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BSK1133 PHYSICAL CHEMISTRY

CHAPTER 5 THERMODYNAMICS (PART A)

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Aims

➢ To understand the First Law of Thermodynamics.

➢ To study the heat capacity, molar heat capacity and specific heat in a chemical reaction.

➢ To learn the principles of calorimetry.

➢ To calculate the enthalpy of reaction based on Hess's Law.

Description

Expected Outcomes

- ❖ Able to describe the First Law of Thermodynamics
- ❖ Able to determine the heat and temperature changes
- ❖ Able to calculate heat or enthalpy from calorimeter data
- ❖ Able to calculate reaction enthalpies by apply Hess's Law

References

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- ✓ Silbey, R. J., Alberty, A. A., & Bawendi, M. G. (2005). Physical Chemistry. New York: John Wiley & Sons.
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Introduction

✓ Most chemical reactions either gain or lost heat energy.
✓ Heat: transferring of thermal energy between two substances with different temperatures.

Thermodynamics:

➢ motion and/or transformation from heat energy into other forms.
➢ a study of the relationship between work and heat or other energy.

Thermochemistry:

➢ a study of the interconversion between heat and other forms of energy in chemical reactions.
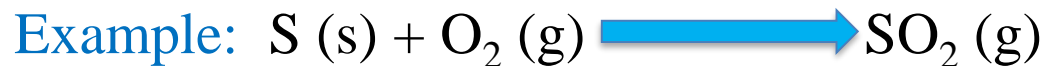
5.1 First Law of Thermodynamics

First Law of Thermodynamics

No creation or destroy of energy, but transformation is allowed. No change of total amount of energy.
Energy is conserved in any process.

❖ **Internal Energy, U** – total energy content (kinetic energy and potential energy) of a system.

$$\Delta U = U_f - U_i$$

- can be changed by doing work **on/by** the system
- can be changed by **absorb/release** heat.

Example: $S\ (s) + O_2\ (g) \longrightarrow SO_2\ (g)$

Release heat as some of the chemical energy in molecules has been converted to thermal energy (from system to surrounding)

Initial state (reactant), U_i : S and O_2
Final state (product), U_f : SO_2

ΔU = energy of 1 mol SO_2 – energy of [1 mol S + 1 mol O_2]

$\Delta U < 0$ cause energy of product < reactants

WORK AND HEAT

✓ The <u>temperature</u> of a system can be raised either by heating it, by doing work on it or a combination of the two.

➤ Heat absorbed from the surrounding (endothermic) = +q
➤ Heat evolved to the surrounding (exothermic) = -q
➤ Work has been done on the system = +w
➤ Work has been done by the system = -w

✓ **Increase of the internal energy**: heat is gained by the system or work is done on the system.

✓ **Decrease of the internal energy:** heat is lost from the system or work is done by the system.

5.2 The Nature and Types of Energy

Law of Conservation of Energy
the total amount of energy in the universe is remained constant

- ✓ Energy is a measurable ability to do work and the amount can be determined (Unit: Joules (J).

- ✓ All living or non-living things need energy.

- ✓ All form of energy can be converted to another form.

- ✓ Example: When fuel is burned, it is converted from chemical energy into heat energy and light energy.

5.3 Enthalpy of Chemical Reactions
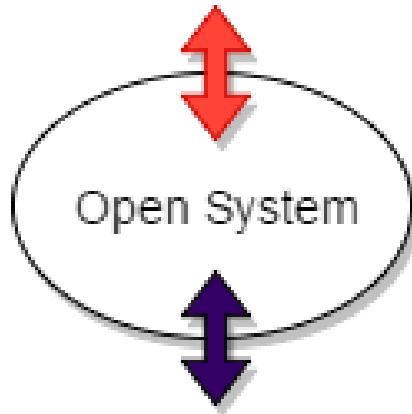
a. Energy Changes in Chemical Reactions

➢ A **system** is a place where the **substances (energy and/or matter)** that are **separated from its surroundings by boundaries**.

➢ A **boundary** is a wall that **allow energy and/or mass may enter or leave the system**.

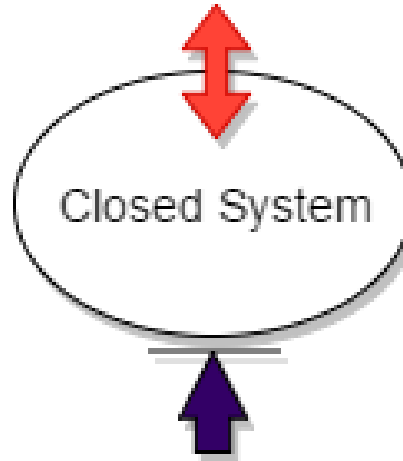➢ **Surroundings** are the **area that out of the system**.

Boundary

System

Surroundings
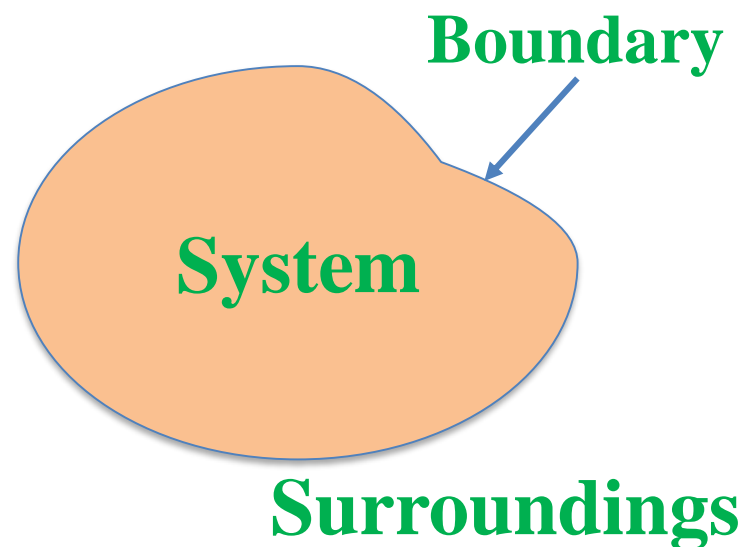
Three types of system:

Open system Mass and energy exchange	Close system Energy exchange only	Isolated system Not applicable

Open System

Closed System

Isolated System
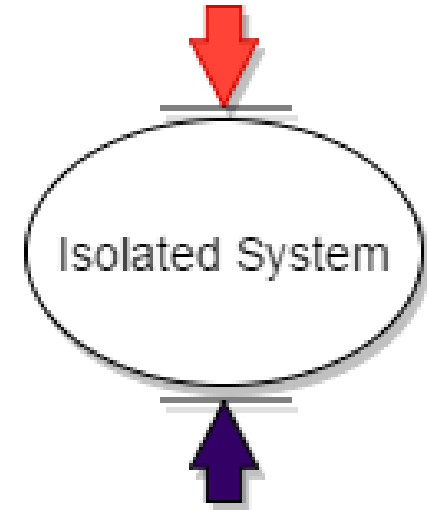
■ Exchange of energy

■ Exchange of matter

Examples:

i. Exothermic – heat given off to the surroundings

Combustion reaction:

$$2H_2 (g) + O_2 (g) \longrightarrow 2H_2O (l) + energy$$

System: reacting mixture (H_2, O_2 and water molecules)

Surroundings: the rest of the universe

Heat that generated from this combustion process is transferred to the surroundings.

ii. Endothermic – heat absorbs from the surroundings

Decomposition reaction:

$$2HgO (s) + energy \longrightarrow 2Hg (l) + O_2 (g)$$

System: reacting mixture (HgO, Hg and O_2)

Surroundings: everything external of system and boundary

Heat is absorbed by the system (that is, to HgO) from the surroundings.

b. Enthalpy of Reactions

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

where H = enthalpy   Unit: J or J/mol

(thermodynamic function)

Since U, P, V are state function, the changes in (U + PV) depends on the initial and final states, hence, ΔH is state function.

If constant pressure,

$$\Delta H = \Delta U + P\Delta V$$ **SIMILAR** ⟶ $\boxed{q_p = \Delta U + P\Delta V}$

NOTES:
i.   constant-volume condition: $\Delta U = q_v$
ii.   constant-pressure condition: $\Delta H = q_p$

i) CONSTANT VOLUME (impossible to achieve)

When a chemical reaction is conducted at constant volume, $\Delta V = 0$, hence $P\Delta V = 0$. (It is impossible.)

$$\Delta U = q - P\Delta V = q_v \qquad \text{Subscript v = constant-volume process}$$

ii) CONSTANT PRESSURE

Most reactions happen at atmospheric pressure

o net increase gas molecules: system does work on the surrounding (expansion)

o net decrease gas molecules: work has been done on the system by the surroundings (compression)

o no net change in gas molecules: no work is done

$$\Delta U = q_p - P\Delta V \qquad \text{Subscript p = constant-pressure process}$$
$$q_p = \Delta U + P\Delta V$$

Generally, almost all reactions are run at constant-pressure processes (or atmospheric pressure), thus, heat change causes the change in enthalpy (ΔH).

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

o $\Delta H > 0$, endothermic process: heat gained by the system from the surroundings

$$H_2O \text{ (s)} \longrightarrow H_2O \text{ (l)} \qquad \Delta H_f^\circ = 6.01 \text{ kJ/mol}$$

o $\Delta H < 0$, exothermic process: heat released by the system to the surroundings

$$CH_4 \text{ (g)} + 2O_2 \text{ (g)} \longrightarrow CO_2 \text{ (g)} + 2H_2O \text{ (l)}$$
$$\Delta H_f^\circ = -890.4 \text{ kJ/mol}$$

c. Standard Enthalpy of Formation and Reactions

❖ **Standard enthalpy of formation, ΔH_f°**

✓ enthalpy of formation of a substance carried out in the standard state at 1 atm

✓ heat change occur as a result of 1 mole of the substance is formed at 1 atm.

   o   Standard enthalpy of formation of any element is zero when it is in most stable form.

   o   **Most of the thermodynamic data is collected at 1 atm and 25 °C.**

ΔH_f° (O_2)= 0 (stable) ΔH_f° (O_3) = 142.2 kJ/mol

ΔH_f° (C, graphite)= 0 (stable) ΔH_f° (C, diamond) = 1.90 kJ/mol

❖ **Standard enthalpy of reaction, ΔH_{rxn}°**

✓ enthalpy of a reaction is conducted at 1 atm as standard state

✓ **$\Delta H_{rxn}^\circ = \Sigma n \Delta H_f^\circ$ (products) - $\Sigma m \Delta H_f^\circ$ (reactants)**

Example: **aA + bB   ⟶   cC + dD**

$$\Delta H_{rxn}^\circ = [c\Delta H_f^\circ (C) + d\Delta H_f^\circ (D)] - [a\Delta H_f^\circ (A) + b\Delta H_f^\circ (B)]$$

i. Direct Method

➢ Measuring ΔH_f° for compounds that can be readily synthesized from their elements.

Example:

$$C \text{ (graphite)} + O_2 \text{ (g)} \longrightarrow CO_2 \text{ (g)} \quad \Delta H_{rxn}^\circ = -393.5 \text{ kJ/mol}$$

(Given: ΔH_f° (C, graphite) = 0, ΔH_f° (O$_2$, g) = 0, ΔH_f° (CO$_2$, g) = -393.5 kJ/mol)

This combustion easily goes to completion.

$$\Delta H_{rxn}^\circ = \Delta H_f^\circ \text{ (CO}_2, \text{ g)} - [\Delta H_f^\circ \text{ (C, graphite)} + \Delta H_f^\circ \text{ (O}_2, \text{ g)]}$$
$$= (-393.5 \text{ kJ/mol}) - [0 + 0]$$
$$= -393.5 \text{ kJ/mol}$$

ii. Indirect Method

➢ Not directly synthesized from their elements.
➢ Slow reaction or may produce intermediate substances.

Hess's Law: the change in enthalpy is same when products are formed, regardless a series of steps that the reaction takes place.

In this case, ΔH_{rxn}° for the overall reaction can be calculated.

RULES:

* ΔH_f° must multiplied or divided by the same factor as the reaction is multiplied or divided.
* The sign of ΔH_f° is reversed if the reaction is reversed.

Example:

The **enthalpy of a reaction** is only depend **on the final state of the products and initial state of the reactants**. If the amount of the sample changes, the enthalpy of the reaction is also changed which is proportional to the moles used in the reaction.

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \longrightarrow H_2O\ (g) \qquad \Delta H° = \text{-572 kJ}$$

i. Scale up the molar amounts results in the increment of enthalpy of the reaction.

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (g) \qquad \Delta H° = \text{-1144 kJ}$$

ii. Switched (change the sign from "negative" sign to "positive" sign

$$H_2O\ (g) \longrightarrow H_2\ (g) + \tfrac{1}{2}O_2\ (g) \qquad \Delta H° = \text{+572 kJ}$$
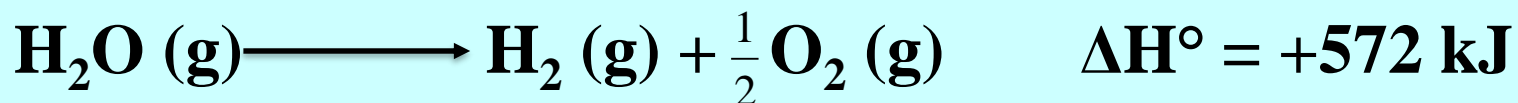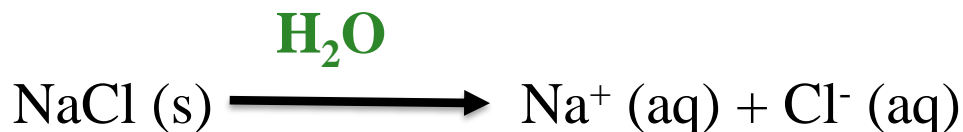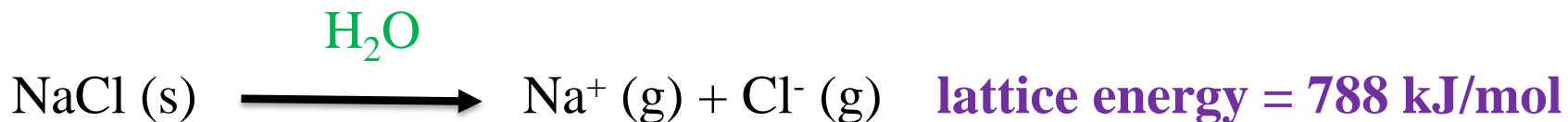
d. Heat of Solution and Heat of Dilution

Heat (Enthalpy) of Solution, ΔH°_{soln} = when a solute dissolves in a solvent, heat is gained or produced.
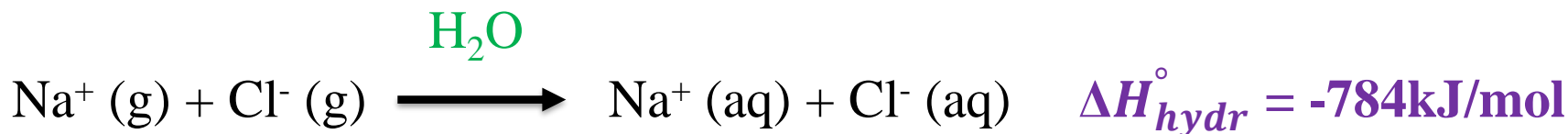
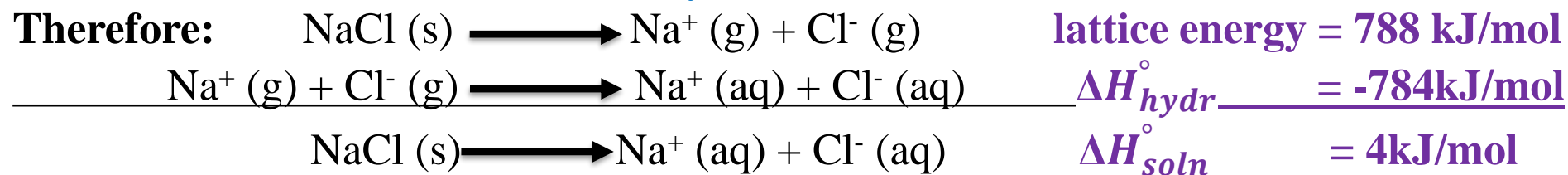**Heat of dilution** = when dilution is carried out, heat change occurred.

$$NaCl\ (s) \xrightarrow{\ H_2O\ } Na^+\ (aq) + Cl^-\ (aq)$$

i. **Lattice energy** – energy to split 1 mole of solid ionic compound into ions of gas.

$$NaCl\ (s) \xrightarrow{\ H_2O\ } Na^+\ (g) + Cl^-\ (g) \quad \textbf{lattice energy = 788 kJ/mol}$$

ii. **Heat of hydrated** – enthalpy changed associated with the hydration process

$$Na^+\ (g) + Cl^-\ (g) \xrightarrow{\ H_2O\ } Na^+\ (aq) + Cl^-\ (aq) \quad \Delta H^{\circ}_{hydr} = \textbf{-784kJ/mol}$$

iii. ΔH°_{soln} = **lattice energy** + ΔH°_{hydr}

Therefore:

$$NaCl\ (s) \longrightarrow Na^+\ (g) + Cl^-\ (g) \qquad \textbf{lattice energy = 788 kJ/mol}$$
$$\underline{Na^+\ (g) + Cl^-\ (g) \longrightarrow Na^+\ (aq) + Cl^-\ (aq) \qquad \Delta H^{\circ}_{hydr} \qquad = \textbf{-784kJ/mol}}$$
$$NaCl\ (s) \longrightarrow Na^+\ (aq) + Cl^-\ (aq) \qquad \Delta H^{\circ}_{soln} \qquad = \textbf{4kJ/mol}$$

When 1 mol NaCl dissolves in water, 4 kJ of heat will be gained.

5.4 Calorimeter

✓ The measurement of heat changes

✓ Specific heat (s) of a substance – amount of heat needed in order to elevate 1 °C of 1 gram of the substance. Unit: J/(g°C).

✓ Heat capacity (C) of a substance – amount of heat needed in order to elevate 1 °C of certain quantity of substance. Unit: J/°C.

$$C = ms \quad \text{where} \quad m = \text{mass of substances in gram}$$

✓ Heat change (q) – amount of heat that has been absorbed or released in a process with changes of temperature (Δt).

$$q = ms\Delta t$$

$$q = C\Delta t \quad \text{where } \Delta t = t_{final} - t_{initial}$$

q > 0: endothermic process   q < 0: exothermic process

i. Constant-Volume Calorimetry (ISOLATED SYSTEM)

Measurement of heat of combustion

✓ Locate sample in **constant-volume bomb calorimeter** (a steel container) which is filled with oxygen (P = 30 atm).

✓ Next, closed bomb calorimeter is put in water (record the quantity of water).

✓ Ignite the sample electrically.

✓ The increment of temperature of the water is recorded in order to calculate the heat produced.

✓ The heat released in combustion process is gained by the water and bomb calorimeter.

Assume: No heat is released to the surroundings, $q_{\text{system}} = 0$

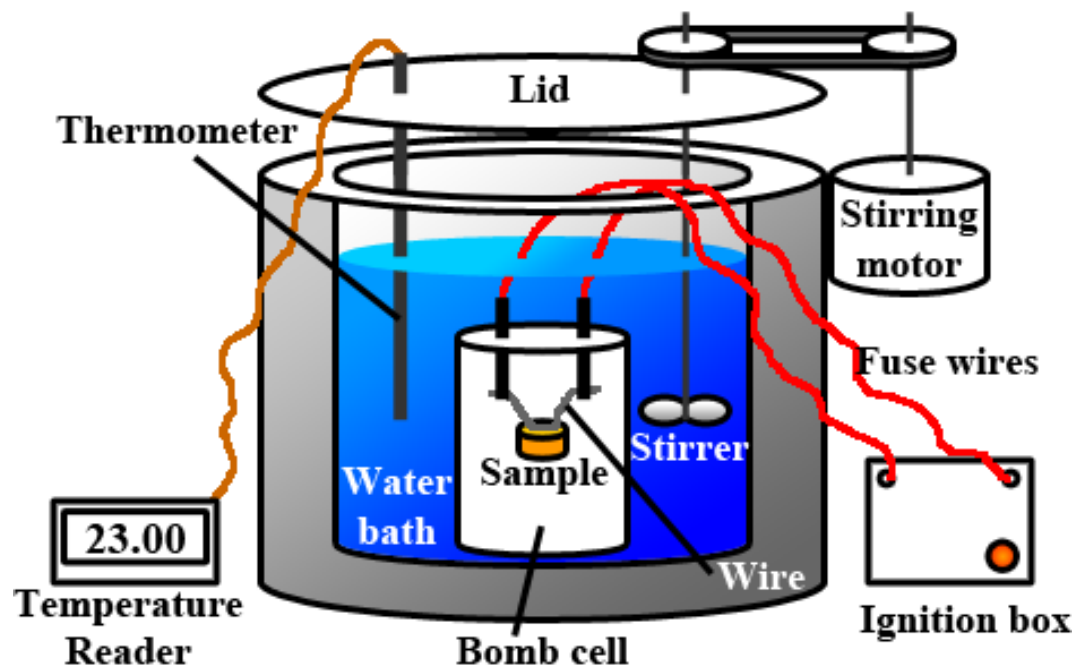$$q_{\text{system}} = q_{\text{cal}} + q_{\text{rxn}} = 0$$

Heat changes for bomb calorimeter and the reaction: $q_{\text{rxn}} = - q_{\text{cal}}$

$$q_{\text{cal}} = C_{\text{cal}}\Delta t$$

ii. Constant-Pressure Calorimetry

Determine the heat change for a non-combustion reaction (heat of neutralization, heat of solution and heat of dilution).
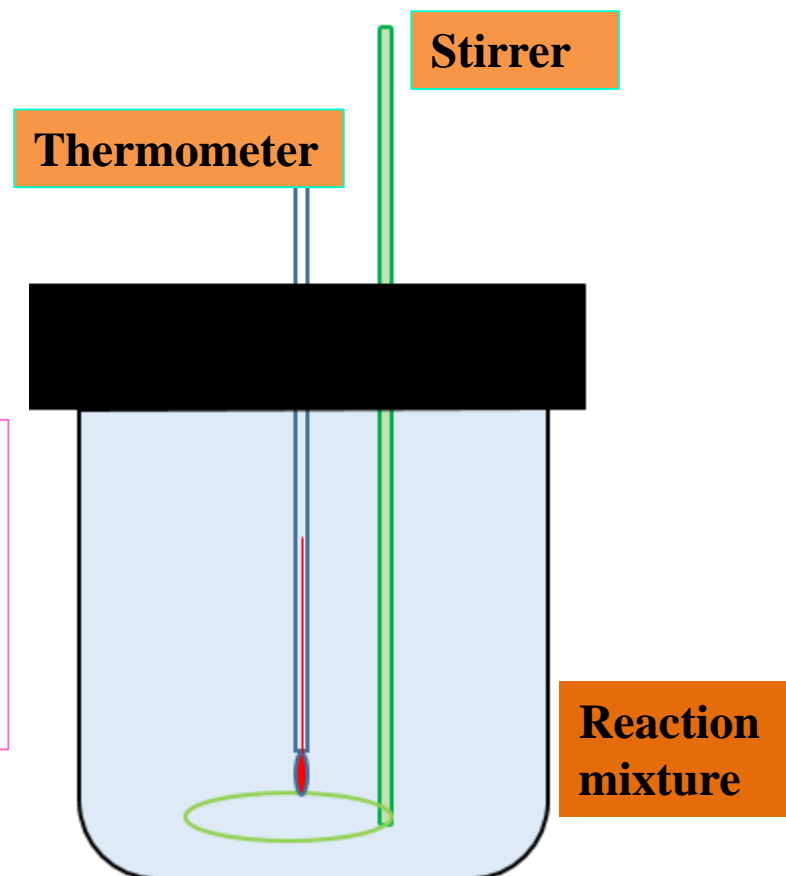
Constant-Volume Bomb Calorimeter

Constant-Pressure Bomb Calorimeter

Stirrer

Thermometer

The heat is gained or lost in a system can be calculated by measuring the temperature change.

Reaction mixture

Conclusion

❖ The different types of energy can be interconvertible.

❖ The change in internal energy refer to the changes in heat and work done of a system.

❖ The heat of reaction or calorimetry can be measured.

❖ The enthalpy of a reaction can be determined based on Hess's law.

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