General Chemistry

Chapter 6

Chap 6 Thermochemistry

- The Nature of Energy
- Enthalpy and Calorimetry
- Hess's law
- standard Enthalpies of Formation
- Present sources of Energy
- New Energy sources

§ 6.1 The Nature of Energy

Energy 定義 : capacity to do work or to produce heat

Law of conservation of energy : the energy can be converted from one form to another but can be neither created nor destroyed.

Energy : kinetic energy (動能) : energy due to motions
potential energy (位能) : energy due to position or composition

Temperature and Heat :

Temperature: a property that reflects the random motions of particles in a particular substance.

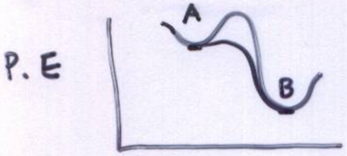
Heat: transfer of energy between two objects due to temp difference

State function (or state property): a property of the system that depends only on its present state. A state function does not depend in any way on the system's past (or future)

↓

A change in this function from one state to another state is independent of the particular pathway taken between the two states

Ex. potential energy



P.E. (A) - P.E. (B) = Δ P.E.

與路徑 (pathway) 無關

A. B. : states

Chemical Energy

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + \underbrace{\text{energy (heat)}}$

exothermic : energy flow from system to surroundings

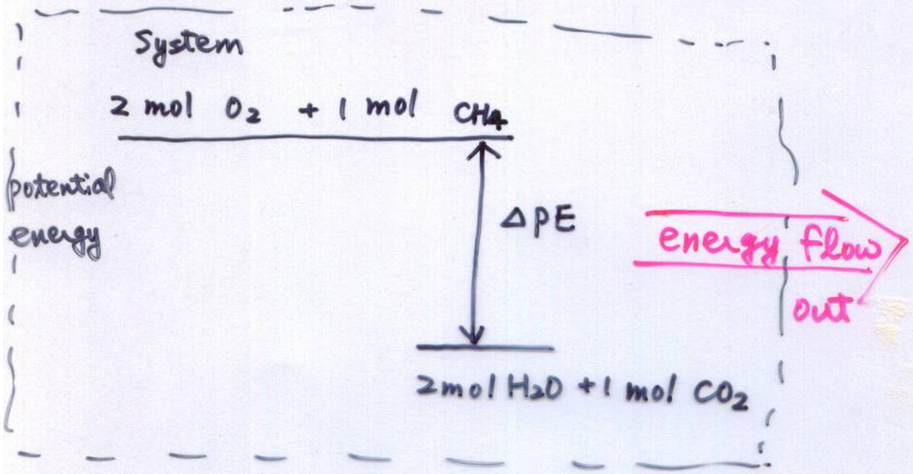
endothermic : energy flow into system from surroundings

$N_2(g) + O_2(g) + \text{energy (heat)} \rightarrow 2NO(g)$

where is the "energy" from?

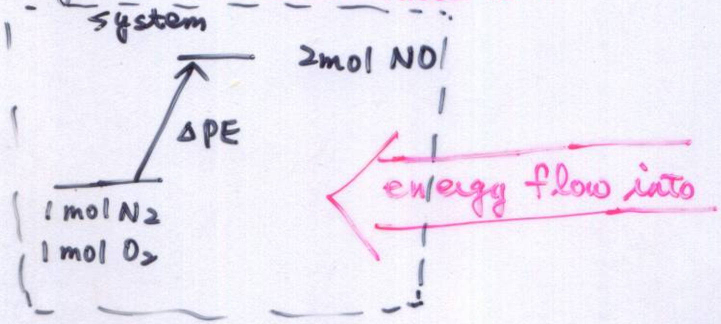
potential energy difference between reactants and products（化學組成的鍵結等 chemical composition 的不同）

Fig. 6-2 Exothermic rx :



Energy stored in the chemical bonds (potential energy) is being converted to thermal energy (random kinetic energy) via heat

Fig 6-3 Endothermic rx :



Thermodynamics (熱力學) : The study of energy and its conversion.

1° law of thermodynamics : the energy of the universe is constant.

Internal **energy** (E) : the sum of the kinetic energy and potential energy of all the "particles" in the system.

$$\underset{\uparrow\ \text{the change of internal energy}}{\Delta E} = \underset{\uparrow\ \text{heat}}{q} + \underset{\nwarrow\ \text{work}}{w}$$

Thermodynamic quantities always consists :

a number : giving the "magnitude" of change

a sign : indicating the "direction" of the flow

exothermic : $\Delta E < 0$ (∵ system's energy ↓)
放熱

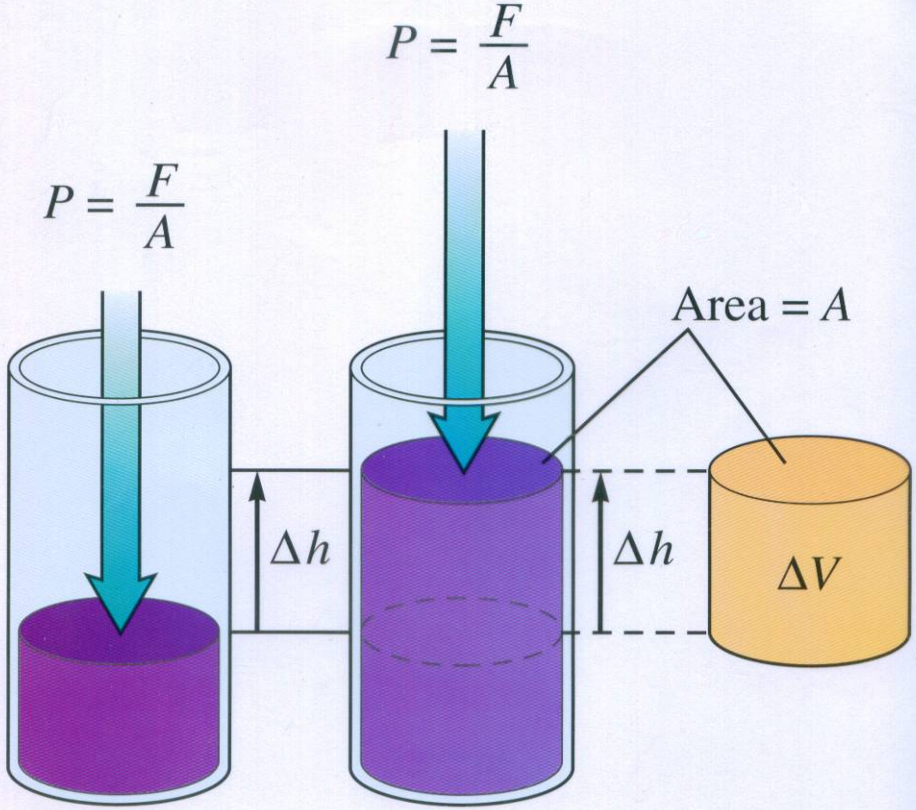
endothermic : $\Delta E > 0$ (∵ system's energy ↑)
吸熱

$q > 0$ when heat flow from surroundings to system

$q < 0$ when heat flow from system to surroundings

$w > 0$ work done to the system

$w < 0$ work done by the system



(a) Initial state

(b) Final state

$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h$$

$$= (\underset{\uparrow\ \text{pressure}}{P} \times \underset{\uparrow\ \text{area}}{A}) \times \Delta h = P\,(A \times \Delta h)$$

$$= \underbrace{P\,(\Delta V)}_{\text{magnitude}}$$

$$w = -P(\Delta V)$$

Figure 6.4
***PV* work**

"expanding" (∵ work done by the system !)

~~6-5~~
6-6

Ex 6.1 Internal energy

Calculate ΔE for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system.

Sol:

$$\Delta E = (+15.6\ \text{kJ}) + (+1.4\ \text{kJ})$$
$$= 17.0\ \text{kJ}$$

Ex 6.2 PV work

Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm

Sol:

$$W = -P\Delta V \quad (\because \text{expanding gas})$$
$$= -15\ \text{atm} \cdot (64-46)\ \text{L}$$
$$= -270\ \text{L} \cdot \text{atm}$$

Ex 6.3. Internal Energy, Heat, and work

A balloon is being inflated to its full extent by heating the air inside it. In the final stage, the volume of the balloon changes from 4.00×10^6 L to 4.5×10^6 L by addition of 1.3×10^8 J of energy as heat. Assuming that the balloon expands against 1.0 atm pressure. calculate $\underset{\sim\sim}{\Delta E}$

$$\Delta E = q + w$$

$$w = -(1\text{ atm}\cdot\Delta V) = -(1\text{ atm}\cdot 0.50\times10^{6}\text{ L})$$

$$= -5.0\times10^{5}\text{ atm}\cdot\text{L} = -5.1\times10^{7}\text{ J}$$

$$(\because 1\text{ atm}\cdot\text{L} = 101.3\text{ J})$$

$$q = +1.3\times10^{8}\text{ J}$$

$$\therefore \Delta E = q + w = (+1.3\times10^{8}\text{ J}) + (-5.1\times10^{7}\text{ J})$$

$$= 8\times10^{7}\text{ J}$$

§ 6.2 Enthalpy and Calorimetry

Enthalpy H :

$$H = E + PV$$

Since internal energy (E), pressure, and volume are state functions.

∴ Enthalpy (H) is a state function !

Ex. a process carried out at constant pressure and where the only work allowed is pressure-volume work. calculate ΔH of the process.

$$\Delta H = \Delta E + \Delta(PV)$$

$\because$ at const P

$$\therefore \Delta H = (q_P - P\Delta V) + P\Delta V$$

$$\therefore \boxed{\Delta H = q_P}$$

6-8

∵ at const P, the change in enthalpy (ΔH) of the system = the energy flow as heat

↓

A reaction studied at const pressure, the flow of heat is a measure of the change in enthalpy for the system

---

For a chemical rx :

$$\Delta H = H_{products} - H_{reactants}$$

Ex. 6.4 enthalpy

1 mol of methane is burned at const P.
890 KJ of energy is released as heat.
calculate ΔH for a process in which a 5.8 g sample of methane is burned at const P

sol : $\Delta H = q_p = -890$ KJ/mol

ΔH of a 5.8 g methane burning

$$= -890 \frac{KJ}{mol} \times \frac{5.8 g}{16.0 \, g/mol}$$

$$= -320 \text{ KJ}$$

Calorimetry （卡計研究 or 熱量測量）

* calorimeter（卡計）: The device used experimentally to determine the heat associated w/ a chemical reaction.

* heat capacity (C) of a substance :

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}} \quad (\text{unit: } J/°C \text{ or } J/K)$$

specific heat capacity (s) : heat capacity per gram

($J/°C\,g$ or $J/K\,g$)

molar heat capacity : heat capacity per mole

($J/°C\cdot mol$ or $J/K\cdot mol$)

See page 257 Fig 6.5

A coffee-cup calorimeter

Ex. 50.0 ml of 1.0 M HCl at 25.0°C w/ 50.0 ml of 1.0 M NaOH at 25.0°C in a calorimeter after rx, the temp increased to 31.9°C calculate the enthalpy change (ΔH) !

sol: $\Delta H = q_p$ = s. heat capacity × mass × temp change

$= -(4.18\ J/°C\cdot g) \times [(50.0+50.0)\,ml \times 1\ g/ml] \times (31.9 - 25.0°C)$

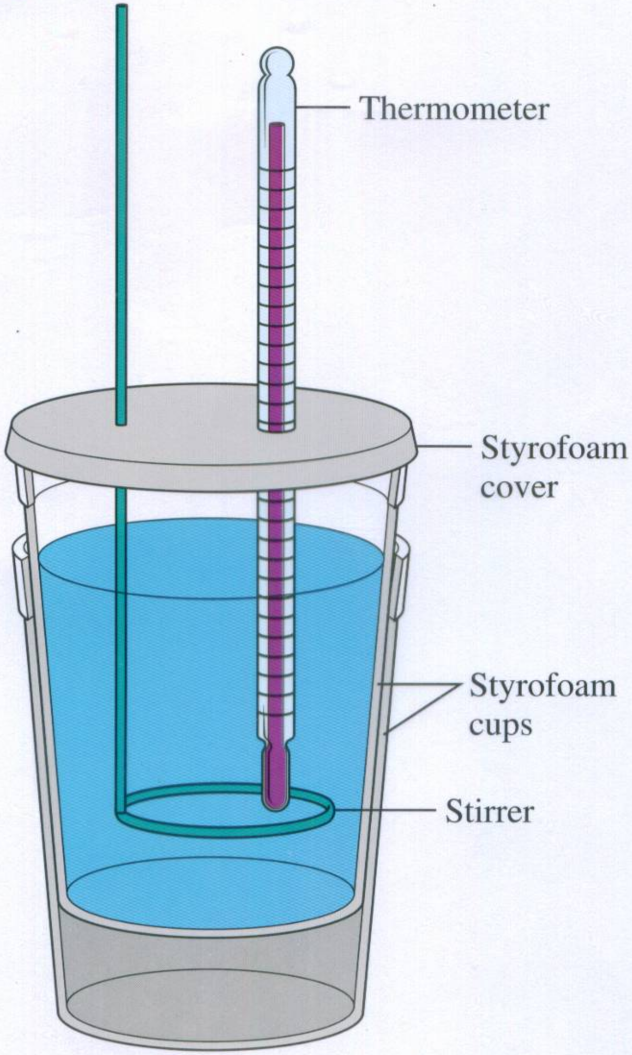
$= -2.9 \times 10^3\ J$ (for 5.0×10^{-2} mol H^+)

$\boxed{\because \text{exothermic !}}$ $\Delta H = -58\ kJ/mol$

coffee cup calorimeter

48

6-10



To measure q_P, that is ΔH

Figure 6.5

Coffee-cup calorimeter

Steven S. Zumdahl, *Chemistry*, © Houghton Mifflin Company. All Rights Reserved.

Ex 6.5. Constant - Pressure Calorimetry

when 1.00 L of 1.00 M $Ba(NO_3)_2$ 25°C mixed w/ 1.00 L of 1.00 M Na_2SO_4 in a calorimeter, the white $BaSO_{4(s)}$ forms and temp increases to 28.1°C. specific heat capacity of the solution = 4.18 J/°C·g, density = 1.0 g/mL calculate ΔH per mol of $BaSO_4$ formed.

sol:

	$Ba^{2+}_{(aq)}$ +	$SO_4^{2-}{}_{(aq)}$ $\rightleftarrows$	$BaSO_{4(s)}$
	1.00 L · 1.00 M	1.00 L · 1.00 M	
initial	1 mol	1 mol	
final	~0 mol	~0 mol	1 mol

$$\text{heat} = - S \times m \times \Delta T$$

(q_p)

(∵ evolved)

$$= -4.18 \ \mathrm{J/^{\circ}C \cdot g} \times (2.00 \ \mathrm{L} \times 1000 \ \mathrm{mL/L} \times 1.0 \ \mathrm{g/mL}) \times (28.1 - 25.0 \ ^{\circ}\mathrm{C})$$

$$= -2.6 \times 10^4 \ \mathrm{J}$$

$$\Delta H = -2.6 \times 10^4 \ \mathrm{J/mol} \ BaSO_{4(s)} \text{ formed.}$$

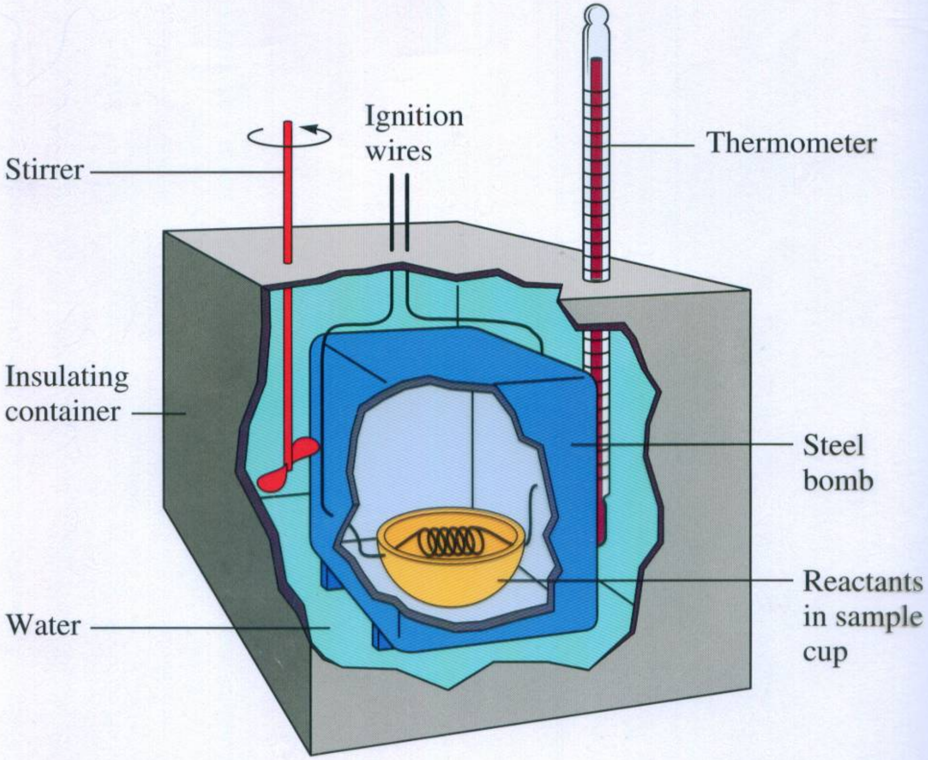
Constant volume calorimeter : 'bomb' calorimeter

$$\Delta E = q + w = q = q_v$$

(∵ $\Delta V = 0$. no work is done !)

6-12

bomb calorimeter



To measure q_v, that is, ΔE

Figure 6.6

Bomb calorimeter

If we ~~use~~ put 0.5269 g of octane in a bomb calorimeter and excess O_2 is present, the sample is burned and the temp of the calorimeter increase 2.25°c. The heat capacity of the calorimeter is 11.3 $\mathrm{kJ}/{}^\circ\mathrm{c}$

calculate ΔE !

Sol: Energy released from the rx

$$= C \cdot \Delta T = -11.3\ \mathrm{kJ}/{}^\circ\mathrm{c} \cdot 2.25\,{}^\circ\mathrm{C}$$

$$= -25.4\ \mathrm{kJ} \quad \text{for } 0.5269\ \mathrm{g} \text{ octane}$$

$$= -25.4\ \mathrm{kJ} \Big/ \frac{0.5269\ \mathrm{g}}{114.2\ \mathrm{g/mol}} = -5.50\times10^{3}\ \mathrm{kJ/mol}$$

$$\Delta E = q_v = -5.50\times10^{3}\ \mathrm{kJ/mol}$$

$\#$

Ex. 6.6. Constant-volume calorimetry

a bomb calorimeter (w/ heat capacity 11.3 $\mathrm{kJ}/{}^\circ\mathrm{c}$) is used to measure the energy of combustion. 1.50 g methane is burned w/ excess O_2. Temp ↑ 7.3°c. calculate the energy of combustion (per gram)

Sol: Energy $(\Delta E) = q_v = C \cdot \Delta T$

$$= -11.3\ \mathrm{kJ}/{}^\circ\mathrm{c} \cdot 7.3\,{}^\circ\mathrm{c}$$

$$= 83\ \mathrm{kJ} \quad \text{for } 1.5\ \mathrm{g} \text{ methane}$$

$$\therefore \Delta E = 83\ \mathrm{kJ} / 1.5\ \mathrm{g} = 55\ \mathrm{kJ/g} = 880\ \mathrm{kJ/mol}$$

§ 6.3 Hess Law

Hess Law: the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

Ex.

$N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)}$ $\Delta H_1 = ?$

If we know,

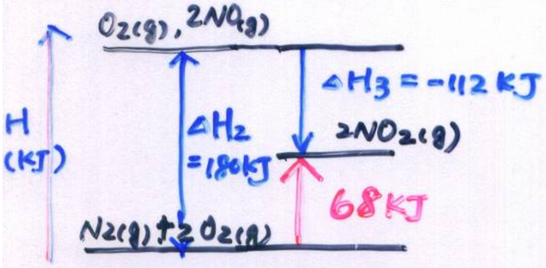
(1) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ $\Delta H_2 = 180\,kJ$

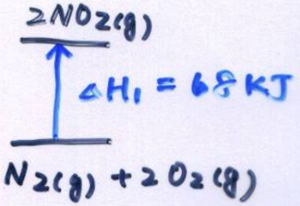
(2) $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ $\Delta H_3 = -112\,kJ$

---

(1)+(2): $N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)}$ $\Delta H_1 = \Delta H_2 + \Delta H_3$
$= 68\,kJ$

see Fig 6.7





不管路徑，只[illegible]管 reactants & products 之 H！（∵ H 是 state function!）

Characteristics of enthalpy changes

6-15

1. If a rx is reversed → the sign of ΔH is reversed.

2. The magnitude of ΔH is directly proportional to the quantities of reactants and products

Ex. $Xe_{(g)} + 2F_{2(g)} \rightarrow XeF_{4(s)}$ $\Delta H = -251$ kJ

$\therefore$ $XeF_{4(s)} \rightarrow Xe_{(g)} + 2F_{2(g)}$ $\Delta H = 251$ kJ

$2Xe_{(g)} + 4F_{2(g)} \rightarrow 2XeF_{4(s)}$

$\Delta H = 2 \times (-251) = -502$ kJ

Ex 6.7 Hess's Law I.

6.8 Hess's Law II.

§6.4 Standard Enthalpies of Formation

see page 260

standard enthalpy of formation (ΔH_f°) of a compound: the change in ~~enthalpy~~ enthalpy that accompanies the formation of one mole of a compound from its elements w/ all substances in their standard states.

standard states: a precisely defined reference state

(∵ all the thermodynamic quantities, we can only measure changes in the properties) ∴ we need reference state!

standard states (not the same as the standard temperature and pressure STP: 1 atm, 0°C

For a compound:

1. For a gaseous sample, Pressure = 1 atm
2. For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid
3. For a substance present in a solution, the standard state is a concentration of exactly 1 M.

For an element:
the standard state is the form in which the element exists under 1 atm and 25°C

Ex :

$\frac{1}{2}N_{2(g)} + O_{2(g)} \rightarrow NO_{2(g)}$ $\Delta H_f^\circ = 34\ \text{kJ/mol}$

$C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(l)}$

elements in standard states $\rightarrow$ compound ΔH_f° $\Delta H_f^\circ = -239\ \text{kJ/mol}$

Hess's Law + standard Enthalpy of Formation

Ex : $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

$\Delta H^\circ = ?$

rx 1 : the formation of $CH_{4(g)}$

$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H_f^\circ = -75\ \text{kJ/mol}$

rx 2 : $2O_{2(g)} \rightarrow 2O_{2(g)}$ $\Delta H_f^\circ = 0\ \text{kJ/mol}$

rx 3 : $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_f^\circ = -394\ \text{kJ/mol}$

rx4 : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ $\Delta H_f^\circ = -286\ \text{kJ/mol}$

$\times 2$

$= -572\ \text{kJ}$

(rx3 + rx4) − (rx 1 + rx 2) :

=

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

$$\therefore\ \Delta H^\circ = [\Delta H_f^\circ(\text{rx3}) + \Delta H_f^\circ(\text{rx4})] - [\Delta H_f^\circ(\text{rx1}) + \Delta H_f^\circ(\text{rx2})]$$

$$= [(-394) + (\underset{\times 2}{-286})] - [(-75) + 0]$$

$$= -891\ \text{kJ}$$

For
∵ Most of the common compounds, their standard enthalpy of formation can be obtained from database

↓

we can predict the change of enthalpy of one rx from the enthalpies of formation of reactants and products ! (Don't need to use calorimeters !)

$$\boxed{\Delta H^{0}_{reaction} = \sum \overset{\text{moles of product}}{n_p}\, \Delta H_f^{0}\,(\text{products}) - \sum \underset{\text{moles of each reactant}}{n_r}\, \Delta H_f^{0}\,(\text{reactants})}$$

- The enthalpy change for a reaction can be calculated by subtracting the enthalpies of formation of reactants from the enthalpies of formation of products.

- Elements are not included. we have defined the enthalpy of formation of an element in its standard state as zero.

page 263. 6-~~19~~ 20

Key concepts when doing enthalpy calculations:

⋮ (see next page)

Ex. 6.9

using the standard enthalpies of formation listed in Table 6.2. calculate the $\Delta H^\circ_{reaction}$ of the reaction:

$$4NH_{3(g)} + 7O_{2(g)} \rightarrow 4NO_{2(g)} + 6H_2O_{(\ell)}$$

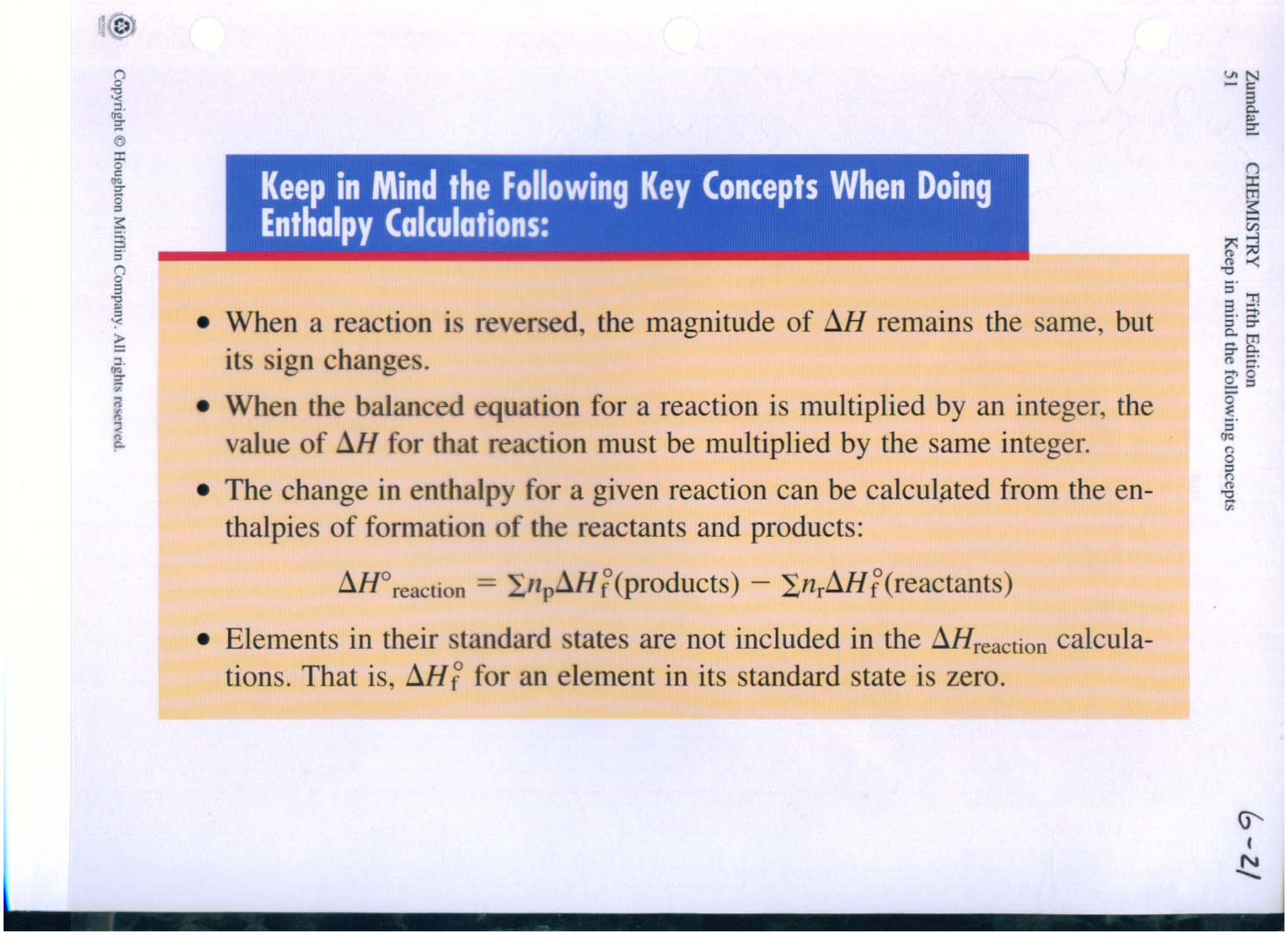
sol:

$$\Delta H^\circ_{reaction} = \sum n_p(\Delta H^\circ_f(\text{products})) - \sum n_r(\Delta H^\circ_f(\text{reactants}))$$

$$\Delta H^\circ_{reaction} = 4(\Delta H^\circ_f(NO_2)) + 6(\Delta H^\circ_f(H_2O)) - [4(\Delta H^\circ_f(NH_3)) + 7(\Delta H^\circ_f(O_2))]$$

$$= 4(34) + 6(-286) - [4(-46) + 7(0)]$$

$$= -1396 \text{ KJ}$$



Zumdahl CHEMISTRY Fifth Edition
51 Keep in mind the following concepts

Keep in Mind the Following Key Concepts When Doing Enthalpy Calculations:

- When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.
- When the balanced equation for a reaction is multiplied by an integer, the value of ΔH for that reaction must be multiplied by the same integer.
- The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^\circ_{\text{reaction}} = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$$

- Elements in their standard states are not included in the $\Delta H_{\text{reaction}}$ calculations. That is, ΔH_f° for an element in its standard state is zero.

6-21

Ex 6.10. Calculate the standard change in enthalpy for :

$$2Al_{(s)} + Fe_2O_{3(s)} \rightarrow Al_2O_{3(s)} + 2Fe_{(s)}$$

Sol: $\Delta H^0 = \sum n_p \, \Delta H_f^0(\text{products}) - \sum n_r \, \Delta H_f^0(\text{reactants})$

$$= [1 \times (-1676) + 2 \times (0)] - [2 \times (0) + 1 \times (-826)]$$

$$= -850.\ \text{KJ}$$ #

Ex 6.11

Compare the standard enthalpy of combustion of methanol and gasoline

↑ 假設為 pure octane

Sol:

rx 1: $2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)}$

rx 2: $2C_8H_{18(l)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(l)}$

rx 1: $\Delta H^0 = [2 \times (-394) + 4(-286)] - [2 \times (-239) + 0]$

$= -1454\ \text{KJ}$ (for 2 mols of methanol burn)

rx 2: $\Delta H^0 = [16 \times (-394) + 18(-286)] - [2 \times (-269) + 0]$

$= -1.09 \times 10^4\ \text{KJ}$ (for 2 moles of octane burn)

$$\frac{-1454\ \text{KJ}}{2\,\text{mol} \times \underset{32}{\cancel{\ \ }}\ \text{g/mol}} = -22.7\ \text{KJ/g} \text{ for methanol}$$

$$\frac{-1.09 \times 10^4\ \text{KJ}}{2\,\text{mol} \times (114.2\ \text{g/mol})} = -47.8\ \text{KJ/g} \text{ for octane}$$

§6.5 Present Sources of Energy

* Plants, coal, petroleum, natural gas

↓

provide energy.

(their energy originally come from sun)

Fig 6.12

* Petroleum and natural gas

↑ 石油

↓

composed of hydrocarbons

(含 5-25 个 C)

C_nH_{2n+2}

or C_nH_{2n}

⋮

↑ 天然氣

↑

methane

\+

ethane

\+

propane

\+

butane

Table 6.3

Table 6.4

* gasoline

↓

加 $(C_2H_5)_4Pb$ anti-knock agent

造成 environmental problem

現用其它 catalytic converters

coal :

plants $(CH_2O)_n$

高压. burning for long period of times

↓

coal

↓

see page 267 Table 6.5

時间愈长. carbon content ↑

單位重量可產生 energy↑

Effects of carbon dioxide on Climate

green house effect

54

6-25

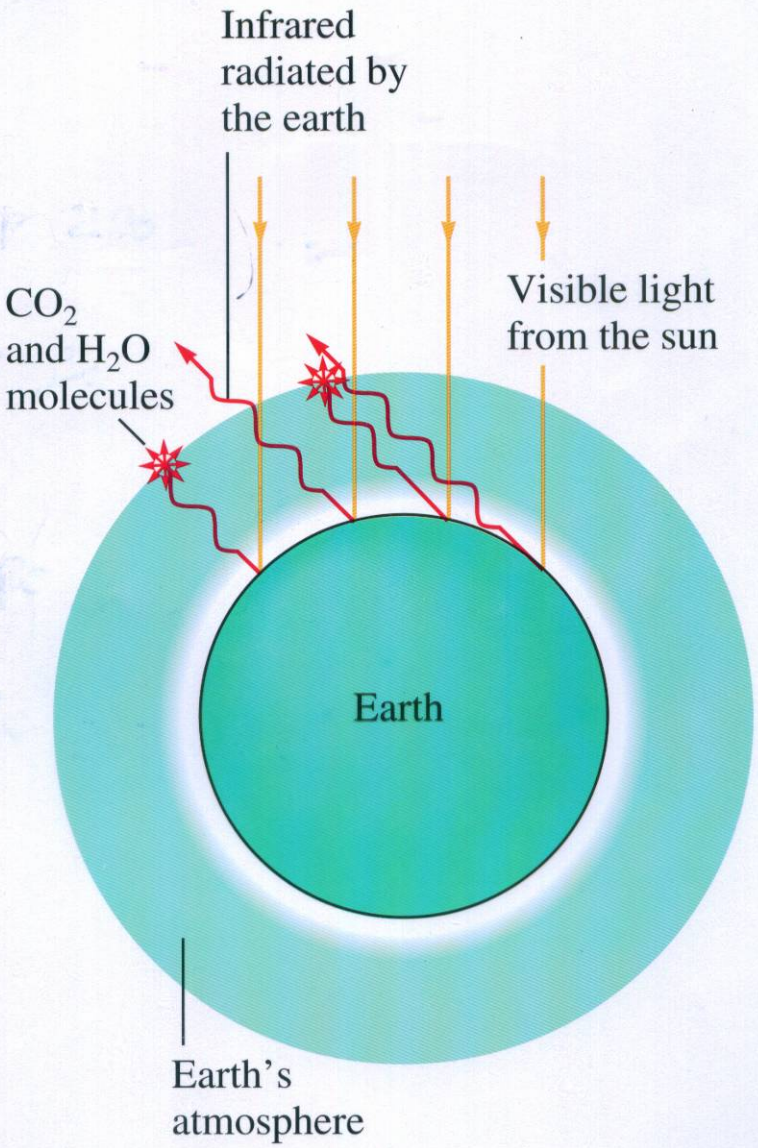


Figure 6.13
Greenhouse effect

Steven S. Zumdahl, *Chemistry*, © Houghton Mifflin Company. All Rights Reserved.