Recall:

- $\Rightarrow$ **Law of conservation of Energy**
- $\Rightarrow$ **Exothermic reaction & Endothermic reaction**
- $\Rightarrow$ **Three types of systems (closed, opened, isolated)**
- $\Rightarrow$ **Calorimetry: q = mcΔT**
- $\Rightarrow$ **Molar enthalpy:** ΔH = nΔH_x
- $\Rightarrow$ **Bond energy:** ΔH = $\sum$ **energy input for break the bonds**
  – $\sum$ **energy released to form the bonds.**

5.4 Hess's Law

- From Experimental evidence, chemists have found that:
  - Change in enthalpy in a chemical process is independent of the path taken.
  - This mean from initial reactant side to final product side, ΔH is always the same regardless of whether the conversion happens in **one step or in a series of steps**.
  - Analogous to you go upstairs, the vertical distance you travel is the same regardless of whether you take the stairs or the elevator.

- For example:

$$N_2(g) + 2\,O_2(g) \rightarrow 2\,NO_2(g) \quad \Delta H = 68\text{ kJ}$$

However, nitrogen dioxide can also be made using a two-step process. The thermochemical equations for the two steps are

$$N_2(g) + O_2(g) \rightarrow 2\,NO(g) \qquad \Delta H = 180\text{ kJ}$$

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g) \quad \Delta H = -112\text{ kJ}$$

If you add these two equations, you get the equation for the overall (net) reaction for the formation of nitrogen dioxide gas. Similarly, the sum of the enthalpy changes of the reactions represented by these equations is equal to the enthalpy change for the net reaction for the formation of nitrogen dioxide gas.

$$N_2(g) + O_2(g) \rightarrow 2\,\cancel{NO}(g) \qquad \Delta H = 180\text{ kJ}$$

$$\underline{2\,\cancel{NO}(g) + O_2(g) \rightarrow 2\,NO_2(g) \quad \Delta H = -112\text{ kJ}}$$

$$N_2(g) + 2\,O_2(g) \rightarrow 2\,NO_2(g) \qquad \Delta H = 68\text{ kJ}$$

This example illustrates that when a reaction proceeds from reactants to products, the change in enthalpy is the same whether the reaction occurs in one step or several. This generalization is now called Hess's law.

Hess's law

The enthalpy change for the conversion of reactants to products is the same whether the conversion occurs in one step or several steps.

Enthalpy Changes during a Two-step and One-step Process to Convert Elemental Nitrogen and Oxygen to Nitrogen Dioxide Gas

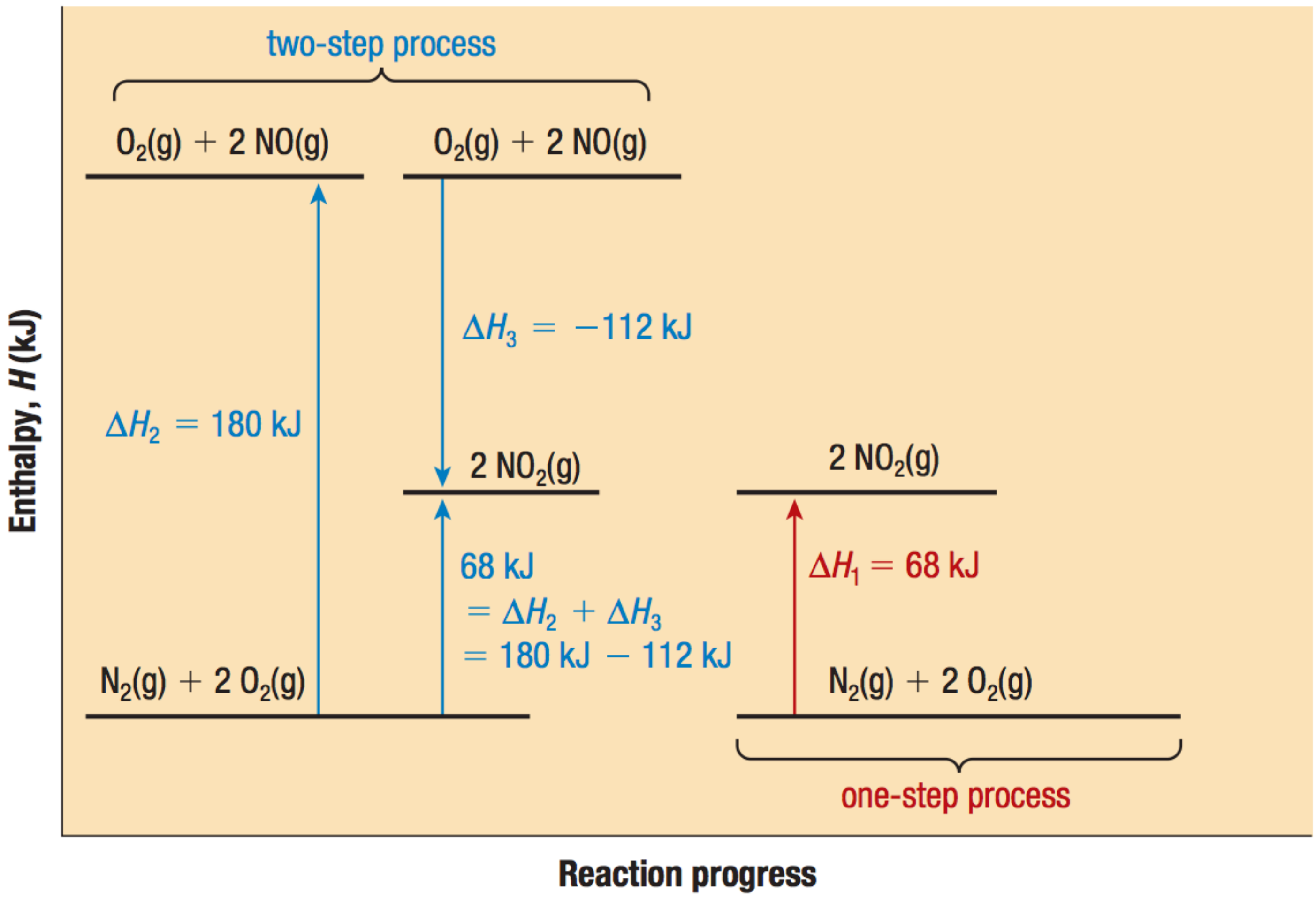

Figure 3 Enthalpy change diagram for the formation of nitrogen dioxide gas from gaseous nitrogen and oxygen. The net enthalpy change is the same whether the process occurs in one step or two.

Rules for Enthalpy Changes

To use Hess's law to calculate enthalpy changes for chemical reactions, you must apply the following two rules:

1. If you reverse a chemical reaction, you must also reverse the sign of ΔH.
2. The magnitude of ΔH is directly proportional to the number of moles of reactants and products in a reaction. If the coefficients in a balanced equation are multiplied by a factor, the value of ΔH is multiplied by the same factor.

Example 1:

Graphite and diamond are two forms of solid carbon. Graphite is a soft, black, slippery material that is the substance in pencils that makes marks. Diamond is a hard, crystalline substance used in making jewellery. Use the data in **Figure 4** and **Figure 5** to calculate the enthalpy change for the conversion of graphite to diamond.

$$C_{graphite}(s) \rightarrow C_{diamond}(s)$$

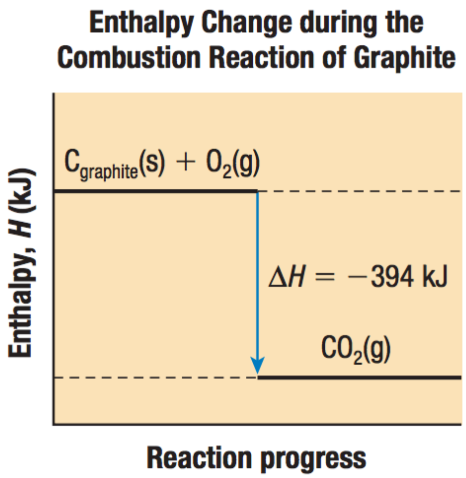

Figure 4 Enthalpy change diagram for the combustion of graphite

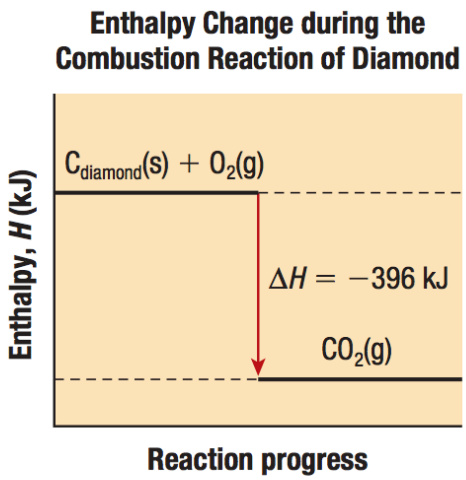

Figure 5 Enthalpy change diagram for the combustion of diamond

Example 2:

Ethene gas, $C_2H_4(g)$, is the raw material for the synthesis of the plastic polyethylene. Engineers designing a process to make ethene from ethane gas, $C_2H_6(g)$, need to know the change in enthalpy of the desired reaction represented by the following balanced chemical equation:

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

The engineers have the following thermochemical equations:

(1) $C_2H_6(g) + 3.5\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) \quad \Delta H = -1559\ kJ$

(2) $C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(l) \quad \Delta H = -1411\ kJ$

(3) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) \quad \Delta H = -572\ kJ$

Practice:

1. Consider the following thermochemical equations:

   $NH_3(g) \rightarrow \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$ $\Delta H = 46$ kJ

   $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$ $\Delta H = -484$ kJ

   (a) Calculate ΔH for the reaction represented by the following equation:

   $2\ N_2(g) + 6\ H_2O(g) \rightarrow 3\ O_2(g) + 4\ NH_3(g)$ [ans: 1268 kJ]

   (b) Draw an enthalpy diagram of the reaction. T/I C

2. Consider the following thermochemical equations:

   $2\ ClF(g) + O_2(g) \rightarrow Cl_2O(g) + F_2O(g)$ $\Delta H = 167.4$ kJ

   $2\ ClF_3(g) + 2\ O_2(g) \rightarrow Cl_2O(g) + 3\ F_2O(g)$ $\Delta H = 341.4$ kJ

   $2\ F_2(g) + O_2(g) \rightarrow 2\ F_2O(g)$ $\Delta H = -43.4$ kJ

   (a) Calculate ΔH for the reaction represented by the following equation:

   $ClF(g) + F_2(g) \rightarrow ClF_3(g)$ [ans: −108.7 kJ]

   (b) Draw an enthalpy diagram of the reaction. T/I C

3. If iron(III) oxide is heated with carbon monoxide, carbon dioxide and metallic iron are produced according to the equation

   $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

   Determine the enthalpy of this reaction given the reactions

   $C(graphite) + \frac{1}{2} O_2 \rightarrow CO$ $\Delta H = -110.5$ kJ

   $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

   $2Fe(s) + 3/2\ O_2(g) \rightarrow Fe_2O_3(s)$ $\Delta H = -824.2$ kJ T/I

   [ans: $\Delta H = -24.8$ kJ]

Homework:

Questions

1. (a) State Hess's law in your own words.
   (b) In a correct equation for a reverse reaction, what happens to the sign and magnitude of ΔH?
   (c) When you multiply the coefficients of a balanced equation by a constant, what changes must you make to the sign and magnitude of ΔH? K/U
2. Explain how Hess's law is consistent with the law of conservation of energy. K/U
3. What characteristic of enthalpy change is the basis of Hess's law? K/U
4. Phosphorus burns spontaneously in air to produce tetraphosphorus decaoxide, $P_4O_{10}(s)$:
   $4\ P(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$
   Using the following thermochemical equations, determine:
   (a) the enthalpy of combustion for phosphorus
   (b) the molar enthalpy of combustion for phosphorus, expressed in kJ/mol K/U T/I
   $4\ P(s) + 3\ O_2(g) \rightarrow P_4O_6(s) \qquad \Delta H = -1640\ kJ$
   $P_4O_6(s) + 2\ O_2(g) \rightarrow P_4O_{10}(s) \qquad \Delta H = -1344\ kJ$
5. Nitric oxide gas, NO(g), can be oxidized in air to produce nitrogen dioxide gas, $NO_2(g)$:
   $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$
   Determine the enthalpy change for this reaction using any of these thermochemical equations: K/U T/I
   $O_2(g) \rightarrow 2\ O(g) \qquad \Delta H = +495\ kJ$
   $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \qquad \Delta H = -199\ kJ$
   $2\ O_3(g) \rightarrow 3\ O_2(g) \qquad \Delta H = -427 kJ$
6. Liquid hydrazine, $N_2H_4(l)$, is a rocket fuel. It combusts in oxygen gas to form nitrogen gas and liquid water:
   $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(l)$
   Use the following thermochemical equations to calculate the enthalpy change for the combustion of liquid hydrazine: K/U T/I
   $2\ NH_3(g) + 3\ N_2O(g) \rightarrow 4\ N_2(g) + 3\ H_2O(l) \qquad \Delta H = -1010\ kJ$
   $N_2O(g) + 3\ H_2(g) \rightarrow N_2H_4(l) + H_2O(l) \qquad \Delta H = -317\ kJ$
   $2\ NH_3(g) + \frac{1}{2}\ O_2(g) \rightarrow N_2H_4(l) + H_2O(l) \qquad \Delta H = -143\ kJ$
   $H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -286\ kJ$
7. Solid calcium carbide, $CaC_2(s)$, reacts with liquid water to produce ethyne, $C_2H_2(g)$ (acetylene):
   $CaC_2(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$
   Using the following thermochemical equations, calculate the enthalpy change for this reaction: K/U T/I
   $Ca(s) + 2\ C_{graphite}(s) \rightarrow CaC_2(s) \qquad \Delta H = -62.8 kJ$
   $Ca(s) + \frac{1}{2}\ O_2(g) \rightarrow CaO(s) \qquad \Delta H = -635.5\ kJ$
   $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \qquad \Delta H = -653.1\ kJ$
   $C_2H_2(g) + \frac{5}{2}\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(l) \qquad \Delta H = -1300.\ kJ$
   $C_{graphite}(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5\ kJ$
8. The neutralization reaction between lithium hydroxide solution, LiOH(aq), and hydrochloric acid, HCl(aq), will produce water and aqueous lithium chloride, LiCl(aq). Using the following thermochemical equations, determine the enthalpy of neutralization for 1 mol of aqueous lithium hydroxide: K/U T/I

$\frac{1}{2}\ H_2(g) + \frac{1}{2}\ Cl_2(g) \rightarrow HCl(g) \qquad \Delta H = -92.3\ kJ$
$H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -285.8\ kJ$
$Li(s) + \frac{1}{2}\ Cl_2(g) \rightarrow LiCl(s) \qquad \Delta H = -815.0\ kJ$
$Li(s) + \frac{1}{2}\ O_2(g) + \frac{1}{2}\ H_2(g) \rightarrow LiOH(s) \qquad \Delta H = -487.0\ kJ$
$LiOH(s) \rightarrow LiOH(aq) \qquad \Delta H = -19.2\ kJ$
$HCl(g) \rightarrow HCl(aq) \qquad \Delta H = -77.0\ kJ$
$LiCl(s) \rightarrow LiCl(aq) \qquad \Delta H = -36.0\ kJ$