以下の文章の内容に基づき、各々の化学反応式に対応する標準反応エンタルピー変化 ( $\Delta H^{\circ}_{rxn}$ ) に関して加成性が成り立つことを具体例を挙げて丁寧に説明せよ。

A useful property of  $\Delta H^{\circ}_{rxn}$  values for chemical equations is their additivity. This property follows directly from the fact that enthalpy is a state function. If we add two chemical equations to obtain a third chemical equation, then the value of  $\Delta H^{\circ}_{rxn}$  for the resulting equation is equal to the sum of the values of  $\Delta H^{\circ}_{rxn}$  for the two equations that are added together. The additivity of  $\Delta H^{\circ}_{rxn}$  values is best illustrated by example. Consider the two chemical equations

(1) 
$$\operatorname{Sn}(s) + \operatorname{Cl}_2(g) \to \operatorname{Sn}\operatorname{Cl}_2(s)$$
  $\Delta H^\circ_{\operatorname{rxn}}(1) = -325.1 \text{ kJ} \cdot \text{mol}^{-1}$   
(2)  $\operatorname{Sn}\operatorname{Cl}_2(s) + \operatorname{Cl}_2(g) \to \operatorname{Sn}\operatorname{Cl}_4(l)$   $\Delta H^\circ_{\operatorname{rxn}}(2) = -186.2 \text{ kJ} \cdot \text{mol}^{-1}$ 

If we add these two chemical equations as if they were algebraic equations, then we get

$$\operatorname{Sn}(s) + \operatorname{SnCl}_2(s) + 2\operatorname{Cl}_2(g) \rightarrow \operatorname{SnCl}_2(s) + \operatorname{SnCl}_4(l)$$

If we cancel  $SnCl_2(s)$  from both sides, we get

(3) 
$$\operatorname{Sn}(s) + 2\operatorname{Cl}_2(g) \to \operatorname{SnCl}_4(l)$$

The additive property of  $\Delta H^{\circ}_{rxn}$  values tells us that  $\Delta H^{\circ}_{rxn}$  for equation (3) is simply

$$\Delta H^{\circ}_{rxn} (3) = \Delta H^{\circ}_{rxn} (1 + 2)$$
  
=  $\Delta H^{\circ}_{rxn} (1) + \Delta H^{\circ}_{rxn} (2)$   
=  $-325.1 \text{ kJ} \cdot \text{mol}^{-1} + (-186.2 \text{ kJ} \cdot \text{mol}^{-1})$   
=  $-511.3 \text{ kJ} \cdot \text{mol}^{-1}$ 

In effect we can imagine equations (1) and (2) as representing a two-step process with the same initial and final steps as equation (3). The total enthalpy change for the two equations together must, therefore, be the same as if the reaction proceeded in a single step (Figure 14.8).

The additivity property of  $\Delta H^{\circ}_{rxn}$  values is known as **Hess's law**. If two or more chemical equations are added together, then the value of  $\Delta H^{\circ}_{rxn}$  for the resulting equation is equal to the sum of the  $\Delta H^{\circ}_{rxn}$  values for the separate equations.

$$Sn(s) + 2Cl_{2}(g) \longrightarrow \Delta H_{rxn}(1) = -325.1 \text{ kJ} \cdot \text{mol}^{-1}$$

$$SnCl_{2}(s) + Cl_{2}(g) \longrightarrow \Delta H_{rxn}(2) = -186.2 \text{ kJ} \cdot \text{mol}^{-1} \longrightarrow \Delta H_{rxn}(3) = -511.3 \text{ kJ} \cdot \text{mol}^{-1}$$

**Figure 14.8** A shematic illustration of the application of Hess's law to the reaction described by  $Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l)$ .  $\Delta H^{\circ}_{rxn}(3) = \Delta H^{\circ}_{rxn}(1) + \Delta H^{\circ}_{rxn}(2)$ 

Suppose now that we add a chemical equation to itself, for example,

(1) 
$$SO_2(g) \rightarrow S(s) + O_2(g)$$
  $\Delta H^\circ_{rxn} (1)$   
(2)  $SO_2(g) \rightarrow S(s) + O_2(g)$   $\Delta H^\circ_{rxn} (2) = \Delta H^\circ_{rxn} (1)$   
(3)  $2SO_2(g) \rightarrow 2S(s) + 2O_2(g)$   $\Delta H^\circ_{rxn} (3)$ 

In this case

$$\Delta H^{\circ}_{rxn} (3) = \Delta H^{\circ}_{rxn} (1) + \Delta H^{\circ}_{rxn} (1)$$
  
=  $2\Delta H^{\circ}_{rxn} (1)$  (14.20)

Notice that adding a chemical equation to itself is equivalent to multiplying both sides of the chemical equation by two, that is,  $2[SO_2(g) \rightarrow S(s) + O_2(g)]$  becomes  $2SO_2(g) \rightarrow 2S(s) + 2O_2(g)$ . Equation 14.20 can be generalized to cover multiplication of a chemical equation by any numerical factor *n*. For example,  $n[SO_2(g) \rightarrow S(s) + O_2(g)]$  becomes  $nSO_2(g) \rightarrow nS(s) + nO_2(g)$ . Multiplication of the chemical equation by n is equivalent to writing the equation out n times and adding the n equations together, so the value of  $\Delta H^{\circ}_{rxn}$  for the resulting equation is

$$\Delta H^{\circ}_{rxn} = n \Delta H^{\circ}_{rxn} (1)$$
(14.21)

Now let's consider the following combination of chemical equations:

(1) 
$$\operatorname{SO}_2(g) \to \operatorname{S}(s) + \operatorname{O}_2(g) \qquad \Delta H^\circ_{\operatorname{rxn}}(1)$$

(2)  $S(s) + O_2(g) \rightarrow SO_2(g)$   $\Delta H^{\circ}_{rxn}(2)$ 

The value of  $\Delta H^{\circ}_{rxn}$  for the sum of these two equations is

$$\Delta H^{\circ}_{rxn} (1+2) = \Delta H^{\circ}_{rxn} (1) + \Delta H^{\circ}_{rxn} (2)$$

But the addition of these two equations yields no net reactants and no net products or, in other words, no net chemical change whatsoever. Because there is no net change, the value of  $\Delta H^{\circ}_{rxn}$ 

(1 + 2) must be zero and we conclude that  $\Delta H^{\circ}_{rxn}(2) = -\Delta H^{\circ}_{rxn}(1)$ . Because equation (2) above is simply the reverse of equation (1), we conclude from Hess's law that

$$\Delta H^{\circ}_{rxn} (reverse) = -\Delta H^{\circ}_{rxn} (forward)$$
(14.22)

Equation 14.22 is easy to apply. If we reverse a chemical equation, then the reactants become the products and the products become the reactants, and so the sigh of  $\Delta H^{\circ}_{rxn}$  changes. That is, if energy is released as heat in one direction, then it is absorbed as heat in the other direction. Equation 14.22 also says that  $\Delta H = 0$  for a **cyclic process**, on other words, one in which the initial state is the same as the final state. We can express this result as an equation by writing

$$\Delta H_{\text{cyclic}} = 0 \tag{14.23}$$