

Topic 8:

Thermochemistry

# **8.0 THERMOCHEMISTRY**

**8.1 Concept of Enthalpy**

**8.2 Calorimetry**

**8.3 Hess's Law**

**8.4 Born-Haber Cycle**

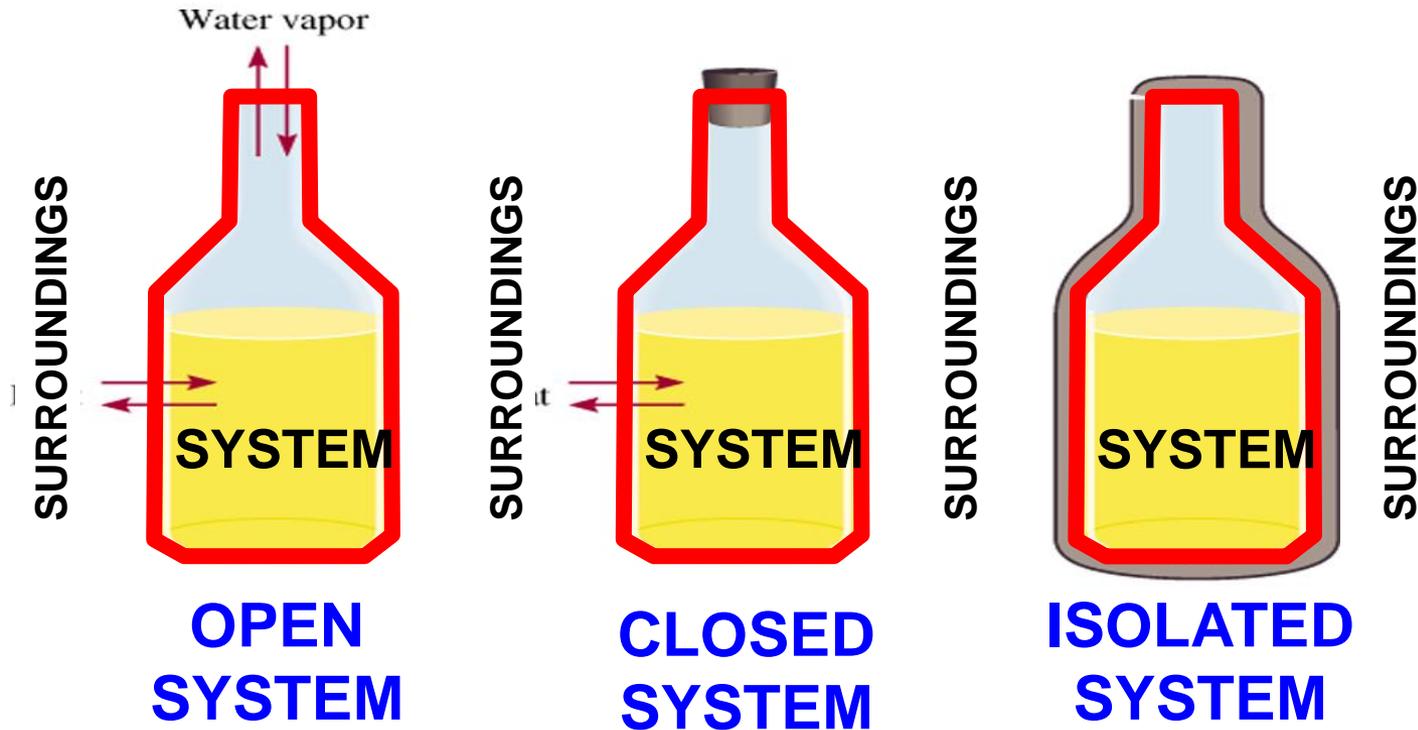
# THERMOCHEMISTRY

- **Thermochemistry** is the study of heat/enthalpy changes in chemical reactions.
- Almost all chemical reactions absorb or release heat energy.
- SI unit for heat is **joule (J)** or **kilojoule (kJ)**.

# Important Terms

- **Heat** is energy transferred between two bodies of different temperatures
- **System** is any specific part of the universe
- **Surroundings** is everything that lies outside the system

## 3 types of system:



### EXCHANGE:

mass &  
energy

only energy

nothing

- **Open system** is a system that can exchange mass and energy with its surroundings
- **Closed system** is a system that allows the exchange of energy with its surroundings
- **Isolated system** is a system that does not allow the exchange of either mass or energy with its surroundings
- **Energy** is the ability to do work
  - SI unit of energy is **kg m<sup>2</sup> s<sup>-2</sup>** or **Joule (J)**
  - Non SI unit of energy is **calorie (Cal)**
  - 1 Cal = 4.184 J

# Objective

At the end of this topic, students should be able to:

- a) Explain endothermic and exothermic reactions using the energy profile diagrams.
- b) State standard conditions of reaction.
- c) Explain standard enthalpy of reactions.
- d) Define enthalpy of
  - Formation, combustion, atomization, neutralization, hydration, solution (dissolution), electron affinity, ionization energy and lattice energy.
- e) Write thermochemical equation for each enthalpy.

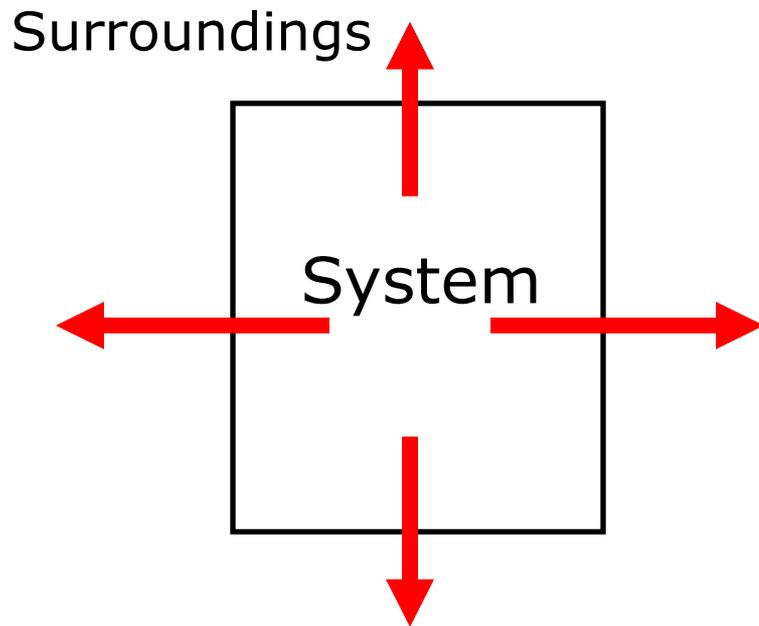
# **8.1 CONCEPT OF ENTHALPY**

# Thermochemistry

- Two types of chemical reactions:
  - Exothermic
  - Endothermic

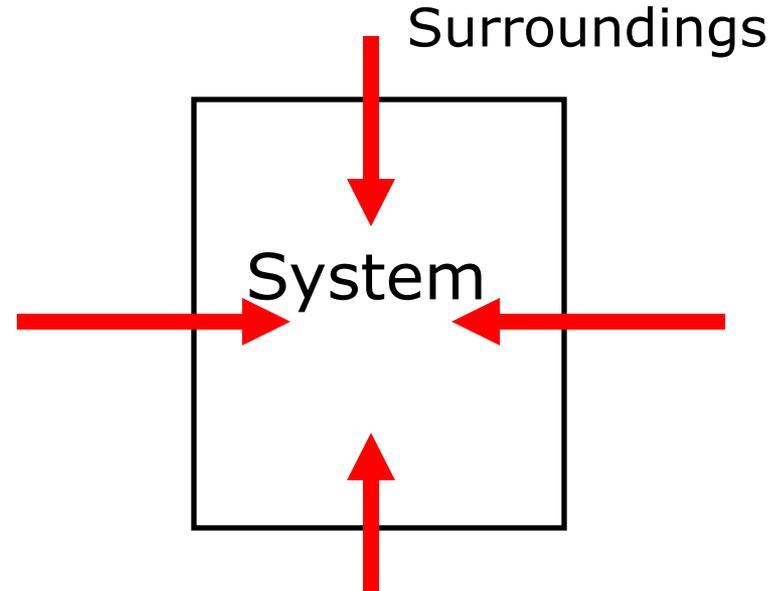
# Types of Chemical Reactions

## EXOTHERMIC



☞ Heat will be released to the surroundings until the system and surrounding are isothermally equal

## ENDOTHERMIC



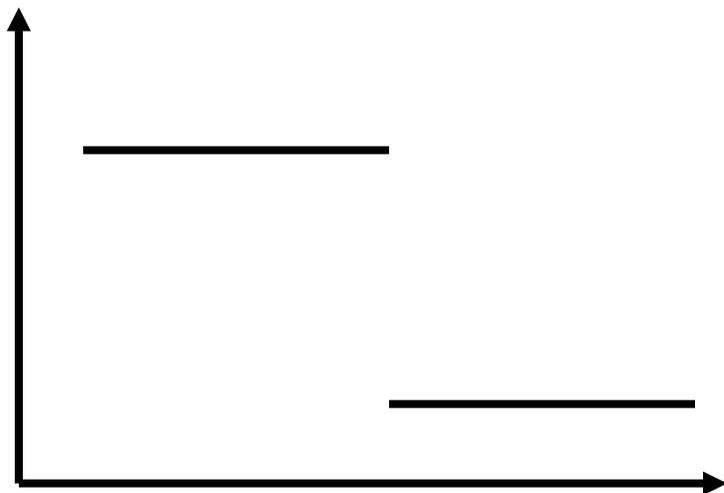
☞ Heat will be absorbed from the surroundings until the system and surrounding are isothermally equal

# Types of Reactions

| <b>EXO</b> thermic Reaction   | <b>ENDO</b> thermic Reaction  |
|---|---|
| A reaction whereby heat energy is <b><u>released</u></b> to the surroundings. | A reaction whereby heat energy is <b><u>absorbed</u></b> from the surroundings. |
| Enthalpy of products < Enthalpy of reactants                                  | Enthalpy of products > Enthalpy of reactants                                    |
| $\Delta H$ is <b><u>negative</u></b> , ( $\Delta H < 0$ )                     | $\Delta H$ is <b><u>positive</u></b> , ( $\Delta H > 0$ )                       |

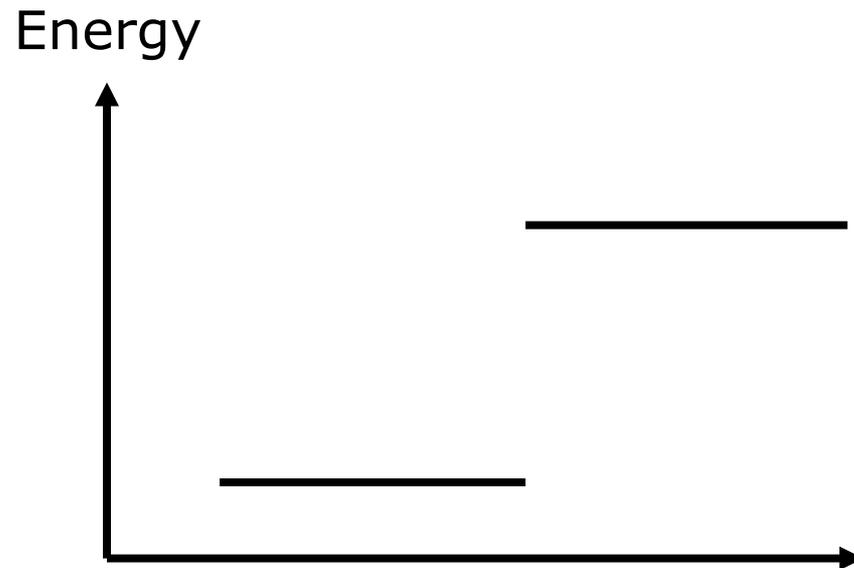
# ENTHALPY OF REACTION ( $\Delta H$ )

## EXOthermic reaction



Enthalpy of products <  
enthalpy of reactants

## ENDOthermic reaction



Enthalpy of products >  
enthalpy of reactants

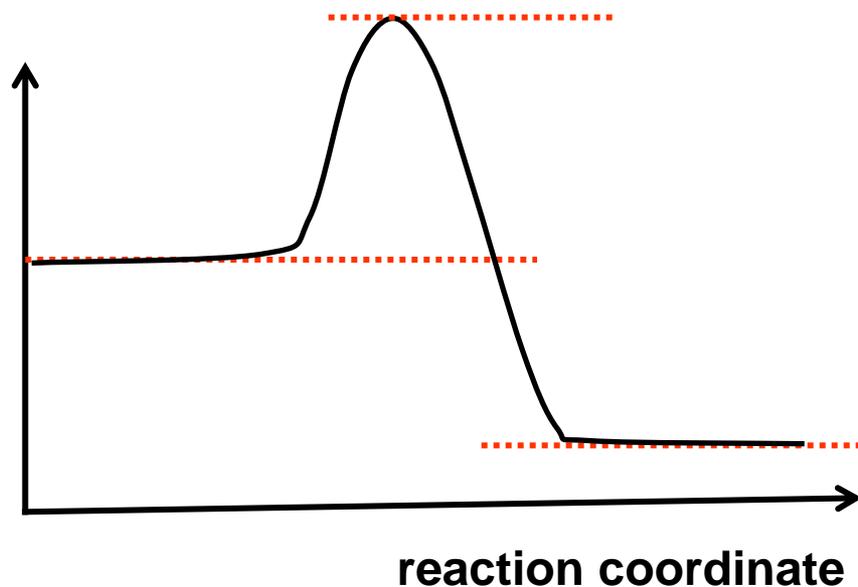
$$\Delta H = \Delta H_{\text{product}} - \Delta H_{\text{reactant}}$$

## ENERGY LEVEL DIAGRAM

# ENTHALPY OF REACTION ( $\Delta H$ )

Enthalpy of reaction,  $\Delta H$  ... is the **difference** in enthalpy between the products and the reactants.

$$\Delta H = H(\text{products}) - H(\text{reactants})$$



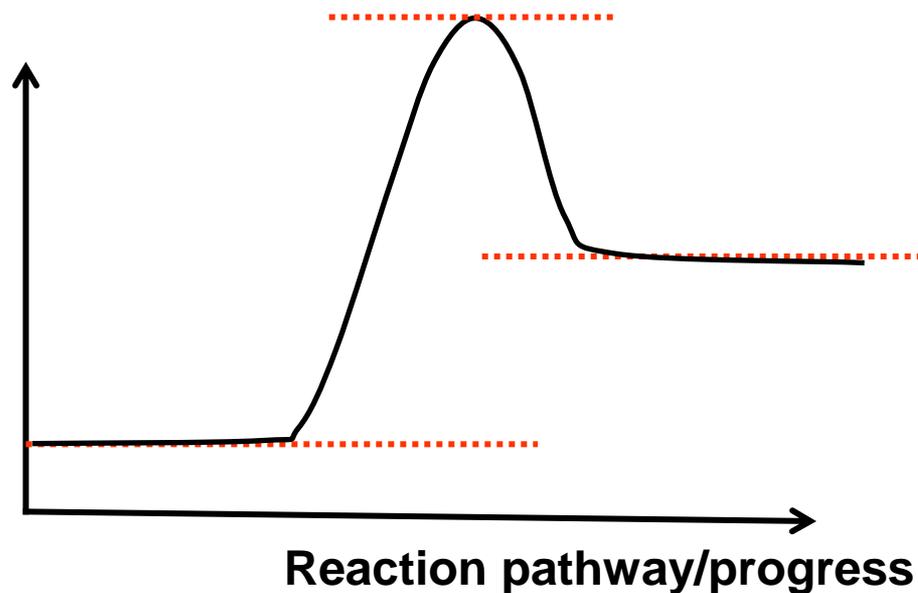
- $H_{\text{products}} < H_{\text{Reactants}}$
- $\Delta H = \text{-ve}$
- Heat is **released** by the system to its surroundings.
- Thermochemical equation:  
 $R(g) \rightarrow P(g) \quad \Delta H = \text{-ve}$

**ENERGY PROFILE DIAGRAM**

# ENTHALPY OF REACTION ( $\Delta H$ )

Enthalpy of reaction,  $\Delta H$  ... the **difference** in enthalpy between the products and the reactants.

$$\Delta H = H (\text{products}) - H (\text{reactants})$$



- $H_{\text{products}} > H_{\text{Reactants}}$
- $\Delta H = +ve$
- Heat is **absorbed** by the system from its surroundings.
- Thermochemical equation:  
 $R(g) \rightarrow P(g) \quad \Delta H = +ve$

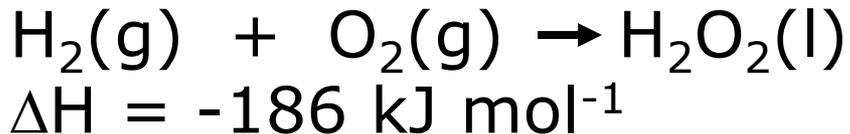
**ENERGY PROFILE DIAGRAM**

## EXOthermic

Weaker bonds are broken while stronger bonds are made

Hence, the energy released is more than the energy absorbed

### Example:

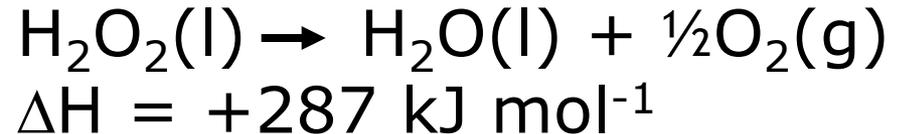


## ENDOthermic

Stronger bonds are broken while weaker bonds are made

Hence, the energy absorbed is more than the energy released

### Example:



# Example 1

Draw the energy level diagram diagram for the reaction:



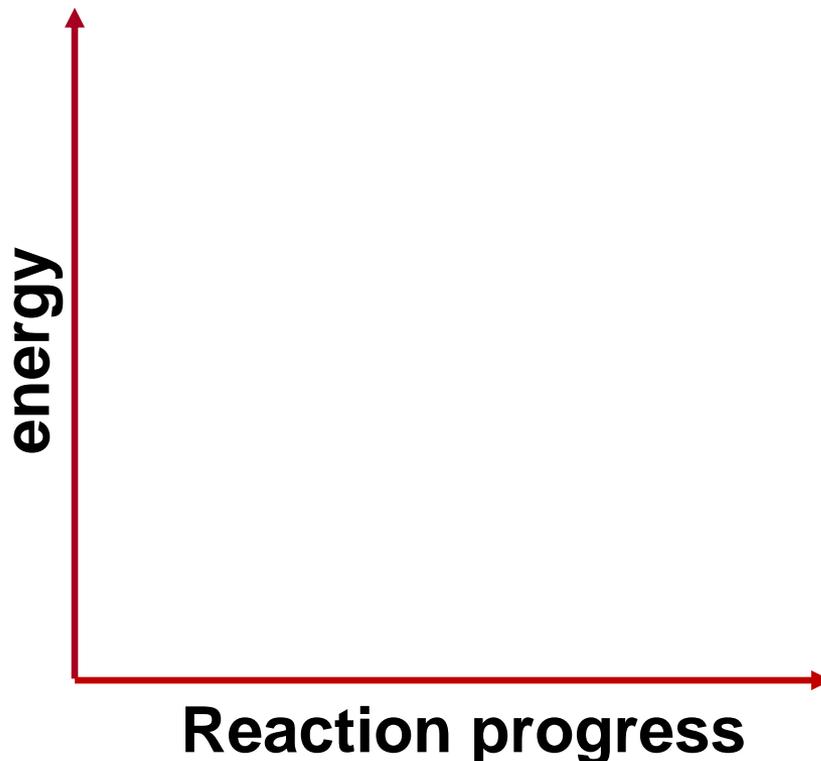
**Solution:**



# Example 2

Draw the energy level diagram for the reaction:  
 $\text{CH}_3\text{COOH}(l) \rightarrow \text{CH}_3\text{COOH}(g)$

**Solution:**



# ENTHALPY, H

- Enthalpy, H refers to the total value of energy of a system at constant pressure.
- Enthalpy cannot be determined directly.
- Only the difference in enthalpy,  $\Delta H$ , or the enthalpy change between products and reactants can be determined.

# STANDARD ENTHALPY, $\Delta H^\circ$

... enthalpy change of a reaction occurs  
at **standard conditions/states:**

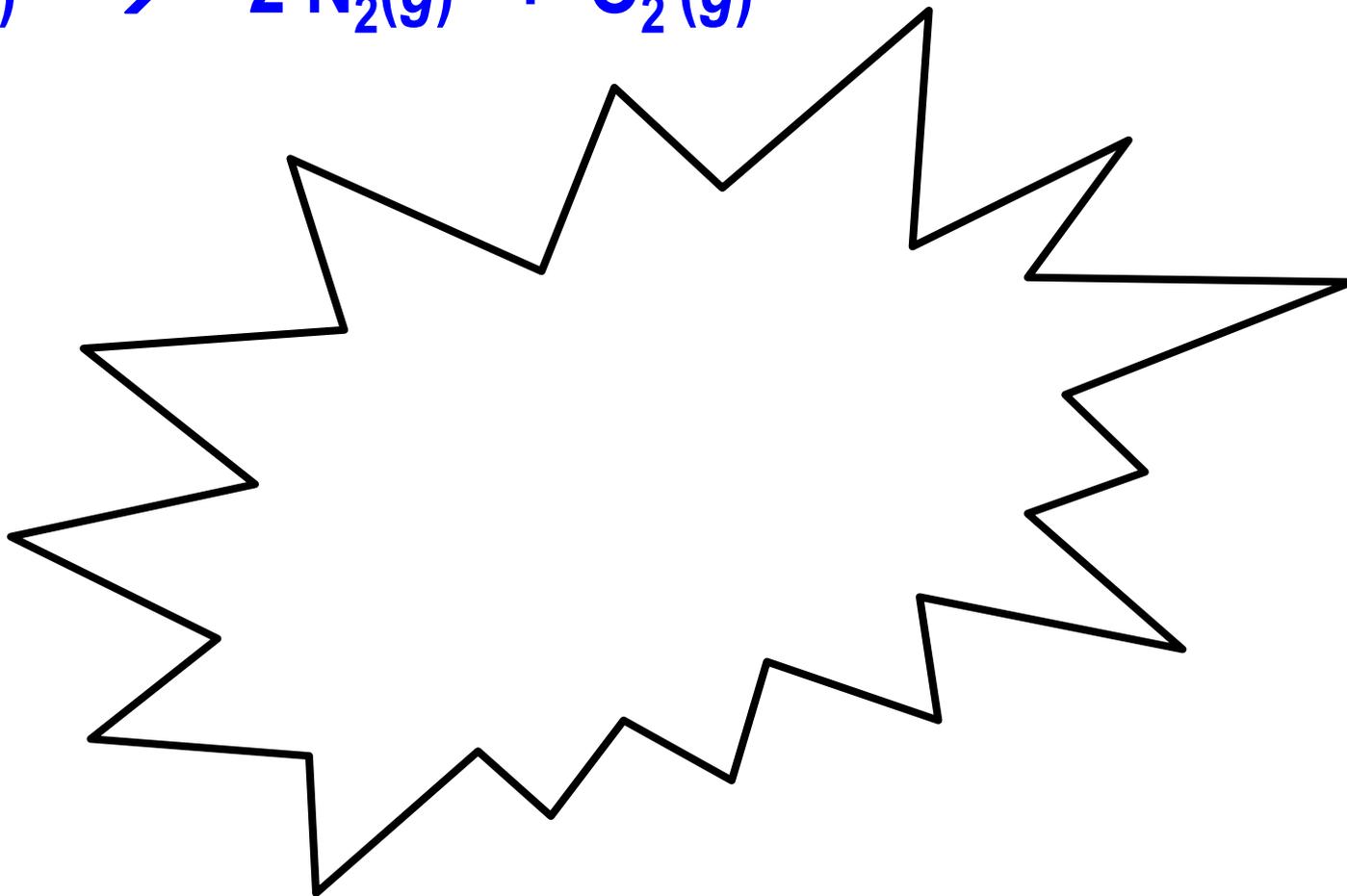
a) temperature: **25°C** or **298 K**

b) pressure: **1 atm**

c) most stable allotropes:

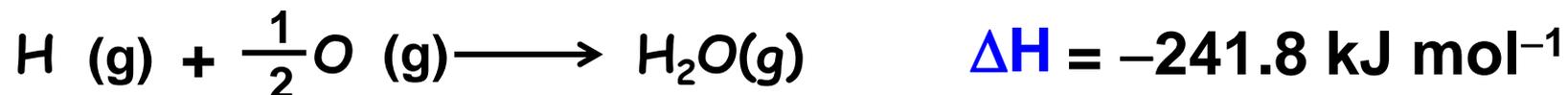
**C (graphite) ; S (rhombic)**

# CHEMICAL EQUATION VS THERMOCHEMICAL EQUATION



# THERMOCHEMICAL EQUATION

- The physical states of all reactants and products as well as enthalpy changes must be specified in thermochemical equations.



- If you flip the equation, the magnitude of  $\Delta H$  remains the same but flip its sign (**Lavoisier-Laplace's law**)





# THERMOCHEMICAL EQUATION

- Thermochemical equation shows the enthalpy change as well as the mass or mole relationships.



Enthalpy change is **directly proportional** to the amounts of substances in a system.

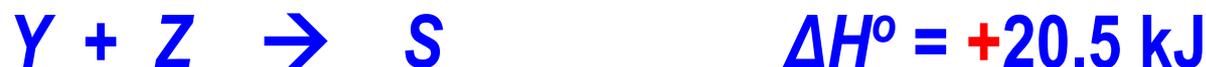
Example:

\_\_\_\_\_ of heat **released** when **2** moles of  $\text{N}_2\text{O}$  decomposed

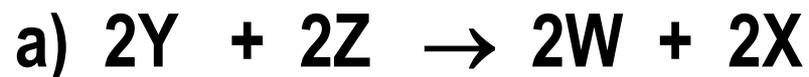
\_\_\_\_\_ of heat **released** when **1** mole of  $\text{N}_2\text{O}$  decomposed

# Have A GO

■ From the data given,



Calculate the enthalpy change for each of the reaction below:



# Have A GO

- Consider the following reaction:



- Calculate the mass of  $\text{N}_2$  produced if **10 kJ** of heat is released.
- Determine the enthalpy change when **2.2 g**  $\text{N}_2\text{O}$  reacted.

# SUMMARY

- **Enthalpy change** = enthalpy products – enthalpy reactants
- Standard conditions: **25°C and 1 atm**
- Characteristics:
  - a) **flip** the equation, **change** the sign of  $\Delta H$
  - b) multiply the **equation** and  **$\Delta H$**  with the same factor

# 8.1 Concept of enthalpy

## Objectives:

- ❑ Define the enthalpies of formation, combustion, sublimation, neutralisation, hydration, solution, atomisation, electron affinity, ionisation energy and lattice energy.
- ❑ Specify and explain the factors that influence the value of lattice energy and hydration energy.



# ENTHALPY



**a) Standard Enthalpy of Formation,  $\Delta H_f^\circ$**

**b) Standard Enthalpy of Combustion,  $\Delta H_c^\circ$**

**c) Standard Enthalpy of Neutralisation,  $\Delta H_n^\circ$**

**d) Standard Enthalpy of Atomisation of an Element,  $\Delta H_a^\circ$**

**e) Standard Enthalpy of Atomisation of a Compound,  $\Delta H_a^\circ$**

**f) Standard Enthalpy of Solution,  $\Delta H_{\text{soln}}^\circ$**

**g) Standard enthalpy of Hydration,  $\Delta H_{\text{hyd}}^\circ$**

**h) Standard Enthalpy of Sublimation,  $\Delta H_{\text{subl}}^\circ$**

**i) Lattice Energy,  $\Delta H_{LE}$**

**j) Ionisation Energy, IE**

**k) Electron Affinity,  $E_A$**

# a) Standard Enthalpy of Formation, $\Delta H_f^\circ$

- Elements in most stable form at standard states

**metals:** monatomic solid, Na(s), Mg(s)... exception Hg(l)

**Diatomic elements:** Hydrogen, oxygen, and nitrogen are H<sub>2</sub>(g); O<sub>2</sub>(g); N<sub>2</sub>(g); F<sub>2</sub>(g); Cl<sub>2</sub>(g); Br<sub>2</sub>(l); I<sub>2</sub>(s)

**Allotropes:** C(graphite); P<sub>4</sub>(white); S(rhombic)

- More **negative**  $\Delta H_f^\circ$ , more **stable** the compound
- The standard enthalpy of formation of any element in its most stable form is **zero**. Why???

$$\Delta H_f^\circ (\text{O}_2) = 0$$

$$\Delta H_f^\circ (\text{C, graphite}) = 0$$

$$\Delta H_f^\circ (\text{O}_3) = +142 \text{ kJ/mol}$$

$$\Delta H_f^\circ (\text{C, diamond}) = +1.92 \text{ kJ/mol}$$