

**IDHAYA COLLEGE FOR WOMEN, KUMBAKONAM**



**DEPARTMENT OF MICROBIOLOGY**

**COURSE : B.Sc., II PHYSICS**  
**SEMESTER : IV**  
**TOPIC : UNIT-V**  
**SUBJECT NAME : GENERAL CHEMISTRY ii**  
**SUB CODE : 16SACCH2**

**Presented by**

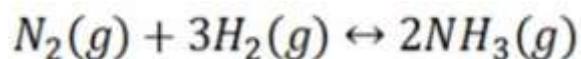
**P.PHILOMINA MARY M.Sc., M.Phil.,**  
**Assistant Professor,**  
**Dept. of Microbiology**

## CHEMICAL EQUILIBRIUM: CRITERIA OF HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

In order to simplify the problems and understand the concept, we divide such reactions into different categories, namely, the homogeneous reactions, where the components involved in the reaction are present in the same phase and the heterogeneous reactions, where the components involved are present in different phases. The methods of dealing with both the reactions are different and so is the determination of the equilibrium state. In this section, we will learn about a homogeneous equilibrium and the calculation of equilibrium constant for a homogeneous reaction.

### Equilibrium Constant for Homogeneous Reaction

Let us consider a homogeneous system, given by the following reaction



Here, we see that gaseous nitrogen reacts with gaseous hydrogen to form gaseous ammonia.

Let us now calculate the equilibrium constant for the above reaction.

In terms of the molar concentration of the components in the reaction, we can write

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

As we know, for reactions involving gases, we express the equilibrium concentration in terms of the partial pressure. Using the ideal gas equation,

$$PV = nRT$$

Where P is the pressure of the system, V is the volume of the system, n is the number of moles of components present in the system, R is the universal gas constant and T is the temperature of the system.

$$P = \frac{n}{v}RT$$

$$P = cRT$$

Here,  $c$  is the concentration of the system. We can also write it as,  $c = \frac{P}{RT}$

$$K_p = \frac{\frac{p_{\text{NH}_3}^2}{RT^2}}{\frac{p_{\text{N}_2} p_{\text{H}_2}^3}{RT \cdot RT^3}}$$

$$K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}} RT^{-2}$$

So equilibrium constant can also be written as,

Here, we note that the general expression for  $K_c$  and  $K_p$  can be written as,

$$K_p = K_c (RT)^{\Delta n}$$

Where  $\Delta n$  is defined as the number of moles of gaseous products – the number of moles of gaseous reactants.

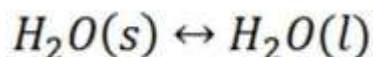
To learn more about homogeneous equilibrium, heterogeneous equilibrium

## CHEMICAL EQUILIBRIUM: CRITERIA OF HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

### Introduction

When the state of equilibrium in a system has components in more than one phase it is termed as a heterogeneous equilibrium. For example, if we take a container with ice and water at a temperature that is allowing the existence of both the phases simultaneously, such that, both ice and water are present in a state of equilibrium. This state is termed as heterogeneous equilibrium.

In terms of its equation, this can be written as:



In another example, we can consider an aqueous solution of a solid such as calcium hydroxide. We notice that the solid calcium hydroxide is in equilibrium with its saturated solution.

Writing the equilibrium constant for heterogeneous reactions is different from that of the homogeneous reactions. For example, consider the thermal dissociation of calcium carbonate into calcium oxide and carbon dioxide. Here, we can see that the equilibrium constant for the dissociation of the reactant into its products is only dependent on the gaseous component, as the solid and the liquid reactants are considered to be constant.



Here, the components  $CaCO_3$  and  $CaO$  are solids, so their molar concentration remains constant throughout the reaction. Therefore the equilibrium constant can be written as,

$$K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$
$$K_c = [CO_2]$$

Also, in terms of  $K_p$ , we can write

$$K_p = pCO_2$$

All chemical reactions have a specific rate defining the progress of reactants going to products. This rate can be influenced by temperature, concentration, and the physical properties of the reactants. The rate also includes the intermediates and transition states that are formed but are neither the reactant nor the product. The rate law defines the role of each reactant in a reaction and can be used to mathematically model the time required for a reaction to proceed. The general form of a rate equation is shown below:

$$rate = k[A]^m[B]^n$$

where  $A$  and  $B$  are concentrations of different molecular species,  $m$  and  $n$  are reaction orders, and  $k$  is the rate constant. The rate of nearly every reaction changes over time as reactants are depleted, making effective collisions less likely to occur. The rate constant, however, is fixed for any single reaction at a given temperature. The reaction order illustrates the number of molecular species involved in a reaction. It is very important to know the rate law, including rate constant and reaction order, which can only be determined experimentally. In this experiment, we will explore one method for determining the rate law and use it to understand the progress of a chemical reaction.

## PRINCIPLES

### Kinetics and Thermodynamics

All chemical reactions are governed by two factors, kinetics and thermodynamics. The thermodynamic factor is the difference in free energy released during a chemical reaction. This free energy, termed spontaneity, is a complex value arising from the enthalpy (heat) and entropy (disorder) within a chemical reaction. Kinetics refers to the rate of a chemical reaction and how fast the system reaches equilibrium. While kinetics can explain the speed of the reaction, thermodynamics yields information about its energetics. Simply stated, thermodynamics relates to stability and kinetics relates to reactivity.

## Determining Rate

Rate is a time-based measurement, meaning it is constantly changing as a reaction proceeds. This can be represented using a differential rate law, expressing the change in concentration over a change in time. Experimentally, the differential rate law is difficult to use, so we can use calculus and represent the rate law as the integrated rate law by integrating the differential rate law. The integrated rate law represents the reaction concentrations at the start of the reaction and at a specified time interval. A table of order, rate law, and integrated rate law is shown below:

Order	Rate law	Integrated Rate Law	Linear plot	Slope	Units of $k$
0 <sup>th</sup>	rate = $k$	$[A]_0 - [A]_t = kt$	$[A]$ vs $t$	$-k$	M/s
1 <sup>st</sup>	rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\ln[A]$ vs $t$	$-k$	s <sup>-1</sup>
2 <sup>nd</sup>	rate = $k[A]^2$	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$	$\frac{1}{[A]}$ vs $t$	$k$	M <sup>-1</sup> s <sup>-1</sup>

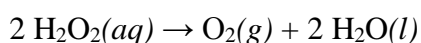
Each order explains the dependence of reactant concentration on reaction rate. For example, a zeroth order rate law, rate =  $k$ , indicates that the rate is only dependent on the rate constant, not on reactant concentration. This is common in catalytic reactions where the catalyst is a solid and the surface area does not change during the reaction. A 1<sup>st</sup> order rate law shows that the rate is dependent on the concentration of one reactant, though other reactants may be present. A 2<sup>nd</sup> order rate law indicates that the rate is dependent on the concentration of two reactants in the reaction. Those reactants can be the same, i.e. rate =  $k[A]^2$ , or different, rate =  $k[A][B]$ . Since the two concentrations are constantly changing, second order rate constants can be difficult to measure in the lab. Regardless of the order, using the integrated rate law simplifies data analysis by allowing for data plotting and applying a linear equation to fit the data. Since only one integrated rate law will fit the data, a reaction's rate constant and reaction order can be immediately identified.

## A Kinetics Experiment

Determining the rate law begins with setting up a kinetics experiment for the chemical reaction. A kinetics experiment is carefully controlled so that measurements are made in timed intervals

in order to determine the change in concentration of a species over time. That species can either be a reactant (decreasing concentration with time) or a product (increasing concentration with time). If multiple reactants are involved, it is also very important that the concentration of only one reactant changes with time. Increasing the concentration of the other reactants much higher than the reactant being studied makes it appear that the concentration of only one reactant changes during the experiment.

In this experiment, the catalytic decomposition of hydrogen peroxide over a platinum catalyst is explored. Since the platinum is a catalyst, only one species is involved which decomposes into two products according to the reaction below:



Because one of the products,  $\text{O}_2$ , is a gas, the increase in pressure of the system over time can be measured and the Ideal Gas Law ( $PV = nRT$ ) used to relate pressure to moles. Once that is done for several different concentrations of the reactant, the reaction order and rate law can be solved.

## PROCEDURE

### 1. Preparing $\text{H}_2\text{O}_2$ Dilutions

1. Stock 3% hydrogen peroxide has a concentration of 0.882 M. Prepare 5 dilutions ranging from 0.882 M to 0.176 M (**Table 1**). Prepare these solutions volumetrically, but prepare them additively since the solute is very dilute and volumes of water are additive.
2. Place the solutions in a constant temperature water bath or leave them on the bench top to equilibrate at room temperature. A temperature range of 20–25 °C (293–298 K) is good for this reaction.

	Required volume of 3% H <sub>2</sub> O <sub>2</sub> solution (mL)	Required volume of water (mL)	Concentration of H <sub>2</sub> O <sub>2</sub> (M)
<b>Trial 1 (3.0%)</b>	50	0	0.882
<b>Trial 2 (2.4%)</b>	40	10	0.706
<b>Trial 3 (1.8%)</b>	30	20	0.530
<b>Trial 4 (1.2%)</b>	20	30	0.353
<b>Trial 5 (0.6%)</b>	10	40	0.176

**Table 1. H<sub>2</sub>O<sub>2</sub> solutions used.**

## 2. Preparing the Reaction Vessel

1. To determine the volume of the reaction vessel, fill a large test tube to the top with water and insert a 1-hole rubber stopper into the test tube until tight and water pushes out the sides and through the top.
2. Remove the stopper and pour the water into a graduated cylinder to determine the *exact* volume of the water. This is the total volume of the reaction vessel (test tube).

## 3. Measuring Oxygen Evolution

1. Replace the water with 50 mL of the first hydrogen peroxide solution and place it back into the water bath. Once equilibrated, add the platinum-coated reaction disc and seal the system with a stopper connected to a gas pressure sensor. These discs are commonly used in contact lens cleaning systems.
2. Once the pressure sensor is setup to acquire data at 2 points/s, run the experiment for 120 s. The Vernier gas pressure sensor, GPS-BTA, is recommended for this experiment.
3. Bubbles should be observed as the peroxide is decomposed to oxygen gas and water. Release the pressure, dispose of the solution, rinse, and replace the solution with the next hydrogen peroxide solution. Repeat the gas pressure measurement until all solutions are tested.

## 4. Data Analysis

### 1. Determining Reaction Order

1. Because pressure of evolved O<sub>2</sub> is directly proportional to the moles of decomposed H<sub>2</sub>O<sub>2</sub>, plotting the **ln(initial rate)** vs. **ln[H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>** yields a slope equivalent to the order of the reaction. The initial concentration of hydrogen peroxide, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>, is what was used in each of the trials.

1. The equation for the rate law is  $rate = k[A]^m$ . Taking the natural logarithm (ln) of the



equation produces a linear equation  $\ln(\text{rate}) = m \ln[A] + k$ , where  $m$ , the slope, is the order of the reaction.

## 2. Determining the Rate Constant, $k$

1. For each trial, convert the rate,  $P_{O_2}/s$ , into units of atm/s if the rate is in a different unit such as torr/s.
2. Because bubbles were evolved in aqueous solution, subtract the vapor pressure of water from the system pressure for each trial. The new rate reflects only the pressure due to oxygen evolution.
3. Apply the Ideal Gas law to convert the rate from atm/s into moles/s in each trial.
  1. Rearrange  $PV = nRT$  to  $n = PV/RT$ . The  $s^{-1}$  unit remains unchanged. The volume is equivalent to the test tube volume minus the solution volume (50 mL).
4. Use the balanced chemical reaction to convert from moles of oxygen produced to moles of hydrogen peroxide decomposed in each trial.
5. Divide the moles of  $H_2O_2$  by the volume of the solution, 0.050 L, to yield the molarity of  $H_2O_2$  decomposed per second,  $[H_2O_2]/s$ .
6. Because this experiment follows first-order kinetics, divide the rate,  $[H_2O_2]/s$ , by the original solution concentration for each trial,  $[H_2O_2]_0$ , to yield a rate constant,  $k$ . This

solution for the rate constant would vary slightly based on the order of the reaction previously determined.

7. Average the rate constants for each trial together since the temperature is constant.