Homework set 2 (partial solution collection)

3.40 Consider the following reaction:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 4H_2O(l) + 2CO_2(g) \qquad \Delta_r H^\circ = -1452.8\ \text{kJ mol}^{-1}$$

What is the value of $\Delta_r H^\circ$ if **(a)** the equation is multiplied throughout by 2, **(b)** the direction of the reaction is reversed so that the products become the reactants and vice versa, and **(c)** water vapor instead of liquid water is the product?

(a) $\Delta_r H^\circ = 2\left(-1452.8\ \text{kJ mol}^{-1}\right) = -2905.6\ \text{kJ mol}^{-1}$

(b) $\Delta_r H^\circ = -\left(-1452.8\ \text{kJ mol}^{-1}\right) = 1452.8\ \text{kJ mol}^{-1}$

(c) The reaction

$$2CH_3OH(l) + 3O_2(g) \rightarrow 4H_2O(g) + 2CO_2(g)$$

is a sum of the following equations:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 4H_2O(l) + 2CO_2(g) \quad \Delta_r H_1^\circ = -1452.8\ \text{kJ mol}^{-1}$$

$$4H_2O(l) \rightarrow 4H_2O(g) \qquad \Delta_r H_2^\circ$$

The standard enthalpy of reaction for vaporization of H_2O is

$$\begin{aligned}\Delta_r H_2^\circ &= 4\Delta_f \overline{H}^\circ\left[H_2O(g)\right] - 4\Delta_f \overline{H}^\circ\left[H_2O(l)\right]\\ &= 4\left(-241.8\ \text{kJ mol}^{-1}\right) - 4\left(-285.8\ \text{kJ mol}^{-1}\right)\\ &= 176.0\ \text{kJ mol}^{-1}\end{aligned}$$

The standard enthalpy of reaction of $2CH_3OH(l) + 3O_2(g) \rightarrow 4H_2O(g) + 2CO_2(g)$ is

$$\Delta_r H^\circ = \Delta_r H_1^\circ + \Delta_r H_2^\circ = -1452.8\ \text{kJ mol}^{-1} + 176.0\ \text{kJ mol}^{-1} = -1276.8\ \text{kJ mol}^{-1}$$

3.44 When 2.00 g of hydrazine decomposed under constant-pressure conditions, 7.00 kJ of heat were transferred to the surroundings:

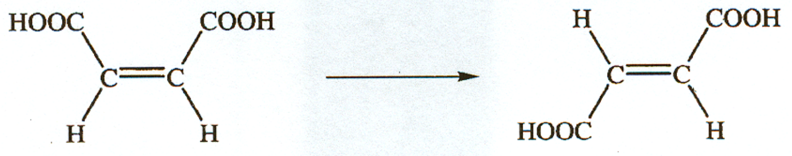
$$3N_2H_4(l) \rightarrow 4NH_3(g) + N_2(g)$$

What is the $\Delta_r H^\circ$ value for the reaction?

The reaction describes the decomposition of 3 moles of hydrazine. Therefore, the amount of heat given must be scaled to this amount of reactant.

$$\Delta_r H^\circ = q_P = \left(\frac{-7.00 \text{ kJ}}{\frac{2.00 \text{ g } N_2H_4}{32.05 \text{ g mol}^{-1} N_2H_4}} \right) (3.00) = -337 \text{ kJ mol}^{-1}$$

3.46 The standard enthalpies of combustion of fumaric acid and maleic acid (to form carbon dioxide and water) are -1336.0 kJ mol^{-1} and -1359.2 kJ mol^{-1}, respectively. Calculate the enthalpy of the following isomerization process:



maleic acid fumaric acid

The chemical equations and the standard enthalpies of combustion of 1 mole of fumaric acid and 1 mole of maleic acid are given below:

$$\text{fumaric} + 3O_2 \rightarrow 4CO_2 + 2H_2O \quad \Delta_r H^\circ = -1336.0 \text{ kJ mol}^{-1}$$

$$\text{maleic} + 3O_2 \rightarrow 4CO_2 + 2H_2O \quad \Delta_r H^\circ = -1359.2 \text{ kJ mol}^{-1}$$

The isomerization reaction (maleic acid → fumaric acid) can be obtained as a combination of these two reactions:

$$4CO_2 + 2H_2O \rightarrow \text{fumaric} + 3O_2 \quad \Delta_r H^\circ = 1336.0 \text{ kJ mol}^{-1}$$

$$\text{maleic} + 3O_2 \rightarrow 4CO_2 + 2H_2O \quad \Delta_r H^\circ = -1359.2 \text{ kJ mol}^{-1}$$

Therefore, the enthalpy of the isomerization process is

$$\Delta_r H = 1336.0 \text{ kJ mol}^{-1} - 1359.2 \text{ kJ mol}^{-1} = -23.2 \text{ kJ mol}^{-1}$$

3.56 Calculate the difference between the values of $\Delta_r H^\circ$ and $\Delta_r U^\circ$ for the oxidation of α-D-glucose at 298 K:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

$\Delta_r H^\circ$ and $\Delta_r U^\circ$ differ from each other if the number of moles of gases after the reaction is not the same as that before the reaction.

$$\Delta_r H^\circ = \Delta_r U^\circ + RT\,\Delta n$$

Since $\Delta n = 0$, $\Delta_r H^\circ = \Delta_r U^\circ$, or $\Delta_r H^\circ - \Delta_r U^\circ = 0$.

HW2

Since the calorimeter has negligible heat capacity, the heat gained by the calorimeter and the solution can be well approximated by that gained by the solution alone. We will also take the density of the solution the same as that of water (1 g mL^{-1} or 1000 g L^{-1}).

$$\begin{aligned}\text{Heat gained by solution} &= m_{\text{solution}} s_{\text{solution}} \Delta T \\ &= (0.085\ \text{L})\left(\frac{1000\ \text{g}}{1\ \text{L}}\right)\left(4.184\ \text{J g}^{-1}\,{}^\circ\text{C}^{-1}\right)(0.044^\circ\ \text{C}) \\ &= 15.6\ \text{J}\end{aligned}$$

This heat gained by the solution comes from the heat given off by the reaction between 6.0 g of deoxygenated hemoglobin and oxygen. For the reaction of 1 mole of deoxygenated hemoglobin and 4 moles of oxygen, the heat given off is

$$q = \frac{-15.6\ \text{J}}{\left(\frac{6.0\ \text{g}}{65000\ \text{g mol}^{-1}}\right)} = -1.69 \times 10^5\ \text{J mol}^{-1}$$

Because the reaction takes place in a constant-pressure calorimeter, the enthalpy of reaction of 1 mole of deoxyhemoglobin with 4 moles of oxygen is the same as q. Thus, the enthalpy of reaction per mole of oxygen bound is $\frac{q}{4} = -42 \times 10^3\ \text{J mol}^{-1} = -42\ \text{kJ mol}^{-1}$