6 Thermochemistry

Energy:

The capacity to do work or to produce heat

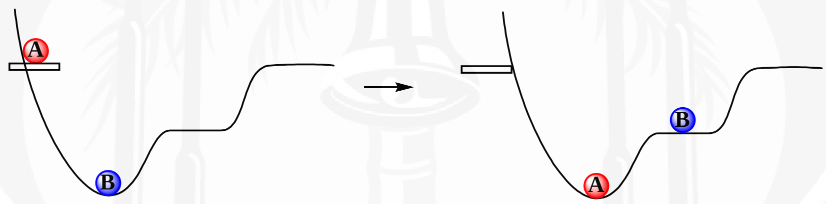
★ The law of conservation of energy

Energy can be converted
but the total is a constant

Two types of energy:

- Kinetic energy — due to motion
  ½ mv^2
- Potential energy — due to position, composition, attraction, repulsion…….

Example



Potential energy has changed for **A** and **B:**

A: decreased
B: increased
Frictional energy is involved

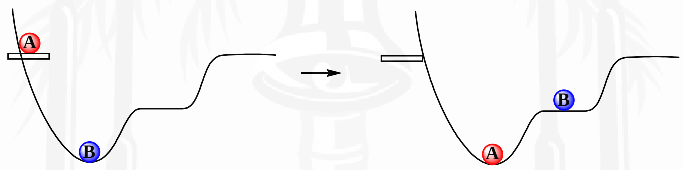
Total energy : no change

◎ Energy transfer:
through work and heat

Work: a force acting over a distance

In previous example: work is done on **B** by **A**

◎ The nature of energy



For **A**:

different path → different heat and work

the change of PE for **A** → the same

★ Energy is a state function — independent of path

Heat and work are path dependent

NOT state function

From one state to another state

→ may go through different path

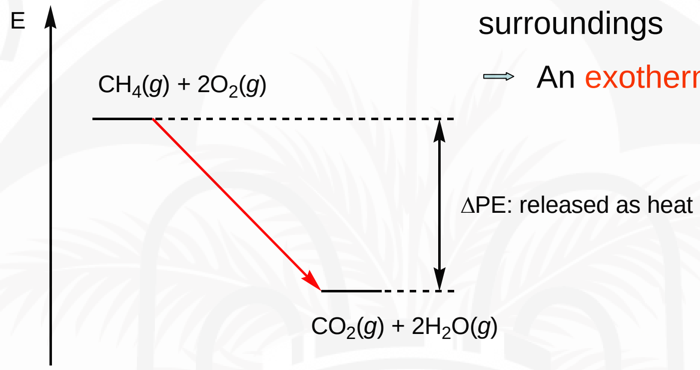
※ Chemical energy

$CH_4(g)$ + $2O_2(g)$ → $CO_2(g)$ + $2H_2O(g)$ + heat

The PE stored in chemical bonds is released to the surroundings

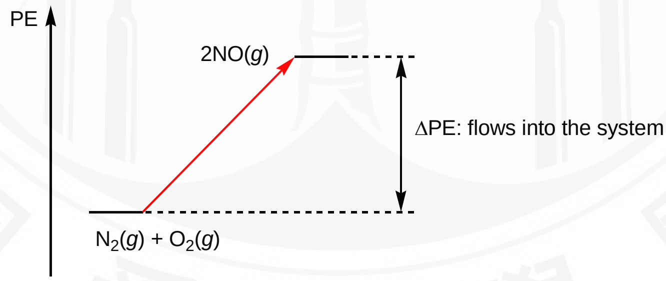
⇨ An exothermic reaction

Energy diagram



Ex:

$N_2(g)$ + $O_2(g)$ + heat → $2NO(g)$



⇨ An endothermic reaction

※ Thermodynamics

The study of energy and its interconversions

Questions:

How far will a reaction proceed?

How much energy will be released or consumed?

★ The first law of thermodynamics

The law of conservation of energy

※ Internal energy (E)

Define internal energy E:

the sum of PE and KE in the system

Difficult to measure

The change is measurable:

$\Delta E = q + w$

heat

work

◎ The sign of q and w

From the system's point of view:

q absorbed by the system is positive

⟹ Increases E of the system

q released by the system is negative

⟹ Decreases E of the system

Ex: endothermic reaction: q (+)
exothermic reaction: q (−)

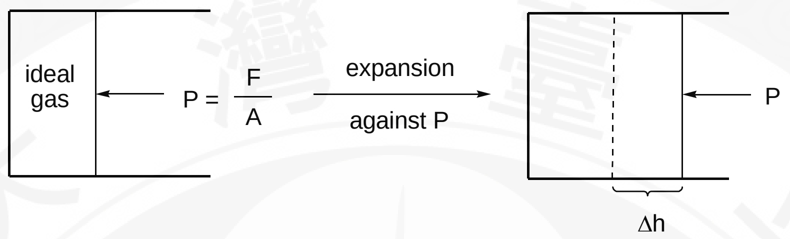
w done by the system is negative

⟹ Decreases E of the system

w done by the surroundings on the system is positive

⟹ Increases E of the system

◎ A model study



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

Since $P = F/A$ → $F = PA$

$|\text{work}| = |P \times A \times \Delta h|$
$= |P \times \Delta V|$

Work is done by the system ⇨ negative

$\Delta V = V_{final} - V_{initial}$

$V_{final} > V_{initial}$ (for expansion)
ΔV ⇨ positive (for expansion)

Therefore we must define
$w = -P\Delta V$

For compression
ΔV → negative
w → positive

Ex: A balloon

$$4.00 \times 10^6\ \text{L} \xrightarrow[\uparrow\ 1.3 \times 10^8\ \text{J}]{\text{heat}} 4.50 \times 10^6\ \text{L}$$

Expands against 1.0 atm, ΔE?

Soln: $\Delta E = q + w$

$q = +1.3 \times 10^8$ J

$w = -P\Delta V$
$= -(1.0\ \text{atm})(0.50 \times 10^6\ \text{L})$
$= -5.0 \times 10^5\ \text{atm} \cdot \text{L}$
$= -(5.0 \times 10^5)(101.3) = -5.1 \times 10^7$ J

$\boxed{1\ \text{atm} \cdot \text{L} = 101.3\ \text{J}}$

$\Delta E = +(1.3 \times 10^8) - 5.1 \times 10^7$ J
$= 8 \times 10^7$ J

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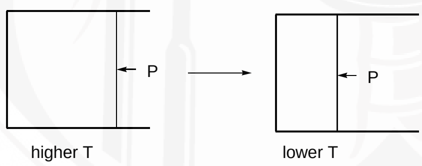
※ Enthalpy (焓) and calorimetry (量熱法)

◎ The definition of enthalpy



$\Delta E = q + w$
$= q - P\Delta V$

At constant P:
$\Delta E = q_P - \Delta(PV)$

$q_P = \Delta E + \Delta(PV)$
$= E_f - E_i + (PV)_f - (PV)_i$
$= E_f + (PV)_f - E_i - (PV)_i$

Define enthalpy $H = E + PV$

→ $H_f = E_f + (PV)_f$ $H_i = E_i + (PV)_i$

→ $q_p = H_f - H_i = \Delta H$

★ $q_P = \Delta H$ at constant P
$= \Delta E + P\Delta V$ at constant P $\Rightarrow$ $q_P \neq \Delta E$ (unless $\Delta V = 0$)

- What's so important?

  Usually reactions are performed at constant P
  q_P is obtained experimentally
  Therefore, ΔH can be measured directly

- The beauty of H

  $H = E + PV$

  A state function
  → Path independent

  For a reaction $\Delta H = H_{products} - H_{reactants}$

  Exothermic reaction: q_P is negative → negative ΔH

  Endothermic reaction: q_P is positive → positive ΔH

- ΔH and ΔE may be different

◎ Calorimetry (量熱學)

The science of measuring heat
⇨ observing T change

$$C = \frac{\text{heat absorbed}}{\text{increase in T}}$$

Heat capacity
熱容

Specific heat capacity: per gram sample

Unit: $\frac{J}{^{o}C \cdot g}$ or $\frac{J}{K \cdot g}$

Molar heat capacity: per mole sample

Unit: $\frac{J}{^{o}C \cdot mol}$ or $\frac{J}{K \cdot mol}$

◎ Constant P calorimetry

Purpose: get q_P

⇨ $q_P = \Delta H$

Ex: Mix 50.0 mL 1.0 M HCl at 25.0 °C ⟹ 31.9 °C
50.0 mL 1.0 M NaOH at 25.0 °C

Soln: $\Delta T = 31.9 - 25.0 = 6.9\ ^{o}C$

mass $\approx$ 100.0 mL $\times$ 1.0 g/mL = 1.0×10^2 g

specific heat capacity

mass

Energy released $= s \times m \times \Delta T$

$= (4.18\ J/^{o}Cg)(1.0 \times 10^2\ g)(6.9\ ^{o}C)$

$= 2.9 \times 10^3\ J$

Heat is an extensive (外延) property

related to the amount of substance

T is an intensive (內涵) property

not related to the amount of substance

50.0 mL 1.0 M HCl ⇨ 5.0×10^{-2} mol H^+

$$\frac{2.9 \times 10^3\ J}{5.0 \times 10^{-2}\ mol} = 5.8 \times 10^4\ J/mol$$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H = -58$ kJ/mol

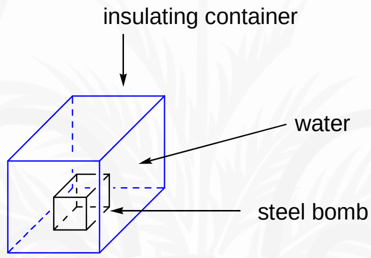
◎ Constant V calorimetry

$\Delta V = 0 \Rightarrow w = 0$

$\Delta E = q_V + w = q_V$

Therefore, $\Delta E = q_V$ at constant V

Use a bomb calorimeter



Ex: Combustion of 0.5269 g octane (C_8H_{18})

The bomb calorimeter used: $C = 11.3$ kJ/°C

$\Delta T = 2.25$ °C

Soln: Heat released = $C\Delta T = 11.3 \times 2.25 = 25.4$ kJ

MW of octane = 114.2 g/mol

$$0.5269 \text{ g octane} \Rightarrow \frac{0.5269 \text{ g}}{114.2 \text{ g/mol}} = 4.614 \times 10^{-3} \text{ mol}$$

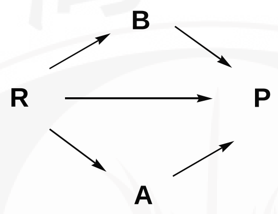
For 1 mol octane:

$$\text{Heat} = \frac{25.4}{4.614 \times 10^{-3}} = 5.50 \times 10^{3} \text{ kJ/mol}$$

$$\Delta E = -5.50 \times 10^{3} \text{ kJmol}^{-1}$$

※ Hess's law

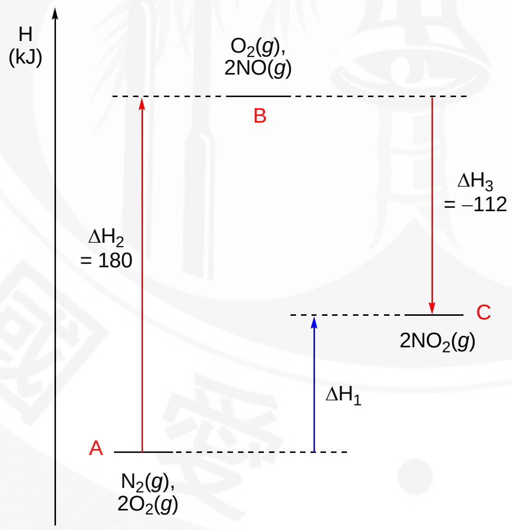
Reactants → Products $\Delta H = \sum n_p H_{products} - \sum n_r H_{reactants}$

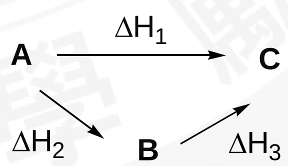


∵ H is a state function

∴ $\Delta H_{R \to P}$ is the same for different pathways

Ex: $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ $\Delta H_1 = 68$ kJ





$\Delta H_1 = \Delta H_2 + \Delta H_3$ ⇨ 180 – 112 must be 68 kJ

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※ Characteristics of ΔH

1. $\Delta H = -\Delta H_{reverse}$

$N_2(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H_2 = +180$ kJ

endothermic

Reverse reaction:

$2NO_2(g) \rightarrow N_2(g) + O_2(g)$ $\Delta H_{-2} = -180$ kJ

exothermic

2. ΔH is an extensive property depending on the amount of reactants

$Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$ $\Delta H = -251$ kJ

$2Xe(g) + 4F_2(g) \rightarrow 2XeF_4(s)$ $\Delta H = 2(-251 \text{ kJ}) = -502$ kJ

Ex: $2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$ $\Delta H = ?$

Data available:

(a) $2B(s) + 3/2O_2(g) \rightarrow B_2O_3(s)$ $\Delta H = -1273$ kJ

(b) $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$ $\Delta H = -2035$ kJ

(c) $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286$ kJ

(d) $H_2O(l) \rightarrow H_2O(g)$ $\Delta H = 44$ kJ

Ex: $2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$ $\Delta H = ?$

Soln:

+a (for B)

$2B(s) + 3/2O_2(g) \rightarrow B_2O_3(s)$ $\Delta H = -1273$ kJ

+3c (for H_2)

$3H_2(g) + 3/2O_2(g) \rightarrow 3H_2O(l)$ $\Delta H = -286 \times 3$ kJ

–b (for B_2H_6)

$B_2O_3(s) + 3H_2O(g) \rightarrow B_2H_6(g) + 3O_2(g)$ $\Delta H = 2035$ kJ

+3d (for H_2O)

$3H_2O(l) \rightarrow 3H_2O(g)$ $\Delta H = 44 \times 3$ kJ

$2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$

$\Delta H = -1273 - (286 \times 3) + 2035 + (44 \times 3)$

$= +36$ kJ

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※ Standard enthalpies of formation

Real interest: calculate ΔH for reactions

Problem: no way to know the exact value of enthalpy

Solution: resolve each compound into the basic elements

Define a standard enthalpy of formation (ΔH_f^o)

— 1 mol of a compound from its elements in their standard states

Standard state:
The physical state in which the substance is most stable at 1 atm and the temperature of interest (usually 25 °C)

gas: a pressure of 1 atm
solution: a concentration of 1 M
a pure liquid or solid compound: the pure liquid or solid
element: the state at 1 atm (25 °C)
Ex: $Na(s)$, $Hg(l)$

*Do not confused with STP

Ex: $1/2N_2(g) + O_2(g) \rightarrow NO_2(g)$ $\quad \Delta H_f^o = 34$ kJ/mol

Elements in standard state $\quad$ 1 mol (in standard state)

$C(s) + 2H_2(g) + 1/2O_2(g) \rightarrow CH_3OH(l)$ $\quad \Delta H_f^o = -239$ kJ/mol

graphite

◎ The use of ΔH_f^o

Ex: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\quad \Delta H^o = ?$

Data available:

$C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\quad \Delta H_f^o = -75$ kJ/mol
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H_f^o = -394$ kJ/mol
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ $\quad \Delta H_f^o = -286$ kJ/mol

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

$C(s)$, $2H_2(g)$ $\quad$ $2O_2(g)$ $\quad$ $C(s)$, $O_2(g)$ $\quad$ $2H_2(g)$, $O_2(g)$

$$\Delta H^o = 75 \quad + 0 \quad - 394 \quad - (286 \times 2)$$
$$= -\Delta H_f^o{}_{(CH_4)} + \Delta H_f^o{}_{(CO_2)} + 2(\Delta H_f^o{}_{(H_2O)})$$
$$= \Delta H_f^o{}_{(CO_2)} + 2(\Delta H_f^o{}_{(H_2O)}) - \Delta H_f^o{}_{(CH_4)}$$

Conclusion:

$$\Delta H_{rxn}^{o} = \sum n_p \Delta H_f^{o}{}_{(products)} - \sum n_r \Delta H_f^{o}{}_{(reactants)}$$

(elements in their standard state are not included)

Cf. $\Delta H = \sum n_p H_{products} - \sum n_r H_{reactants}$

Ex: $4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(l)$

ΔH_f^{o} : -46 $\qquad$ 34 $\qquad$ -286 kJ/mol

$$\Delta H^{o} = 6(-286) + 4(34) - 4(-46) = -1396 \text{ kJ}$$