General Chemistry

Thermochemistry I

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Chapter Description

- Expected Outcome:

  At the end of the lecture, the students should be able to understand and solve the problems regarding on the heat, enthalpy, exothermic and endothermic.

- References:

  1) Stephen B. Barone. Introduction to general chemistry. Blackwell Science.
  2) James E. Bradry General Chemistry: Principles & Structure. John Wiley.

Contents

- System and surrounding
- Heat
- Enthalphy and Enthalphy Change
- Exothermic and Endothermic
- Standard Enthalphy Change
- Standard Formation Enthalphy
- Standard Fusion Enthalphy

CONCEPT OF ENTHALPY

Energy

- The ability to do work

- Units of energy
  - **SI Unit: Joule (J)**

    $1\ J = 1\ kgm^2s^{-2}$

  - **Older unit: calorie (cal)**

    $1\ cal = 4.184\ J$

Exothermic reaction

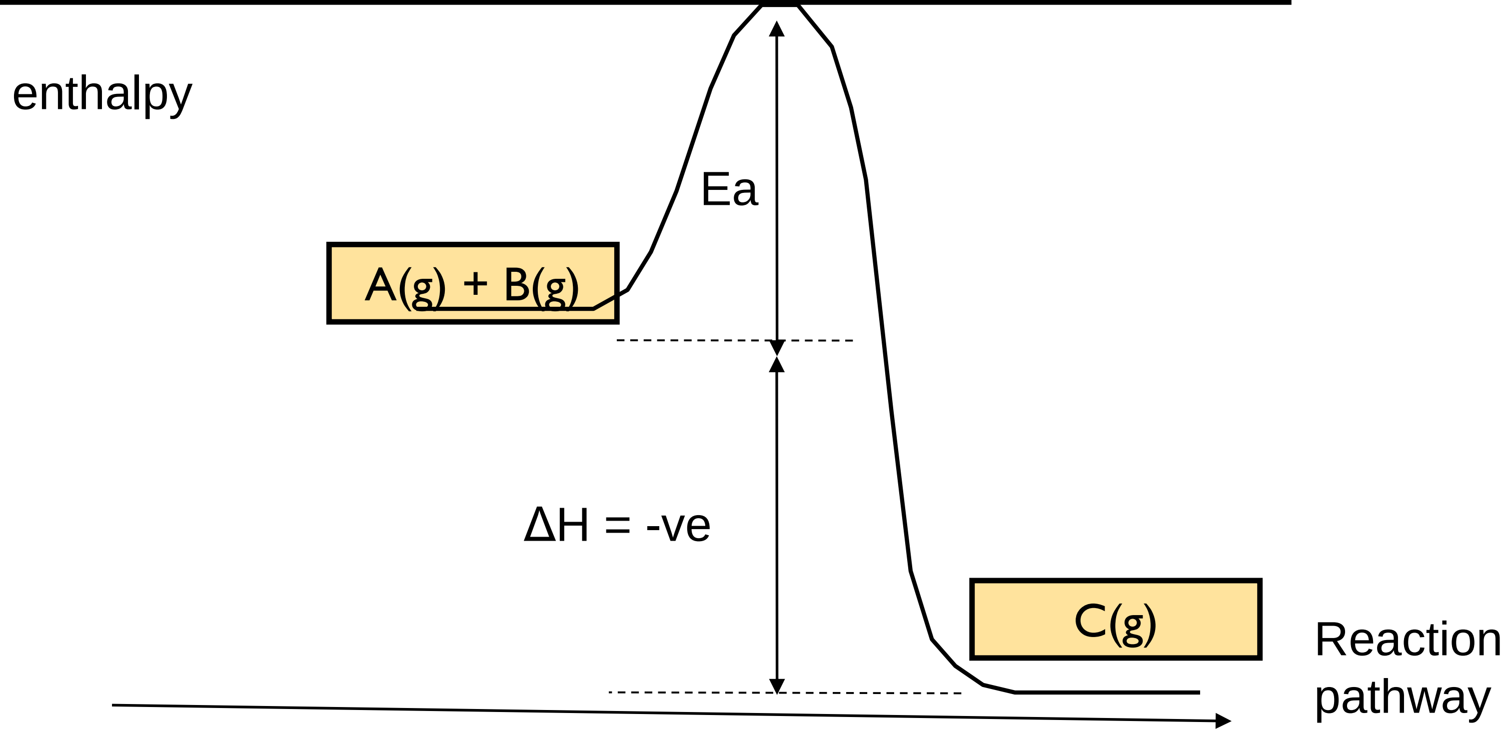
- **ΔH is (-ve)**
- Enthalpy of products **<** Enthalpy of reactants
- **Heat** is **released** from the system to the surroundings.
- E.g: combustion, neutralization etc.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + \text{heat}$$

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

Energy profile diagram for exothermic reaction

A (g) + B (g) → C (g) ΔH = –ve
(reactants) (product)



Endothermic reaction

- **ΔH is (+ve)**
- Enthalpy of products **>** enthalpy of reactants
- **Heat** is **absorbed** by the system from the surrounding
- E.g: ice melting

$$\text{Heat} + H_2O(s) \longrightarrow H_2O(l)$$

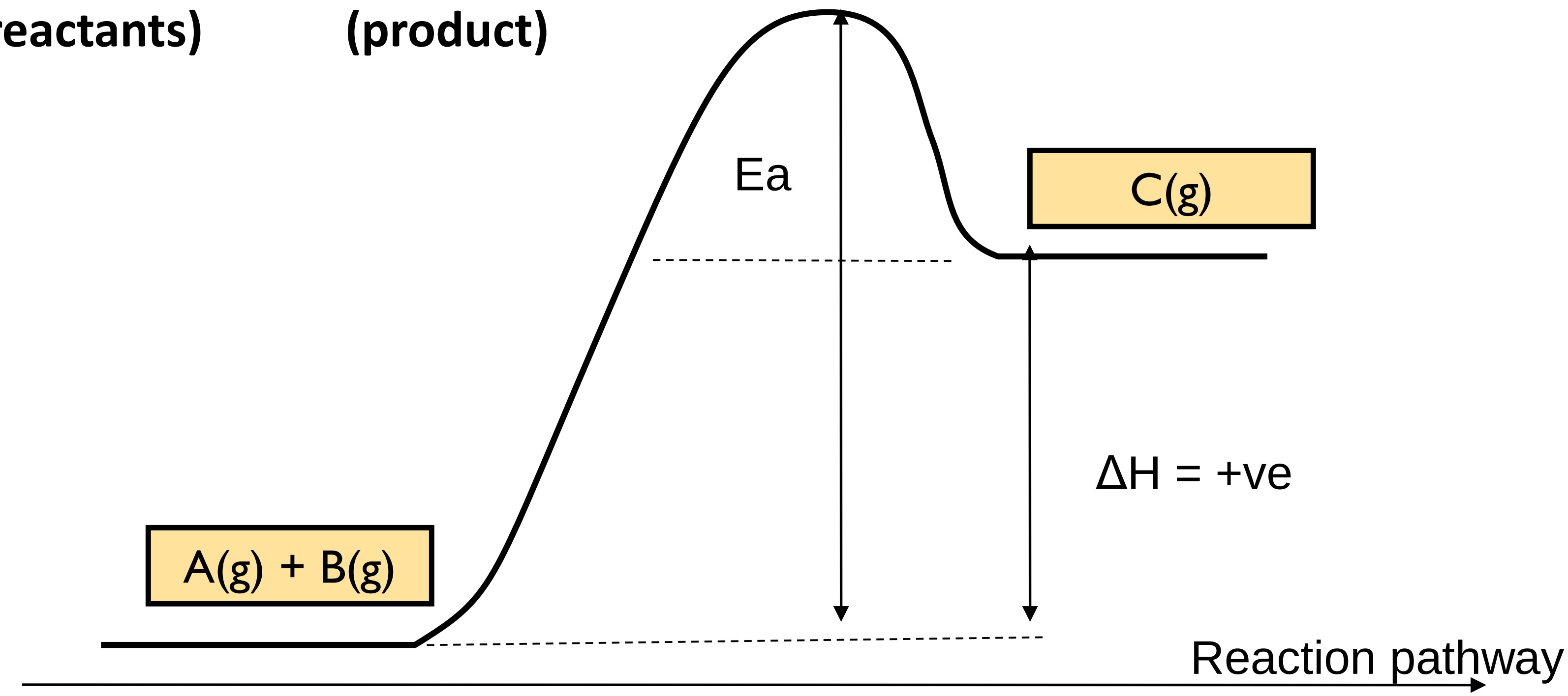
$$\text{heat} + H_2O(l) \rightarrow H_2O(g)$$

Enthalpy

Consider the following reaction:-

A (g) + B (g) → C (g) **ΔH = +ve**

(reactants) **(product)**

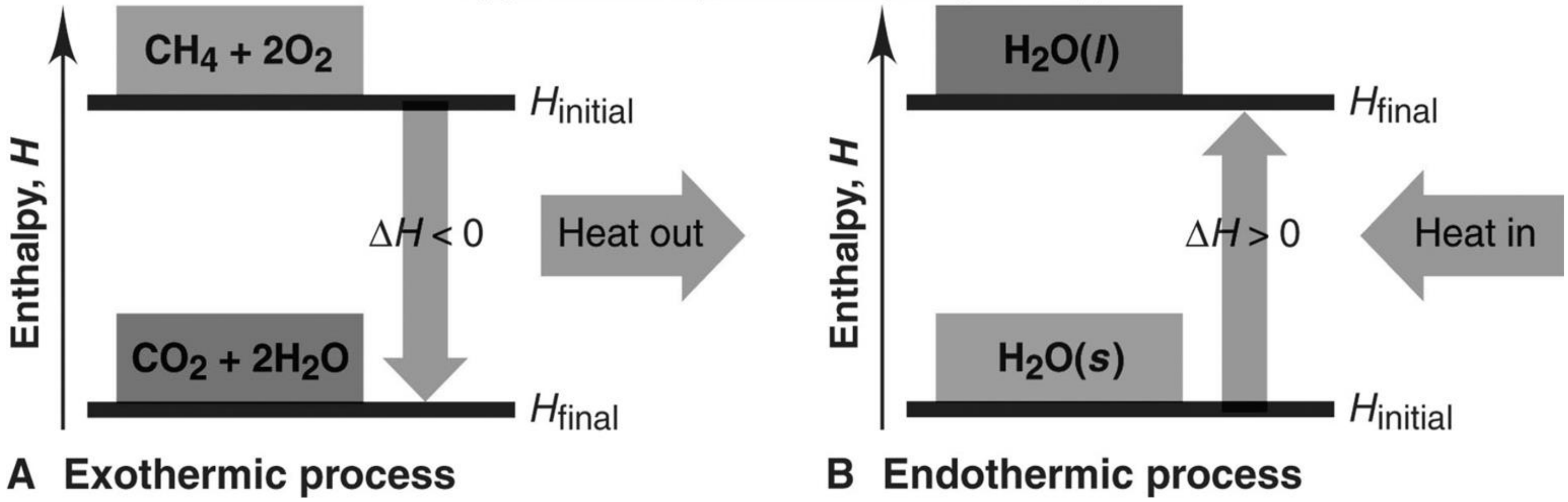


Enthalphy

- The heat content or total energy in the system
- Commonly measured through heat change.
- Examples: system undergoes combustion or ionization.

Enthalphy Change

- **Heat given off or absorbed during a reaction at constant pressure**



- $H_{products} < H_{reactants}$
- $H_{products} > H_{reactants}$

Enthalphy of reaction and standard condition

- **Enthalpy of reaction:**
  - The enthalpy change associated with a chemical reaction.

    ($\Delta H_{reaction} = \Sigma \Delta H_f \text{ product} - \Sigma \Delta H_f \text{ reactant}$)
- **Standard enthalpy, ΔH°**
  - The enthalpy change for a particular reaction that occurs at 298K and 1 atm (standard state)

Types of Enthalpies

~ Enthalpy of formation

~ Enthalpy of combustion

~ Enthalpy of atomisation

~ Enthalpy neutralisation

~ Enthalpy hydration

~ Enthalpy solution (dissolution)

Enthalphy formation

- The heat changed when 1 mole of a compound is formed from its elements in their most stable state.

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2(g)} \rightarrow H_2O_{\,(l)} \qquad \Delta H_f = -286\ \text{kJ}$$

$$K(s) + \tfrac{1}{2}\,Br_2(l) \rightarrow KBr(s) \qquad \Delta H = \Delta H_f$$

- The standard enthalpy of formation of any element in its most stable state form is zero.

E.g. :-

$$\Delta H_{\,f}(O_{2\,(g)}) = 0$$

$$\Delta H_{\,f}\,(Cl_{2\,(g)}) = 0$$

Enthalphy combustion

The heat released when 1 mole of substance is burned completely in excess oxygen.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H = \Delta H_{comb}$$

$$C_4H_{10}(l) + 13/2\ O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \qquad \Delta H = \Delta H_{comb}$$

Enthalphy automization

- The heat absorbed when 1 mole of gaseous atoms is formed from its element
- ΔH_a is always positive because it involves only breaking of bonds
- E.g:-

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad \Delta H_a = +109 \text{ kJ}$$

$$\tfrac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad \Delta H_a = +123 \text{ kJ}$$

Neutralization enthalphy

- The heat released when 1 mole of water, H_2O is formed from the neutralization of acid and base.

- E.g:-

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} \quad \Delta H_n = -58\ kJ$$

Hydration enthalphy

- The heat released when 1 mole of gaseous ions is hydrated in water.

- E.g:-

$Na^+_{(g)} \longrightarrow Na^+_{(aq)}$ $\Delta H_{hyd} = -406\ kJ$

$Cl^-_{(g)} \longrightarrow Cl^-_{(aq)}$ $\Delta H_{hyd} = -363\ kJ$

Solution enthalphy

- The heat **changed** when 1 mole of a **substance** is dissolves in water.

- **E.g:**

$$\mathbf{KCl_{(s)} \longrightarrow K^{+}_{(aq)} + Cl^{-}_{(aq)} \qquad \Delta H_{soln} = +690\ kJ}$$

ΔH^{o}_{rxn} or ΔH^{o}

- Standard enthalpy of reaction
- The enthalpy change of a reaction carried out at standard states (1 atm, 25°C)

ΔH^{o} — standard states

Thermochemical equation

- Shows the enthalpy changes.

E.g : $H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H = +6.01$ kJ

- 1 mole of **$H_2O_{(l)}$** is formed from 1 mole of **$H_2O_{(s)}$** at 0°C, ΔH is +6.01 kJ

- However, when 1 mole of **$H_2O_{(s)}$** is formed from 1 mole of **$H_2O_{(l)}$**, the **magnitude** of **ΔH remains** the same but with the **opposite sign** of it.

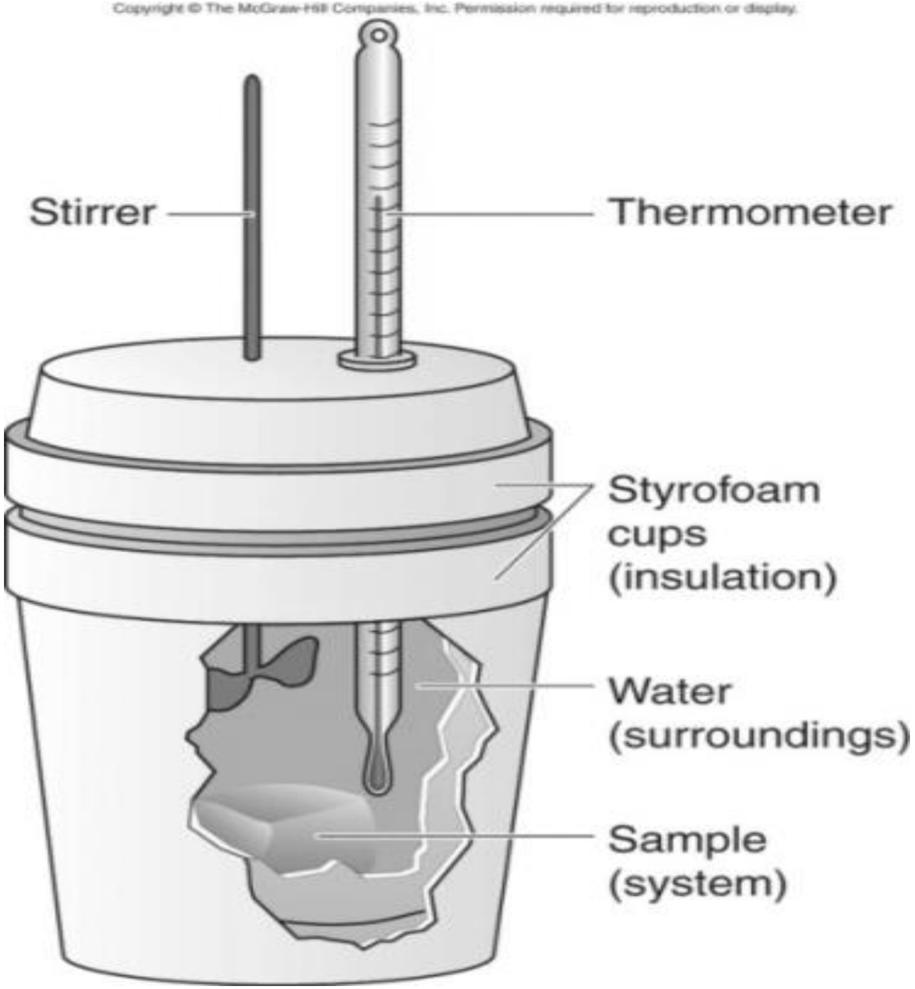
$$H_2O_{(l)} \rightarrow H_2O_{(s)} \qquad \Delta H = -6.01 \text{ kJ}$$

CALORIMETRY

- Examples of calorimeter
  - Simple calorimeter
  - Bomb calorimeter

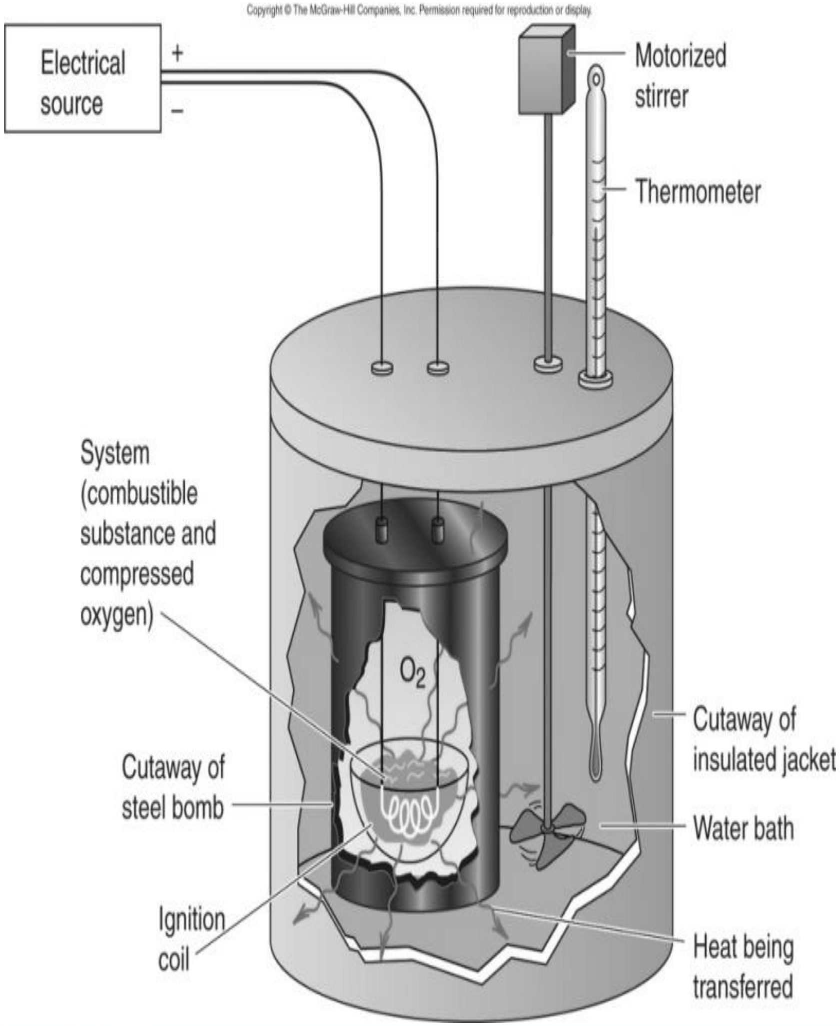
- A method used in the laboratory to measure the heat change of a reaction.
- Apparatus used is known as the calorimeter

Constant–pressure calorimeter



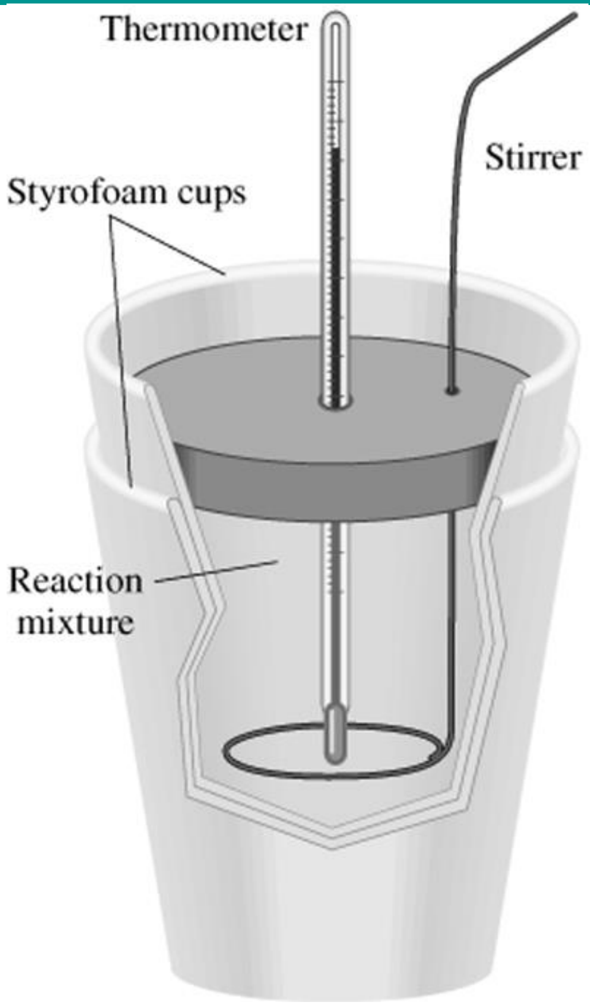
- **constant–pressure calorimeter (simple calorimeter)**

Bomb calorimeter



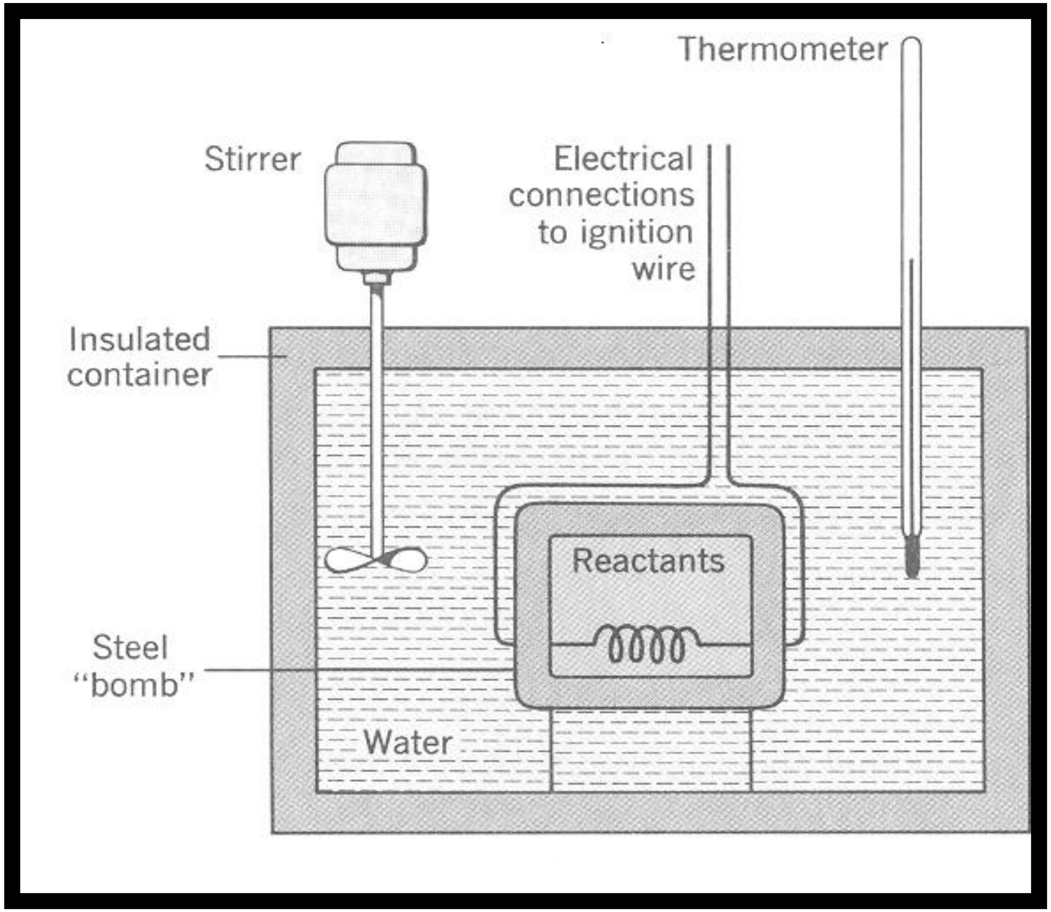
- constant–volume calorimeter (bomb calorimeter)

Constant–Pressure Calorimeter



- The outer Styrofoam cup insulate the reaction mixture from the surroundings (it is assumed that **no heat is lost** to the surroundings)
- **Heat release** by the reaction is **absorbed by solution and the calorimeter**

Constant–Volume Calorimeter



- **Specific heat capacity, c**

Is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius **($Jg^{-1}°C^{-1}$)**.

- **Heat capacity, C**

Is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius **($J°C^{-1}$)**

Basic principle in calorimeter

Heat released by a reaction	=	Heat absorbed by surroundings (calorimeter+water)

- **Surroundings may refer to the:**
  i. Calorimeter itself or;
  ii. The water and calorimeter

$q_{reaction} = m_w c_w \Delta T$ or $C_c \Delta T$

Heat released by reaction = Heat absorbed by calorimeter+water

$$q = C_c\Delta T + m_w c_w \Delta T$$

q = heat released by reaction

m_w= mass of water

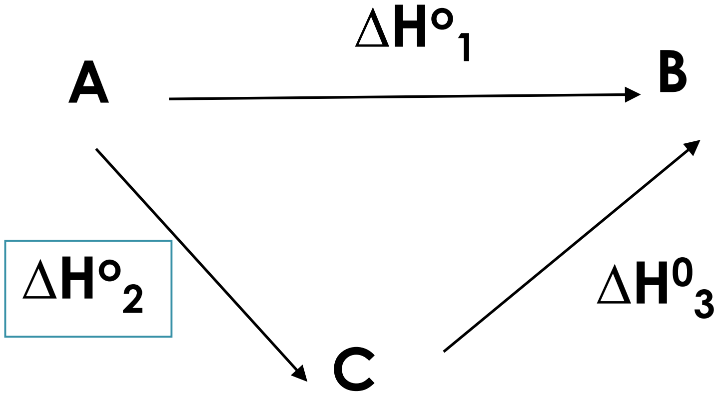
C_w= specific heat capacity for water

C_c = heat capacity for calorimeter

ΔT = temperature change

Hess's law

- Hess's Law states that when reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in the series of steps.
- The enthalpy change depends only on the initial and final states of the reactants and products but is independent of the path taken.



$$\Delta H^\circ_1 = \Delta H^\circ_2 + \Delta H^\circ_3$$

Hess's law- using 2 methods

Algebraic method

Energy cycle method

Algebraic method

QUESTION :

Given the following enthalpies of reaction,

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393\ kJ$

$H_{2(g)} + 1/2O_2 \longrightarrow H_2O_{(g)}$ $\Delta H = -286\ kJ$

$C_2H_{6(g)} + 7/2O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$ $\Delta H = -1560 kJ$

Calculate the enthalpy formation for , $C_2H_{6(g)}$

Step 1

List all the thermochemical equations involved

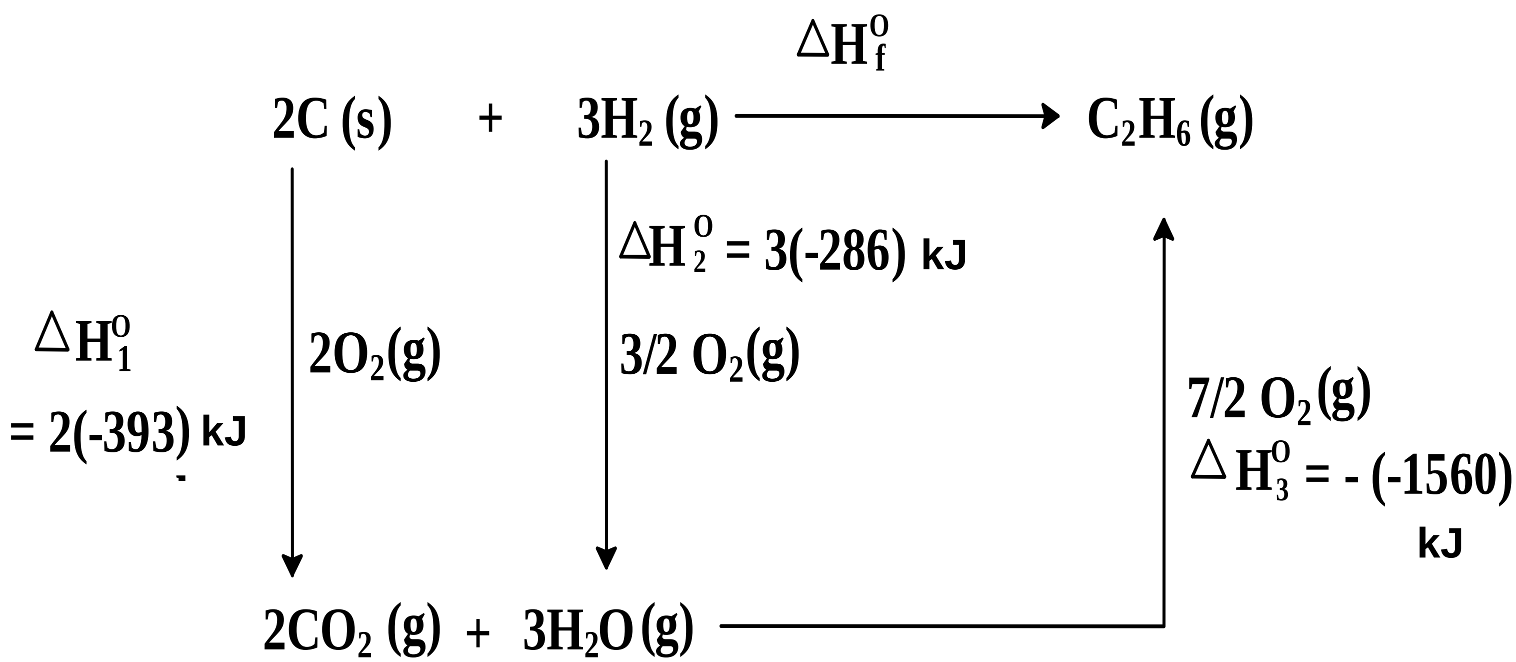
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393\ kJ$$

$$H_{2(g)} + 1/2O_2 \longrightarrow H_2O_{(g)} \qquad \Delta H = -286\ kJ$$

$$C_2H_{6(g)} + 7/2O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)} \qquad \Delta H = -1560 kJ$$

Energy Cycle Method

Draw the energy cycle and apply Hess's Law to calculate the unknown value.



Enthalpy Formation

$$\Delta H^o_f = 2(\Delta H^o_1) + 3(\Delta H^o_2) + \Delta H^o_3$$

$= -786-858+1560$

$= -84$ kJmol^{-1}

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Author Information

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