SOLUTIONS

PROBLEM SET 3

CHM 3400, Dr. Chatfield

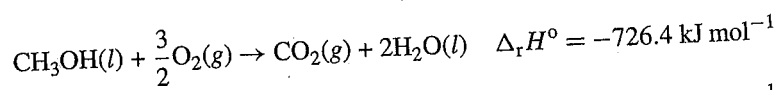**3.50** The hydrogenation for ethylene is

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$
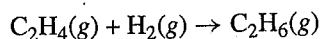
Calculate the change in the enthalpy of hydrogenation from 298 K to 398 K. The $\overline{C}_P^{\,o}$ values are: C_2H_4: 43.6 J K^{-1} mol^{-1} and C_2H_6: 52.7 J K^{-1} mol^{-1}.


Assume the heat capacities are temperature independent.

$$\Delta_r H_{398} - \Delta_r H_{298} = \Delta C_P^{\,o}\ (398\ \text{K} - 298\ \text{K})$$

$$= \left\{ \overline{C}_P^{\,o}\ [C_2H_6(g)] - \overline{C}_P^{\,o}\ [C_2H_4(g)] - \overline{C}_P^{\,o}\ [H_2(g)] \right\}\ (10\ \text{K})$$

$$\doteq \left(52.7\ \text{J K}^{-1}\,\text{mol}^{-1} - 43.6\ \text{J K}^{-1}\,\text{mol}^{-1} - 28.8\ \text{J K}^{-1}\,\text{mol}^{-1} \right)\ (10\ \text{K})$$

$$= -197\ \text{kJ mol}^{-1}$$

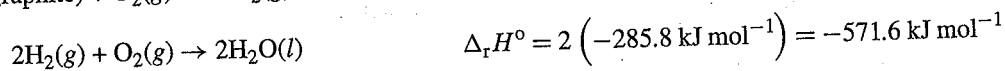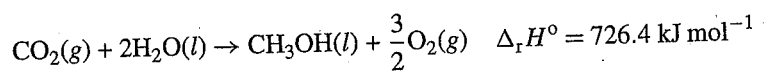**3.54** From the following heats of combustion,

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta_r H^\circ = -726.4\ \text{kJ mol}^{-1}$$

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \quad \Delta_r H^\circ = -393.5\ \text{kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta_r H^\circ = -285.8\ \text{kJ mol}^{-1}$$

calculate the enthalpy of formation of methanol (CH_3OH) from its elements:

$$C(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$$
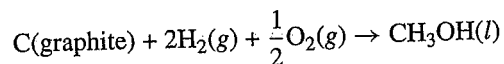
The formation reaction of methanol can be thought of as a sum of the reactions:

$$CO_2(g) + 2H_2O(l) \rightarrow CH_3OH(l) + \frac{3}{2}O_2(g) \quad \Delta_r H^\circ = 726.4\ \text{kJ mol}^{-1}$$

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \quad \Delta_r H^\circ = -393.5\ \text{kJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta_r H^\circ = 2\left(-285.8\ \text{kJ mol}^{-1}\right) = -571.6\ \text{kJ mol}^{-1}$$

Therefore, the standard enthalpy of formation of methanol is the sum of the standard enthalpies of reaction of the three reactions above:

$$\Delta_f H^\circ\ [CH_3OH(l)] = 726.4\ \text{kJ mol}^{-1} - 393.5\ \text{kJ mol}^{-1} - 571.6\ \text{kJ mol}^{-1} = -238.7\ \text{kJ mol}^{-1}$$

3.60 Use the bond enthalpy values in Table 3.4 to calculate the enthalpy of combustion for ethane,

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$$
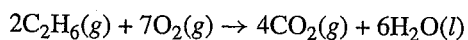
Compare your result with that calculated from the enthalpy of formation values of the products and reactants listed in Appendix 2.

Calculation of the enthalpy of combustion using bond enthalpies:

Type of bonds broken	Number of bonds broken	Bond enthalpy / kJ·mol^{-1}	Enthalpy change / kJ·mol^{-1}
C—H	12	414	4968
C—C	2	347	694
O=O	7	498.8	3491.6

Type of bonds broken	Number of bonds broken	Bond enthalpy / kJ·mol^{-1}	Enthalpy change / kJ·mol^{-1}
C=O	8	799	6392
O—H	12	460	5520

$$\Delta_r H^\circ = (4968 + 694 + 3491.6) \text{ kJ mol}^{-1} - (6392 + 5520) \text{ kJ mol}^{-1} = -2758 \text{ kJ mol}^{-1}$$
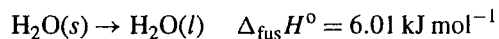
Calculation of the enthalpy of combustion using enthalpies of formation:

$$\Delta_r H^\circ = 4\Delta_f \overline{H}^\circ \left[CO_2(g) \right] + 6\Delta_f \overline{H}^\circ \left[H_2O(l) \right] - 2\Delta_f \overline{H}^\circ \left[C_2H_6(g) \right] - 7\Delta_f \overline{H}^\circ \left[O_2(g) \right]$$

$$= 4 \left(-393.5 \text{ kJ mol}^{-1} \right) + 6 \left(-285.8 \text{ kJ mol}^{-1} \right) - 2 \left(-84.7 \text{ kJ mol}^{-1} \right) - 7 \left(0 \text{ kJ mol}^{-1} \right)$$

$$= -3119.4 \text{ kJ mol}^{-1}$$

The value of $\Delta_r H^\circ$ so calculated is 13% greater than that calculated using bond enthalpies. The value determined using enthalpies of formation is the correct value, since it relies on the first law of thermodynamics. Bond enthalpies are averages determined for similar bonds in many molecules and provide estimates that are typically within 10% of the experimental value for any given, particular reaction.

3.71 The molar enthalpies of fusion and vaporization of water are 6.01 kJ mol^{-1} and 44.01 kJ mol^{-1} (at 298 K), respectively. From these values, estimate the molar enthalpy of sublimation of ice.

The sublimation process can be considered a sum of the following processes:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta_{fus} H^\circ = 6.01 \text{ kJ mol}^{-1}$$

$$H_2O(l) \rightarrow H_2O(g) \quad \Delta_{vap} H^\circ = 44.01 \text{ kJ mol}^{-1}$$

Thus,

$$\Delta_{sub} H^\circ = 6.01 \text{ kJ mol}^{-1} + 44.01 \text{ kJ mol}^{-1} = 50.02 \text{ kJ mol}^{-1}$$

This value is an approximation, since the value of $\Delta_{vap} H^\circ$ is given at 298 K, whereas ice would not typically be found above 273 K.