3.40 Consider the following reaction:

$$2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \rightarrow 4\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$$
 $\Delta_r H^0 = -1452.8 \text{ kJ mol}^{-1}$

What is the value of $\Delta_r H^o$ 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)
$$\Delta_{\mathbf{r}} H^{0} = 2 \left(-1452.8 \text{ kJ mol}^{-1} \right) = -2905.6 \text{ kJ mol}^{-1}$$

(b)
$$\Delta_r H^0 = -(-1452.8 \text{ kJ mol}^{-1}) = 1452.8 \text{ kJ mol}^{-1}$$

(c) The reaction

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

is a sum of the following equations:

$$2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \rightarrow 4\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$$
 $\Delta_{\text{r}}H_1^{\text{o}} = -1452.8 \text{ kJ mol}^{-1}$ $4\text{H}_2\text{O}(l) \rightarrow 4\text{H}_2\text{O}(g)$ $\Delta_{\text{r}}H_2^{\text{o}}$

The standard enthalpy of reaction for vaporization of H₂O is

$$\begin{split} \Delta_{\rm r} H_2^{\rm o} &= 4 \Delta_{\rm f} \overline{H}^{\rm o} \left[{\rm H_2O}(g) \right] - 4 \Delta_{\rm f} \overline{H}^{\rm o} \left[{\rm H_2O}(l) \right] \\ &= 4 \left(-241.8 \text{ kJ mol}^{-1} \right) - 4 \left(-285.8 \text{ kJ mol}^{-1} \right) \\ &= 176.0 \text{ kJ mol}^{-1} \end{split}$$

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

$$\Delta_{\rm r} H^{\rm o} = \Delta_{\rm r} H^{\rm o}_1 + \Delta_{\rm r} H^{\rm o}_2 = -1452.8~{\rm kJ~mol}^{-1} + 176.0~{\rm kJ~mol}^{-1} = -1276.8~{\rm kJ~mol}^{-1}$$

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 $\Delta_r H^o$ 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.

$$\Delta_{\rm r} H^{\rm o} = q_P = \left(\frac{-7.00 \text{ kJ}}{\frac{2.00 \text{ g N}_2 \text{H}_4}{32.05 \text{ g mol}^{-1} \text{ N}_2 \text{H}_4}}\right) (3.00) = -337 \text{ kJ mol}^{-1}$$

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:

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

fumaric +
$$3O_2 \rightarrow 4CO_2 + 2H_2O$$
 $\Delta_r H^o = -1336.0 \text{ kJ mol}^{-1}$
maleic + $3O_2 \rightarrow 4CO_2 + 2H_2O$ $\Delta_r H^o = -1359.2 \text{ kJ mol}^{-1}$

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

$$4\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{fumaric} + 3\text{O}_2 \quad \Delta_{\text{r}} H^{\text{o}} = 1336.0 \text{ kJ mol}^{-1}$$

$$\text{maleic} + 3\text{O}_2 \rightarrow 4\text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta_{\text{r}} H^{\text{o}} = -1359.2 \text{ kJ mol}^{-1}$$

Therefore, the enthalpy of the isomerization process is

$$\Delta_{\rm r}H = 1336.0 \text{ kJ mol}^{-1} - 1359.2 \text{ kJ mol}^{-1} = -23.2 \text{ kJ mol}^{-1}$$

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

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

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

$$\Delta_{\rm r} H^{\rm o} = \Delta_{\rm r} U^{\rm o} + RT \Delta n$$

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