# Chapter 4 : CHEMICAL KINITICS

TEACHER ORIENTATION.The rate law.

Student orientation. To make the students understand the basic concept of the Rate law and its applications.

CONCEPT DETAILS :

In chemical kinetics, the **order of reaction** with respect to a given substance (such as reactant, catalyst or product) is defined as the index, or exponent, to which its concentration term in the rate equation is raised. For the typical rate equation of form $r = k[A]^x[B]^y \cdots$, where [A], [B], ... are concentrations, the reaction orders (or *partial* reaction orders) are x for substance A, y for substance B, etc. The *overall* reaction order is the sum x + y + ...

For example, the chemical reaction between mercury (II) chloride and oxalate ion

$$2\ HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2\ Cl^-(aq) + 2\ CO_2(g) + Hg_2Cl_2(s)$$
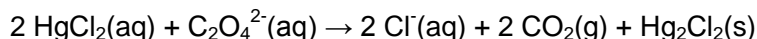
has the observed rate equation

$$r = k[HgCl_2]^1[C_2O_4^{2-}]^2$$

In this case, the reaction **order with respect to** the reactant $HgCl_2$ is 1 and with respect to oxalate ion is 2; the **overall reaction order** is 1 + 2 = 3. As is true for many reactions, the reaction orders (here 1 and 2 respectively) differ from the stoichiometric coefficients (2 and 1). Reaction orders can be determined only by experiment. Their knowledge allows conclusions to be drawn about the reaction mechanism, and may help to identify the rate-determining step.

Elementary (single-step) reactions do have reaction orders equal to the stoichiometric coefficients for each reactant, but complex (multi-step) reactions may or may not have reaction orders equal to their stoichiometric coefficients.

Orders of reaction for each reactant are often positive integers, but they may also be zero, fractional, or negative.

A reaction can also have an *undefined* reaction order with respect to a reactant if the rate is not simply proportional to some power of the concentration of that reactant; for example, one cannot talk about reaction order in the rate equation for a bimolecular reaction between adsorbed molecules:

$$r = k\frac{K_1 K_2 C_A C_B}{(1 + K_1 C_A + K_2 C_B)^2}.$$

Method of initial rates

The order of a reaction for each reactant can be estimated from the variation in initial rate with the concentration of that reactant, using the natural logarithm of the typical rate equation

$$\ln r = \ln k + x \ln[A] + y \ln[B] + \ldots$$

For example the initial rate can be measured in a series of experiments at different initial concentrations of reactant A with all other concentrations [B], [C], ... kept constant, so that

$$\ln r = x \ln[A] + \text{constant}$$

The slope of a graph of $\ln r$ as a function of $\ln[A]$ then corresponds to the order x with respect to reactant A.

However this method is not always reliable because

1. measurement of the initial rate requires accurate determination of small changes in concentration in short times (compared to the reaction half-life) and is sensitive to errors, and
2. the rate equation will not be completely determined if the rate also depends on substances not present at the beginning of the reaction, such as intermediates or products.

The tentative rate equation determined by this method is therefore normally verified by comparing the concentrations measured over a longer time (several half-lives) with theintegrated form of the rate equation.

First order

If a reaction rate depends on a single reactant and the value of the exponent is one, then the reaction is said to be first order. In organic chemistry, the class of S_N1 (nucleophilic substitution unimolecular) reactions consists of first-order reactions. For example,[4] in the reaction of aryldiazonium ions with nucleophiles in aqueous solution $ArN_2^+ + X^- \rightarrow ArX + N_2$, the rate equation is $r = k[ArN_2^+]$, where Ar indicates an aryl group.

Another class of first-order reactions is radioactive decay processes which are all first order. These are, however, nuclear reactions rather than chemical reactions.

Second order

A reaction is said to be second order when the overall order is two. The rate of a second-order reaction may be proportional to one concentration squared $r = k[A]^2$, or (more commonly) to the product of two concentrations $r = k[A][B]$. As an example of the first type, the reaction $NO_2 + CO \rightarrow NO + CO_2$ is second-order in the reactant NO_2 and zero order in the reactant CO. The observed rate is given by $r = k[NO_2]^2$, and is independent of the concentration of CO.[5]

The second type includes the class of S_N2 (nucleophilic substitution bimolecular) reactions, such as the alkaline hydrolysis of ethyl acetate:[4]

$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$.
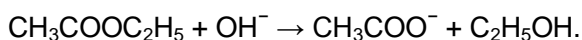
> This reaction is first-order in each reactant and second-order overall: $r = k[CH_3COOC_2H_5][OH^-]$
>
> If the same hydrolysis reaction is catalyzed by imidazole, the rate equation becomes[4] $r = k[imidazole][CH_3COOC_2H_5]$. The rate is first-order in one reactant (ethyl acetate), and also first-order in imidazole which as a catalyst does not appear in the overall chemical equation.

Pseudo-first order[edit]

> If the concentration of a reactant remains constant (because it is a catalyst or it is in great excess with respect to the other reactants), its concentration can be included in the rate constant, obtaining a **pseudo–first-order** (or occasionally pseudo–second-order) rate equation. For a typical second-order reaction with rate equation $r = k[A][B]$, if the concentration of reactant B is constant then $r = k[A][B] = k'[A]$, where the pseudo–first-order rate constant $k' = k[B]$. The second-order rate equation has been reduced to a **pseudo–first-order** rate equation, which makes the treatment to obtain an integrated rate equation much easier.

For example, the hydrolysis of sucrose in acid solution is often cited as a first-order reaction with rate $r = k[sucrose]$. The true rate equation is third-order, $r = k[sucrose][H^+][H_2O]$; however, the concentrations of both the catalyst H^+ and the solvent H_2O are normally constant, so that the reaction is pseudo–first-order.[6]

Zero order[edit]

For *zero-order* reactions, the reaction rate is independent of the concentration of a reactant, so that changing its concentration has no effect on the speed of the reaction. This is true for many enzyme-catalyzed reactions, provided that the reactant concentration is much greater than the enzyme concentration which controls the rate. For example, the biological oxidation of ethanol to acetaldehyde by the enzyme liver alcohol dehydrogenase (LADH) is zero order in ethanol.[7]

Fractional order[edit]

In **fractional order** reactions, the order is a non-integer, which often indicates a chemical chain reaction or other complex reaction mechanism. For example, the pyrolysis ofethanal (CH_3-CHO) into methane and carbon monoxide proceeds with an order of 1.5 with respect to ethanal: r = k[CH_3-CHO]$^{3/2}$.[8] The decomposition of phosgene ($COCl_2$) to carbon monoxide and chlorine has order 1 with respect to phosgene itself and order 0.5 with respect to chlorine: r = k[$COCl_2$] [Cl_2]$^{1/2}$.

Mixed order[edit]

More complex rate laws have been described as being **mixed order** if they approximate to the laws for more than one order at different concentrations of the chemical species involved. For example, a rate law of the form $r = k_1[A] + k_2[A]^2$ represents concurrent first order and second order reactions (or more often concurrent pseudo-first order and second order) reactions, and can be described as mixed first and second order.[9] For sufficiently large values of [A] such a reaction will approximate second order kinetics, but for smaller [A] the kinetics will approximate first order (or pseudo-first order). As the reaction progresses, the reaction can change from second order to first order as reactant is consumed.

Another type of mixed-order rate law has a denominator of two or more terms, often because the identity of the rate-determining step depends on the values of the concentrations. An example is the oxidation of an alcohol to a ketone by hexacyanoferrate (III) ion [$Fe(CN)_6^{3-}$] with ruthenate (VI) ion (RuO_4^{2-})

as catalyst.[10] For this reaction, the rate of disappearance of hexacyanoferrate (III)

is $$r = \frac{[Fe(CN)_6]^{2-}}{k_\alpha + k_\beta[Fe(CN)_6]^{2-}}$$

This is zero-order with respect to hexacyanoferrate (III) at the onset of the reaction (when its concentration is high and the ruthenium catalyst is quickly regenerated), but changes to first-order when its concentration decreases and the regeneration of catalyst becomes rate-determining.

Negative order[edit]

A reaction rate can have a negative partial order with respect to a substance. For example the conversion of ozone (O_3) to oxygen fonolloireactws the rate

equation $$r = k\frac{[O_3]^2}{[O_2]}$$ in an excess of oxygen. This corresponds to second order in ozone and order (-1) with respect to oxygen.

When a partial order is negative, the overall order is usually considered as undefined. In the above example for instance, the reaction is not described as first order even though the sum of the partial orders is 2 + (-1) = 1, because the rate equation is more complex than that of a simple first-order reaction.

ACTIVITY

Determine the order of hydrolysis of cane sugar.

Instant diagnostic assignment

1. what is order of reaction ?

2.Differentiate between first and second order of reaction ?

3. How rate of reaction is determimed ?

level1.

1 .List the factors on which the rate of a chemical reaction depends?

2.   What is meant by i) order ii) molecularity of a reaction.

3.   A reaction is of first order in A and of second order in B. Write the differential rate equation.

level 2

1. Why do reaction rate depend on the temperature . Explain.

2. For an elementary reaction , 2A +B->3C the rate of the appearance of C at a time 'T' is 1.3*10-4 mol/l/s. Calculate at this time i) rate of the reactionii)rate of disappearance of 'A'?

3. What is meant by rate constant 'k' of a reaction ?If the concentration be expressed in mol/l units and time in second. What would be the units for 'K'.i) for a Zero order reaction ii) For a first order reaction?

level 3

1. A certain reaction is 50% complete in 20 min at 300 K and the same reaction is again 50% complete in 5min at 350 K. Calculate the activation energy if it is a first order reaction?(R=8.314J/K/mol, log 4=0.6021)

2. A first order reaction has a rate constant of 1.15*10 $^{-3}$/sec . How long will it take for5g of this to reduce to 3g?

3. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at constant vol.-> SO_2Cl_2->SO_2 +Cl_2

Exp.	TIME(s)	TOTAL PRESSURE(atm)
	0	0.5
1		

	100	0.6
2		