

# Lecture 13

Pseudo first and second order reactions

An expression for second order reaction



Can be written as,

$$-dA/dt = k [A]^2$$

And the integration,

$$\int -1/A^2 dA = k dt$$

$$1/A_t - 1/A_0 = kt$$

This integration is rather easy. The amount of reactant present at any time can be calculated knowing k.

Look at the expression,  $-dA/dt = k [A] [B]$

**is not very easy.** If there is a relation between the concentration of A and B, an expression could be derived since,

$$dA/dt = d(A-x)/dt = -dx/dt$$

$$dx/dt = k (A)_t (B)_t = k (A-x) (B-x)$$

Integrating

$$kt = [1/A_0 - B_0] \ln [(A)_t (B)_0 / (A)_0 (B)_t]$$

This kind of expressions gets complicated as the relation between compositions of the reacting species gets complex.

Simplification by **Ostwald's isolation method.**

This depends on the approximation that when the reactant is present in large excess, the concentration is hardly changed during the course of the reaction.  $-dA/dt = k [A] [B]$  gets reduced to  $-dA/dt = k'[A]$  when B is present in large excess  $B_o \approx B_t$ .

$$k_t = [1/A_o - B_o] \ln [(A_t) (B_o) / (A_o) (B)_t]$$

This is the pseudo first order rate law.

The third order rate law

$$-dA/dt = k [A^2] [B]$$

Reduces to pseudo first order, if A is present in excess.

If B is in excess, it becomes pseudo second order.

## Reactions in stages

It is generally accepted that third order reactions are hard to occur. Higher order reactions (more than three) are very rare, may not even occur. In reactions it is necessary for the reacting species to come close in a particular geometry at one instant. This is rather difficult for three or more molecules.

Then how is that third order reactions are occurring?

The fact that in all of the third order reactions NO is an ingredient seems to suggest that an intermediate reagent involving NO is taking part. The dimer of NO,  $(\text{NO})_2$  is long-lived. Thus it can take part in the reaction like,



The reaction is kinetically third order since rate dependence on the square of the NO concentration.

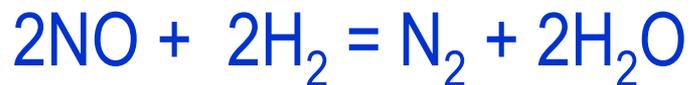
Concept of intermediate

Valid in solutions also

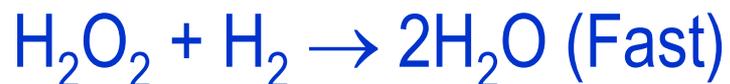
Reactions may happen in steps!

This simplifies equations.

The reaction of NO and H<sub>2</sub> forming N<sub>2</sub> and H<sub>2</sub>O seems to occur in two states.



The steps appear to be,



→ Indicates intermediate stage although the exact nature of the intermediate steps is not clear, it appears that one step involves 2NO and H<sub>2</sub>.

In the case of a complex reaction, the rate is determined by the slowest process.

It could be any one of the steps.

All the kinetic studies have shown that even for the moderately complex reactions, the reaction occurs in stages. The stoichiometric reaction does not always represent the true reaction.

From the stoichiometric reaction, it is hard to arrive at the mechanism of the reaction as well. How would one understand the mechanism of a reaction from the rate? Let us consider the following reaction. It involves the hydrolysis of an ester in dilute acid medium. The reaction rate is independent of the anion for strong acids. This shows that the hydrolysis of the ester is essentially catalysed by protons.

# Determination of the order of reactions

## Method of trial

Order of the reaction is the one corresponding to the best formula.

**Graphical method** can be adopted if data at number of time intervals is available.

For first order,  $t = \text{constant} - (2.303/k) \log c$

For order,  $n$   $t = \text{constant} + [1/k(n-1)] 1/c^{n-1}$

Plot of  $t$  vs.  $1/c^{n-1}$  should give a straight line.  $1/c$  for second and  $1/c^2$  for third.

Thus one can write the first probable reaction.



At any acid concentration, the rate depends only on the concentration of the ester. Thus one can say that the equilibrium lies to the left.

Otherwise the acidity decreases upon addition of further acid.

We know that the reaction is first order in both the ester and the acid.

We suggest the following mechanism,



the reaction involves the breakage of covalent O – R' bond.

This is slow. The next step involves the regeneration of acid, since it is a catalyst.



This reaction almost goes to completion. In these steps it can be seen that step 2 is the rate limiting step.

# Time to complete a definite fraction of the reaction

For a reaction of order  $n$ , the time to complete half the

$$t_{0.5}^n = \text{constant} * 1/c_0^{n-1}$$

Time required to decompose half the reactants is constant for first order. In general it is proportional to  $1/c_0^{n-1}$ . In other words  $t_{0.5} * c_0^{n-1}$  is a constant.

By varying the initial concentration of the reactants and measuring the time taken for a definite fraction to decompose, one can determine the order.

# Differential method

$$-dc_1/dt = kc_1^n \qquad -dc_2/dt = kc_2^n$$

Where  $c_1$  and  $c_2$  are two different concentrations of the reactants.

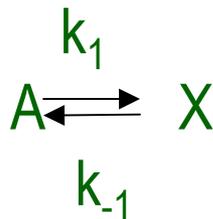
Take log and subtract

$$n = [\log(-dc_1/dt) - \log(-dc_2/dt)] / [\log c_1 - \log c_2]$$

$dc_1/dt$  and  $dc_2/dt$  can be determined by plotting con.  $c$  against time and taking slope ( $dc/dt$ ) at two different concentrations. Plot of  $\log(-dc/dt)$  against  $\log(c)$  gives  $n$ . Alternatively one can determine  $-dc/dt$  at two concentrations and insert in the equation. The results are independent of concentration units if all are expressed similarly.

# Opposing Reactions

Reactions may proceed to a state of equilibrium which differs appreciably from completion. The simplest case of this occurs when both forward and reverse reactions are of the first order, so that the situation can be represented as,



Assume that  $k_1$  and  $k_{-1}$  are the rate constants in the forward and reverse directions. If the experiment is started using pure A, of concentration  $a_0$ , and if after the time  $t$  the concentration of X is  $x$ , then that of A is  $a_0 - x$ . The net rate of production of X is ,

$$dx/dt = k_1(a_0 - x) - k_{-1}x \quad (1)$$

X is being produced by the forward reaction (first term) and removed by the reverse reaction (second term). If  $x_e$  is the concentration of X at equilibrium, when the net rate of reaction is zero,

$$0 = k_1(a_0 - x_e) - k_{-1}x_e \quad (2)$$

Which rearranges to

$$k_{-1} = k_1(a_0 - x_e)/x_e$$

Substitution of this expression in Eq. (1) gives rise to,

$$dx/dt = (k_1 a_0 / x_e) (x_e - x)$$

Integration of this equation, using the fact that  $x = 0$  when  $t = 0$ , gives

$$k_1 = x_e/a_0 t [\ln x_e/(x_e - x)] \quad (3)$$

If  $x_e$  is known, it is possible to calculate  $k_1$  from measurements of  $x$  as a function of the time.

For certain purposes it is convenient to have this equation in a different form.

From (2),

$$x_e(k_1 + k_{-1}) = k_1 a_0$$

$$x_e/a_0 = k_1/(k_1 + k_{-1})$$

Equation (3) may therefore be written as

$$k_1 = k_1/(k_1 + k_{-1}) \cdot 1/t \ln x_e/(x_e - x)$$

or

$$k_1 + k_{-1} = 1/t \ln x_e/(x_e - x) \quad (4)$$

Comparison of this equation with that for a simple first-order reaction shows that the two are formally analogous,  $x_e$  replacing  $a_0$ , and  $k_1 + k_{-1}$  replacing  $k$ .

Here it has been assumed that the initial concentration of the product X is zero. If this is not the case, and the initial concentrations of A and X are  $a_0$  and  $x_0$ , the net rate at time t is given by,

$$dx/dt = k_1(a_0 - x) - k_{-1}(x + x_0)$$

By methods similar to those used earlier it can be shown that this equation integrates to

$$k_1 + k_{-1} = 1/t \ln [(k_1 a_0 - k_{-1} x_0)/(k_1 a_0 - k_{-1} x_0 - (k_1 + k_{-1})x)] \quad (5)$$

The concentration  $x_e$ , at equilibrium, is defined by

$$x_e = (k_1 a_0 - k_{-1} x_0)/(k_1 + k_{-1})$$

Equation (5) reduces to

$$k_1 + k_{-1} = 1/t \ln x_e/(x_e - x)$$

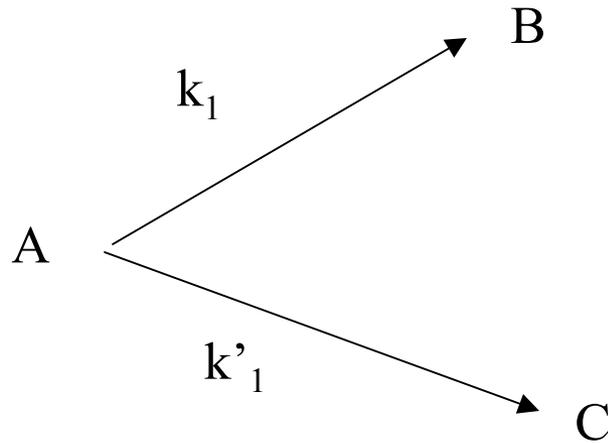
which is the same as Eq. (4)

# RATE EQATIONS FOR OPPOSING REACTIONS

Stoichiometric equation	Rate equation	Integrated rate equation
$A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1}x$	
$A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1}(x + x_0)$	$x_e/a_0 \ln x_e/x_e - x = k_1 t$
$2 A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1} x/2$	
$A \rightleftharpoons 2X$	$dx/dt = k_1(a_0 - x/2) - k_{-1}x$	
$A \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x) - k_{-1}x^2$	$x_e/(2a_0 - x_e) \ln a_0 x_e + x(a_0 - x_e)/a_0(x_e - x) = k_1 t$
$A + B \rightleftharpoons X$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}x$	$x_e/(a_0^2 - x_e^2) \ln x_e(a_0^2 - x x_e)/a_0^2(x_e - x) = k_1 t$
$A + B \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}x^2$	$X_e/2a_0(a_0 - x_e) \ln x(a_0 - 2x_e) + a_0 x_e/a_0(x_e - x)$
$2 A \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}(x/2)^2$	

# Parallel Reactions

These reactions are those in which the reacting molecules convert through more than one channel yielding different sets of products. The reaction resulting in the product is known as the main or the major reaction and the other reactions are referred to as the side or parallel reactions. To calculate the overall rate, the rate of the side reactions should be taken into account. Consider a reaction,

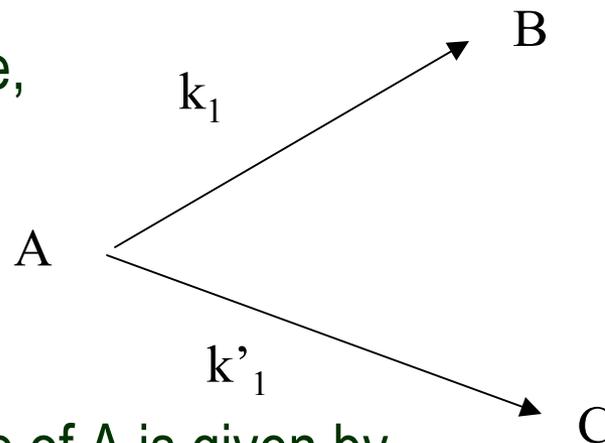


The rates these two reactions are,

$$d[B]/dt = k_1[A]$$

and

$$d[C]/dt = k'_1[A]$$



The overall rate of disappearance of A is given by

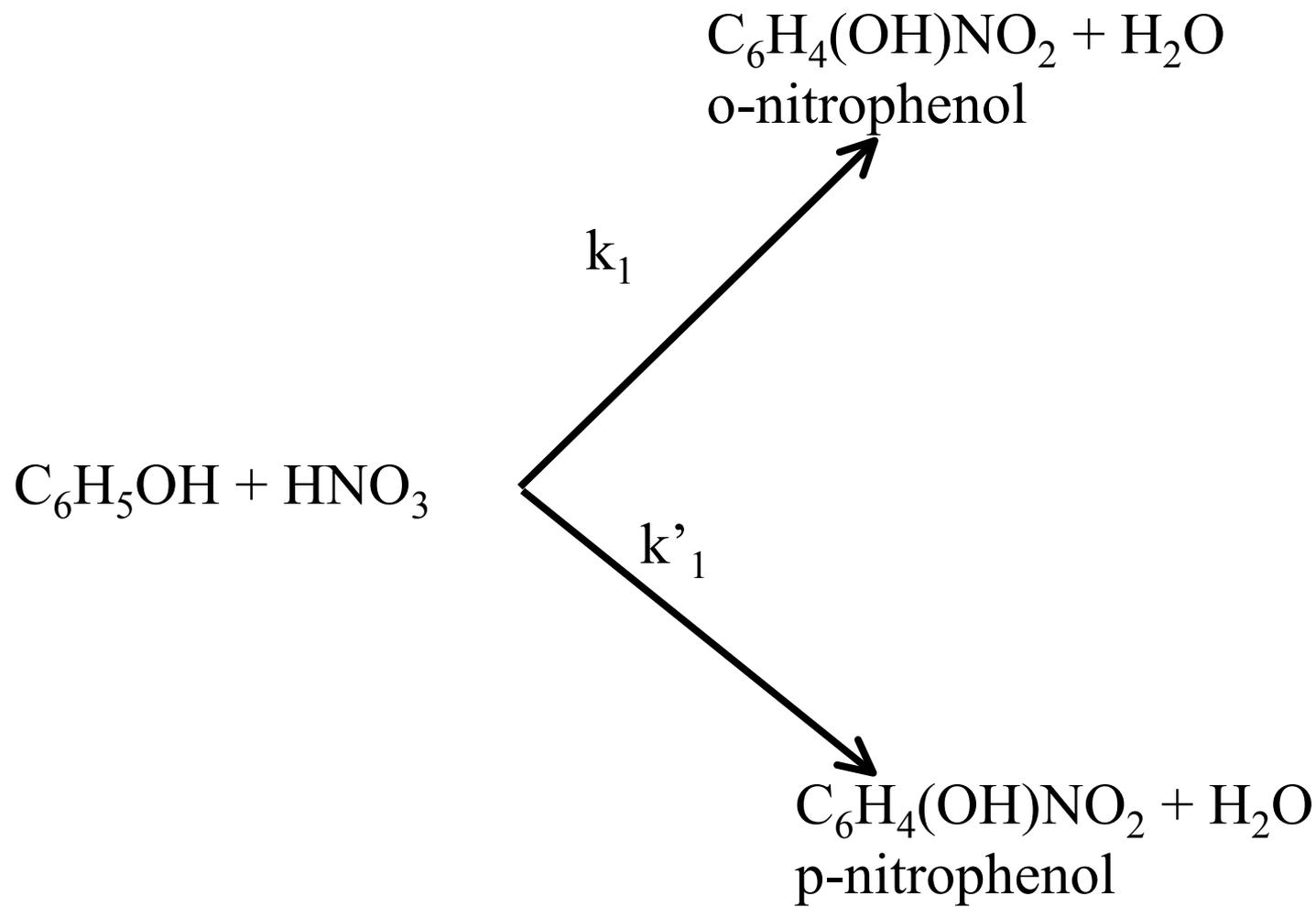
$$\begin{aligned} -d[A]/dt &= k_1[A] + k'_1[A] \\ &= [k_1 + k'_1][A] \end{aligned} \quad (1)$$

The ratio of the two rates is given as

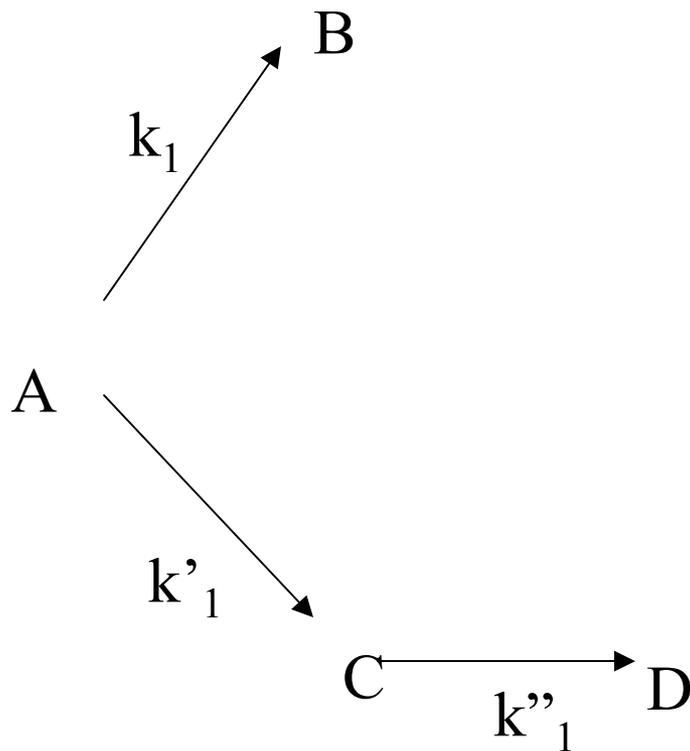
$$d[B]/dt / d[C]/dt = k_1/k'_1 \quad (2)$$

With the help of these equations (1 and 2), the rate constants for individual steps can be calculated.

An example of parallel reaction is the nitration of phenol.



The parallel reaction depicted above can get complicated. In the situation below, if  $k''_1$  is large in comparison to  $k'_1$ , all the C formed will become D immediately.



Therefore, the set of reactions actually will be just as the kind written in the beginning, instead of C, the product observed will be D. If  $k_1$  and  $k'_1$  have similar magnitude, amount of A and D formed will be the similar.

# Equilibrium constant and specific reaction rate

$$K = k/k'$$

This relation is already implied in,

$$k(a-x_e) = k'x_e$$

This values of  $k$  and  $k'$  derived from this equation cannot be used to calculate  $K$ . In general the values of  $k$  and  $k'$  can be determined by studying the rates of forward and backward reactions in the early states when the opposing reaction is negligible. The value of  $K$  can be determined by analysing the reacting system at equilibrium. The equilibrium constant determined from  $k$  and  $k'$  may not exactly correspond with the true equilibrium constant.

In the esterification of acetic acid by ethanol, if one wants to determine the equilibrium constant, first  $k$  for the forward reaction is measured assuring that the backward reaction is negligible. Similarly, the forward reaction rate constant of the hydrolysis of ethyl acetate is determined under identical conditions. Here again the reverse reaction is neglected. The equilibrium constant calculated, as the ratio of these rate constants vary slightly from the true value determined from the concentration.