Ch. 8 Thermochemistry 熱化學

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1. $\Delta U = q + w$
2. ΔH Versus ΔU; $\Delta H = \Delta U + \Delta n_g RT$

§ 8-1 Principles of heat flow

Chemical reaction：

System：reactants and products.

Surroundings：the vessel in which the reaction takes place and the air or other material in thermal contact with the reaction system.

State property (狀態性質)：

Any thermodynamic property whose value for the process is independent of the path. It depends only on the state of the system. 一性質與初態和終態有關, 與其過程和途徑無關.

例如：composition, T and P

例： 50.0 g of $H_2O(l)$ at 50℃, 1atm

⇓

50.0 g of $H_2O(l)$ at 80℃, 1atm

$$\Delta X = X_{final} - X_{initial}$$

Heat flow (熱流量; q) is not a state property (non-state property); its magnitude depends on how a process is carried out.

Non-state property of a system：一性質與其過程和途徑有關. 如: 功 (work; w); 熱流量 (heat flow; q)

§ Direction and Sign of Heat Flow：

Heat flow (q)

q：” + “ when heat flows into the system from the surroundings. 吸熱

q：” - “ when heat flows out of the system into the surroundings. 放熱

An endothermic(吸熱) process (q > 0)

例： $H_2O(s) \longrightarrow H_2O(l)$ q > 0

An exothermic(放熱) process ($q < 0$)

例： $CH_4(g) + 2O_2(g) \xrightarrow[\text{燃燒}]{\Delta} CO_2(g) + 2H_2O(g)$ $q < 0$

放熱至環境中

§ Magnitude of heat flow:

q： 單位 J, kJ

1 cal = 4.184 J 1 kcal = 4.184 kJ

$q = C \times \Delta T$ $(\Delta T = T_{final} - T_{initial})$

C：heat capacity of the system

$\Downarrow J/K$

The amount of heat required to raise the temperature of the system 1K.

For a pure substance of mass m

$q = m \times c \times \Delta T$ c : specific heat capacity 比熱

c：the amount of heat required to raise the temperature of

one gram of a substance one Kelvin. $J/g \cdot K$

$C = m \times c$

Table 8.1

$H_2O(\mathbf{l})$: $c = 4.18\ J/g \cdot K$; $H_2O(g)$: $c = 1.87\ J/g \cdot K$

Ex 8.1. Compare the amount of heat given off by 1.40 mol of liquid water when it cools from 100.0℃ to 10.0℃ to that given off when 1.40 mol of steam cools from 200℃ to 110℃.

Ans: $q_1 = m \times c \times \Delta T$ c value from Table 8.1.

$= (18.02 \text{ x } 1.40) \times (4.18) \times (10.0 - 100.0)$

$= (25.228) \text{ x } (4.18) \text{ x } (-90.0)$

$= -9491 \text{ J}$

$= -9.49 \text{ kJ}$

$q_2 = m \times c \times \Delta T$

$= (18.02 \text{ x } 1.40) \times (1.87) \times (110 - 200)$

$= (25.228) \text{ x } (1.87) \text{ x } (-90)$

$= -4246 \text{ J}$

$= -4.25 \text{ kJ}$

Steam gives off less heat than water when it cools.

§ 8-2 Measurement of Heat flow; Calorimetry 熱卡計

Calorimeter 卡計：測反應熱之儀器，儀器內含水或其它已知比熱物質,

卡計可隔絕外界空氣對熱量之影響。

$$q_{reaction} = - q_{calorimeter}$$

$$q_{calorimeter} = C_{cal} \times \Delta T$$

$$q_{reaction} = - C_{cal} \times \Delta T$$

$$= - m \times c_{cal} \times \Delta T$$

§ Coffee-cup Calorimeter

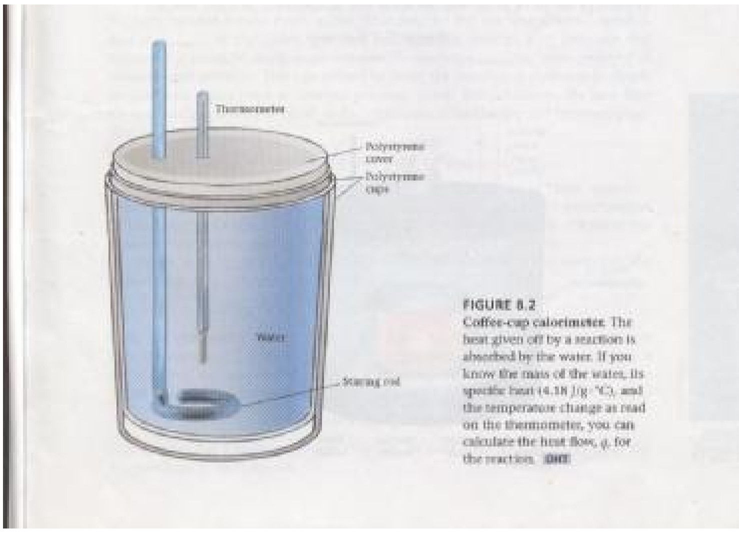


Fig 8.2. 實驗室用, polystyrene foam cup 內含水，外加溫度計攪拌棒

$$q_{reaction} = -\text{m} \times \text{c}_{cal} \times \Delta T$$
$$= -\text{m} \times 4.18 \times \Delta T$$

Ex 8.2. Calcium chloride, $CaCl_2$, is added to canned vegetables to maintain the vegetables' firmness. When added to water, it dissolves:

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

A calorimeter contains 50.0 g of water at 25.00℃. When 1.00 g of calcium chloride is added to the calorimeter, the temperature rises to 28.51℃. Assume that all the heat given off by the reaction is transferred to the water.

(a) Calculate q for the reaction system.

(b) How much $CaCl_2$ must be added to raise the temperature of the solution 9.00℃？

Ans:

$$(a)\ \ q_{H_2O} = m \times c_{cal} \times \Delta T$$
$$= 50.0 \times 4.18 \times (28.51 - 25.00)$$
$$= 734\ J$$
$$q_{reaction} = -\,q_{H_2O}$$
$$= -734\ J$$
$$(b)\ \ q_{reaction} = -\,m \times c_{cal} \times \Delta T$$
$$= -50.0 \times 4.18 \times 9.00$$
$$= -1.88 \times 10^3\ J$$
$$1.00 : -734 = m_{CaCl_2} : -1880$$
$$m_{CaCl_2} = 2.56\ g$$

§ Bomb calorimeter 彈形卡計

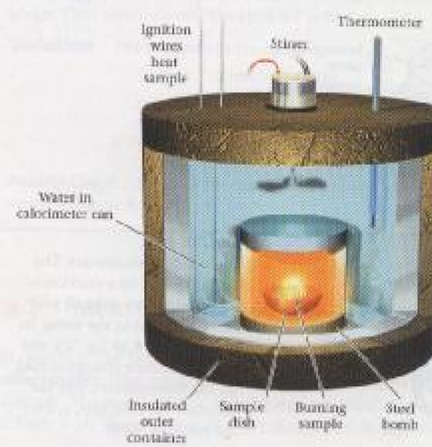


FIGURE 8.3
Bomb calorimeter. The heat flow, *q*, for the reaction is calculated from the temperature change multiplied by the heat capacity of the calorimeter, which is determined in a preliminary experiment. OHT

Coffee cup calorimeter 不適合含氣體之反應及高溫產物之反應.

⇓

bomb calorimeter

└→ heavy-walled metal vessel

浸入水中

$$q_{reaction} = -q_{calorimeter} = -C_{cal} \times \Delta T$$

C_{cal} 可由一已知反應熱之反應測得之，如下例:

例： 一反應放熱 93.3 kJ，而 Bomb calorimeter 升溫由 20.00℃至 30.00℃

$$-93.3\ \text{kJ} = -C_{cal} \times \Delta T$$
$$= -C_{cal} \times (30.00 - 20.00)$$
$$C_{cal} = \frac{93.3}{10.00} = 9.33\ {kJ}/{K}$$

Ex 8.3. Hydrogen chloride is used in etching semiconductors. It can be prepared by reacting hydrogen and chlorine gases.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

It is found that when 1.00 g of H_2 is made to react completely with Cl_2 in a bomb calorimeter, the temperature in the bomb (heat capacity = 9.33 kJ/K) rises from 20.00℃ to 29.82℃. How much heat is evolved by the reaction?

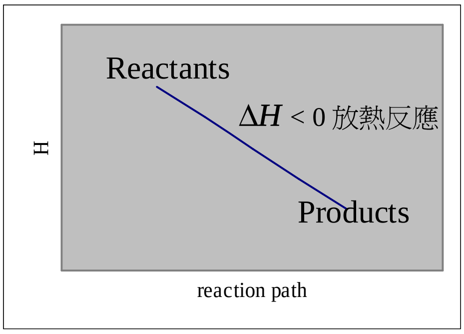
Ans:

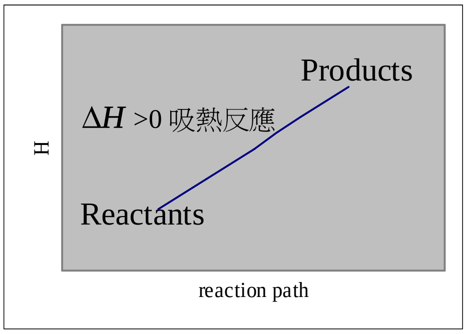
$$q_{reaction} = -C_{cal} \times \Delta T$$
$$= -9.33 \times (29.82 - 20.00)$$
$$= -91.6\ \text{kJ}$$

§ 8-3 Enthalpy 焓; H

At constant pressure (P = C), the heat flow for the reaction system is equal to the difference in enthalpy (H) between products and reactants.

P = C; $q_{reaction} = \Delta H = \sum H_{f\ 生成物} - \sum H_{f\ 反應物}$





例: $CH_4(g) + 2O_2 \longrightarrow CO_2(g) + 2H_2O(g)$

$\Delta H < 0$ 放熱反應

例: $H_2O(s) \longrightarrow H_2O(\mathbf{l})$

$\Delta H > 0$ 吸熱反應

1.00g $H_2O(l)$ (25℃, 1atm) $\longrightarrow$ 1.00g $H_2O(l)$ (26℃, 1 atm)

ΔH = 4.18 J

╰→= c; 比熱

§ 8-4 Thermochemical equations：

A chemical equation also shows the **enthalpy relation** between products and reactants.

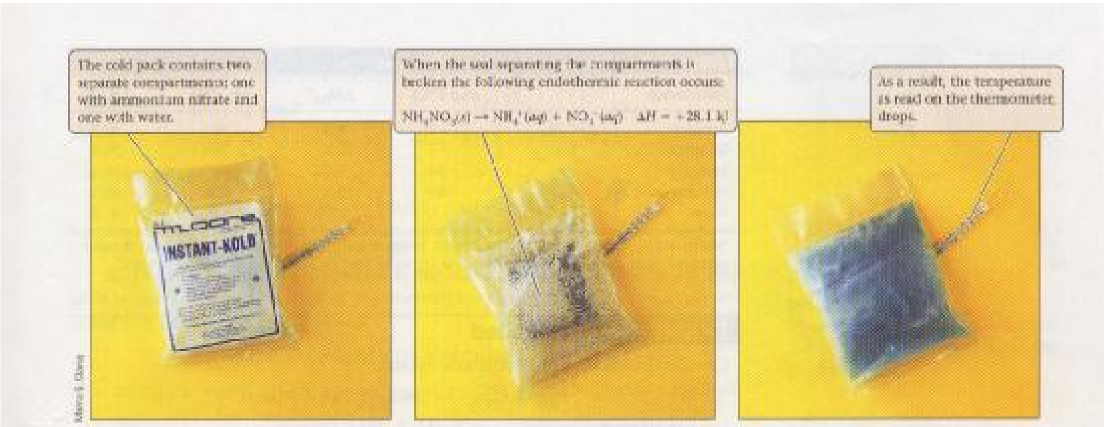


FIGURE 8.5
Endothermic reaction in a cold pack.

$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$

1.00g NH_4NO_3 $q_{reaction}$ = 351 J

ΔH = 351 J = 0.351 kJ for 1.00g NH_4NO_3

for 1 mole NH_4NO_3

ΔH = (0.351) × (80.05) = +28.1 kJ

∴

$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$ ΔH = +28.1 kJ

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ ΔH = -185 kJ

Thermochemical equations：

1. P = C, ΔH " + " endothermic 吸熱反應
   " – " exothermic 放熱反應

2. 平衡常數代表 mole 數
   1 mole $H_2(g)$ + 1 mole $Cl_2(g) \longrightarrow$ 2 mole $HCl(g)$ ΔH = -185 kJ
   反應熱之值隨平衡係數值改變而變.

3. 反應物及生成物狀態需明確標示 (**l**), (s), (g), (aq).

4. ΔH 一般未標明下，指 25℃狀況下.

§ Rules of Thermochemistry

1. The magnitude of ΔH is directly proportional to the amount of reactant or product.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -185 \text{ kJ}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H = \frac{1}{2}\times(-185 \text{ kJ}) = -92.5 \text{ kJ}$$

Ex 8.4. The Bunsen burners in your labs are fueled by natural gas, which is mostly methane, CH_4. The thermochemical equation for the combustion (burning in oxygen) of methane is

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\mathbf{l}) \qquad \Delta H = -890.3 \text{ kJ}$$

Calculate ΔH when

(a) 5.00 g of CH_4 react with an excess of oxygen.
(b) 2.00 L of O_2 at 49.0℃ and 782 mmHg react with an excess of methane.
(c) 2.00 L of CH_4 react with 5.00 L of O_2 in a reaction vessel kept at 25℃ and 1.00 atm. Followed the ideal gas behavior.

Ans:

(a) $\Delta H = \frac{5.00}{16.04} \times \frac{-890.3}{1 \text{ mol } CH_4}$ = -278 kJ

(b) $n_{O_2} = \frac{PV}{RT} = \frac{(782/760) \times 2.00}{0.0821 \times (49 + 273)}$ = 0.0778 mol

$\Delta H = 0.0778 \times \frac{-890.3 \text{ kJ}}{2 \text{ mol } O_2}$ = -34.6 kJ

(c) P = C and T = C; V ∞ n

$n_{CH_4} : n_{O_2} = 1 : 2$ ∴ CH_4 is the limiting reagent.

$n_{CH_4} = \frac{PV}{RT} = \frac{1.00 \times 2.00}{0.0821 \times (25 + 273)}$ = 0.0817 mol

$\Delta H = 0.0817 \times \frac{-890.3}{1 \text{ mol } CH_4}$ = -72.7 kJ

s $\longrightarrow$ *l* heat of fusion ΔH_{fus}

l $\longrightarrow$ g heat of vaporization ΔH_{vap} ⇒ Table 8.2

2. $\Delta H_{正反應} = -\Delta H_{逆反應}$

$H_2O(s) \longrightarrow H_2O(l)$ ΔH = +6.00 kJ

⇒ $H_2O(l) \longrightarrow H_2O(s)$ ΔH = -6.00 kJ

Ex 8.5. Given

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ ΔH = -571.6 kJ

Calculate ΔH for the equation

$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + H_2(g)$

Ans：

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H = \frac{-571.6}{2} = -285.8\ kJ$

$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + H_2(g)$ ΔH = -(-285.8) kJ = +285.8 kJ

3. The value of ΔH for a reaction is **the same** whether it occurs in one step or in a series of step.

反應熱 ΔH 與反應物及生成物狀態有關，

$$\Delta H = \sum H_{f\,生成物} - \sum H_{f\,反應物}$$; 與反應步驟無關 ⇒ 狀態性質.

Hess's law: ⇒ fundamental basis of thermodynamics as applied to chemical reactions.

- Specific chemical changes are accompanied by a characteristic change in energy.
- New chemical changes can be devised by combing known chemical changes. This is done algebraically.
- The change in energy of the combined reaction is the equivalent algebraic combination of the energy changes of the component chemical reaction.

Hess's law 黑斯定律

1) 反應熱依化學反應之初態及終態而定，與中間反應過程無關.

2) 熱化學反應與代數方程式一般，可以彼此加減.

Ex 8.6. Carbon monoxide, CO, is a poisonous gas. It can be obtained by burning carbon in a limited amount of oxygen. Given

(1) $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_1 = -393.5\ kJ$

(2) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H_2 = -566.0\ kJ$

Calculate ΔH for the reaction

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = ?$$

Ans:

$1 \times (1) - \frac{1}{2} \times (2)$:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

$$CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g)$$

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = 1 \times \Delta H_1 - \frac{1}{2} \times \Delta H_2$$

$$= 1 \times (-393.5) - \frac{1}{2} \times (-566.0)$$

$$= -110.5\ kJ$$

Thermochemistry 重點整理：

1. ΔH 與反應物及生成物之量成正比

2. $\Delta H_{\text{正反應}} = -\Delta H_{\text{逆反應}}$

3. ΔH 與反應過程無關,僅與反應初態及終態有關.

§ 8-5 Enthalpies of Formation:

利用生成焓可以更方便計算反應之 ΔH .

$$\Delta H^{\circ} = \sum \Delta H^{\circ}_{f\ \text{生成物}} - \sum \Delta H^{\circ}_{f\ \text{反應物}}$$

§ Meaning of ΔH_f° ：

Standard molar enthalpy of formation 標準莫耳生成焓：

The enthalpy change when one mole of compound is formed at P = 1 atm, T = 25℃ from the elements.

$$Ag(s)\,(25℃) + \frac{1}{2}Cl_2(g)\,(1\text{ atm, }25℃) \longrightarrow AgCl(s)\,(25℃) \quad \Delta H = -127.1\text{ kJ}$$

$$\Delta H^{\circ}_f \quad AgCl(s) \;= -127.1\,{}^{kJ}\!/_{mol}$$

$$\frac{1}{2}N_2(g)\,(1\text{ atm, }25℃) + \; O_2(g) \;\; (1\text{ atm, }25℃) \longrightarrow NO_2(g) \;\; (1\text{ atm, }25℃)$$

$$\Delta H \;= +\,33.2\text{ kJ}; \qquad \Delta H^{\circ}_f \quad NO_2(g) \;= +\,33.2\,{}^{kJ}\!/_{mol}$$

Table 8.3 ΔH°_f

TABLE 8.3 Standard Enthalpies of Formation at 25°C (kJ/mol) of Compounds at 1 atm, Aqueous Ions at 1 *M* ΔH_f°, kJ/mol

Compounds

$AgBr(s)$	−100.4	$CaCl_2(s)$	−795.8	$H_2O(g)$	−241.8	$NH_4NO_3(s)$	−365.6
$AgCl(s)$	−127.1	$CaCO_3(s)$	−1206.9	$H_2O(l)$	−285.8	$NO(g)$	+90.2
$AgI(s)$	−61.8	$CaO(s)$	−635.1	$H_2O_2(l)$	−187.8	$NO_2(g)$	+33.2
$AgNO_3(s)$	−124.4	$Ca(OH)_2(s)$	−986.1	$H_2S(g)$	−20.6	$N_2O_4(g)$	+9.2
$Ag_2O(s)$	−31.0	$CaSO_4(s)$	−1434.1	$H_2SO_4(l)$	−814.0	$NaCl(s)$	−411.2
$Al_2O_3(s)$	−1675.7	$CdCl_2(s)$	−391.5	$HgO(s)$	−90.8	$NaF(s)$	−573.6
$BaCl_2(s)$	−858.6	$CdO(s)$	−258.2	$KBr(s)$	−393.8	$NaOH(s)$	−425.6
$BaCO_3(s)$	−1216.3	$Cr_2O_3(s)$	−1139.7	$KCl(s)$	−436.7	$NiO(s)$	−239.7
$BaO(s)$	−553.5	$CuO(s)$	−157.3	$KClO_3(s)$	−397.7	$PbBr_2(s)$	−278.7
$BaSO_4(s)$	−1473.2	$Cu_2O(s)$	−168.6	$KClO_4(s)$	−432.8	$PbCl_2(s)$	−359.4
$CCl_4(l)$	−135.4	$CuS(s)$	−53.1	$KNO_3(s)$	−494.6	$PbO(s)$	−219.0
$CHCl_3(l)$	−134.5	$Cu_2S(s)$	−79.5	$MgCl_2(s)$	−641.3	$PbO_2(s)$	−277.4
$CH_4(g)$	−74.8	$CuSO_4(s)$	−771.4	$MgCO_3(s)$	−1095.8	$PCl_3(g)$	−287.0
$C_2H_2(g)$	+226.7	$Fe(OH)_3(s)$	−823.0	$MgO(s)$	−601.7	$PCl_5(g)$	−374.9
$C_2H_4(g)$	+52.3	$Fe_2O_3(s)$	−824.2	$Mg(OH)_2(s)$	−924.5	$SiO_2(s)$	−910.9
$C_2H_6(g)$	−84.7	$Fe_3O_4(s)$	−1118.4	$MgSO_4(s)$	−1284.9	$SnO_2(s)$	−580.7
$C_3H_8(g)$	−103.8	$HBr(g)$	−36.4	$MnO(s)$	−385.2	$SO_2(g)$	−296.8
$CH_3OH(l)$	−238.7	$HCl(g)$	−92.3	$MnO_2(s)$	−520.0	$SO_3(g)$	−395.7
$C_2H_5OH(l)$	−277.7	$HF(g)$	−271.1	$NH_3(g)$	−46.1	$ZnI_2(s)$	−208.0
$CO(g)$	−110.5	$HI(g)$	+26.5	$N_2H_4(l)$	+50.6	$ZnO(s)$	−348.3
$CO_2(g)$	−393.5	$HNO_3(l)$	−174.1	$NH_4Cl(s)$	−314.4	$ZnS(s)$	−206.0

Cations				Anions			
$Ag^+(aq)$	+105.6	$Hg^{2+}(aq)$	+171.1	$Br^-(aq)$	−121.6	$HPO_4^{2-}(aq)$	−1292.1
$Al^{3+}(aq)$	−531.0	$K^+(aq)$	−252.4	$CO_3^{2-}(aq)$	−677.1	$HSO_4^-(aq)$	−887.3
$Ba^{2+}(aq)$	−537.6	$Mg^{2+}(aq)$	−466.8	$Cl^-(aq)$	−167.2	$I^-(aq)$	−55.2
$Ca^{2+}(aq)$	−542.8	$Mn^{2+}(aq)$	−220.8	$ClO_3^-(aq)$	−104.0	$MnO_4^-(aq)$	−541.4
$Cd^{2+}(aq)$	−75.9	$Na^+(aq)$	−240.1	$ClO_4^-(aq)$	−129.3	$NO_2^-(aq)$	−104.6
$Cu^+(aq)$	+71.7	$NH_4^+(aq)$	−132.5	$CrO_4^{2-}(aq)$	−881.2	$NO_3^-(aq)$	−205.0
$Cu^{2+}(aq)$	+64.8	$Ni^{2+}(aq)$	−54.0	$Cr_2O_7^{2-}(aq)$	−1490.3	$OH^-(aq)$	−230.0
$Fe^{2+}(aq)$	−89.1	$Pb^{2+}(aq)$	−1.7	$F^-(aq)$	−332.6	$PO_4^{3-}(aq)$	−1277.4
$Fe^{3+}(aq)$	−48.5	$Sn^{2+}(aq)$	−8.8	$HCO_3^-(aq)$	−692.0	$S^{2-}(aq)$	+33.1
$H^+(aq)$	0.0	$Zn^{2+}(aq)$	−153.9	$H_2PO_4^-(aq)$	−1296.3	$SO_4^{2-}(aq)$	−909.3

常溫常壓下(1 atm, 25℃)，所有穩定狀態元素之莫耳生成焓 = 0

$$\Delta H_f^\circ\ Br_2(l) \;=\; \Delta H_f^\circ\ O_2(g) \;=0$$

§ Calculation of ΔH° standard enthalpy change.

$$\Delta H^\circ \;=\; \sum \Delta H^\circ_{f\ products} - \sum \Delta H^\circ_{f\ reactants}$$

Thermite (鋁熱劑)：

$$2\,Al(s) \;+\; Fe_2O_3(s) \;\longrightarrow\; 2\,Fe(s) \;+\; Al_2O_3(s)$$

$$\Delta H^\circ \;=\; \sum \Delta H^\circ_{f\ 生成物} - \sum \Delta H^\circ_{f\ 反應物}$$

$$= \left[2\times\Delta H_f^\circ Fe(s) + \Delta H_f^\circ Al_2O_3(s)\right] - \left[2\times\Delta H_f^\circ Al(s) + \Delta H_f^\circ Fe_2O_3(s)\right]$$

= (-1675.7) – (-824.2)

= -851.5 kJ

．平衡係數，必需列入計算

$$2\,Al(s) + 3\,Cu^{2+}(aq) \longrightarrow 2\,Al^{3+}(aq) + 3\,Cu(s)$$

$$\Delta H^{\circ} = \sum \Delta H^{\circ}_{f\,生成物} - \sum \Delta H^{\circ}_{f\,反應物}$$

$$= 2 \times \Delta H^{\circ}_{f}\ Al^{3+}(aq) - 3 \times \Delta H^{\circ}_{f}\ Cu^{2+}(aq)$$

$$= 2 \times (-531.0) - 3 \times (+64.8)$$
$$= -1256.4 \text{ kJ}$$

Ex 8.7. Benzene, C_6H_6, used in the manufacture of plastics, is a carcinogen affecting the bone marrow. Long-term exposure has been shown to cause leukemia and the blood disorders. The combustion of benzene is given by the following equation:

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l) \qquad \Delta H^{\circ} = -3267.4 \text{ kJ}$$

(a) Calculate the heat of formation of benzene.

(b) Calculate ΔH° for the reaction

$$12CO_2(g) + 6H_2O(l) \rightarrow 2C_6H_6(\mathbf{l}) + 15O_2(g)$$

(c) Calculate ΔH° for the reaction

$$C_6H_6(g) + \frac{15}{2}O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(g)$$

Given that ΔH_{vap} for benzene at 25°C is 33.6 kJ/mol；
ΔH_{vap} for water at 25°C is 44.0 kJ/mol。

Ans：

(a) $$\Delta H^{\circ} = \sum \Delta H^{\circ}_{f\,生成物} - \sum \Delta H^{\circ}_{f\,反應物}$$

$$\Delta H^{\circ} = \left[6 \times \Delta H^{\circ}_{f} CO_2(g) + 3 \times \Delta H^{\circ}_{f} H_2O(l)\right] - \left[\Delta H^{\circ}_{f} C_6H_6(l)\right]$$

$$-3267.4 = \left[6 \times (-393.5) + 3 \times (-285.8)\right] - \Delta H^{\circ}_{f} C_6H_6(l)$$

$$\Delta H^{\circ}_{f} C_6H_{6(l)} = \left[(-2361) + (-857.4)\right] + 3267.4$$

$$= +49.0\ \text{kJ/mol}$$

(b) $$[C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)] \quad \text{x} \quad (-2)$$

$$\Rightarrow \quad 12CO_2(g) + 6H_2O(l) \rightarrow 2C_6H_6(\mathbf{l}) + 15O_2(g)$$
$$\Delta H^{\circ} = (-3267.4) \times (-2) = +6534.8 \text{ kJ}$$

(c) (1) $C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$ ΔH_1° = -3267.4 kJ

(2) $H_2O(l) \longrightarrow + H_2O(g)$ ΔH_2° = +44.0 kJ

(3) $C_6H_6(l) \longrightarrow C_6H_6(g)$ $\Delta H_3^\circ = \Delta H_{vap}$ = 33.6 kJ

1 × (1) + 3 × (2) - 1 × (3):

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

$$+ \quad 3H_2O(l) \longrightarrow + \ 3H_2O(g)$$

$$+ \quad C_6H_6(g) \longrightarrow + \ C_6H_6(l)$$

$$C_6H_6(g) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$$

ΔH° = 1 × ΔH_1° + 3 × ΔH_2° - 1 × ΔH_3°

= (-3267.4) + 3 × (44.0) – (33.6)
= -3169.0 kJ

Ex 8.8. Sodium carbonate is a white powder used in the manufacture of glass. When hydrochloric acid is added to a solution of sodium carbonate, carbon dioxide gas is formed. The equation for the reaction is

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O(l)$$

(a) Calculate ΔH° for the thermochemical equation.

(b) Calculate ΔH° when 25.0 mL of 0.186 M HCl is added to sodium carbonate.

Ans：

(a) $\Delta H^\circ = \sum \Delta H^\circ_{f\ 生成物} - \sum \Delta H^\circ_{f\ 反應物}$

$= [\Delta H^\circ_f CO_2(g) + \Delta H^\circ_f H_2O(l)] - [2\Delta H^\circ_f H^+(aq) + \Delta H^\circ_f CO_3^{2-}(aq)]$

$= [(-393.5) + (-285.8)] - [2 \times (0.00) + (-677.1)]$

= -2.2 kJ

(b)

$$n_{HCl} = n_{H^+} = V \times M = \frac{25.00}{1000} \times 0.186 = 0.00465 \text{ mol}$$

$$\Delta H^\circ = 0.00465 \text{ mol H}^+ \times \frac{-2.2\text{kJ}}{2 \text{ mol H}^+} = -5.1 \times 10^{-3} \text{ kJ}$$

§ 8-6 Bond enthalpy 鍵結焓：均爲”+”值

When one mole of bonds is broken in the gases state.

$H_2(g) \longrightarrow 2H(g)$ $\Delta H^\circ = 436$ kJ H-H bond enthalpy = 436 kJ

$Cl_2(g) \longrightarrow 2Cl(g)$ $\Delta H^\circ = 243$ kJ Cl-Cl bond enthalpy = 243 kJ

§ 8-7 The First law of Thermodynamics 熱力學第一定律

Thermochemistry is a branch of thermodynamics.

Thermodynamics distinguishes between two types of energy one of these is heat (q); the other is work (w). Work includes all forms of energy except heat.

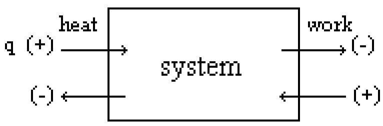
The law of conservation of energy：能量不滅定律

$$\Delta U_{system} = -\Delta U_{surroundings}$$

The first law of Thermodynamics：

In any process, the total change in energy of a system, ΔU is equal to the sum of the heat, q, and the work , w , transfer between the system and the surroundings.

$$\Delta U = q + w$$



For an isolated system, the total energy of the system remains constant.

$\Delta U = \mathbf{q + w}$

Isolated system 獨立系統: A system does not allow matter or energy come in or get out of the system.

Ex 8-9： Calculate ΔU of a gas for a process in which the gas.

a) absorbs 20 J of heat and does 12 J of work by expanding.
b) evolves 30 J of heat and has 52 J work done on it as it contacts.

Ans： $\Delta U = q + w$

a) q = +20 J w = -12J
ΔU = +20 + (-12) = +8 J

b) q = -30 J w= +52 J
ΔU = -30 + 52 = +22 J

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ ΔU = -885 kJ

	ΔU	q	w
本生燈	-885 kJ	-890 kJ	+5 kJ
汽車引擎	-885 kJ	-665 kJ	-220 kJ
燃料電池*	-885 kJ	-67 kJ	-818 kJ

* 以功率而言，此項最佳.

§ ΔH versus ΔU

Coffee-cup calorimeter P = C $\Delta H = q_P$

Bomb calorimeter V = C w = 0 $\Delta U = q_V$

H = U + PV 1 mole 25℃
PV = 1 × 0.0821 × (25+273)
= 24.5 L-atm × 0.1013 kJ
= 2.48 kJ

1 L-atm = 0.1013 kJ

$\Delta H = \Delta U + \Delta PV$

$$= \Delta U + \left[(PV)_{產物} - (PV)_{反應物}\right]$$

$\Delta H = \Delta U + \Delta n_g RT$　　　　Δn_g :氣體物質莫耳數改變量

25℃下，$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$　　ΔU = -885 kJ

Δn_g = 1- (1 + 2) = -2 mol

R：8.314 $J/mol.k$　　T：298 K

$\Delta H = \Delta U + \Delta n_g RT$

= (-885 kJ) + (-2) × 8.314 × 298

= (-885 kJ) + (-5.0×10^3 J)

= (-885 kJ) + (-5.0 kJ)

= -890 kJ

ΔH = -890 kJ;　ΔU = -885 kJ

大多反應, 其 w 佔不到 1%，可忽略.

Ex 8.10. Calculate ΔH and ΔU at 25℃ for the reaction takes place when an oxyacetylene torch is used.

$$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$$

Ans：

$$\Delta H = \sum \Delta H^{o}_{f\,生成物} - \sum \Delta H^{o}_{f\,反應物}$$

$$= \left[2 \times \Delta H^{o}_{f} CO_2(g) + \Delta H^{o}_{f} H_2O(g)\right] - \left[\Delta H^{o}_{f} C_2H_2(g)\right]$$

$$= \left[2 \times (-393.5) + (-241.8)\right] - (226.7)$$

= -1255.5 kJ

$\Delta n_g = (2 + 1) - (1 + \frac{5}{2})$ = -0.5 mol

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta U = \Delta H - \Delta n_g RT$$

$$= -1255.5 - (-0.5) \times (8.314) \times (25 + 273)$$

$$= -1255.5 \text{ kJ} + 1.2 \text{ kJ}$$

$$= -1254.3 \text{ kJ}$$