9 Energy, Enthalpy and Thermochemistry

Energy:

The capacity to do work or to produce heat

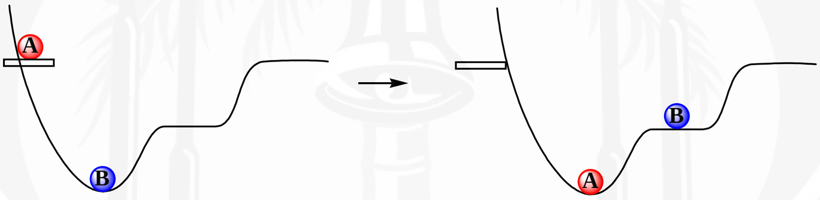
★ The law of conservation of energy

Energy can be converted
but the total is a constant

Two types of energy:

Kinetic energy — due to motion
$\frac{1}{2} mv^2$
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

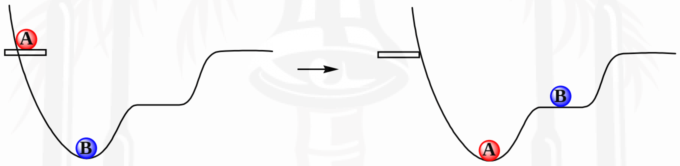
Total energy : no change

◎ 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

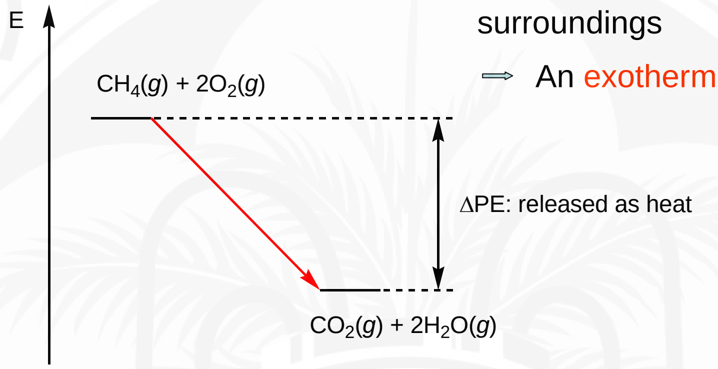
※ Chemical energy

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

The PE stored in chemical bonds is released to the surroundings

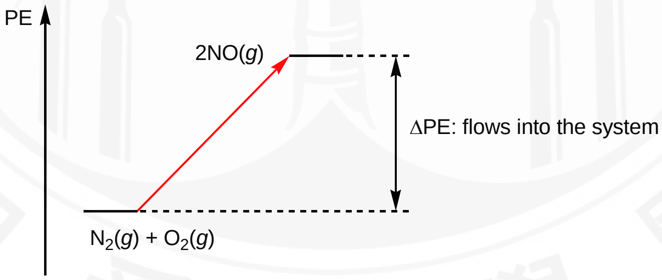
⟹ An exothermic reaction

Energy diagram



Ex:

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



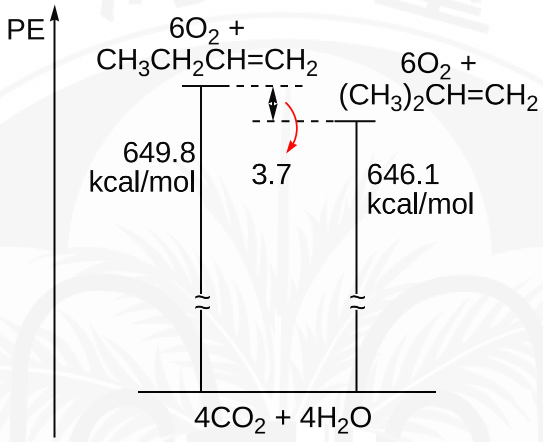
⟹ An endothermic reaction

Ex. $CH_3CH_2CH{=}CH_2 + 6O_2 \rightarrow 4CO_2 + 4H_2O$

$\Delta H = -649.8$ kcal/mol

$(CH_3)_2C{=}CH_2 + 6O_2 \rightarrow 4CO_2 + 4H_2O$

$\Delta H = -646.1$ kcal/mol



※ 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

臺灣大學化學系
NTU Chemistry

※ Internal energy (E)

Define internal energy E:
the sum of PE and KE in the system

Difficult to measure

The change is measurable:

$$\Delta E = q + w$$

work

heat

◎ 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* (−)

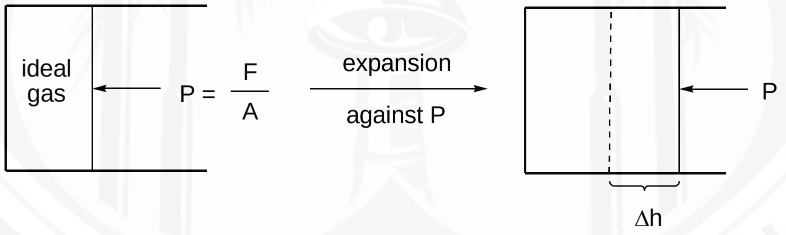
w done by the system is negative

⇨ 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 $P = F/A \rightarrow F = PA$

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

Work is done by the system ⇨ negative

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

$V_{\text{final}} > V_{\text{initial}}$ (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

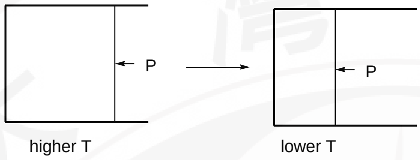
$$\begin{aligned} w &= -P\Delta V \\ &= -(1.0\ \text{atm})(0.50 \times 10^6\ \text{L}) \\ &= -5.0 \times 10^5\ \text{atm} \cdot \text{L} \\ &= -(5.0 \times 10^5)(101.3) = -5.1 \times 10^7\ \text{J} \end{aligned}$$

1 atm • L = 101.3 J

$$\begin{aligned} \Delta E &= +(1.3 \times 10^8) - 5.1 \times 10^7\ \text{J} \\ &= 8 \times 10^7\ \text{J} \end{aligned}$$

※ Enthalpy (焓)

◎ 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 $H = E + PV$

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

→ $q_p = H_f - H_i = \Delta H$

★ $q_P = \Delta H$ 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 $\quad \Delta H = H_{\text{products}} - H_{\text{reactants}}$

  Exothermic reaction: q_P is negative → negative ΔH

  Endothermic reaction: q_P is positive → positive ΔH

- ΔH and ΔE may be different

※ Thermodynamics of ideal gases

◎ Heating 1 mol of an ideal gas at constant V

$T_1 \rightarrow T_2 \qquad \Delta V = 0$

$(\text{KE})_{\text{avg}} = {}^{3}\!/_{2}RT \qquad$ (note: total $E = KE + \overset{\overset{\text{No change}}{\downarrow}}{PE}$)

$\Delta\text{KE} = {}^{3}\!/_{2}RT_2 - {}^{3}\!/_{2}RT_1 = {}^{3}\!/_{2}R\Delta T = \Delta E$

$\Delta V = 0$ ⇨ no PV work ($w = 0$)

⇨ $\Delta E = q_v + w = {}^{3}\!/_{2}R\Delta T$ ⇨ $q_v = {}^{3}\!/_{2}R\Delta T$

☆ $\Delta E = q_v$ at constant V

✓ Molar heat capacity (熱容)

$$C = \frac{\text{heat absorbed}}{\text{increase in T}} = \frac{q}{\Delta T} \quad \text{(per mol)}$$

$C_v = \dfrac{q_v}{\Delta T}$ ⇨ $C_v = {}^{3}\!/_{2}R$

↑

Heat required to change T of 1 mol
ideal gas by 1 K at constant V

◎ Heating an ideal gas at constant P

$T_1 \rightarrow T_2$ (KE increases)
$V_1 \rightarrow V_2$ (PV work is done)

$\Delta \text{KE} = {}^3/_2 R\Delta T$ (1 mol)

$w = -P\Delta V = -nR\Delta T$ (note: $PV_1 = nRT_1$)

For 1 mol of ideal gas
$\Delta E = q_p + w \quad ⇨ \quad q_p = \Delta E - w = {}^3/_2 R\Delta T + R\Delta T = \Delta H$

$$C_p = \frac{q_p}{\Delta T} \quad ⇨ \quad \underset{\uparrow}{C_p} = {}^3/_2 R + R = C_v + R$$

Heat required to change T of 1 mol ideal gas by 1 K at constant P

	C_v		C_p		$C_p - C_v$ ($JK^{-1}mol^{-1}$)
He, Ne, Ar	12.47		20.80		8.33
H_2	20.54	$>{}^3/_2R$	28.86	$>{}^5/_2R$	8.32
CO_2	28.95		37.27		8.32
C_2H_6	44.60		52.92		8.32

$\boxed{{}^3/_2R = 12.47}$

Extra E is required to increase the rotational and vibrational E of polyatomic molecule

The difference is due to the expansion work
→ No change

◎ Heating a gas: energy and enthalpy

Translational E for 1 mol of ideal gas:

$E = {}^{3}/_{2}RT$ ← T dependent only

$\Delta E = {}^{3}/_{2}R\Delta T$

General form: $\Delta E = {}^{3}/_{2}nR\Delta T$

Since $C_v = {}^{3}/_{2}R$ ⇨ $\Delta E = nC_v\Delta T$

Recall $H = E + PV$

$$\begin{aligned}\Delta H &= \Delta E + \Delta(PV)\\ &= \Delta E + nR\Delta T\\ &= nC_v\Delta T + nR\Delta T\\ &= n(C_v + R)\Delta T\end{aligned}$$

$\Delta H = nC_p\Delta T$ ← T dependent only

$E \propto T$ ⇨ slope = nC_v

$H \propto T$ ⇨ slope = nC_p

} Independent of P or V

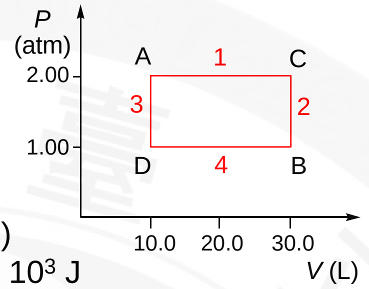
But $q = nC\Delta T$
is dependent on condition

Summary

$C_v = {}^{3}/_{2}R$	Monoatomic ideal gas
$C_v > {}^{3}/_{2}R$	Polyatomic ideal gas (measured by exp.)
$C_p = C_v + R$	All ideal gases
$C_p = {}^{5}/_{2}R = {}^{3}/_{2}R + R$	Monoatomic ideal gas
$C_p > {}^{5}/_{2}R$	Polyatomic ideal gas (measured by exp.)
$\Delta E = nC_v\Delta T$	All ideal gases
$\Delta H = nC_p\Delta T$	All ideal gases

Ex. From state A → state B

Q: q, w, ΔE, ΔH ?



Step 1

$w_1 = -P\Delta V$

$= -(2.00\text{ atm})(30.0\text{ L} - 10.0\text{ L})$

$= -4.00 \times 10\text{ L}\bullet\text{atm} = -4.05 \times 10^3\text{ J}$

At A: $P_1V_1/nR = T_1$ At C: $P_2V_2/nR = T_2$

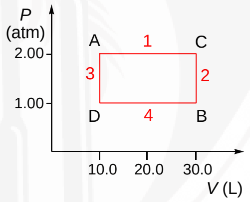
$$\Delta T = T_2 - T_1 = \frac{P(V_2 - V_1)}{nR} = \frac{(2.00)(20.0)}{nR} = \frac{40.0\text{ L}\bullet\text{atm}}{nR}$$

$$= \frac{4.05\times10^3\text{ J}}{nR}$$

$$q_1 = q_\text{p} = nC_\text{p}\Delta T = n(\frac{5}{2}R)(\frac{4.05\times10^3}{nR}) = 1.01\times10^4\text{ J}$$

$$\Delta E_1 = nC_\text{v}\Delta T = n(\frac{3}{2}R)(\frac{4.05\times10^3}{nR}) = 6.08\times10^3\text{ J}$$

$\Delta H_1 = q_\text{p} = q_1 = 1.01 \times 10^4$ J



Step 2

$w_2 = 0$

$$\Delta T = \frac{(P_\text{f} - P_\text{i})V}{nR} = \frac{(1.00 - 2.00)(30.0)}{nR} = \frac{-30.0\text{ L}\bullet\text{atm}}{nR}$$

$$= \frac{-3.04\times10^3\text{ J}}{nR}$$

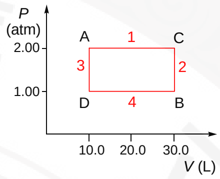
$$q_2 = q_\text{v} = nC_\text{v}\Delta T = n(\frac{3}{2}R)(\frac{-3.04\times10^3}{nR}) = -4.56\times10^3\text{ J}$$

$\Delta E_2 = q_\text{v} = q_2 = -4.56 \times 10^3$ J

$$\Delta H_2 = nC_\text{p}\Delta T = n(\frac{5}{2}R)(\frac{-3.04\times10^3}{nR}) = -7.60\times10^3\text{ J}$$

Another way to calculate ΔH_2

$$\Delta H_2 = \Delta E_2 + \Delta(PV) = \Delta E_2 + (1.00 - 2.00)30.0\ \text{L}\cdot\text{atm}$$
$$= -4.56 \times 10^3 - 3.04 \times 10^3\ \text{J}$$



Step 3

$w_3 = 0$

$$\Delta T = \frac{(P_f - P_i)V}{nR} = \frac{(-1.00)(10.0)}{nR} = \frac{-10.0\ \text{L}\bullet\text{atm}}{nR} = \frac{-1.01\times10^3\ \text{J}}{nR}$$

$$q_3 = q_v = nC_v\Delta T = n(\frac{3}{2}R)(\frac{-1.01\times10^3}{nR}) = -1.52\times10^3\ \text{J}$$

$$\Delta E_3 = q_v = q_3 = -1.52 \times 10^3\ \text{J}$$

$$\Delta H_3 = nC_p\Delta T = n(\frac{5}{2}R)(\frac{-1.01\times10^3}{nR}) = -2.53\times10^3\ \text{J}$$

Step 4

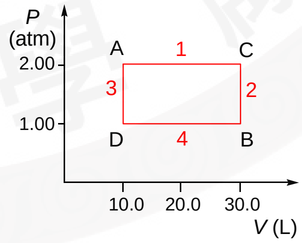
$$w_4 = -P\Delta V = -(1.00\ \text{atm})(30.0\ \text{L} - 10.0\ \text{L})$$
$$= -2.00 \times 10\ \text{L}\cdot\text{atm} = -2.03 \times 10^3\ \text{J}$$

$$\Delta T = \frac{P(V_f - V_i)}{nR} = \frac{(1.00)(20.0)}{nR} = \frac{20.0\ \text{L}\bullet\text{atm}}{nR} = \frac{2.03\times10^3\ \text{J}}{nR}$$

$$q_4 = q_p = nC_p\Delta T = n(\frac{5}{2}R)(\frac{2.03\times10^3}{nR}) = 5.08\times10^3\ \text{J}$$

$$\Delta E_4 = nC_v\Delta T = n(\frac{3}{2}R)(\frac{2.03\times10^3}{nR}) = 3.05\times10^3\ \text{J}$$

$$\Delta H_4 = q_p = q_4 = 5.08 \times 10^3\ \text{J}$$



Summary

$w_1 = -4.05 \times 10^3$ J
$\Delta E_1 = 6.08 \times 10^3$ J
$w_2 = 0$ J
$\Delta E_2 = -4.56 \times 10^3$ J

$q_1 = 1.01 \times 10^4$ J
$\Delta H_1 = 1.01 \times 10^4$ J
$q_2 = -4.56 \times 10^3$ J
$\Delta H_2 = -7.60 \times 10^3$ J

$$A \xrightarrow{1} C \xrightarrow{2} B$$

$q = q_1 + q_2 = 5.5 \times 10^3$ J
$\Delta E = q + \mathrm{w} = 1.5 \times 10^3$ J

$w = w_1 + w_2 = -4.05 \times 10^3$ J
$\Delta H = \Delta H_1 + \Delta H_2 = 2.5 \times 10^3$ J

$w_3 = 0$ J
$\Delta E_3 = -1.52 \times 10^3$ J
$w_4 = -2.03 \times 10^3$ J
$\Delta E_4 = 3.05 \times 10^3$ J

$q_3 = -1.52 \times 10^3$ J
$\Delta H_3 = -2.53 \times 10^3$ J
$q_4 = 5.08 \times 10^3$ J
$\Delta H_4 = 5.08 \times 10^3$ J

$$A \xrightarrow{3} D \xrightarrow{4} B$$

$q = q_3 + q_4 = 3.56 \times 10^3$ J
$\Delta E = q + \mathrm{w} = 1.52 \times 10^3$ J

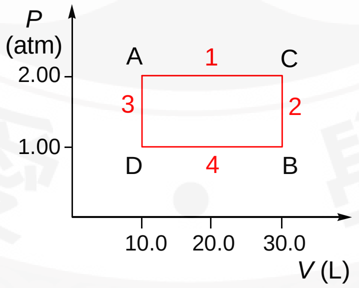
$w = w_3 + w_4 = -2.03 \times 10^3$ J
$\Delta H = \Delta H_3 + \Delta H_4 = 2.55 \times 10^3$ J

Conclusion

From A → B

ΔE, and ΔH are the same for the two pathways

q, and w are path dependent



※ 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: $\frac{J}{{}^{o}C \bullet g}$ or $\frac{J}{K \bullet g}$

Molar heat capacity: per mole sample

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

◎ Constant P calorimetry

Purpose: get q_P
⇨ $q_P = \Delta H$

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

Soln: $\Delta T = 31.9 - 25.0 = 6.9\ {}^{o}C$
mass ≈ $100.0\ mL \times 1.0\ g/mL = 1.0 \times 10^2\ g$

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^+

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

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

◎ At constant P with PV work

Example above: reaction in solution
assumption: $\Delta V = 0$ ⇨ $w = 0$
$\Delta E = q_p + w = q_p = \Delta H$

Ex. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

There is volume change – volume decreased

$$\underset{\uparrow \atop (+)}{w} = -P\Delta \underset{\nwarrow\ (-)}{V}$$

$$\underset{\nwarrow}{\Delta E} = q_p + w = \underset{\nearrow}{\Delta H} + w$$

Different values

2.00 mol $SO_2(g)$ + 1.00 mol $O_2(g)$ at 25 °C, 1.00 atm
$q = -198$ kJ (T kept constant)

Q: ΔH , ΔE ?

Soln: $w = -P\Delta V = -P(V_2 - V_1) = -(n_2RT - n_1RT)$
$= -(-1.00 \text{ mol})(8.3145 \text{ J/K} \cdot \text{mol})(298 \text{ K})$
$= 2.48 \times 10^3$ J
$= 2.48$ kJ

$\Delta E = q + w = -198 + 2.48 = -196$ kJ

$\Delta H = q_p = -198$ kJ

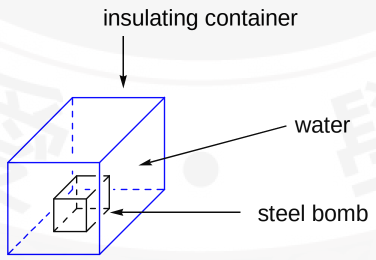
◎ Constant V calorimetry

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

$\Delta E = q_V + w = q_V$

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:

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

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

Ex. Same bomb calorimeter

1.50 g methane + O_2 (excess) → $\Delta T = 7.3$ °C

1.15 g H_2 + O_2 (excess) → $\Delta T = 14.3$ °C

For methane

$$\frac{C\Delta T}{\text{mass}} = \frac{(11.3)(7.3)}{1.50} = 55 \text{ kJ/g}$$

For H_2

$$\frac{C\Delta T}{\text{mass}} = \frac{(11.3)(14.3)}{1.15} = 141 \text{ kJ/g}$$

More efficient fuel

Cf. Octane: 48.2 kJ/g

※ Hess's law

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

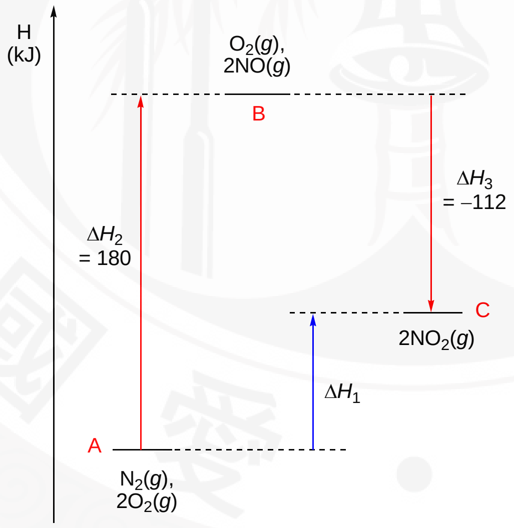
$$\begin{tikzcd}
 & B \arrow[dr] & \\
R \arrow[ur] \arrow[rr] \arrow[dr] & & P \\
 & A \arrow[ur] &
\end{tikzcd}$$

∵ H is a state function

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

---

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



$$\begin{tikzcd}
A \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_2"'] & & C \\
 & B \arrow[ur, "\Delta H_3"'] &
\end{tikzcd}$$

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

※ Characteristics of ΔH

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

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H_2 = +180$ kJ
↑
endothermic

Reverse reaction:
$2NO(g) \rightarrow N_2(g) + O_2(g)$ $\Delta H_{-2} = -180$ 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

※ 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 be confused with STP

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

Elements in standard state

1 mol (in standard state)

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

graphite

◎ The use of ΔH_f^o

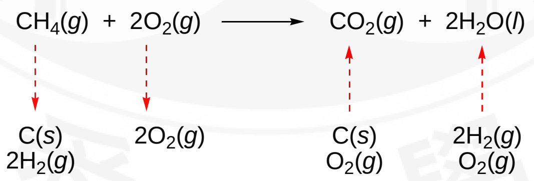
Ex: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\qquad \Delta H^o = ?$

Data available:

$C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\qquad \Delta H_f^o = -75$ kJ/mol

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\qquad \Delta H_f^o = -394$ kJ/mol

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\qquad \Delta H_f^o = -286$ kJ/mol



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

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

$$\Delta H^o = 75 \quad +0 \quad -394 \quad -(286 \times 2) = -891 \text{ kJ}$$
$$= -\Delta H_f^o{}_{(CH_4)} + \Delta H_f^o{}_{(CO_2)} + 2(\Delta H_f^o{}_{(H_2O)})$$
$$= \Delta H_f^o{}_{(CO_2)} + 2(\Delta H_f^o{}_{(H_2O)}) - \Delta H_f^o{}_{(CH_4)}$$

Conclusion:

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

(elements in their standard state are not included)

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

Ex: $\underset{\underset{-46}{\uparrow}}{4NH_3(g)} + 7O_2(g) \rightarrow \underset{\underset{34}{\uparrow}}{4NO_2(g)} + \underset{\underset{-286\ kJ/mol}{\uparrow}}{6H_2O(l)}$

ΔH_f^{o} : -46 34 -286 kJ/mol

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

※ Present sources of energy

- ✓ Natural gas

  Mainly CH_4 with some ethane
  propane
  butane

- ✓ Petroleum $\xrightarrow[\text{distillation}]{}$ C_{5-10} gasoline
  C_{10-18} kerosene
  C_{15-25} diesel

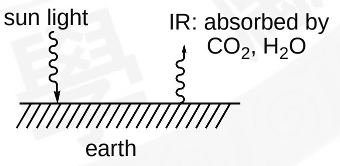
  cracking $\Big\downarrow$ 700 ^{o}C catalyst

  More gasoline fraction

- ✓ Coal: contains sulfur

  $\xrightarrow[O_2]{}$ gives off SO_2, and CO_2

  $\downarrow$ Acid rain $\uparrow$ Absorbs IR



※ New energy sources

✓ Coal gasification

$C(s)$ + steam + air:

~600 °C ⟶ $C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H^o = -75$ kJ
~900 °C ⟶ $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H^o = -111$ kJ
~1200 °C ⟶ $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^o = -394$ kJ
(+ sulfur compounds)
~900 °C ⟶ $C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$ $\Delta H^o = 131$ kJ

Water gas shift reaction

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$
$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$

Remove CO_2, H_2O & impurities
Left with CH_4, CO, and H_2

400 °C
Catalyst: Fe_2O_3 or Ni

Used in synthesis

$$CO(g) + 2H_2(g) \xrightarrow[\text{300 atm}]{\text{230–400 °C}} CH_3OH(l)$$

Ag or Cu catalyst

Fischer-Tropsch synthesis

$$nCO(g) + (2n+1)H_2(g) \xrightarrow[\text{1 to several hundred atm catalyst}]{\text{150–350 °C}} C_nH_{2n+2} + nH_2O(g)$$

Oxo process

$$RCH{=}CH_2 + H_2(g) + CO(g) \xrightarrow[\text{catalyst}]{\text{200–250 °C}} RCH_2CH_2CHO$$

✓ Hydrogen

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H^o = -286$ kJ

Highly exothermic
No pollution

Problems

△ Costs

Main source: $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$

Electrolysis of water?
Cheap electricity required

Thermolysis of water?
Efficient catalytic system required

Photo-biological decomposition of water?
New biological system required

△ Storage

Reacts with metals to give hydrides
— causing structural change

Large volumes are required

Ex. 80.0 L gasoline ⇨ 59200 g
assume hydrogen is three times more efficient
59200/3 = 19700 g H_2 ⇨ 277 L liquid H_2
⇨ 238000 L gaseous H_2

Better way:

$H_2(g) + \underset{\substack{\uparrow\\ \text{metal}}}{M}(s) \rightarrow MH_2(s)$

$MH_2(s) \rightarrow H_2(g) + M(s)$

Efficient system required

✓ Other source of energy

Ethanol

Gasohol (10% ethanol in gasoline)

Pure ethanol has too high a bp

Methanol

Possible

Biodiesel

From seed oil

臺灣大學化學系 NTU Chemistry

※ Exercise

Knowing: $\Delta H_f^o{}_{H_2O(l)} = -285.8$ kJ/mol

Q: $H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$

At 298 K and 1 atm, $\Delta E^o = $?

Soln: $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\qquad \Delta H_f^o{}_{H_2O(l)}$

⇨ $H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$ $\qquad \Delta H^o = 285.8$ kJ/mol

Assuming $V_{H_2} + \frac{1}{2} V_{O_2} >> V_{H_2O(l)}$

⇨ $\Delta V = V_{H_2} + \frac{1}{2} V_{O_2} = 1.5(24.6 \text{ L}) = 36.9$ L

⇨ $\Delta E^o = \Delta H^o + w = \Delta H^o - P\Delta V$

⇨ $\Delta E^o = 285.8 - (1)(36.9)(0.1013) = 282.1$ kJ/mol