Homework #3

3.17 At 373.15 K and 1 atm, the molar volume of liquid water and steam are 1.88×10^{-5} m^3 an 3.06×10^{-2} m^3, respectively. Given that the heat of vaporization of water is 40.79 kJ mol^{-} calculate the values of ΔH and ΔU for 1 mole in the following process:

$$H_2O(l, 373.15\text{ K}, 1\text{ atm}) \rightarrow H_2O(g, 373.15\text{ K}, 1\text{ atm})$$

ΔH for the above process is the heat of vaporization, that is, $\Delta H = 40.79$ kJ for 1 mole of wate

It is necessary to calculate w and q before determining ΔU. Since the process occurs at constan pressure, $q = \Delta H = 40.79$ kJ when 1 mol liquid H_2O vaporizes. In the same process,

$$\begin{aligned} w &= -P_{ex}\Delta V \\ &= -(1.00\text{ atm})\left(3.06 \times 10^{-2}\text{ m}^3 - 1.88 \times 10^{-5}\text{ m}^3\right)\left(\frac{1000\text{ L}}{1\text{ m}^3}\right)\left(\frac{101.3\text{ J}}{1\text{ L atm}}\right) \\ &= -3.098 \times 10^3\text{ J} \end{aligned}$$

Note that we could have safely ignored the volume of liquid H_2O, since it is negligible comparec with that of gaseous H_2O above.

Using the first law,

$$\Delta U = q + w = 40.79\text{ kJ} - 3.098\text{ kJ} = 37.69\text{ kJ}$$

3.19 Calculate the value of ΔH when the temperature of 1 mole of a monatomic gas is increased from 25° C to 300° C.

ΔH is directly related to change in temperature of a system:

$$\Delta H = C_P \Delta T$$

Assuming that the gas is ideal,

$$C_P = C_V + nR$$

A monatomic gas has only translational degrees of freedom, $C_V = \frac{3}{2}nR$. Therefore, $C_P = \frac{5}{2}nR$ and

$$\Delta H = \frac{5}{2}(1\text{ mol})\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)(573\text{ K} - 298\text{ K}) = 5.72 \times 10^3\text{ J}$$

3.25 The constant-pressure molar heat capacity of nitrogen is given by the expression

$$\overline{C}_P = \left(27.0 + 5.90 \times 10^{-3}T - 0.34 \times 10^{-6}T^2\right) \text{ J K}^{-1}\text{ mol}^{-1}$$

Calculate the value of ΔH for heating 1 mole of nitrogen from 25.0° C to 125° C.

Since $\overline{C}_P$ is temperature dependent, it has to be integrated over T to yield ΔH:

$$\Delta H = \int_{298\text{ K}}^{398\text{ K}} n\,\overline{C}_P\,dT$$

$$= \int_{298\text{ K}}^{398\text{ K}} (1\text{ mol})\left[\left(27.0 + 5.90 \times 10^{-3}T - 0.34 \times 10^{-6}T^2\right) \text{ J K}^{-1}\text{ mol}^{-1}\right] dT$$

$$= \left[27.0T + 5.90 \times 10^{-3}\frac{T^2}{2} - 0.34 \times 10^{-6}\frac{T^3}{3}\right]_{298\text{ K}}^{398\text{ K}} \text{ J}$$

$$= \left[27.0\,(398) + 5.90 \times 10^{-3}\frac{398^2}{2} - 0.34 \times 10^{-6}\frac{398^3}{3}\right] \text{ J}$$

$$- \left[27.0\,(298) + 5.90 \times 10^{-3}\frac{298^2}{2} - 0.34 \times 10^{-6}\frac{298^3}{3}\right] \text{ J}$$

$$= 2.90 \times 10^3 \text{ J}$$

3.35 One mole of an ideal monatomic gas initially at 300 K and a pressure of 15.0 atm expands to a final pressure of 1.00 atm. The expansion can occur via any one of four different paths: **(a)** isothermal and reversible, **(b)** isothermal and irreversible, **(c)** adiabatic and reversible, and **(d)** adiabatic and irreversible. In irreversible processes, the expansion occurs against an external pressure of 1.00 atm. For each case, calculate the values of q, w, ΔU, and ΔH.

(a) When an ideal gas undergoes an isothermal process, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -nRT\ln\frac{P_1}{P_2} = -(1\text{ mol})\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)(300\text{ K})\ln\frac{15.0\text{ atm}}{1.00\text{ atm}} = -6.75 \times 10^3\text{ J}$$

(b) When an ideal gas undergoes an isothermal process, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -P_{ex}(V_2 - V_1)$$

V_1 and V_2 can be determined using the ideal gas law:

$$V_1 = \frac{nRT}{P_1} = \frac{(1\text{ mol})\left(0.08206\text{ L atm K}^{-1}\text{ mol}^{-1}\right)(300\text{ K})}{15.0\text{ atm}} = 1.641\text{ L}$$

$$V_2 = \frac{nRT}{P_2} = \frac{(1\text{ mol})\left(0.08206\text{ L atm K}^{-1}\text{ mol}^{-1}\right)(300\text{ K})}{1.00\text{ atm}} = 24.62\text{ L}$$

Therefore,

$$w = -(1.00\text{ atm})(24.62\text{ L} - 1.641\text{ L})\left(\frac{101.3\text{ J}}{1\text{ L atm}}\right) = -2.33 \times 10^3\text{ J}$$

and

$$q = \Delta U - w = -w = 2.33 \times 10^3\text{ J}$$

(c) $q = 0$ for an adiabatic process.

To determine ΔU and ΔH, T_2 needs to be calculated. Using the same procedure as Problem 3.34(a),

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} = (300\text{ K})\left(\frac{1.00\text{ atm}}{15.0\text{ atm}}\right)^{\left(\frac{5}{3}-1\right)/\frac{5}{3}} = 101.6\text{ K}$$

Now the rest of the quantities can be calculated:

$$\Delta U = C_V\Delta T = \frac{3}{2}(1\text{ mol})\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)(101.6\text{ K} - 300\text{ K}) = -2.47 \times 10^3\text{ J}$$

$$w = \Delta U - q = \Delta U = -2.47 \times 10^3\text{ J}$$

$$\Delta H = C_P\Delta T = \frac{5}{2}(1\text{ mol})\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)(101.6\text{ K} - 300\text{ K}) = -4.12 \times 10^3\text{ J}$$

(d) $q = 0$ for an adiabatic process.

To determine ΔU and ΔH, T_2 needs to be calculated. Using the same procedure as Problem 3.34(b),

$$T_2 = \frac{2}{5}\left(\frac{P_{ex}}{P_1} + \frac{3}{2}\right)T_1$$

$$= \frac{2}{5}\left(\frac{1.00\text{ atm}}{15.0\text{ atm}} + \frac{3}{2}\right)(300\text{ K}) = 188\text{ K}$$

$$\Delta U = C_V\Delta T = \frac{3}{2}(1\text{ mol})\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)(188\text{ K} - 300\text{ K}) = -1.40 \times 10^3\text{ J}$$

$$w = \Delta U - q = \Delta U = -1.40 \times 10^3\text{ J}$$

$$\Delta H = C_P\Delta T = \frac{5}{2}(1\text{ mol})\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)(188\text{ K} - 300\text{ K}) = -2.33 \times 10^3\text{ J}$$

3.39 When 1.034 g of naphthalene ($C_{10}H_8$) are completely burned in a constant-volume bomb calorimeter at 298 K, 41.56 kJ of heat is evolved. Calculate the values of $\Delta_r U$ and $\Delta_r H$ for the reaction.

Since volume is constant, $w = 0$, and therefore,

$$\Delta_r U = q = \frac{-41.56\ \text{kJ}}{(1.034\ \text{g})\left(\frac{1\ \text{mol}}{128.16\ \text{g}}\right)} = -5151.2\ \text{kJ mol}^{-1} = -5151\ \text{kJ mol}^{-1}$$

The change in number of moles of gases needs to be determined before $\Delta_r H$ can be evaluated. From the combustion of 1 mole of naphthalene,

$$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l)$$

$\Delta n = 10 - 12 = -2$. Thus,

$$\Delta_r H = \Delta_r U + RT\Delta n = -5151.2\ \text{kJ mol}^{-1} + \left(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\right)(298\ \text{K})(-2)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$= -5156\ \text{kJ mol}^{-1}$$

3.43 Determine the amount of heat (in kJ) given off when 1.26×10^4 g of ammonia is produced according to the equation

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta_r H^\circ = -92.6\ \text{kJ mol}^{-1}$$

Assume the reaction takes place under standard-state conditions at 25° C.

The equation gives standard enthalpy of reaction (or, since P is constant, the amount of heat given off) when 2 moles of NH_3 are produced. When 1.26×10^4 g of ammonia is produced, the amount of heat given off is

$$\left(\frac{-92.6\ \text{kJ}}{2\ \text{mol NH}_3}\right)\left(\frac{1.26 \times 10^4\ \text{g NH}_3}{17.03\ \text{g mol}^{-1}\ \text{NH}_3}\right) = -3.43 \times 10^4\ \text{kJ}$$

3.57 Alcoholic fermentation is the process in which carbohydrates are broken down into ethanol and carbon dioxide. The reaction is very complex and involves a number of enzyme-catalyzed steps. The overall change is

$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

Calculate the standard enthalpy change for this reaction, assuming that the carbohydrate is α-D-glucose.

$$\Delta_r H^\circ = 2\Delta_f \overline{H}^\circ\left[C_2H_5OH(l)\right] + 2\Delta_f \overline{H}^\circ\left[CO_2(g)\right] - \Delta_f \overline{H}^\circ\left[C_6H_{12}O_6(s)\right]$$

$$= 2\left(-277.0\ \text{kJ mol}^{-1}\right) + 2\left(-393.5\ \text{kJ mol}^{-1}\right) - \left(-1274.5\ \text{kJ mol}^{-1}\right)$$

$$= -66.5\ \text{kJ mol}^{-1}$$

4.7 The molar heat of vaporization of ethanol is 39.3 kJ mol^{-1}, and the boiling point of ethanol is 78.3° C. Calculate the value of $\Delta_{\text{vap}}S$ for the vaporization of 0.50 mole of ethanol.

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_b} = \frac{(0.50 \text{ mol})\left(39.3 \times 10^3 \text{ J mol}^{-1}\right)}{351.5 \text{ K}} = 56 \text{ J K}^{-1}$$

4.11 One mole of an ideal gas is first, heated at constant pressure from T to $3T$ and second, cooled back to T at constant volume. (**a**) Derive an expression for ΔS for the overall process. (**b**) Show that the overall process is equivalent to an isothermal expansion of the gas at T from V to $3V$, where V is the original volume. (**c**) Show that the value of ΔS for the process in (**a**) is the same as that in (**b**).

(**a**) For Step 1,

$$\Delta S_1 = C_P \ln \frac{T_2}{T_1} = \frac{5}{2} nR \ln \frac{3T}{T}$$
$$= \frac{5}{2} R \ln 3$$

For step 2,

$$\Delta S_2 = C_V \ln \frac{T_2}{T_1} = \frac{3}{2} nR \ln \frac{T}{3T} \qquad \text{(See Problem 4.10)}$$
$$= -\frac{3}{2} R \ln 3$$

For the overall process,

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{5}{2} R \ln 3 - \frac{3}{2} R \ln 3 = R \ln 3$$

(**b**) Assume initially the system is at P_1, V_1, and T_1. Step 1 carries it to P_2, V_2, and T_2, which in turn is converted to P_3, V_3, and T_3 by Step 2. The relationship between the pressures, volumes, and temperatures are shown in the following.

Since the pressure is constant in Step 1, $P_1 = P_2$. Furthermore, it is given that $T_2 = 3T_1$. V_1 and V_2 are related by

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \frac{P_1 (V_2)}{3T_1}$$
$$V_2 = 3V_1$$

In Step 2, the volume is kept constant. That is, $V_3 = V_2 = 3V_1$. The temperature decreases to $T_3 = \frac{1}{3}T_2 = T_1$. The pressures are related by

$$\frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \frac{P_3V_2}{\frac{1}{3}T_2}$$

$$P_3 = \frac{1}{3}P_2 = \frac{1}{3}P_1$$

Therefore, the overall process is $P_1\ V_1\ T_1 \rightarrow \frac{1}{3}P_1\ 3V_1\ T_1$. This is an isothermal expansion from V to $3V$ where V is the original volume.

(c) ΔS for the overall process in part **(b)** is

$$\Delta S = nR\ln\frac{3V}{V} = R\ln 3$$

which is the same as ΔS for the process in part **(a)**.

4.17 The absolute molar entropies of O_2 and N_2 are 205 $J\,K^{-1}\,mol^{-1}$ and 192 $J\,K^{-1}\,mol^{-1}$, respectively, at 25° C. What is the entropy of a mixture made up of 2.4 moles of O_2 and 9.2 moles of N_2 at the same temperature and pressure?

The entropy of the mixture, S_f, is related to the entropy of mixing, $\Delta_{mix}S$, and the initial entropy of the system, S_i. Before these quantities can be calculated, the mole fractions of O_2 and N_2 need to be determined.

$$x_{O_2} = \frac{2.4\text{ mol}}{2.4\text{ mol} + 9.2\text{ mol}} = 0.207$$

$$x_{N_2} = 1 - 0.207 = 0.793$$

The entropy of mixing is

$$\begin{aligned}\Delta_{mix}S &= -R\left(n_{O_2}\ln x_{O_2} + n_{N_2}\ln x_{N_2}\right)\\ &= -\left(8.314\text{ J K}^{-1}\text{mol}^{-1}\right)[(2.4\text{ mol})\ln 0.207 + (9.2\text{ mol})\ln 0.793]\\ &= 49.2\text{ J K}^{-1}\end{aligned}$$

The initial entropy of system is the sum of the entropies of O_2 and N_2:

$$\begin{aligned}S_i &= n_{O_2}\bar{S}_{O_2} + n_{N_2}\bar{S}_{N_2} = (2.4\text{ mol})\left(205\text{ J K}^{-1}\text{mol}^{-1}\right) + (9.2\text{ mol})\left(192\text{ J K}^{-1}\text{mol}^{-1}\right)\\ &= 2.26\times 10^3\text{ J K}^{-1}\end{aligned}$$

Since $\Delta_{mix}S = S_f - S_i$,

$$S_f = \Delta_{mix}S + S_i = 49.2\text{ J K}^{-1} + 2.26\times 10^3\text{ J K}^{-1} = 2.3\times 10^3\text{ J K}^{-1}$$