 = 5 \times S_m(\text{H}_2\text{O}) + 4 \times S_m(\text{CO}_2) - 13/2 \times S_m(\text{O}_2) - S_m(\text{C}_4\text{H}_{10}) = -439 \, \text{J/K mol} \]
\[ \Delta G^0 = -2878 \times 10^3 - 298 \times (-439) = -2747 \, \text{kJ = non-expansion work} \]
\[ w = -p_{\text{ext}} \Delta V = -\Delta nRT = - (4 - 13/2 - 1) \times 8.314 \times 298 = 8.7 \, \text{kJ = expansion work} \]
\[ w_{\text{tot}} = -2738 \, \text{kJ} \]

5. Using \( \Delta G^0 \) and \( \Delta H^0 \) values for combustion of glucose at 25°C determine whether the reaction will be more favored at 37°C.

\[ \Delta G^0 = -RT \ln K \]
\[ \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]
\[ \Delta H^0 = -2808 \, \text{kJ/mol} \]
\[ \Delta S^0 = \text{use the entropy values from the problem (4) and } S(\text{C}_6\text{H}_{12}\text{O}_6) = 212 \, \text{J/K mol} \]
\[ \Delta S^0 = 259 \, \text{J/K} \]
\[ \Delta G^0 = -2808 \times 10^3 J - 298 \times 259 \text{ J/K} = -2885 \, \text{kJ} \]
\[-2885 \times 10^3 J = -8.314 \times 298 \ln K \rightarrow K = 1 \times 10^{500} \]
\[ \ln K(310) = \ln K(298) + \left[ (-2808 \times 10^3) / 8.314 \right] (1/298 - 1/310) \]
\[ K(310) = 5.2 \times 10^{486} \]
Reaction is less favored at 37°C.

6. When 2 mol of a gas at 300 K and 3 bar is isothermally compressed, its entropy decreases by 20 J/K. Calculate:
   a) the final pressure of the gas
   \[ n = 2 \text{ moles} \quad T = 300 \, \text{K = const} \quad p = 3 \, \text{bar} \quad \Delta S = -20 \, \text{J/K} \]
   \[ \Delta S = nR \ln \left( \frac{V_f}{V_i} \right) = nR \ln \left( \frac{p_f}{p_i} \right) \]
   \[ p_f = 10 \, \text{bar} \]
   
   b) \( \Delta G \) for the compression
   \[ dG = V dp = nRT dp / p \]
   \[ \Delta G = nRT \ln \left( \frac{p_f}{p_i} \right) = 6 \, \text{kJ} \]

THE PROBLEM BELOW HAS BEEN MODIFIED

7. The equilibrium constant for the reaction \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \) is \( 1.69 \times 10^{-3} \) at 2300 K. A mixture consisting of 5 g of \( \text{N}_2\text{O}_4 \) and 2 g of \( \text{NO}_2 \) in a container of volume 1 L is heated to
2300 K and allowed to come to equilibrium. Calculate the mole fraction of NO$_2$ at equilibrium. Assume that the total pressure at the equilibrium is 1 bar.

\[
K = \frac{x^2(\text{NO}_2)}{x(\text{N}_2\text{O}_4)}
\]
\[
1.69 \times 10^{-3} = \frac{x^2}{(1-x)} \quad \rightarrow \quad \text{solving quadratic equation gives } x = 0.0403
\]