CHAPTER 11

THERMOCHEMISTRY

The study of heat changes during a chemical reaction is called thermochemistry.

UNITS OF ENERGY:

Joule : $J = kgm^2s^{-2} = Nm$

$Kwh = 3.6 \times 10^6 J$

$1\ cal = 4.184 J$

$1 J = 10^7$ ergs

EXOTHERMIC REACTIONS

It is a natural tendency of any system to go to the lower energy state by itself. Such changes are called spontaneous changes.

A spontaneous change is accompanied by decrease in heat energy, in other words heat is evolved. A process in which heat is evolved is called an exothermic process. The heat of reaction in this case is written with negative sign.

ENDOTHERMIC REACTION

An endothermic process is one in which heat is absorbed and its heat of reaction is indicated by a positive sign.

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PROPERTIES	EXOTHERMIC	ENDOTHERMIC
1. Flow of heat energy:	System to surrounding	Surrounding to system
2. Temperature of surrounding:	Increases	Decrease
3. Temperature of system:	Decrease	Increase
4. Energy of products:	Low	High
5. Stability of product:	More stable than reactant	Less stable than reactan
6. Energy of reactants:	High	Low
7. Strength of bonds in products:	Strong	Weak
8. Strength of bonds in reactants:	Weak	Strong
9. Enthalpy Change (ΔH):	Negative.	Positive

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EXAMPLES OF EXOTHERMIC REACTIONS

1. $C + O_2 \rightarrow CO_2$
2. Respiration:

   $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$
3. Neutralization:

   $NaOH + HCl \longrightarrow NaCl + H_2O$

EXAMPLES OF ENDOTHERMIC REACTIONS

1. $N_2 + O_2 \longrightarrow 2NO$
2. Thermal Decomposition:

   $CaCO_3 \rightarrow CaO + CO_2$
3. Dissolution:

   $NH_4NO_{3(s)} \rightarrow NH_4NO_{3\,(aq)}$

* It is expected that all exothermic reactions are spontaneous. But it is not always true.
* Some endothermic reactions are also spontaneous in nature.
* The spontaneity of a reaction can be measured by study of the free energy of the system

$$\Delta G = \Delta H - \Delta TS$$

$T\Delta S_{total}$ — Gibb's free energy (ΔG)

$T\Delta S_{surrounding}$ (ΔH)

$T\Delta S_{system}$ (ΔTS)

ΔS : Entropy change

T : temperature in kelvin

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ΔG = +ve → non-spontaneous reaction
ΔG = −ve → spontaneous reaction

SYSTEM

A system is that part of the universe which is under scientific consideration.

SURROUNDING

The portion of universe except system is called surrounding.

STATE

The condition of a system is called state of the system.

STATE FUNCTION

A macroscopic property of a system which has some definite values for initial and final states, and which is independent of the path adopted to bring about a change

→ Pressure (P), temperature (T), volume (V), internal energy (E) and enthalpy (H) are all state functions.
→ Capital symbols are used for state function.
→ Heat and work are not state functions.

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INTERNAL ENERGY

The sum of potential energy and kinetic energy of a substance is called its internal energy

OR

The sum of all possible kinds of energies of all particles of a system is called its internal energy (E)

KINETIC ENERGY

1. Translational K.E (mono-atomic)
2. Rotational K.E (tetra atom)
3. Vibrational KE (di-atomic)

POTENTIAL ENERGY

1. Intramolecular forces
2. Inter-molecular forces

EFFECT OF INCREASE IN INTERNAL ENERGY

1. The temperature of the system may increase
2. A phase change may occur
3. A chemical reaction may take place.

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FIRST LAW OF THERMODYNAMICS

This law states that energy can neither be created nor destroyed although it may change from one form to another.

OR

The total energy of the system and its surroundings is conserved.

→ Based on law of conservation of energy.

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

$$\Delta E = q_v$$

The only ~~those~~ type of work in thermodynamics is the PV work. Hence, work is done when a system expands.

$\Delta E = q_v$

Heat absorbed at constant volume is used to increase the internal energy only and no work is done.

SIGN CONVENTIONS

1. Work done by the system on the surroundings '–'
2. Work done on the system by the surroundings '+'
3. Heat absorbed by system (endothermic) '+'
4. Heat absorbed by surround from system (exothermic) '–'

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ENTHALPY

The amount of heat evolved or absorbed in a chemical reaction is called heat of reaction.

Heat of reaction is measured at 25°C (298 K) and one atmospheric pressure is known as enthalpy change. It is denoted by ΔH°

* If a reaction is exothermic when going in one direction, it will be endothermic in the reverse direction. When a reaction is reversed, the magnitude of ΔH° remains the same but its sign changes.

$$C + O_2 \rightarrow CO_2 \qquad \Delta H^\circ = -393.5\ kJ$$
$$CO_2 \rightarrow C + O_2 \qquad \Delta H^\circ = +393.5\ kJ$$

Change In Enthalpy:

$$\Delta H = H_{products} - H_{reactants}$$

For exothermic , $\Delta H = -ve$

For endothermic , $\Delta H = +ve$

→ The standard state of any substance is taken as its natural state at 298k (25°C) under one atmospheric pressure.

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ENTHALPY OF REACTION (ΔH_r°)

The enthalpy change which occurs when certain number of moles of reactants as indicated by the balanced chemical equation, react together completely to give the products under standard conditions.

$$2H_2 + O_2 \rightarrow 2H_2O \qquad \Delta H^\circ = -285.8 \, kJ\,mol^{-1}$$

ENTHALPY OF FORMATION (ΔH_f°)

The change of enthalpy when one mole of a compound is formed from atoms of its elements

$$C + O_2 \rightarrow CO_2 \qquad \Delta H_f^\circ = -393.7 \, kJ\,mol^{-1}$$

ENTHALPY OF ATOMIZATION (ΔH_{at}°)

The enthalpy change when one mole of gaseous atoms are formed from a molecule or an element under standard conditions.

$$\tfrac{1}{2} H_{2(g)} \rightarrow H_{(g)} \qquad \Delta H_{at}^\circ = -218 \, kJ\,mol^{-1}$$

ENTHALPY OF NEUTRALIZATION (ΔH_n)

The amount of heat evolved when one mole of hydrogen ions H^+ from an acid, react with one mole of hydroxide ions (OH^-) from a base to form one mole of water.

The enthalpy of neutralization of NaOH by HCl is $-57.4 \, kJ\,mol^{-1}$

$$NaOH + HCl \rightarrow NaCl + H_2O \qquad \Delta H_n = -57.4 \, kJ\,mol^{-1}$$

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ENTHALPY OF COMBUSTION (ΔH_c°)

The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad \Delta H_c^\circ = -1368\ kJmol^{-1}$$

ENTHALPY OF SOLUTION (ΔH_{sol}°)

The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change

$$NH_4Cl_{(s)} + (aq) \rightleftharpoons NH_4Cl_{(aq)} \qquad \Delta H_{sol}^\circ = +16.2\ kJmol^{-1}$$

* EXAMPLES OF REACTIONS WHEN $\Delta H^\circ = +ve$
  1. Enthalpy of atomization
  2. Enthalpy of ionization

* EXAMPLES OF REACTIONS WHEN $\Delta H^\circ = -ve$
  1. Enthalpy of neutralization
  2. Enthalpy of combustion

* EXAMPLES OF REACTIONS WHEN $\Delta H^\circ = +ve$ or $-ve$
  1. Enthalpy of formation
  2. Enthalpy of solution

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DIFFERENCE BETWEEN INTERNAL ENERGY AND ENTHALPY

INTERNAL ENERGY

1. It is defined as the total energy of the system
2. It is denoted by 'E'
3. It is the sum of kinetic and potential energies
4. Formula:

$$E = K \cdot E + P \cdot E$$

5. It is expressed in joules or calories

ENTHALPY

1. It is defined as sum of internal energy and product of pressure and volume of the system.
2. It is denoted by 'H'
3. It is calculated by

$$H = E + PV$$

4. It is expressed in kcal mol^{-1} or kJmol^{-1}

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HEAT CAPACITY

"Heat capacity is the capacity of the system to absorb (heat) and store energy"

The heat capacity of a system is the heat absorbed by a system in raising the temperature by one degree (K or °C)

SI Unit : JC^{-1}

Heat capacity is expressed in two ways:

1) Specific Heat 2) Molar heat capacity

SPECIFIC HEAT

It is the amount of heat absorbed by 1 gram of a substance to the raise the temperature by 1 ~~Kelvin~~ degree.

MOLAR HEAT CAPACITY

The amount of heat required to raise the temperature of one mole of the substance through 1°C or 1K

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MEASUREMENT OF ENTHALPY OF REACTION

There are two basic methods to measure the enthalpy of reaction:

1. Experimental methods
   a. Direct calorimetry
   b. Indirect calorimetry

2. Theoretical methods
   a. Hess's law for constant heat summation
   b. Born Haber's cycle

1. DIRECT CALORIMETRY

→ A calorimeter consists of an insulated container filled with water in which a reaction chamber is immersed

→ In the case of an exothermic reaction, the heat generated is transferred to water and the rise in temperature of water is measured with thermometer.

→ From specific heat, temperature change, ~~and~~ the amount of heat evolved or absorbed in reaction can be calculated by using equation

$$q = nC\Delta T$$

n: mole of substance

C: molar heat capacity

ΔT: change in temperature

Hence $C = \frac{q}{n}(T_2 - T_1)$

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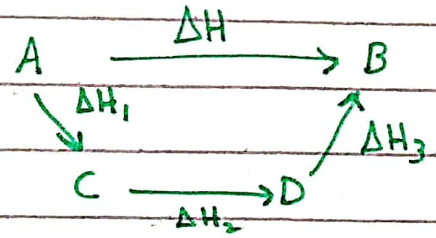
Heat of reaction of those reactions can be measured by calorimeter, which are in single step.

2. INDIRECT CALORIMETRY

In this method enthalpy change is calculated indirectly using Hess's Law.

HESS'S LAW

"The amount of energy evolved or absorbed in a chemical reaction is the same whether the reaction takes place in a single or several steps"



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

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BORN HABER CYCLE

Sum of energy change which occurs in a closed cycle, from the same initial and final states, is zero.

It enables us to calculate lattice energy of binary compounds (ionic)

$$\Sigma \Delta H_{(cycle)} = 0$$

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* The standard enthalpy of formation for an element in its standard state is zero.

* Specific Heat Capacity (c) = $\frac{\text{Heat}}{\text{gram} \times \Delta T}$

* Molar Heat capacity (c) = $\frac{\text{Heat}}{\text{moles} \times \Delta T}$

* To find molar heat capacity when specific heat capacity is given:

  Multiply specific heat with molar mass

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