



MOUNTAIN TOP UNIVERSITY

E-Courseware

**COLLEGE OF BASIC AND APPLIED
SCIENCES**

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Published By:

Mountain Top University



COURSE GUIDE

COURSE TITLE: General Chemistry I

COURSE CODE: CHM 101

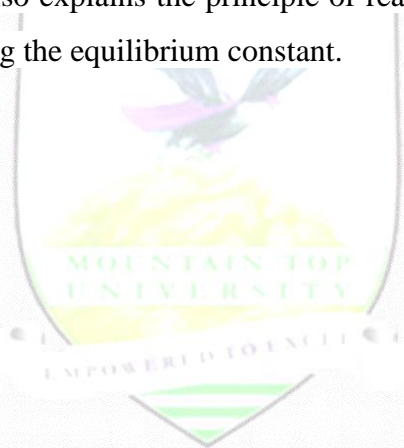
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COURSE OBJECTIVES

GENERAL INTRODUCTION AND COURSE OBJECTIVES

This course aims at explaining the concept of heat flow or heat change during chemical reactions. It deals with the various heat contents involving the evolution or absorption of heat from or by a system. It also explains the principle of reactions occurring at equilibrium and the various factors affecting the equilibrium constant.



COURSE CONTENTS

| | | |
|---------------------|--|-----------|
| Lecture One: | Thermochemistry and Thermodynamic | 6 |
| Lecture Two: | Chemical Equilibrium | 13 |



LECTURE ONE

Thermochemistry and Thermodynamic

1.0 Introduction

In studying and evaluating the flow of energy into or out of a system, it will be useful to consider changes in certain properties of the system. These properties include temperature, pressure, volume and concentration of the system. Measuring the changes in these properties from initial state to final state, can provide information concerning changes in energy and related quantities such as heat and work.

Objectives

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

1. Define thermochemistry and thermodynamic;
2. Define the various heat changes such as heat of formation, atomization, neutralization, combustion and perform some simple calculations base on them ;
3. Define entropy change and free energy change and perform some simple calculations'
4. Explain the concept of spontaneous process;

Pre-Test

1. Define thermochemistry.
2. Distinguish between endothermic and exothermic reactions.
3. What do you understand by enthalpy, entropy and free energy changes?

CONTENT

1.1 Thermochemistry and Thermodynamics

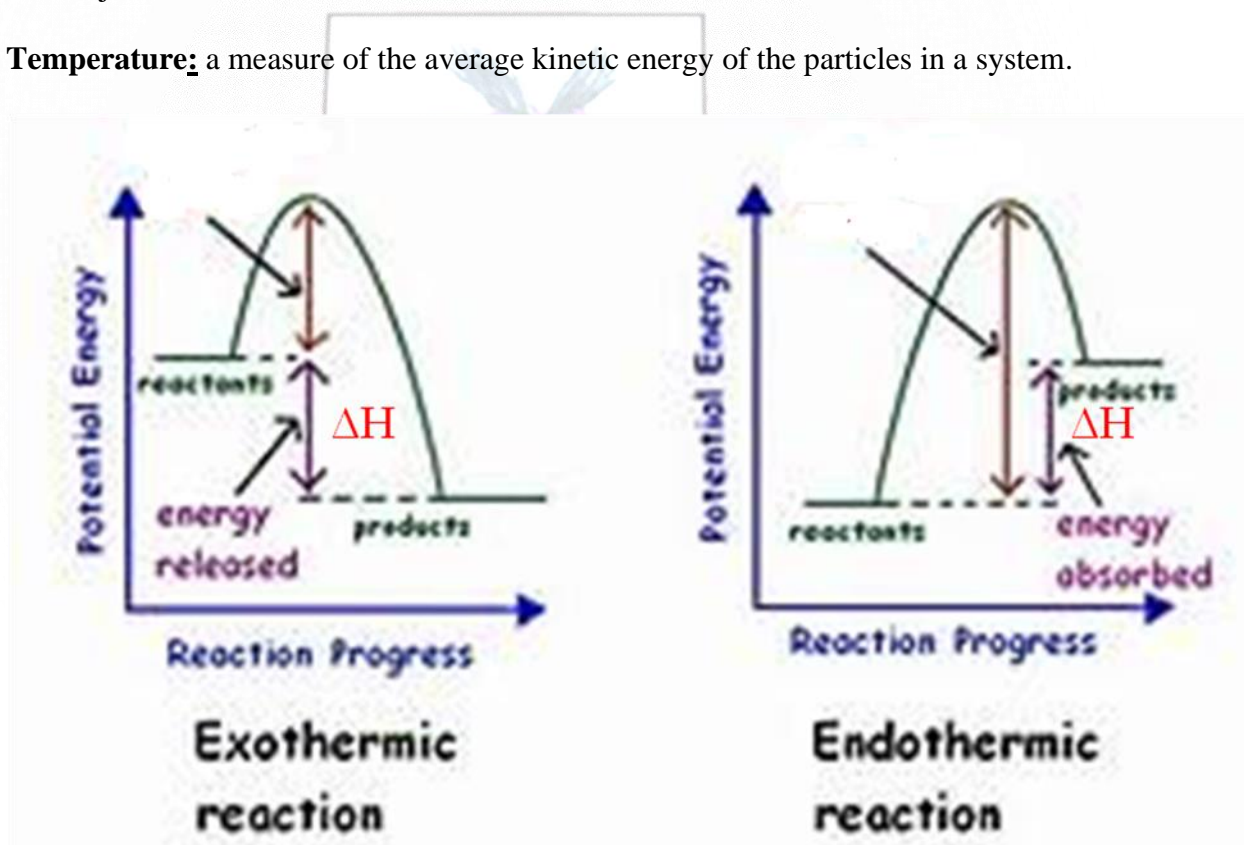
Thermochemistry is concerned with the heat changes that occur during a reaction and thermochemistry is a branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.

Thermodynamic is the study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation.

1.2 Thermodynamic Terms and Basic Concept

- **System:** part of the universe which is set aside for investigation.
- **Surrounding:** This is an imaginary line between system & surrounding.
- **Boundary:** This is an imaginary line between system & surrounding.
- **Open System:** An open system is one in which matter and energy can be exchanged with the surroundings.

- **Isolated system:** An isolated system is one in which matter and energy cannot be exchanged with the surroundings
- **Closed system:** A closed system is one that exchange energy but not matter with its surroundings.
- **Exothermic:** This occurs when energy in form of heat is released by system to surrounding.
- **Endothermic:** This occurs when energy in form heat is absorbed by system from surrounding.
- **Work (w):** The product of force applied to an object over distance
- **Heat (q):** is the energy that is transfers from one object to another because of a temperature different between them. Heat always flows from a warm body/object to a cool object
- **Temperature:** a measure of the average kinetic energy of the particles in a system.



For exothermic reaction, $H_P < H_R$ and $\Delta H = H_P - H_R$ which is negative and for endothermic reaction, $H_P > H_R$ and as such, $\Delta H = H_P - H_R$ which is positive

1.3 First Law of Thermodynamic

States that: Energy cannot be created or destroyed it can only be transformed from one form to another i.e. energy is conserved. The internal energy E of a system is the sum of all kinetic and potential energies of all its components.

The change in internal energy ΔE is the difference between final and initial. A positive value ΔE indicates the system has gained energy from its surrounding, but if the value of ΔE is negative, it indicates that the system has lost energy to its surroundings.

Mathematically, the first law may be stated as $\Delta E = q + w$, where q is the heat absorbed or evolved by the system.

E increases when work is done on a system or heat is added to a system.

Example:

Calculate the energy change for a system undergoing an exothermic process in which 15.4 kJ of heat flows and where 6.3 kJ of work is done on the system.

Solution:

Using $\Delta E = q + w$

$$\Delta E = 15.4 + 6.3 = 21.7 \text{ kJ}$$

1.4 ENTHALPY CHANGE



Enthalpy, H : Is the heat transferred between the system and surroundings carried out under constant pressure. Enthalpy is a state function i.e when all its properties are fixed.

If the process occurs at constant pressure,

Since we know that $PV = nRT$

$$\begin{aligned}\Delta H &= \Delta(E + PV) \\ &= \Delta E + P\Delta V\end{aligned}$$

We can write $P\Delta V = RT\Delta n$, where n is the number of mole difference.

Therefore, $\Delta H = \Delta E + RT\Delta n$, When ΔH is positive, the system gains heat from the surroundings i.e endothermic reaction and when ΔH is negative, the surroundings gain heat from the system i.e exothermic reaction.

1.5. Examples of Enthalpies of Reaction

1. Enthalpy or heat of Combustion

This is the heat changes (evolved) when a mole of a substance is burned completely in (excess) oxygen gas. The instrument used for determination of heat of combustion is the bomb calorimeter.

$$\text{Heat of combustion} = \frac{MC\theta}{m} \times \frac{M}{1}$$

$$\text{Heat of combustion} = \frac{\text{heat energy produced}}{\text{mass burnt}} \times \frac{\text{Molar mass}}{1}$$

Where mass burnt = mass of the substance combusted or burned, molar mass = the molar mass of the substance, $MC\theta$ = mass of water x specific heat capacity of water x change in temperature and $\theta = \theta_2 - \theta_1$

$MC\theta$ gives the energy produced.

Example 1: 50 J of energy was produced by combustion of 10 g of carbon(II) oxide. Calculate the heat of combustion of carbon (II) oxide (C=12, O=16)

Solution

$$\text{Heat of combustion} = \frac{\text{heat energy produced}}{\text{mass burnt}} \times \frac{\text{Molar mass}}{1}$$

$$\text{Heat of combustion} = \frac{50 \text{ J}}{10 \text{ g}} \times \frac{28 \text{ g/mol}}{1}$$

$$= -140 \text{ J/mol}$$

Example 2: 5.27 g of methanal (CH_4) was combusted in excess oxygen in a bomb calorimeter at 25 °C, and 119.5 kJ of heat was evolved. Calculate the ΔE and ΔH for the reaction. (H=1, C=12, O=16, $R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

2. Enthalpy or heat of formation

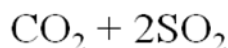
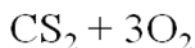
This is the heat change when one mole of a substance is formed from its constituent elements under standard conditions.

$$\Delta H_f = H_{\text{final}} - H_{\text{initial}}$$

$$= H_{\text{products}} - H_{\text{reactants}}$$

Example 1: The heat of formation of SO_2 and CO_2 are 71 J mol^{-1} and 94.3 kJ mol^{-1} respectively and the heat of combustion of carbon(IV) sulphide is 265.1 kJ mol^{-1} . Calculate the heat of formation of carbon(IV) sulphide.

Solution



$$\Delta H_f = 94.3 + 2(71) - (-265.1) = 501.3 \text{ kJ/mol}$$



From the reaction above, calculate the standard heat change if the standard enthalpies of $\text{CO}_{2(\text{g})}$, $\text{H}_2\text{O}_{(\text{g})}$ and $\text{CO}_{(\text{g})}$ in kJmol^{-1} are -394, -242 and -110 respectively. (Ans = -42 kJmol^{-1})

3. Enthalpy or heat of neutralization

This is the heat change when one mole of hydrogen ions, H^+ , from an acid reacts with one mole of hydroxide ions, OH^- , from alkali to form one molecule of water under standard conditions.



Note that ΔH for strong acid and base is always constant because of complete ionization

1.6 Hess's law of constant heat of summation

It states that provided heat is the only form of energy to enter or leave a system, the enthalpy change for any chemical reaction is constant whether the reaction occurs in a single step or several steps.

The law is important because it is often used to calculate the heat changes for reactions and processes that are not conveniently monitored directly and it can also be use to determine the heat of transition.

1.7 Spontaneous Processes

A process which proceeds of its own accord, without any outside assistance is called a spontaneous process. Other factors aside enthalpy that determine whether a reaction will be spontaneous or not are entropy and free energy change.

1.8 Entropy Change (ΔS)

This is a measure of the degree of disorder or randomness of a substance or a system. It is represented as S and its change as ΔS .

Note

- ❑ An increase in temperature, increases the entropy and vice versa.

- ❑ A perfectly ordered system at temperature zero, has an entropy of zero.

$$\Delta S = H_{\text{Product}} - H_{\text{Reactant}}$$

Example 1: Calculate the standard entropy, ΔS , of formation, of $\text{CO}_{2(g)}$. Given the standard entropies of $\text{CO}_{2(g)}$, $\text{C}_{(s)}$, $\text{O}_{2(g)}$ to be 213.6, 5.740 and 205.0 $\text{JK}^{-1}\text{mol}^{-1}$

Solution

$$\Delta S = H_{\text{Product}} - H_{\text{Reactant}}$$

$$\Delta S = 213.6 - (5.740 + 205.0)$$

$$\Delta S = 2.86 \text{ JK}^{-1}\text{mol}^{-1}$$

1.9 Free Energy Change (ΔG)

It defined as the energy available to do work or is the driving force that brings about a chemical change.. It is represented as G and its change as ΔG .

Note

- ❑ For a reaction to be spontaneous, ΔS must be positive, since the total energy must increase.
- ❑ For all spontaneous process, ΔG must be negative. When ΔG is zero, the system is at equilibrium.

$$\Delta G = \Delta H - T\Delta S$$

Example: Given that the enthalpy change for a reaction at 27 °C is -5000 kJmol^{-1} and the entropy is 109.5 $\text{JK}^{-1}\text{mol}^{-1}$, calculate the free energy change for the reaction and state with reason whether the process is spontaneous or not.

Solution

$$\Delta G = -5000 - (300 \times 109.5)$$

$$\Delta G = -37850 \text{ kJK}^{-1}\text{mol}^{-1}$$

The process will be spontaneous since the value of free energy change is negative.

Post-Test

1. With the aid of a schematic diagram, explain what you understand by exothermic and endothermic reactions.
2. Define thermodynamic and thermodynamic.
3. What is enthalpy change?
4. When is a reaction said to be spontaneous?

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- **Bahl, A and Bahl, B.S. *Essentials of physical chemistry*, S.Chand and Company Ltd. 2007**
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LECTURE TWO

Chemical Equilibrium

2.0 Introduction

Objectives

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

1. Explain the concept of chemical equilibrium, and
2. Explain the various factors affecting the equilibrium position.

Pre-Test

1. What is a reversible reaction?
2. Explain the various factors affecting the position of equilibrium.

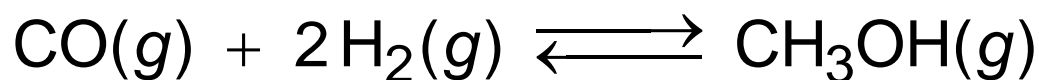
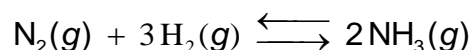
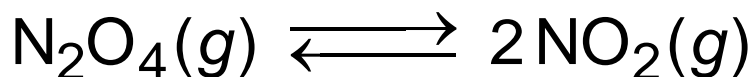
CONTENT

2.1 Reversible Reaction

A chemical equilibrium occurs when the rate of forward reaction equals that of backward reaction.

Reversible reaction = a reaction that proceeds simultaneously in both directions.

Examples



2.2 Chemical Equilibrium

At equilibrium,

the forward reaction: $\text{N}_2\text{O}_4(g) \longrightarrow 2\text{NO}_2(g)$, and

the reverse reaction: $2\text{NO}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$

both processes proceed at equal rates.

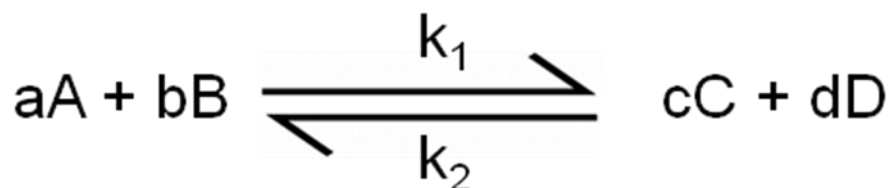
Chemical equilibria are **dynamic**, not static – the reactions do not stop.

The point of Chemical equilibrium can be obtained from either direction.

2.3 Law of mass action

This states that the rate at which a chemical reaction takes place at a given temperature is directly proportional to the product of the active masses of the reaction.

Consider the reaction below



Where a, b, c and d are the reacting moles, k_1 and k_2 are the equilibrium constants for the forward and backward equation

Rate of forward reaction (R_f) = $k_1[A]^a[B]^b$ (1)

Rate of backward reaction (R_b) = $k_2[C]^c[D]^d$ (2)

Rate of backward reaction (R_b) = $k_2[C]^c[D]^d$ (3)

$$k_1[A]^a[B]^b = k_2[C]^c[D]^d$$

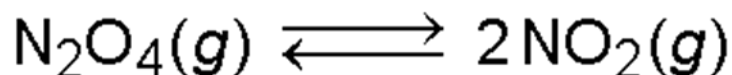
$$\frac{k_1}{k_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\text{If } K_c = \frac{k_1}{k_2}$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

For gases:
$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

Examples:



$$k_f[\text{N}_2\text{O}_4]_{\text{eq}} = k_r[\text{NO}_2]_{\text{eq}}^2$$

or

$$\frac{k_f}{k_r} = \frac{[\text{NO}_2]_{\text{eq}}^2}{[\text{N}_2\text{O}_4]_{\text{eq}}} = K_c$$

where K_c is the equilibrium constant

2.4. Factors That Affect Chemical Equilibrium

Le Châtelier's Principle

"If an equilibrium system variable is changed, the equilibrium will shift in the direction (right or left) that tends to reduce the change."

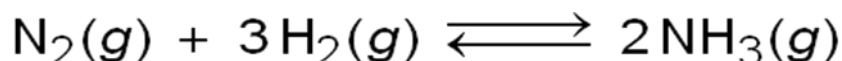
1. Effect of change in concentration:- When a reactant or product is added to a system in equilibrium, the position of equilibrium will shift away from the added substance. But when a reactant or product is removed from a system in equilibrium, the equilibrium position will shift towards the removed substance. E.g

2. Effect of change in change in pressure:-

For reactions involving an increase in volume, an increase in pressure will lead to a decrease in volume and the equilibrium position will shift backward favouring the reactants. E.g



For reactions involving a decrease in volume of the system, an increase in pressure or decrease in volume will shift the equilibrium position to the right favouring the formation of the product and vice versa. E.g



3. Effect of change in change in Temperature:-

For exothermic reactions, an increase in temperature will shift the equilibrium position backward and a decrease in temperature will shift it to the right or forward.

For endothermic reactions, an increase in temperature will shift the equilibrium position to the right or forward and a decrease in temperature will shift it to the left or backward

Note: Always check out for the value of the enthalpy change whether it is positive or negative

4. Effect of change in change in Catalyst:-

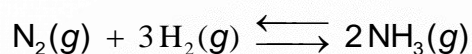
A catalyst has no effect on the position of equilibrium in a reversible reaction.

A catalyst is used to speed up the rate of establishment of the equilibrium.

It is often employed in endothermic reactions.

Post-Test

1. With the aid of diagram, explain what you understand by chemical equilibrium.
2. When N_2 is added to the reaction below, what happen to the equilibrium position?



Bibliography

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