Homework set #3

4.8 Calculate the values of ΔU, ΔH, and ΔS for the following process:

$$1 \text{ mole of liquid water at } 25^\circ \text{ C and } 1 \text{ atm} \rightarrow 1 \text{ mol of steam at } 100^\circ \text{ C and } 1 \text{ atm}$$

The molar heat of vaporization of water at 373 K is 40.79 kJ mol^{-1}, and the molar heat capacity of water is 75.3 J K^{-1} mol^{-1}. Assume the molar heat capacity to be temperature independent and ideal-gas behavior.

The problem can be solved readily by breaking down the process into two steps, each carried out at 1 atm: (1) $H_2O(l)$ is heated from 25° C to 100° C, then (2) $H_2O(l)$ at 100° C is heated to effect the phase transformation to $H_2O(g)$ at 100° C.

Step 1

$$H_2O(l),\ 25^\circ \text{ C} \rightarrow H_2O(l),\ 100^\circ \text{ C}$$

$$\Delta H = C_P \Delta T = (1 \text{ mol}) \left(75.3 \text{ J K}^{-1}\text{mol}^{-1}\right) (373.2 \text{ K} - 298.2 \text{ K}) = 5.648 \times 10^3 \text{ J}$$

ΔU is related to ΔH by

$$\Delta U = \Delta H - P \Delta V$$

Since both reactant and product are in the liquid phase, ΔV is negligible. Therefore,

$$\Delta U = \Delta H = 5.648 \times 10^3 \text{ J}$$

$$\Delta S = C_P \ln \frac{T_2}{T_1} = (1 \text{ mol}) \left(75.3 \text{ J K}^{-1} \text{ mol}^{-1}\right) \ln \frac{373.2 \text{ K}}{298.2 \text{ K}} = 16.89 \text{ J K}^{-1}$$

Step 2

$$H_2O(l),\ 100^\circ \text{ C} \rightarrow H_2O(g),\ 100^\circ \text{ C}$$

$$\Delta H = n \Delta_{\text{vap}} \overline{H} = (1 \text{ mol}) \left(40.79 \text{ kJ mol}^{-1}\right) = 40.79 \text{ kJ}$$

To calculate ΔU, the change in volume must first be determined. Since the volume of $H_2O(g)$, V_g is much greater than that of $H_2O(l)$, V_l, the latter is ignored.

$$\Delta U = \Delta H - P \Delta V = \Delta H - P \left(V_g - V_l\right) = \Delta H - P V_g$$

$$= \Delta H - P \frac{nRT}{P} = \Delta H - nRT$$

$$= 40.79 \text{ kJ} - (1 \text{ mol}) \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\right) (373.2 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= 37.687 \text{ kJ}$$

$$\Delta S = \frac{\Delta_{\text{vap}} H}{T_b} = \frac{40.79 \times 10^3 \text{ J}}{373.15 \text{ K}} = 109.31 \text{ J K}^{-1}$$

The values of ΔH, ΔU, and ΔS for the entire process can be obtained by summing the corresponding quantities calculated in the two steps:

$$\Delta H = 5.648 \text{ kJ} + 40.79 \text{ kJ} = 46.44 \text{ kJ}$$

$$\Delta U = 5.648 \text{ kJ} + 37.687 \text{ kJ} = 43.34 \text{ kJ}$$

$$\Delta S = 16.89 \text{ J K}^{-1} + 109.31 \text{ J K}^{-1} = 126.2 \text{ J K}^{-1}$$

4.10 A quantity of 6.0 moles of an ideal gas is reversibly heated at constant volume from 17° C to 35° C. Calculate the entropy change. What would be the value of ΔS if the heating were carried out irreversibly?

At constant volume, $dq_{\text{rev}} = C_V dT$.

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{C_V dT}{T} = C_V \ln \frac{T_2}{T_1} = \frac{3}{2} nR \ln \frac{T_2}{T_1}$$

$$= \frac{3}{2} (6.0 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{mol}^{-1}\right) \ln \frac{308 \text{ K}}{290 \text{ K}}$$

$$= 4.5 \text{ J K}^{-1}$$

If heating were carried out irreversibly, ΔS is still 4.5 J K^{-1} because S is a state function so that ΔS depends only on the final and initial states. ΔS must be calculated, however, using a reversible pathway.

4.14 A sample of neon (Ne) gas initially at 20° C and 1.0 atm is expanded from 1.2 L to 2.6 L and simultaneously heated to 40° C. Calculate the entropy change for the process.

The number of moles of Ne can be determined using the initial conditions and the ideal gas law.

$$n = \frac{(1.0 \text{ atm})\ (1.2 \text{ L})}{\left(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}\right) (293 \text{ K})} = 4.99 \times 10^{-2} \text{ mol}$$

The problem can be solved by breaking down the process into 2 steps: (1) isothermal expansion from 1.2 L at 1.0 atm to 2.6 L. The temperature is kept at 20° C; (2) heating at constant volume (2.6 L) from 20° C to 40° C. The entropy changes for these two steps, ΔS_1 and ΔS_2 are

$$\Delta S_1 = nR \ln \frac{V_2}{V_1} = \left(4.99 \times 10^{-2} \text{ mol}\right) \left(8.314 \text{ J K}^{-1} \text{mol}^{-1}\right) \ln \frac{2.6 \text{ L}}{1.2 \text{ L}} = 0.321 \text{ J K}^{-1}$$

$$\Delta S_2 = C_V \ln \frac{T_2}{T_1} = \frac{3}{2} nR \ln \frac{T_2}{T_1} = \frac{3}{2} \left(4.99 \times 10^{-2} \text{ mol}\right) \left(8.314 \text{ J K}^{-1} \text{mol}^{-1}\right) \ln \frac{313 \text{ K}}{293 \text{ K}}$$

$$= 4.11 \times 10^{-2} \text{ J K}^{-1}$$

The entropy change for the entire process is

$$\Delta S = \Delta S_1 + \Delta S_2 = 0.321 \text{ J K}^{-1} + 4.11 \times 10^{-2} \text{ J K}^{-1} = 0.36 \text{ J K}^{-1}$$

4.22 One mole of an ideal gas is isothermally expanded from 5.0 L to 10 L at 300 K. Compare the entropy changes for the system, surroundings, and the universe if the process is carried out **(a)** reversibly, and **(b)** irreversibly against an external pressure of 2.0 atm.

(a) For the reversible process,

$$\Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} = (1\ \text{mol})\left(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\right) \ln \frac{10\ \text{L}}{5.0\ \text{L}} = 5.8\ \text{J K}^{-1}$$

$$\Delta S_{\text{surr}} = -5.8\ \text{J K}^{-1}$$

$$\Delta S_{\text{univ}} = 0\ \text{J K}^{-1}$$

(b) ΔS_{sys} is the same as above, that is, 5.8 J K^{-1}.

ΔS_{surr} can be calculated once q_{surr} is determined. The latter quantity is related to q_{sys}, which in turn can be calculated from the work done by the system, w, and the first law of thermodynamics.

$$w = -P_{ex}\Delta V = -\ (2.0\text{ atm})\ (10\text{ L} - 5.0\text{ L})\left(\frac{101.3\text{ J}}{1\text{ L atm}}\right) = -1.01 \times 10^3\text{ J}$$

According to the first law, $\Delta U = q + w$. For an ideal gas, $\Delta U = 0$ for an isothermal process, and $q_{sys} = q = -w = 1.01 \times 10^3$ J. The entropy change of the surroundings is

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q_{sys}}{T_{surr}} = \frac{-1.01 \times 10^3\text{ J}}{300\text{ K}} = -3.4\text{ J K}^{-1}$$

Therefore,

$$\Delta S_{univ} = 5.8\text{ J K}^{-1} - 3.4\text{ J K}^{-1} = 2.4\text{ J K}^{-1}$$

4.24 Consider the reaction

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Calculate the values of $\Delta_r S^o$ for the reaction mixture, surroundings, and the universe at 298 K. Why is your result reassuring to Earth's inhabitants?

$$\begin{aligned}\Delta_r S^o &= 2\overline{S}^o\,[NO(g)] - \overline{S}^o\,[N_2(g)] - \overline{S}^o\,[O_2(g)]\\ &= 2\left(210.6\text{ J K}^{-1}\text{mol}^{-1}\right) - 191.6\text{ J K}^{-1}\text{mol}^{-1} - 205.0\text{ J K}^{-1}\text{mol}^{-1}\\ &= 24.6\text{ J K}^{-1}\text{mol}^{-1}\end{aligned}$$

ΔS^o_{surr} is determined from $\Delta_r H^o$ and the temperature of the surroundings.

$$\begin{aligned}\Delta_r H^o &= 2\Delta_f\overline{H}^o\,[NO(g)] - \Delta_f\overline{H}^o\,[N_2(g)] - \Delta_f\overline{H}^o\,[O_2(g)]\\ &= 2\left(90.4\text{ kJ mol}^{-1}\right) - 0\text{ kJ mol}^{-1} - 0\text{ kJ mol}^{-1}\\ &= 180.8\text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta H^o_{surr} = -\Delta_r H^o = -180.8\text{ kJ mol}^{-1}$$

$$\Delta S^o_{surr} = \frac{\Delta H^o_{surr}}{T} = \frac{-180.8 \times 10^3\text{ J mol}^{-1}}{298\text{ K}} = -607\text{ J K}^{-1}\text{mol}^{-1}$$

Therefore,

$$\Delta S_{univ} = 24.6\text{ J K}^{-1}\text{mol}^{-1} - 607\text{ J K}^{-1}\text{mol}^{-1} = -582\text{ J K}^{-1}\text{mol}^{-1}$$

This is not a spontaneous process at 298 K. Therefore, O_2, which is essential to us, does not react with N_2 in the atmosphere at 298 K.