Chemical Kinetics - Part 2

Objectives

After going through this lesson, the learners will be able to understand the following:

- Discuss the Dependence of Rate of Reaction on Concentration
- Define Rate Law and Rate Constant
- Differentiate between the Molecularity and the Order of a Reaction

Contents Outline

- Factors Affecting the Rate of the Reaction
- Effect of Concentration on the Rate of the Reaction
- Rate Law and Rate Constant
- Order of a Reaction
- Molecularity of a Reaction
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Factors Affecting the Rate of the Reaction

Rate of a reaction is influenced by a number of factors as follows:

i. Experimental conditions such as concentration of reactants (pressure in case of gases);
ii. Temperature of the reactants or products;
iii. Nature of the reacting substances;
iv. Presence of catalyst.

Effect of Concentration on the Rate of the Reaction

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. It is found that the concentrations of the reactants decrease while the concentrations of the products increase with passage of time (Fig. 1).

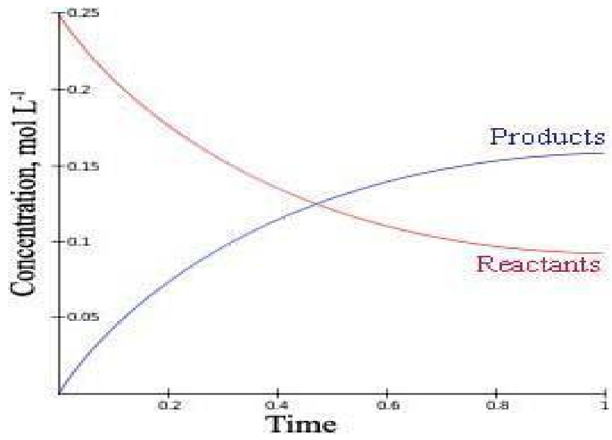

Fig. 1: Variation of concentration with passage of time

(Source:https://upload.wikimedia.org/wikipedia/commons/thumb/2/24/ChemicalEquilibrium.svg/300px-ChemicalEquilibrium.svg.png)

The representation of the rate of a reaction in terms of concentration of the reactants is known as rate law. It is also known as the rate equation or rate expression.

Rate Law and Rate Constant

In the first module, we have calculated the average rate of the reaction for hydrolysis of butyl chloride with passage of time. We found that the rate of a reaction decreases with the passage of time as the concentration of reactants decreases. Conversely, rates generally increase when reactant concentrations increase. So, the rate of a reaction depends upon the concentration of reactants.

Consider a general reaction

$aA \ + \ bB \rightarrow cC \ + \ dD$

where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is

$$Rate \propto [A]^x[B]^y \qquad (1)$$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as

$$Rate = k[A]^x[B]^y \qquad (2)$$

$$\frac{-d[R]}{dt} = k[A]^x[B]^y \qquad (3)$$

This form of equation (3) is known as differential rate equation where k is a proportionality constant called rate constant. The equation like (1), which relates the rate of a reaction to concentration of reactants, is called rate law or rate expression. Thus, rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be the same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Rate constant (k) also known as velocity constant or specific reaction rate, is defined as the rate of the reaction when concentration of each reactant is taken as unity.

As [A] = [B] = 1 mol L^{-1} , $Rate = k$

Thus, the rate constant gives an idea about the speed of the reaction, i.e. a reaction with higher value of rate constant proceeds at faster rate. The rate constant depends upon temperature while independent of concentration of the reacting species.

The rate law expression can be explained using the following example:

$$2\,NO\,(g)\ +\ O_2(g) \rightarrow 2\,NO_2\,(g)$$

We can measure the rate of this reaction as a function of initial concentrations either by keeping the concentration of one of the reactants constant and changing the concentration of the other reactant or by changing the concentration of both the reactants. The following results are obtained (Table 1).

Table 1. Initial rate of formation of NO_2

Experiment	**Initial [NO] / mol L^{-1}**	**Initial [O_2] / mol L^{-1}**	**Initial rate of formation of NO_2 / mol L^{-1} s^{-1}**
1	0.30	0.30	0.096
2	0.60	0.30	0.384
3	0.30	0.60	0.192
4	0.60	0.60	0.768

It is obvious, after looking at the results, that when the concentration of NO is doubled and that of O_2 is kept constant then the initial rate increases by a factor of four from 0.096 to 0.384 mol L^{-1} s^{-1}. This indicates that the rate depends upon the square of the concentration of NO (i.e. rate $\propto [NO]^2$). When concentration of NO is kept constant and concentration of O_2 is doubled the rate also gets doubled indicating that rate depends on concentration of O_2 to the first power (i.e. rate $\propto [O_2]$). Hence, the rate equation for this reaction will be

$$Rate\ =\ k\,[NO]^2\,[O_2]$$

The differential form of this rate expression is given as

$\frac{-d[R]}{dt} = k[NO]^2[O_2]$

Now, we observe that for this reaction, in the rate equation derived from the experimental data, the exponents of the concentration terms are the same as their stoichiometric coefficients in the balanced chemical equation.

Some other examples are given below:

1. $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$; the experimental rate expression is

   $rate = k[CHCl_3][Cl_2]^{\frac{1}{2}}$

2. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$; the experimental rate expression is

   $rate = k[CH_3COOC_2H_5]^1[H_2O]^0$

In these reactions, the exponents of the concentration terms are not the same as their stoichiometric coefficients. Thus, we can say that:

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

Before going on further, it is very important to know the difference between the rate of the reaction and the rate constant of the reaction. As discussed above, the rate of the reaction is expressed as the speed of the reaction at which reactants are converted into products, while the rate constant is the proportionality constant in the rate law expression. Also, the rate of the reaction depends upon the concentration of the reactant species at a particular moment of time, while rate constant is equal to the rate of the reaction when concentration terms are unity at that moment of time. The rate of the reaction generally decreases with progress of the reaction; on the other hand, the rate constant is a constant value for a reaction at given conditions.

Order of a Reaction

In the rate equation (2)

$Rate = k[A]^x[B]^y$

where x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y in (2) gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.

Hence, the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called elementary reactions. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called complex reactions. These may be consecutive reactions (e.g., oxidation of ethane to CO_2 and H_2O passes through a series of intermediate steps in which alcohol, aldehyde and acid are formed), reverse reactions and side reactions (e.g., nitration of phenol yields o-nitrophenol and p-nitrophenol).

Units of rate constant: For a general reaction,

$$aA \ + \ bB \rightarrow cC \ + \ dD$$

$$Rate \ = \ k\,[A]^x\,[B]^y$$

where x + y = n = order of the reaction $k \ = \frac{Rate}{[A]^x[B]^y}$

$$= \frac{concentration}{time} \times \frac{1}{(concentration)^n}$$

$$= \ (concentration)^{1-n} \times time^{-1}$$

(where [A] = [B])

Taking SI units of concentration, mol L^{-1} and time, sec, the units of k for different reaction order are listed in Table 2.

Table 2. Units of rate constant

Reaction	**Order**	**Units of rate constant**
Zero order reaction	0	$\frac{molL^{-1}}{s} \times \frac{1}{(molL^{-1})^0} = molL^{-1}s^{-1}$
First order reaction	1	$\frac{molL^{-1}}{s} \times \frac{1}{(molL^{-1})^1} = s^{-1}$
Second order reaction	2	$\frac{molL^{-1}}{s} \times \frac{1}{(molL^{-1})^2} = mol^{-1}Ls^{-1}$
n^{th} order reaction	n	$\frac{molL^{-1}}{s} \times \frac{1}{(molL^{-1})^n} = (molL^{-1})^{1-n}s^{-1}$

Example 1: Calculate the overall order of a reaction which has the rate expression:

(a) Rate = k $[A]^{1/2}$ $[B]^{3/2}$

(b) Rate = k $[A]^{3/2}$ $[B]^{-1}$

Solution:

(a) $Rate = k\,[A]^x\,[B]^y$

Order of the reaction = x + y

Here, x = ½ and y = 3/2

So order = 1/2 + 3/2 = 2, i.e., the reaction is a second order reaction.

(b) Here, x = 3/2 and y = -1

So order = 3/2 + (–1) = 1/2, i.e., the reaction is a half order reaction order.

Example 2: Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}

(ii) $k = 3 \times 10^{-4}$ s^{-1}

Solution:

(i) From table 2, we know that the unit of second order rate constant is mol^{-1} L s^{-1}. In this case $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} and hence it represents a second order reaction.

(ii) Again from table 2, the unit of a first order rate constant is s^{-1}. Here, $k = 3 \times 10^{-4}$ s^{-1} and thus it represents a first order reaction.

Example 3: Find out the order of the reaction and units of rate constant in the following reactions. Also state the order with respect to each of the reactants.

(a) $CH_3CHO \rightarrow CH_4 + CO\,;\ Rate = k\,[CH_3CHO]^{\frac{3}{2}}$

(b) $CO + Cl_2 \rightarrow COCl_2;\ Rate = k\,[CO]^2\,[Cl_2]^{\frac{1}{2}}$

(c) $NO + O_2 \rightarrow 2\,NO_2\,;\ Rate = k\,[NO]^2\,[O_2]$

Solution:

(a) $Rate = k[CH_3CHO]^{\frac{3}{2}}$

Order with respect to CH_3CHO = 3/2 = 1.5

Overall order of the reaction = 3/2 =1.5

Units of rate constant, k = $(mol\ L^{-1})^{1-n}$ s^{-1}

Here, n = 1.5, therefore, units of k = $(mol\ L^{-1})^{1-1.5}\ s^{-1} = mol^{-1/2}\ L^{1/2}\ s^{-1}$

(b) $Rate = k\,[CO]^2\,[Cl_2]^{\frac{1}{2}}$

Order with respect to CO = 2 and order with respect to Cl_2 = ½ =0.5

Overall order of the reaction = 2 + ½ = 2½ = 5/2 = 2.5

Units of rate constant, k = $(mol\ L^{-1})^{1-n}\ s^{-1}$

Here, n = 2.5, therefore, units of k = $(mol\ L^{-1})^{1-2.5}\ s^{-1} = mol^{-3/2}\ L^{3/2}\ s^{-1}$

(c) $Rate = k\,[NO]^2\,[O_2]$

Order with respect to NO = 2 and order with respect to O_2 = 1

Overall order of the reaction = 2 + 1 = 3

Units of rate constant, k = $(mol\ L^{-1})^{1-n}\ s^{-1}$

Here, n = 3, therefore, units of k = $(mol\ L^{-1})^{1-3}\ s^{-1} = mol^{-2}\ L^{2}\ s^{-1}$

Molecularity of a Reaction

Another property of a reaction called molecularity helps in understanding its mechanism. The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$$2\,HI \rightarrow H_2 + I_2$$

Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example,

$$2\,NO + O_2 \rightarrow 2NO_2$$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed.

It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.

$$KClO_3 + 6\,FeSO_4 + 3\,H_2SO_4 \rightarrow KCl + 3\,Fe_2(SO_4)_3 + 3\,H_2O$$

This reaction which apparently seems to be of tenth order is actually a second order reaction. This shows that this reaction takes place in several steps. Which step controls the rate of the overall reaction? The question can be answered if we go through the mechanism of reaction, for example, chances to win the relay race competition by a team depend upon the slowest person in the team. Similarly, the overall rate of the reaction is controlled by the slowest step in a reaction called the rate determining step. Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in an alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline Medium}]{I^-} 2H_2O + O_2$$

The rate equation for this reaction is found to be

$$Rate = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

This reaction is first order with respect to both H_2O_2 and I^-. Evidences suggest that this reaction takes place in two steps:

Step 1: $H_2O_2 + I^- \rightarrow H_2O + IO^-$

Step 2: $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

Both the steps are bimolecular elementary reactions. Species IO^- is called as an intermediate since it is formed during the course of the reaction but not in the overall balanced equation. The first step, being slow, is the rate determining step. Thus, the rate of formation of intermediate will determine the rate of this reaction. The detailed description of various steps involved in a reaction is known as the mechanism of a reaction.

We have to keep this in mind that each and every step involved in a reaction proceeds with different rates; only the slowest step of the reaction depicts the overall rate of the reaction. In cases of complex reactions, the molecularity of the overall reaction, in general, has no significance.

Thus, from the discussion till now, we conclude the following:

i. Order of the reaction is the sum of the powers of the concentration terms in the rate law expression while molecularity is simply the number of the reacting species.
ii. Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity is a theoretical concept and cannot be zero or a non-integer.

iii. Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no significance.

For complex reactions, order is given by the slowest step and hence depicts the mechanism of the reaction; on the other hand, the molecularity of the slowest step is the same as the order of the overall reaction and gives no clue about the mechanism.

Order of the reaction depends upon the experimental conditions like temperature and pressure while molecularity of the reaction does not.

Example 4: For a reaction, A + B → Product, the rate law is given by, $Rate = k\,[A]^{\frac{1}{2}}\,[B]^2$. What is the order of the reaction?

Solution: The order of the reaction is the sum of powers of the concentration terms in the rate law expression. Here, we have

$$Rate = k\,[A]^{\frac{1}{2}}\,[B]^2$$

Therefore, order of the reaction = ½ +2 = 5/2 =2.5

Example 5: The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

Solution: The reaction X → Y follows second order kinetics. Therefore, the rate equation for this reaction will be given as:

$$Rate = k\,[X]^2$$

Let the concentration of X, i.e. [X] be 'a' mol L^{-1}, then rate of the reaction is:

$$Rate = k\,(a)^2 = k\,a^2$$

If the concentration of X is increased to three times, then [X] = 3 × a mol L^{-1}

Therefore, rate of the reaction will be:

$$Rate_{New} = k\,(3a)^2 = 9\,ka^2$$

Hence, the rate of the reaction or rate of the formation of Y will increase by 9 times.

Example 6: For what type of reactions the rate constant shall have the same units as the rate of the reaction?

Solution: It is for the zero-order reaction.

Summary

In the first module we have learnt about the rate of the reaction; in this module, we learnt that the number of factors such as temperature, concentration of reactants, and catalyst affect the rate of a reaction. It was observed that with passage of time the concentration of reactant decreases while that of products increases. Also, the rate of the reaction decreases with decrease in concentration of the reactants.

Mathematical representation of rate of a reaction in terms of concentration of the reactants is given by rate law. It has to be determined experimentally and cannot be predicted. The proportionality factor in the rate law is known as rate constant, k. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation.

Order of a reaction with respect to a reactant is the power of its concentration which appears in the rate law equation. The order of a reaction is the sum of all such powers of concentration of terms for different reactants. Order of a reaction can be 0, 1, 2 or any non-integer. Molecularity is defined only for an elementary reaction. Its values are limited from 1 to 3 whereas order can be 0, 1, 2, 3 or even a fraction. Molecularity cannot be zero or a non-integer. Molecularity and order of an elementary reaction are the same. Many reactions occur in a number of steps that make the overall mechanism of the reaction and the rate of the reaction is determined by the slowest step of the reaction.