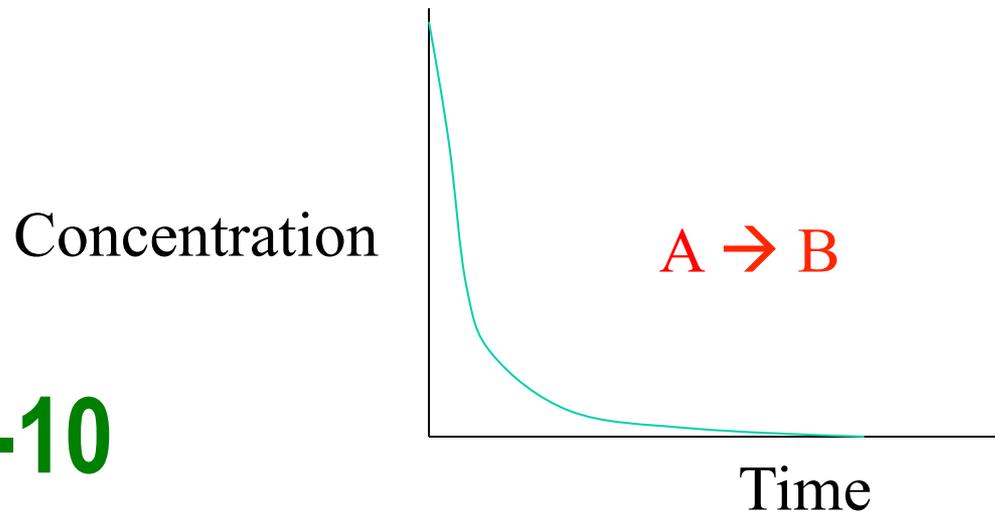


## Lecture 9-10

# Elementary chemical kinetics

Steady state approximation



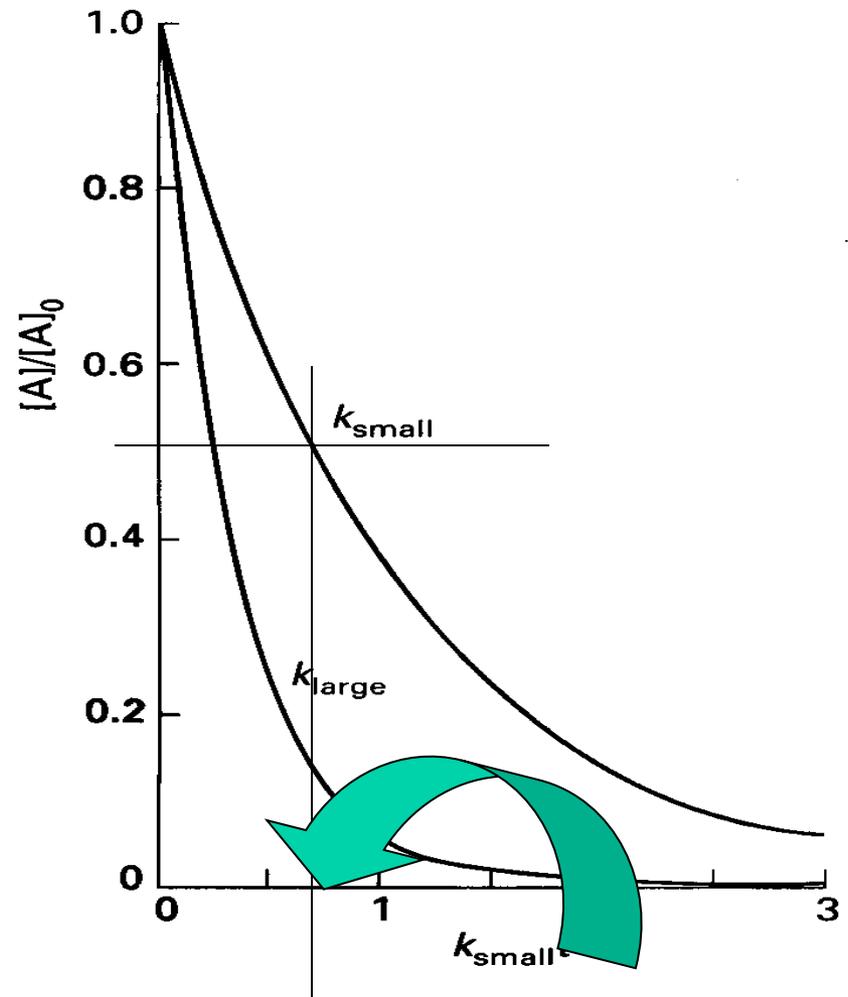
$$-d[C]/dt = k[C]$$

$$k = 1/t \ln (a/a-x)$$

A → Products

$$k = 1/t (1/C - 1/C_0)$$

$$1/n-1 [ 1/C^{n-1} - 1/C_0^{n-1} ] = kt$$



Half life

## RATE EQUATIONS FOR OPPOSING REACTIONS

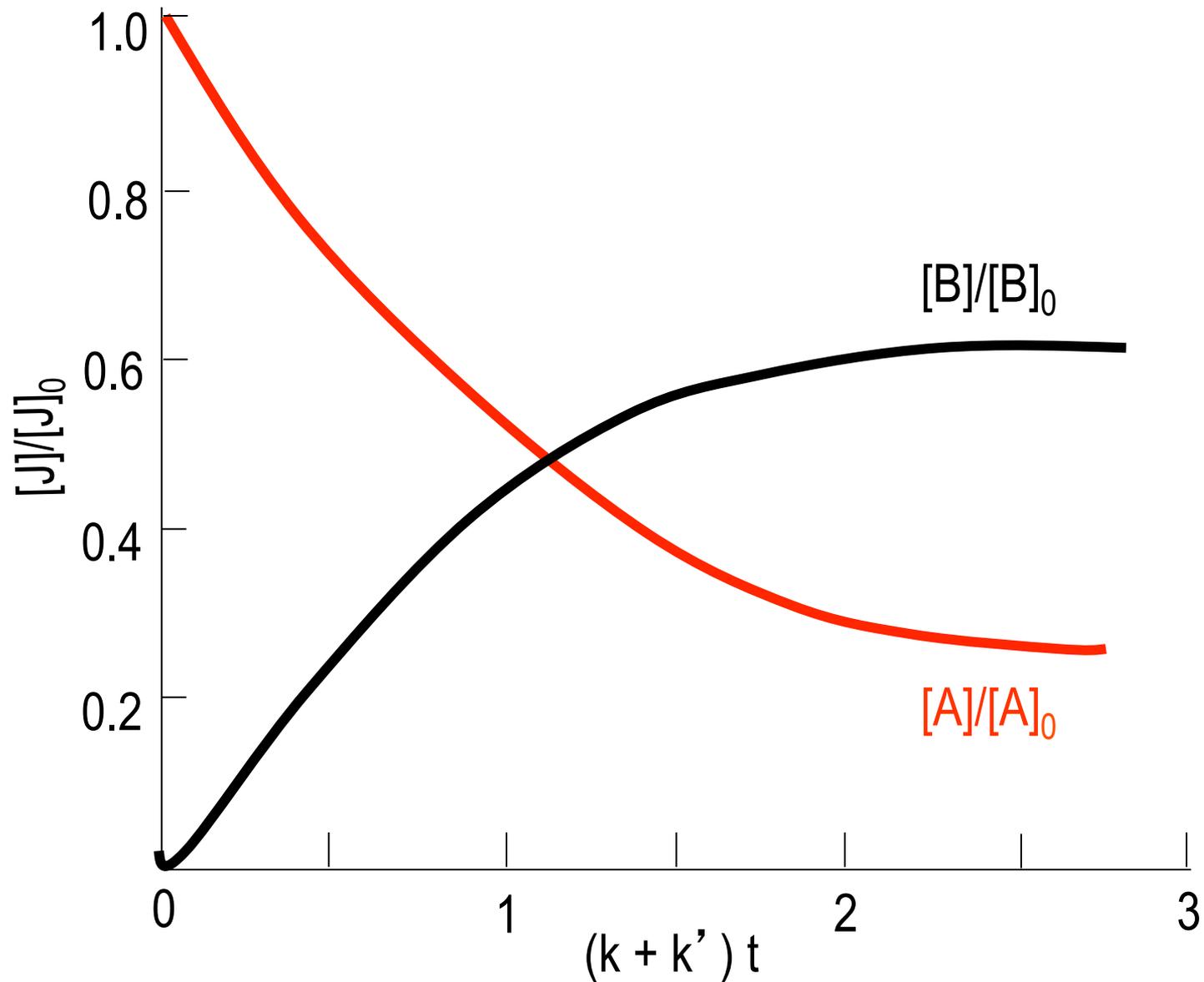
Stoichiometric equation	Rate equation	Integrated rate equation
$A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1}x$	
$A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1}(x + x_0)$	$x_e/a_0 \ln x_e/x_e - x = k_1t$
$2A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1}x/2$	
$A \rightleftharpoons 2X$	$dx/dt = k_1(a_0 - x/2) - k_{-1}x$	
$A \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x) - k_{-1}x^2$	$x_e/(2a_0 - x_e) \ln a_0x_e + x(a_0 - x_e)/a_0(x_e - x) = k_1t$
$A + B \rightleftharpoons X$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}x$	$x_e/(a_0^2 - x_e^2) \ln x_e(a_0^2 - xx_e)/a_0^2(x_e - x) = k_1t$
$A + B \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}x^2$	$x_e/2a_0(a_0 - x_e) \ln x(a_0 - 2x_e) + a_0x_e/a_0(x_e - x)$
$2A \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}(x/2)^2$	

In general, discussions of kinetics disregard reverse reaction. However, this is important when the product concentration is significant.

Consider the case of A going to B and the reaction is reversible.

At equilibrium,  $k[A]_{\text{eq}} = k'[B]_{\text{eq}}$ .

This rearranges to,  $K = [B]_{\text{eq}}/[A]_{\text{eq}} = k/k'$



This is the situation depicted in the figure where  $k = 2k'$ .

In a generalised situation involving multiple steps,

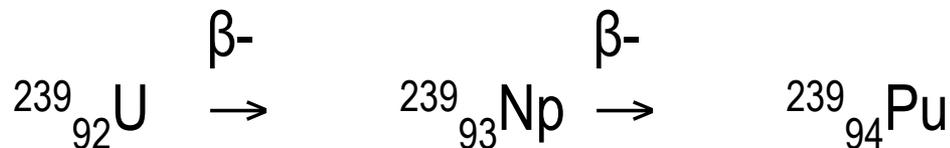
$$K = k_a/k_a' \cdot k_b/k_b' \cdot \dots$$

Where  $k_a$  refers to the forward reaction rate constant of the step a and  $k_a'$  refers to that of the reverse reaction.

Consider a consecutive reaction,



An examples would be,



The kinetics of this reaction can be studied in the following way,

For the first step,

$$1. \quad dA/dt = -k_1 A$$

$$2. \quad dB/dt = k_1 A - k_1' B \quad \text{since it forms from A and decomposes to C}$$

$$3. \quad dC/dt = k_1' B$$

Relation 1 corresponds to exponential decay. Suppose the concentration of A initially is  $A_0$

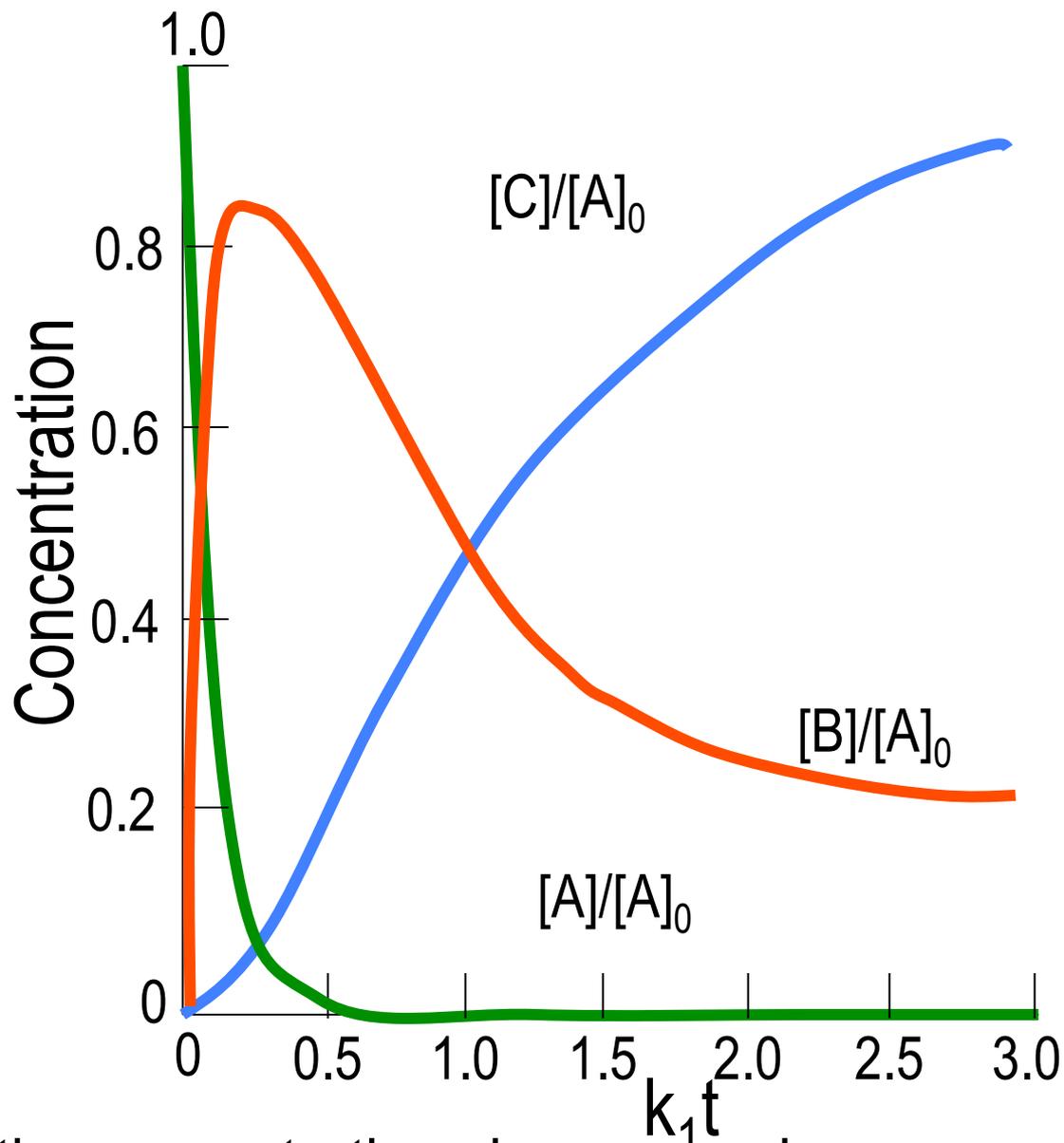
$$A_t = A_0 \exp(-k_1 t)$$

For relation 2, if a condition  $B_0 = 0$  is imposed, we get,

$$B_t = A_0 [k_1 / (k_1' - k_1)] (e^{-k_1 t} - e^{-k_1' t}) \quad (1)$$

At all times,  $[A] + [B] + [C] = A_0$

$$[C] = \left\{ 1 + \frac{[(k_1 e^{-k_1' t} - k_1' e^{-k_1 t}) / (k_1' - k_1)]}{k_1} \right\} A_0 \quad (2)$$



All the concentration change can be represented graphically for  $[A_t]$ ,  $[B_t]$  and  $[C_t]$  using equations,  $k_1 = 10k_1'$ .

Let us assume that  $k_1' \gg k_1$ . Then every molecule of B formed will decay to C quickly. Then the rate of formation of C depends on the formation of B.

Look at the earlier equation:

$$[C] = \left\{ 1 + \frac{[(k_1 e^{-k_1' t} - k_1' e^{-k_1 t})]}{(k_1' - k_1)} \right\} A_0 \quad (2)$$

If  $k_1' \gg k_1$ ,  $e^{-k_1' t}$  is much smaller than  $e^{-k_1 t}$  and may be neglected.  $k_1' - k_1 = k_1'$

$$C \sim A_0 (1 - e^{-k_1 t})$$

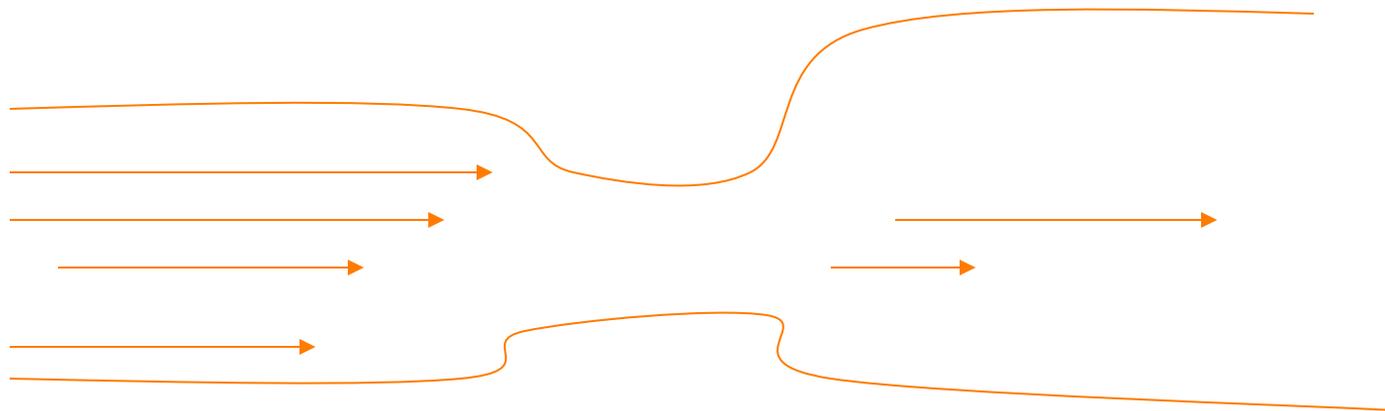
when  $k_1$  in the denominator is neglected in comparison with  $k_1'$ .

The concentration of C depends on smaller rate coefficient. The step with smaller rate constant is called the rate determining step.

If  $k_1' \ll k_1$

$$C \sim A_0 (1 - e^{-k_1't})$$

**Rate depends upon the rate determining reaction.**



Look at the rapidity with which equations become complex. Can we reduce the complexity?

Let us assume that  $k'_1 \gg k_1$ . Then for the equation of  $B_t$ ,

$$B_t = A_0 [k_1 / (k'_1 - k_1)] (e^{-k_1 t} - e^{-k'_1 t}) \quad (1)$$

it can be seen that the concentration of  $B_t$  is lesser than that of  $A$  by a factor  $k_1 / k'_1$ .

Thus if  $A$  reacts slowly, it can be seen that the concentration of  $A$  remains at the same constant value for a long time such that,  $dB/dt \sim 0$

This is not true only in the beginning of the reaction. The assumption the major part of the reaction takes place when the reagent concentration is constant is called the **steady state approximation**.

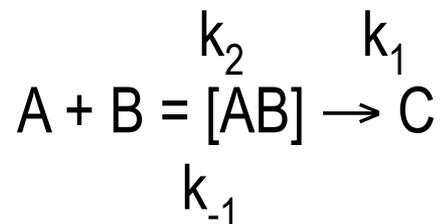
Thus the  $dB/dt$  equation ( $dB/dt = k_1 A - k'_1 B$ ) reduces to,

$$k_1 A - k'_1 B \sim 0$$

$$B \approx (k_1 / k'_1) A$$

Thus,  $dC/dt = k_1' B \sim k_1 A$

Similar type of equation can be used when intermediate attains equilibrium with the reactants called pre equilibrium.



If the intermediate reacts slowly to form C,  $k_1$  can be neglected in the rate equation.

$$d[AB]/dt \sim k_2 [A] \cdot [B] - k_{-1} [AB]$$

If intermediate is in a **steady state**,

$$k_2 [A] \cdot [B] - k_{-1} [AB] = 0$$

or

$$[AB] = k_2/k_{-1} [A] \cdot [B]$$

but,  $[AB] = K [A] \cdot [B]$  ←  $K = \text{equilibrium constant}$

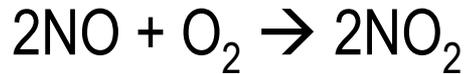
Thus,  $dC/dt = k_1 K [A] \cdot [B]$  or  $dC/dt = k_1 k_2 / k_{-1} [A] \cdot [B]$

Thus, the reaction is overall second order.

Using steady state

Using equilibrium constant

Let us look at an example.

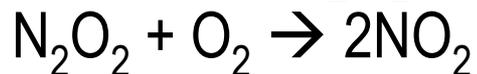


the reaction shows third order kinetics. The assumption that the reaction is termolecular does not appear correct since the reaction rate decreases with temperature which should have increased trimolecular collisions.

Thus we can assume it to involve steps.

Assume the pre equilibrium.

$\text{NO} + \text{NO} = \text{N}_2\text{O}_2$ , the equilibrium constant is K



Applying steady state to  $\text{N}_2\text{O}_2$

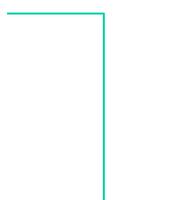
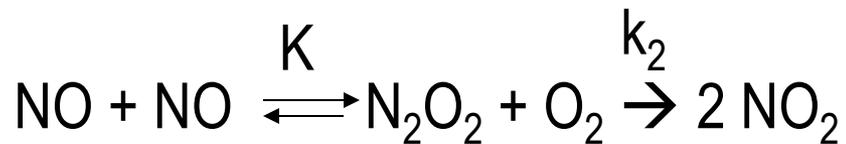
$$[\text{N}_2\text{O}_2] = K [\text{NO}]^2$$

$$\begin{aligned} d[\text{NO}_2]/dt &= k_2 [\text{N}_2\text{O}_2] [\text{O}_2] \\ &= k_2 K [\text{NO}]^2 [\text{O}_2] \end{aligned}$$

this is third order rate law

$$k_3 = k_2 K$$

The temperature dependence is also explained this way. Although  $k_2$  increases with  $T$ ,  $K$  decreases because the dimerisation is exothermic.



Pre-equilibrium

Kinetic control



$$\text{Rate 1/Rate 2} = k_1/k_2$$

Kinetic control

Thermodynamic control

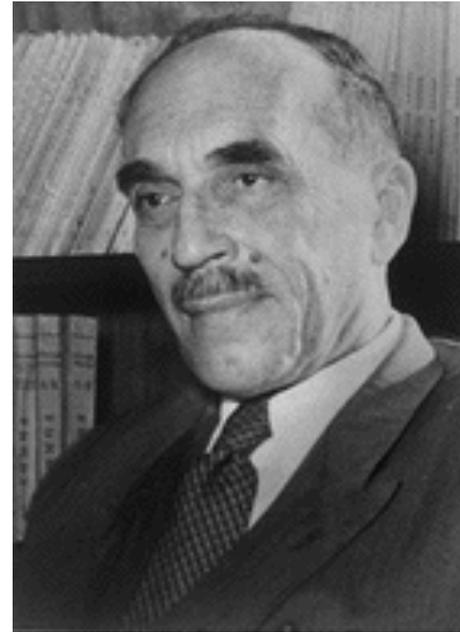
## Applications of this concept

Enzyme kinetics **Michaelis-Menten Mechanism**

Unimolecular reactions

Radical reactions

# Complex reactions



Nikolai Nikolaevic Semenov  
1896-1986, Nobel 1956

Complex reactions, explosions  
Oscillations and chaos  
Belousov-Zhabotinskii reaction

Chain reactions are examples of complex reactions, with complex rate expressions.

In a chain reaction, the intermediate produced in one step generates an intermediate in another step.

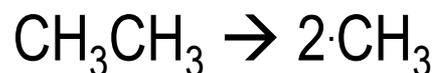
This process goes on.

Intermediates are called **chain carriers**. Sometimes, the chain carriers are radicals, they can be ions as well. In nuclear fission they are **neutrons**.

There are several steps in a chain reaction.

## 1. Chain initiation

This can be by **thermolysis** (heating) or **photolysis** (absorption of light) leading to the breakage of a bond.



## 2. Propagation

In this, the chain carrier makes another carrier.



### 3. Branching

One carrier makes more than one carrier.



(oxygen has two unpaired electrons)

### 4. Retardation

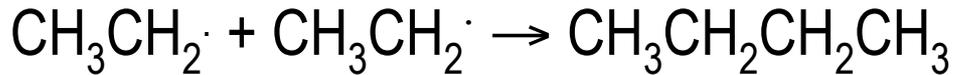
Chain carrier may react with a product reducing the rate of formation of the product.



Retardation makes another chain carrier, but the product concentration is reduced.

## 5. Chain termination

Radicals combine and the chain carriers are lost.



## 6. Inhibition

Chain carriers are removed by other processes, other than termination, say by foreign radicals.



All need not be there for a given reaction.

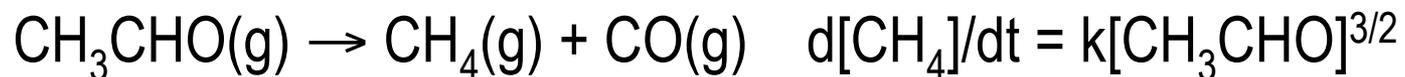
Minimum necessary are,

Initiation, propagation and termination.

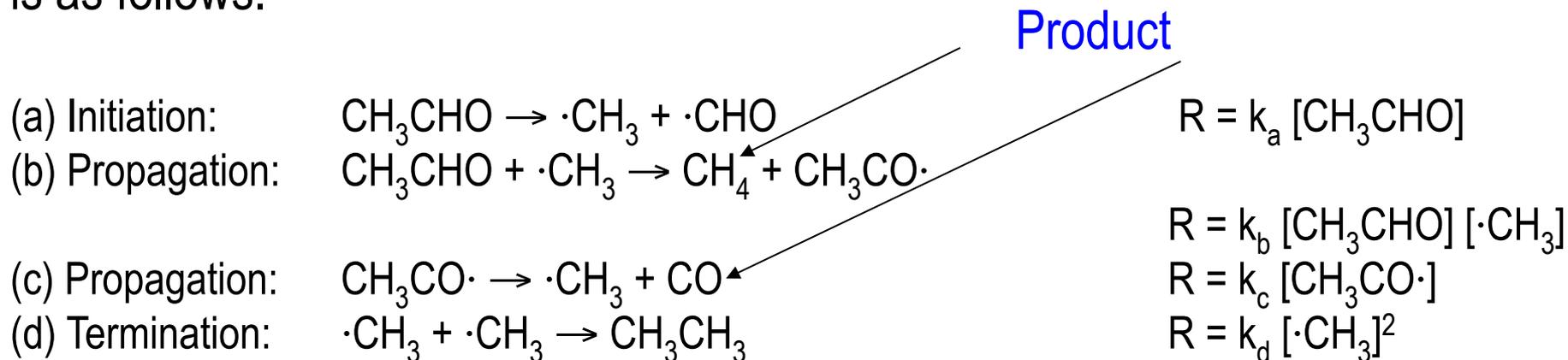
# How do we account for the rate of laws of chain reactions?

Look at the thermal decomposition of acetaldehyde. This appears to follow three-halves order in acetaldehyde.

Overall reaction,



The mechanism for this reaction known as **Rice-Herzfeld mechanism** is as follows.



Although the mechanism explains the principal products, there are several minor products such as acetone ( $\text{CH}_3\text{COCH}_3$ ) and propanal ( $\text{CH}_3\text{CH}_2\text{CHO}$ ).

The rate equation can be derived on the basis of **steady-state approximation**. The rate of change of intermediates may be set equal to zero.

$$\begin{aligned} d[\cdot\text{CH}_3]/dt &= k_a[\text{CH}_3\text{CHO}] - k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k_c[\text{CH}_3\text{CO}\cdot] \\ &\quad - 2k_d[\cdot\text{CH}_3]^2 = 0 \end{aligned}$$

$$d[\text{CH}_3\text{CO}\cdot]/dt = k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k_c[\text{CH}_3\text{CO}\cdot] = 0$$

The sum of the two equation is,

$$k_a[\text{CH}_3\text{CHO}] - 2k_d[\cdot\text{CH}_3]^2 = 0$$

The steady-state concentration of  $\cdot\text{CH}_3$  radicals is,

$$[\cdot\text{CH}_3] = (k_a/2k_d)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

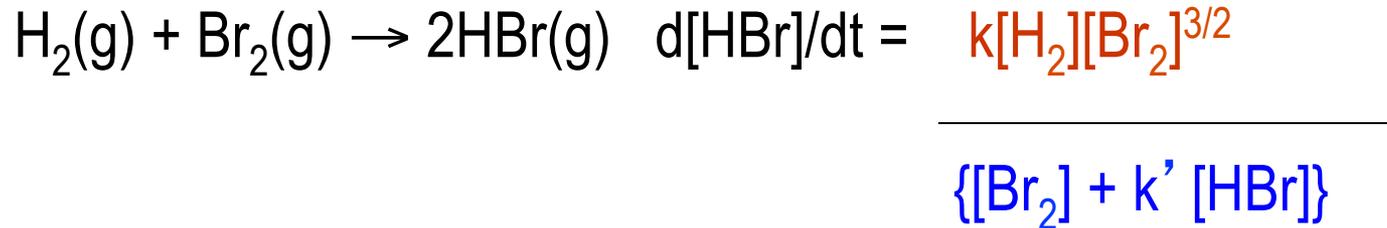
It follows that the rate of formation of  $\text{CH}_4$  is

$$d[\text{CH}_4]/dt = k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] = k_b (k_a/2k_d)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Thus the mechanism explains the observed rate expression. It is sure that the true rate law is more complicated than that observed experimentally.

There are several cases where the reaction is complicated.

An example is,



The following mechanism has been proposed to account for this rate law.

- (a) Initiation:  $\text{Br}_2 + \text{M} \rightarrow \text{Br}\cdot + \text{Br}\cdot + \text{M}$      $R = k_a[\text{Br}_2][\text{M}]$   
where M is either  $\text{Br}_2$  or  $\text{H}_2$ .
- (b) Propagation:  $\text{Br}\cdot + \text{H}_2 \rightarrow \text{HBr} + \text{H}\cdot$      $R = k_b[\text{Br}\cdot][\text{H}_2]$   
 $\text{H}\cdot + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}\cdot$      $R = k'_b[\text{H}\cdot][\text{Br}_2]$
- (c) Retardation:  $\text{H}\cdot + \text{HBr} \rightarrow \text{H}_2 + \text{Br}\cdot$      $R = k_c[\text{H}\cdot][\text{HBr}]$
- (d) Termination:  $\text{Br}\cdot + \text{Br}\cdot + \text{M} \rightarrow \text{Br}_2 + \text{M}^*$      $R = k_d[\text{Br}\cdot]^2 [\text{M}]$

The third body collision removes the excess energy.

There can be other recombinations also, such as H. + H. and H. + Br..

The net rate of formation of HBr is,

$$d[\text{HBr}]/dt = k_b[\text{Br}\cdot][\text{H}_2] + k'_b[\text{H}\cdot][\text{Br}_2] - k_c[\text{H}\cdot][\text{HBr}]$$

We can apply steady state.

$$d[\text{H}\cdot]/dt = k_b[\text{Br}\cdot][\text{H}_2] - k'_b[\text{H}\cdot][\text{Br}_2] - k_c[\text{H}\cdot][\text{HBr}] = 0$$

$$d[\text{Br}\cdot]/dt = 2k_a[\text{Br}_2][\text{M}] - k_b[\text{Br}\cdot][\text{H}_2] + k'_b[\text{H}\cdot][\text{Br}_2] + k_c[\text{H}\cdot][\text{HBr}] - 2k_d[\text{Br}\cdot]^2 [\text{M}] = 0$$

$$[\text{Br}\cdot] = (k_a/k_d)^{1/2} [\text{Br}_2]^{1/2}$$

$$[\text{H}\cdot] = k_b(k_a/k_d)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2} / \{k'_b[\text{Br}_2] + k_c[\text{HBr}]\}$$

Substitute in the HBr rate law.

$$d[\text{HBr}]/dt = 2k_b(k_a/k_d)^{1/2}[\text{H}_2][\text{Br}_2]^{3/2}/\{[\text{Br}_2] + (k_c/k'_b)[\text{HBr}]\}$$

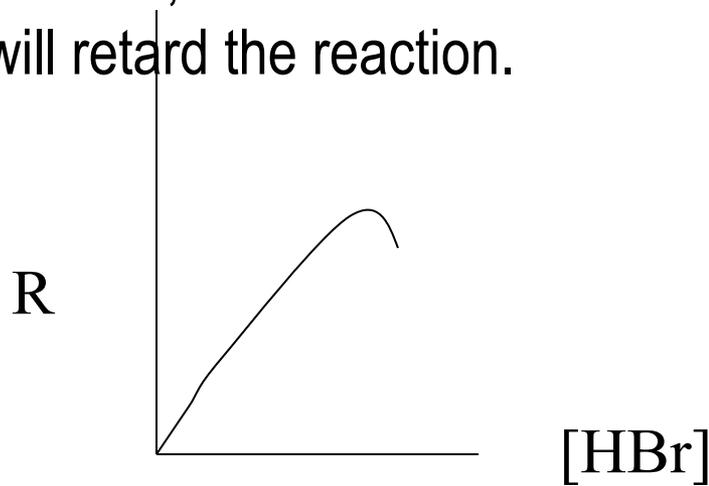
If it is compared with the experimental rate law one can see,

$$k = 2k_b(k_a/k_d)^{1/2} \quad k' = k_c/k'_b$$

Presence of **HBr in the denominator** indicates that it is an **inhibitor**.

Presence of  $\text{Br}_2$  in the denominator is because of the fact that its presence removes reactive radicals from the chain mechanism.

If we plot HBr concentration as a function of time, it will reach a maximum as increased presence of HBr will retard the reaction.



# **Applications of SSA**

**Michaelis-Menten Mechanism**

**Unimolecular reactions**

# Michaelis-Menten Mechanism of Enzyme Kinetics

Enzyme kinetics is very efficient.

Basic characteristics:

- 1. For a given substrate concentration  $[S]_0$ , initial rate is proportional to total enzyme concentration,  $[E]_0$ .
- 2. For a given  $[E]_0$  and  $[S]_0$ , rate is proportional to  $[S]$ .
- 3. For a given  $[E]_0$  and large  $[S]_0$ , rate is independent of  $[S]_0$  and reaches a max. called max. velocity.

M-M mechanism accounts for these features.



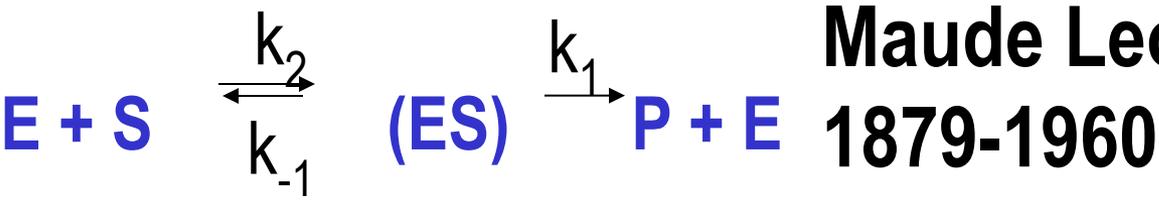
enzyme + substrate  $\rightarrow$  product + enzyme

Net  $S \rightarrow P$  but kinetics show that rate depends on E.

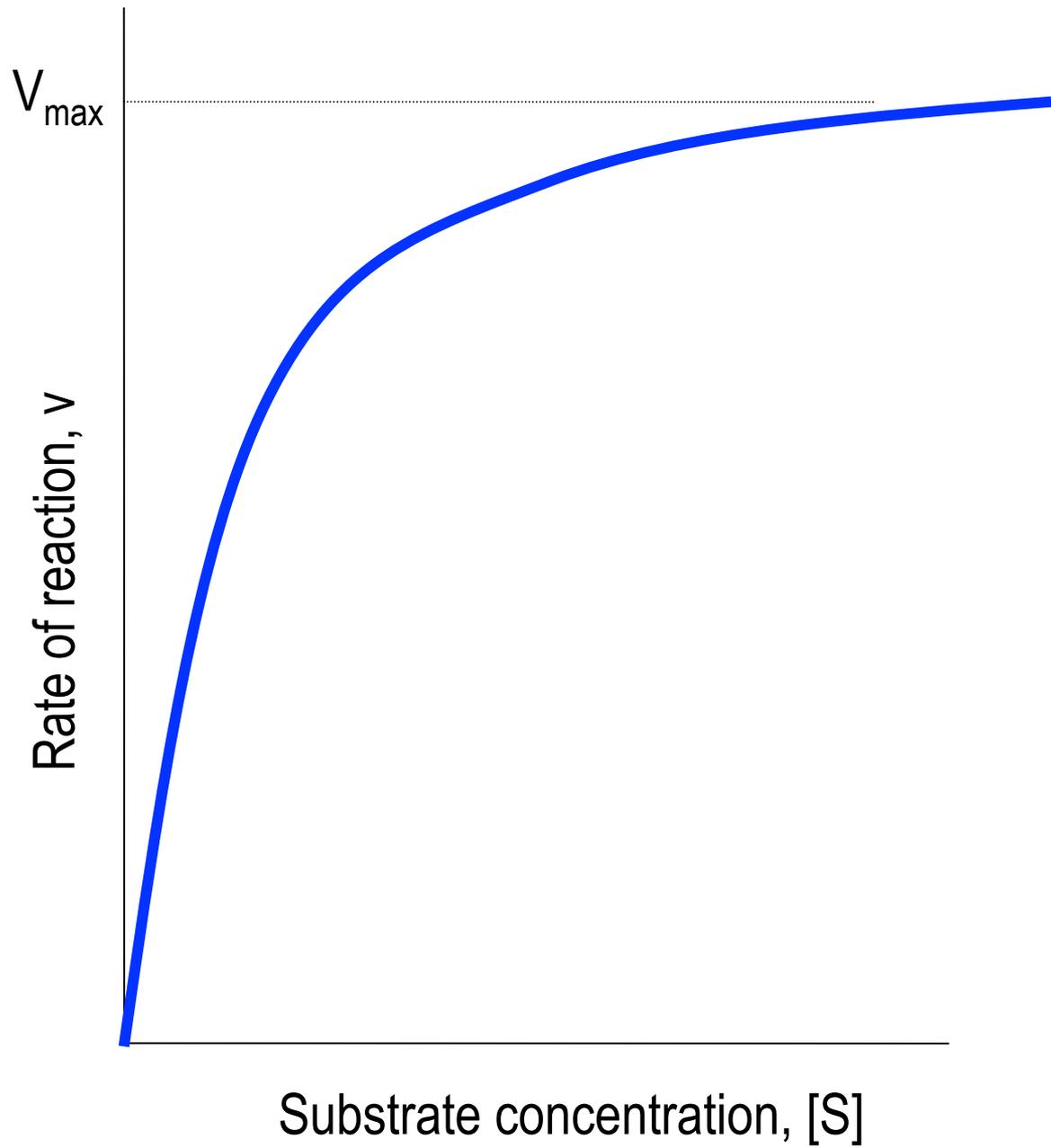
The mechanism,

**Leonor Michaelis 1875-1949**

**Maude Leonora Menten**



**1879-1960**



$$dP/dt = k_1 [ES]$$

$$d[ES]/dt = k_2[E][S] - k_{-1} [ES] - k_1 [ES]$$

at steady state,

$$k_2[E][S] - k_{-1} [ES] - k_1[ES] \sim 0$$

So,

$$[ES] \sim k_2 [E] [S] / \{k_1 + k_{-1}\}$$

[E] and [S] are the free enzyme and substrate concentrations. Enzyme is added only to a small quantity and  $[E] + [ES] = [E]_0$ , the initial enzyme concentration which is a constant. Only small amount of enzyme is added, and the concentration is much smaller than the substrate, free substrate

$$[S] \approx [S]_0$$

$$[ES] = k_2 \{[E]_0 - [ES]\} [S] / \{k_1 + k_{-1}\}$$

$$[ES] \{k_1 + k_{-1} + k_2[S]\} = k_2 [E]_0[S]$$

$$[ES] = k_2 [E]_0 [S] / \{k_1 + k_{-1} + k_2[S]\}$$

Thus,

$$dP/dt = k_1 k_2 [E]_0 [S] / \{k_1 + k_{-1} + k_2 [S]\}$$

Enzymolysis depends linearly on the amount of the enzyme added,

$$= k_1 [E]_0 [S] / \{K_M + [S]\} \quad (1)$$

where  $K_M = (k_1 + k_{-1})/k_2$

$K_M$  is the Michaelis constant. This is a constant for a given enzyme and a substrate pair. This mechanism for the mode of action was proposed by Michaelis and Menten in 1913 and therefore called, Michaelis and Menten mechanism of enzyme kinetics.

Equation (1) can be written as,

$$dP/dt = k [E]_0; \text{ where } k = k_1 [S] / \{K_M + [S]\} \quad (2)$$

Thus enzymolysis depends on the amount of enzyme.

Look at the condition,  $[S] \gg K_M$

$dP/dt = k_1 [E]_0$  and the reaction is zero order in S. Thus the rate is constant. When S is large, the change in substrate concentration is constant. The rate of formation of product is highest under this condition and  $k_1 [E]_0$  is called the **maximum velocity** of enzymolysis.  $k_1$  is called the **maximum turnover number**.

When  $[S] \ll K_M$ ,

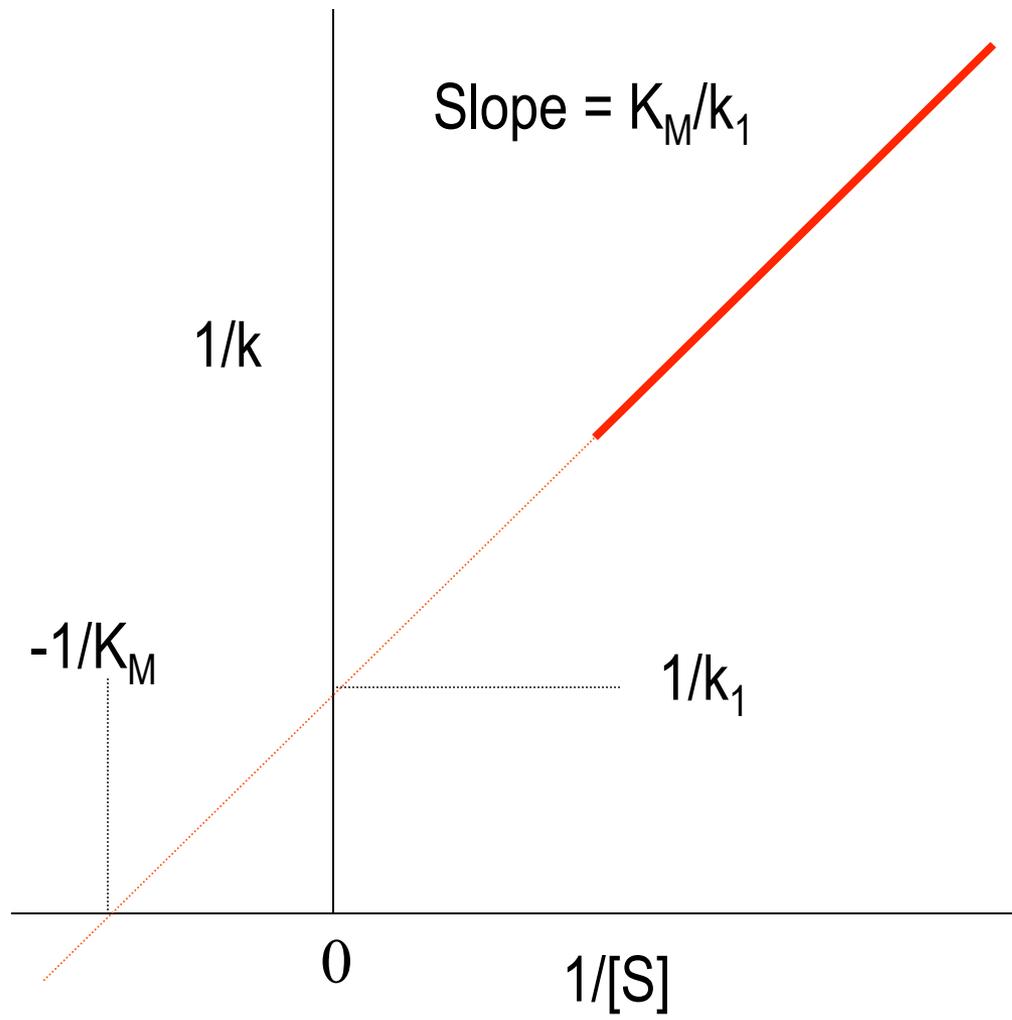
$$dP/dt = \{k_1/K_M\} [E]_0 [S]$$

Rate depends on both enzyme and substrate.

Equation (2) gives,

$$1/k = 1/k_1 + K_M/k_1 [S]$$

A plot of  $1/k$  vs.  $1/[S]$  will give intercept  $(1/k_1)$  when  $1/[S] = 0$ . The slope will give  $K_M/k_1$  and therefore  $K_M$ . The method will not give  $k_2$  and  $k_{-1}$ , separately. Additional data will be needed to evaluate these. This plot is called the **Lineweaver-Burk plot**.



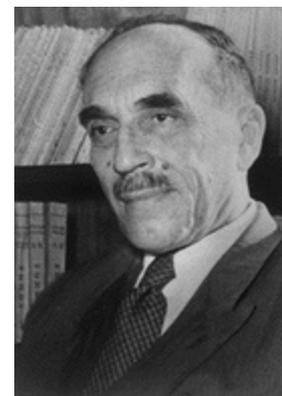
# Unimolecular Reactions

How do they occur?

Look at the following reaction.



Sir Cyril Hinshelwood  
1897-1967, Nobel 1956



Nikolai Nikolaevic Semenov  
1896-1986, Nobel 1956



These are unimolecular reactions.

The reactant molecules somehow have enough energy to react by themselves. How can energy transfer occur without collisions?

The first successful explanation of unimolecular reactions is by Frederick Lindemann in 1921 and elaborated later by Cyril Hinshelwood. This mechanism is called as Lindemann- Hinshelwood mechanism.

The generalised explanation is as follows.

The reactant molecule A gets activated by collisions with another molecule.



Collisions with other molecule can result in loss of this energy.



Some activated molecules may form products.



In case the unimolecular decay is slow, the net reaction is first order.

This can be demonstrated by applying steady state for the formation of  $A^*$ .

$$d[A^*]/dt = k_a[A]^2 - k'_a[A][A^*] - k_b[A^*] \approx 0$$

Solution is,

$$[A^*] = k_a[A]^2 / \{k_b + k'_a[A]\}$$

The rate law for the formation of P is,

$$d[P]/dt = k_b[A^*] = k_a k_b [A]^2 / \{k_b + k'_a [A]\}$$

As can be seen, the rate law is not first order.

The important aspect is the rate of deactivation of A\* by collisions with A is much larger than the rate of unimolecular decay.

$$k'_a [A^*][A] \gg k_b [A^*] \text{ or } k'_a [A] \gg k_b$$

Thus we can neglect  $k_b$  in the denominator and write,

$$d[P]/dt \approx k[A] \quad \text{where} \quad k = k_a k_b / k'_a$$

This is a first order rate law.

The rate expression also shows that when the concentration (partial pressure) of A is small, then  $k'_a [A] \ll k_b$ , we get

$$d[P]/dt \approx k_a [A]^2$$

If we write the rate expression as,

$$d[P]/dt = k[A]$$

where

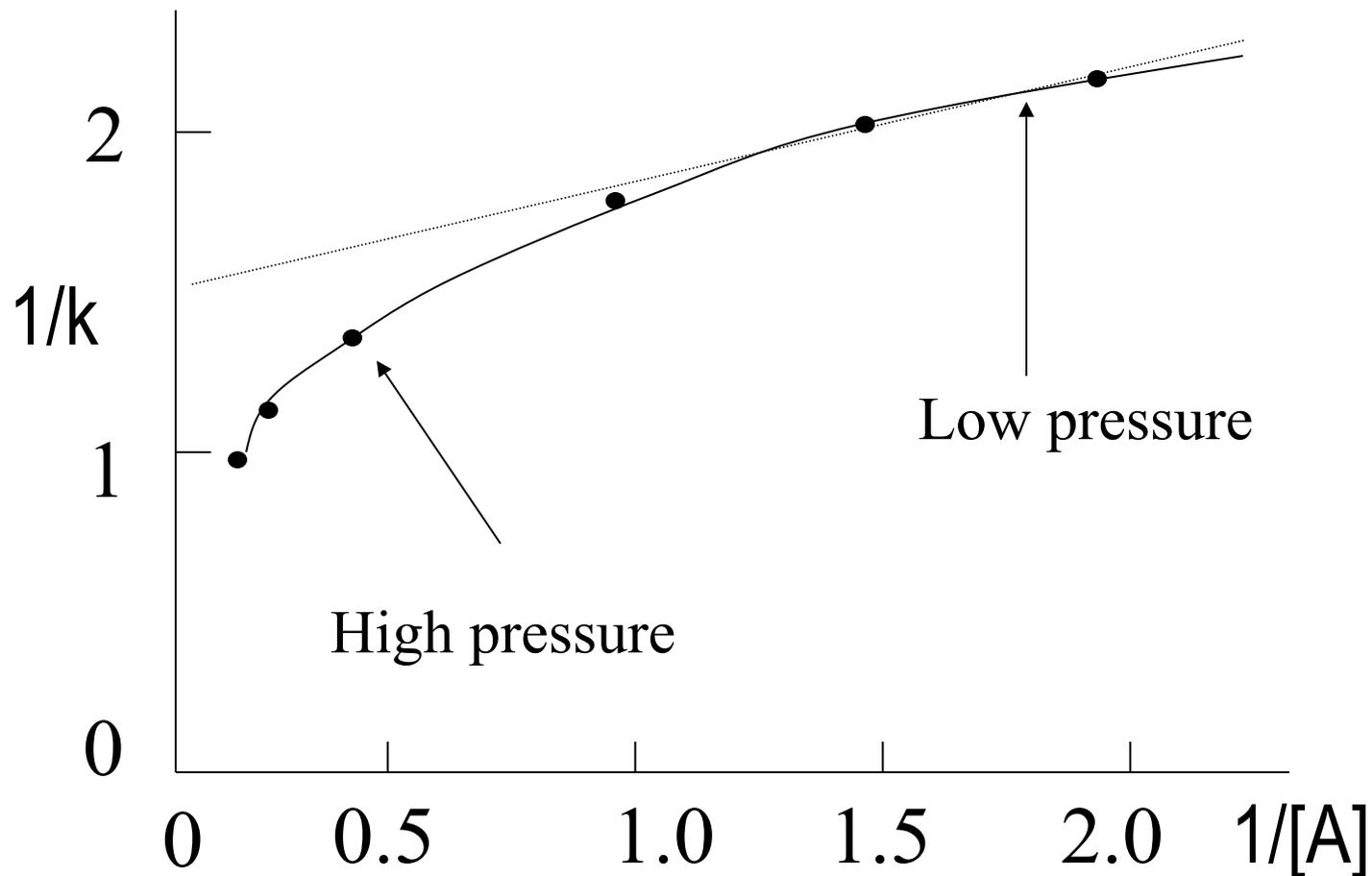
$$k = k_a k_b [A] / \{k_b + k'_a [A]\}$$



The effective rate constant

$$1/k = k'_a / (k_a k_b) + 1/k_a [A]$$

The test for the theory is to get a straight line for  $1/k$  vs.  $1/[A]$  plot.  
A typical plot is seen below.



The behaviour is in gross agreement with the theory. At high pressures (lower  $1/[A]$ ) the value of  $k$  higher (lower  $1/k$ ) than expected from a linear behaviour. The reaction studied is the unimolecular isomerization of trans-CHD=CHD. The Lindemann-Hinshelwood mechanism is the straight line, extrapolation from lower pressure (larger  $1/[A]$ ) to higher pressure (smaller  $1/[A]$ ).

Background material – not to be discussed in the class  
Review of concepts you know

Feasibility of processes?

Thermodynamics - thermodynamic state functions

Time dependence?

Chemical kinetics – rate equations

# A BRIEF HISTORY OF CHEMICAL KINETICS

Ref: "The World of Physical Chemistry," by K. J. Laidler, Oxford Univ. Press, 1993)

- 1850**: Wilhelmy (Germany) studied the rate of inversion of sucrose (hydrolysis into D-(+)-glucose and D-(-)-fructose in the presence of an acid) and found it to be proportional to the concentrations of both the sugar and the acid.
- 1864**: Guldberg and Waage (Norway) formulated their "law of mass action," according to which the reaction "forces" are proportional to the product of the concentrations of the reactants:  
$$K = \frac{[R]^r [S]^s}{[A]^a [B]^b}$$
 where a, b, r and s are the stoichiometric coefficients in the chemical equation  $A+B=R+S$ . So the rate of the forward reaction is proportional to  $[A]^a [B]^b$  and that of the reverse reaction is proportional to  $[R]^r [S]^s$ .
- 1865-67**: Harcourt and Esson (UK) analyzed the reactions between  $H_2O_2$  and HI and between  $KMnO_4$  and  $(COOH)_2$ . They wrote the corresponding differential equations, integrated them and determined the concentration vs. time relationships. They also proposed an equation for the temperature dependence of the reaction rate,  $k = A T^C$ . Mathematical expressions.
- 1884**: van't Hoff (The Netherlands) published his "Studies of Chemical Dynamics" (Études de dynamique chimique), in which he generalized and further developed the work of Wilhelmy, Harcourt and Esson. In particular, he introduced the differential method of analysis. He also analyzed the temperature dependence of the equilibrium constant (now called the "van't Hoff equation") and of forward and reverse reaction rates.
- 1887**: Ostwald (Germany; Latvia) introduces the terms "reaction order" and "half-life" in his "Lehrbuch der allgemeinen Chemie."
- 1889**: Arrhenius (Sweden) further analyzed the temperature dependence of reaction rate,  $k = A \exp(-B/T)$ , and gave it an "energy barrier" interpretation; this is now called the "Arrhenius equation."

Kinetics refers to a branch of mechanics dealing with the motion of particles without considering any external forces acting on the particles. This differs from dynamics which takes into account of the external forces acting on the particles.

In the gas phase, chemical kinetics can be treated in terms of the kinetic theory of gases and the statistical mechanics of isolated atoms. In the liquid phase, the molecules are closer and applications of molecular theories are difficult. In the liquid phase, many reactions are diffusion controlled and the rate constants depend upon the rate with which the reactants can diffuse together.

**Chemical reactions occur at a definite rate.**

**Slow... Fast....in kinetics.**

**One is concerned with reactions in-between.**

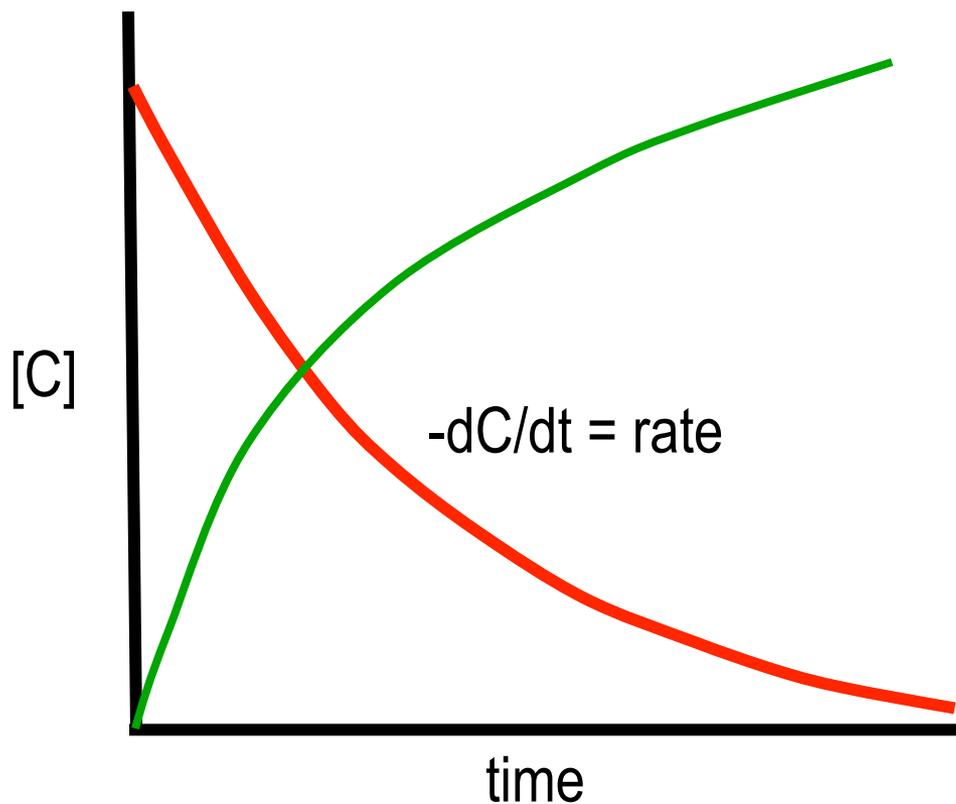
**Some of them are very slow...**

**Neutralisation of an acid by alkali in aqueous solution.... fast**

**Diamond to graphite... slow**



Rate of a chemical reaction depends upon the concentration of the reacting substances. In the gas phase, it depends upon the pressure. Since the concentration is decreasing steadily, the rate decreases. A variation of rate with time is shown in the figure.





The rate depends only on the concentration of  $\text{N}_2\text{O}_5$  except at very low pressures.



Although both ester and water are involved in the reaction, the concentration of water does not undergo any significant change during the reaction. Thus the reaction is first order although there are two reacting species.

Dissociation of HI is second order.

Reaction of NO and O<sub>2</sub> giving NO<sub>2</sub> is third order depending on the square of the NO concentration and the concentration of O<sub>2</sub>.

Rate constant

$$\text{Rate} = k C_1^{n1} C_2^{n2} C_3^{n3} \dots$$

The overall order n is

$$n = n1 + n2 + n3 + \dots$$

The reaction is of order n1 in reactant 1, and n2 in reactant 2, etc.

It may appear that any order is possible, but in reality order does not exceed three.

Chemical reactions can be classified in terms of the **molecularity**. This number is the number of molecules or atoms taking part in each act of chemical reaction.

The dissociation of nitrogen pentoxide is a **unimolecular** reaction. This can occur in the gaseous or solution phase.

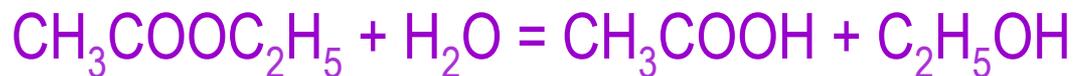


In HI dissociation, two molecules take part.



The reaction is not,  $\text{HI} = \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{I}_2$

Another **biomolecular** reaction is



If three molecules are involved, the overall process is termolecular.



In simple reactions, the number of reactants appearing in the stoichiometric reaction is the molecularity. However, reactions can occur in multiple steps referred to as elementary processes.

Molecularity can be assigned to each individual step, which indicates the species reacting in that step. This form of assignment is possible only if the mechanism is known.

**Molecularity is concerned with the mechanism.** But the order of a reaction expresses the dependence of measured rate on the concentration of the reactants.

**Order and molecularity can be same or different.** In reactions where one of the reactant is present in large excess, this is invariably the case. Order of a reaction can be zero and even fractional, but molecularity is never zero and always an integer. The decomposition of gaseous acetaldehyde has been shown to have an order of  $3/2$ . The reaction of  $H_2$  and  $Br_2$  to form  $HBr$  has a rate proportional to  $(Br_2)^{1/2}$  in the absence  $HBr$  and  $(Br_2)^{3/2}$  in the presence of sufficient amount of  $HBr$ . The rate of formation of phosgene ( $COCl_2$ ) from  $CO$  and  $Cl_2$  is given by  $k(Cl_2)^{3/2}(CO)$ . Order and molecularity are not completely independent, however. Measurements of order are sometimes used to confirm or contradict a proposed mechanism.

**We shall consider only homogeneous, simple reactions taking place at a constant temperature.**

How do you probe the system?

Physical and chemical methods

Physical method is preferred, no variation of concentration.

Pressure of a gas, the conductance of an electrolyte, extent of light absorption, rotation of polarisation of an incident light beam, extent of fluorescence of a species etc. are monitored.

In the chemical method, a small portion of the sample is taken from time to time, and the product concentration is analysed.

# First order reaction

In first order, rate is proportional to the concentration of one of the reactants.

$$-d[C]/dt = k[C]$$

[C] is the concentration of the reactant at time t. k is the proportionality constant or the rate constant or the velocity constant or the specific reaction rate.

When [C] = 1 rate = k. Rate at any concentration C is the product of k and [C].

In practice, it is advantageous to use the relation in a different form.

$$-d[C]/[C] = k dt$$

Upon integration,

$$-\int_{[C]_0}^C d[C]/[C] = k \int_0^t dt$$

Where [C]<sub>0</sub> is the concentration of the reactant at time 0 and [C] at time t

$$\ln [C]_0/[C] = kt$$

$$k = 1/t \ln [C]_0/[C]$$

[C]<sub>0</sub> is proportional to a and [C] to a-x.

$$k = 1/t \ln (a/a-x)$$

## Important characteristics of the first order rate equation

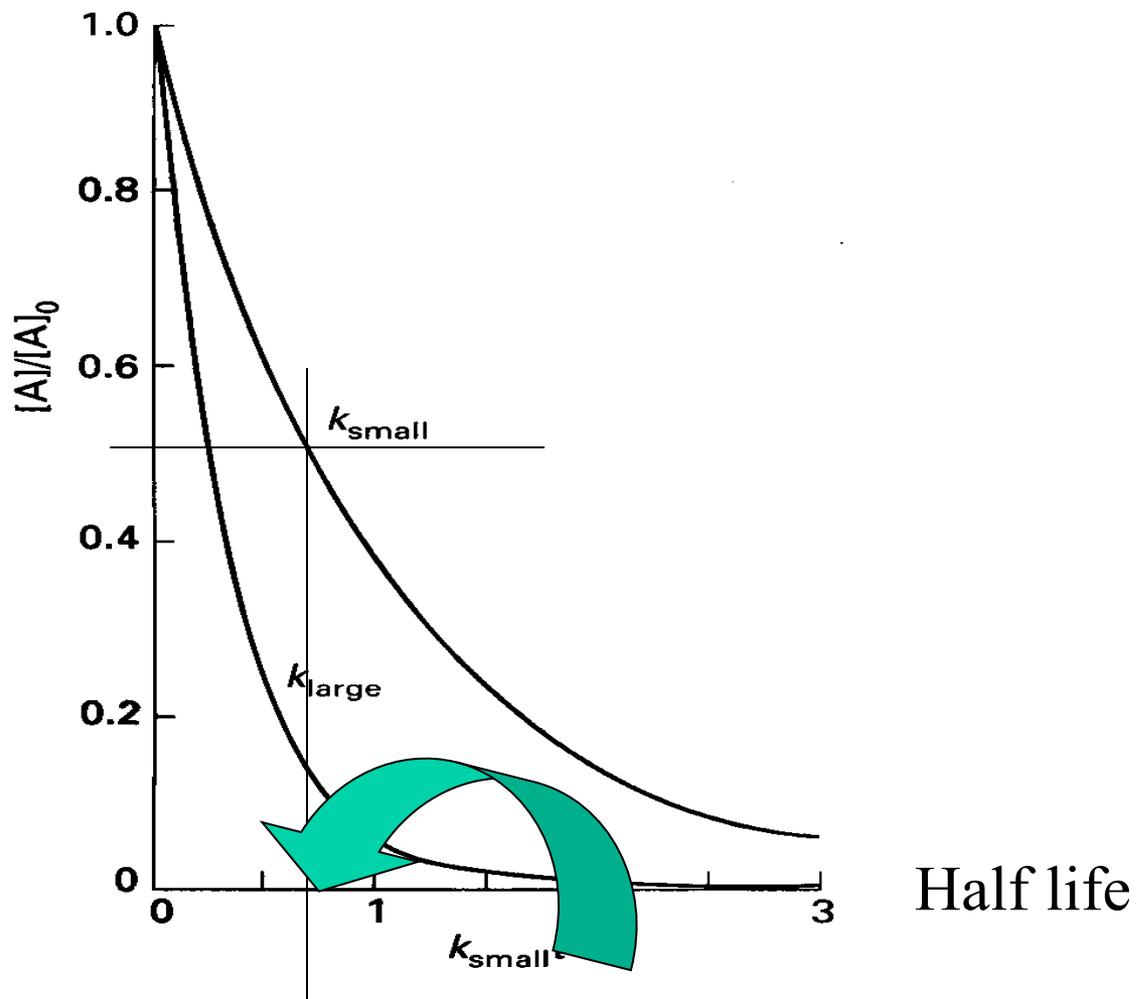
Any unit of concentration could be used as long as both  $a$  and  $a-x$  are expressed in the same units. The specific reaction rate has unit of  $\text{time}^{-1}$  and is generally expressed as  $\text{sec}^{-1}$ .

Important characteristic of a first order reaction is the time taken for the completion of a fraction the reaction. If  $t_{0.5}$  is the time required for the completion of half of the reaction,

$$t_{0.5} = (2.303/k) \log 2 = 0.693/k = t_{0.5}$$

This value is called the half-life, which is a constant for the reaction.

Time to complete any definite fraction of the reaction is constant.



The value of  $k$  can tell us quickly the rate at which products are formed.

## Examples of first order reactions



For every mole of  $\text{N}_2\text{O}_5$  decomposed, the number of moles of the system increases by  $1\frac{1}{2}$  in a constant volume apparatus, the partial pressure  $x$  of  $\text{N}_2\text{O}_5$  decomposed is equal to double the increase in gas pressure.

Measurement of pressure will not directly give the amount of  $\text{N}_2\text{O}_5$  decomposed since  $\text{N}_2\text{O}_4$  formed will undergo further decomposition to form  $\text{NO}_2$ . This can however be accounted for by knowing the equilibrium constant of this reaction.

The measured rate constant is approximately constant at  $1.3 \times 10^{-4} \text{ sec}^{-1}$  which shows that the reaction is first order.

$\text{N}_2\text{O}_5$  equilibrium has also been studied in solution. By keeping the appropriate solvents it is possible to keep  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  formed in solution and the volume of oxygen evolved is measured. The amount of  $\text{O}_2$  produced corresponds to double the amount of  $\text{N}_2\text{O}_5$  decomposed. The final  $\text{O}_2$  volume will give the value of  $a$ .

Instead of individual values of  $k$ , a graphical method can be employed.

$$t = (2.303/k) \ln a - (2.303/k) \log (a-x)$$

A plot of  $t$  against  $\log (a-x)$  should give a straight line with  $- 2.303/k$  as the slope.

Another first order reaction.



The hydrolysis of an ester is very slow if only water is present. In the presence of an acid catalyst, the reaction has a measurable rate. Hydrolysis of methyl acetate in presence of HCl is such a reaction. The concentration of acid is small and it does not change during the reaction. Water concentration is high and it does not change appreciably. Thus the rate depends only on the concentration of methyl acetate and the rate is first order. To follow the reaction, a small volume of the mixture is withdrawn at definite intervals and it is titrated against standard alkali. The volume of alkali consumed at time 0,  $\infty$  and  $t$  will give the rate constant of the reaction.

$$k = 2.303/t \log (T_{\infty} - T_0 / T_{\infty} - T_t)$$

$T_{\infty} - T_0$  refers to a.  $T_t - T_0$  is x.

Experimental studies show that k determined remains a constant. It has to be said that k does depend upon the amount of water and the concentration of acid. With these, the value of k will change.

Another example is the inversion of sucrose. This is also catalysed by acid. The course of the reaction can be measured by determining the angle of rotation of polarised light. Sucrose rotates it to right and a mixture of dextrose and laevulose makes it to left. If  $\alpha_0$  and  $\alpha_{\infty}$  and  $\alpha_t$  are the angles of rotation including the sign,  $\alpha_0 - \alpha_{\infty}$  is proportional to a and  $\alpha_t - \alpha_{\infty}$  is proportional to a-x.

$$\text{Thus, } k = 2.303/t \log(\alpha_0 - \alpha_{\infty} / \alpha_t - \alpha_{\infty} )$$

Here again the value of k depends on the concentration of water and acid.

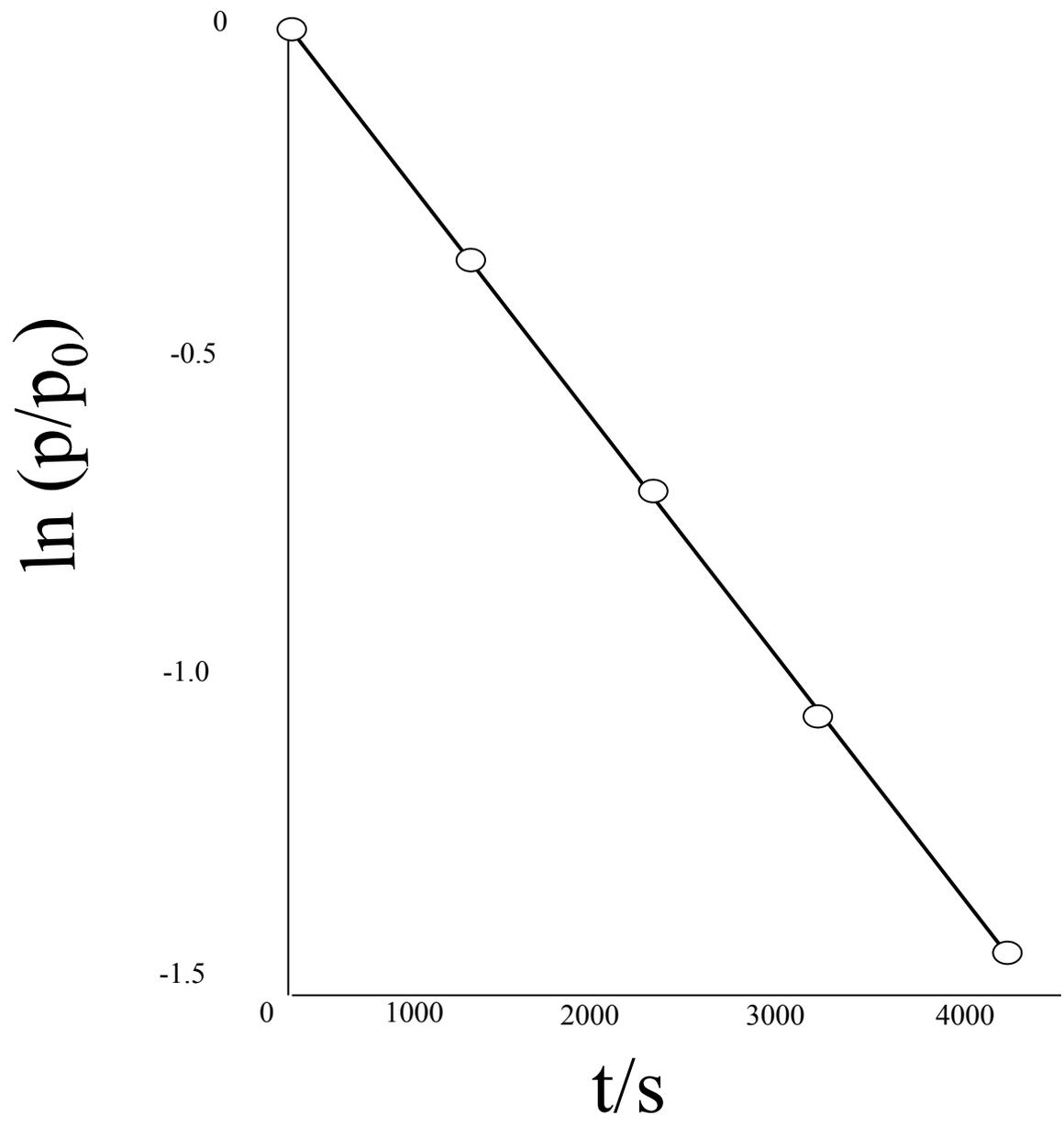


A typical decomposition reaction is that of azomethane.



This reaction can be monitored by measuring the total pressure as a function of time. Since all the species are in the gas phase, the pressure is a direct measure of the concentration. This is depicted below.

The shape of the graph (logarithm of concentration is linear with time) illustrates that the reaction is first order.



## Second order reactions

The rate of a second order reaction depends upon two concentration terms. It can be



$$-dC_A/dt = kC_A^2 \text{ or } -dC_A/dt = -dC_B/dt = kC_A C_B$$

In general,

$$-dC/dt = kC^n \text{ or}$$

$$-dC/C^n = kdt$$

$$-C^{-n}dC = kdt$$

$$-[C^{-n+1}/-n+1]_c^{co} = kt$$

$$1/n-1 [ 1/C^{n-1} - 1/C_o^{n-1} ] = kt$$

For a second order reaction,

$$k = 1/t (1/C - 1/C_0)$$

If  $C_0$  is  $a$ , and  $C$  is  $a-x$

$$k = 1/t (1/a-x - 1/a) = 1/t [x/(a-x)a]$$

Let us consider,



$$-dC_A/dt = -dC_B/dt = kC_A C_B$$

If  $a$  and  $b$  represents initial moles of  $A$  and  $B$  and  $x$  represents the amount of each that has reacted after time  $t$ ,

$$dx/dt = k (a-x) (b-x) \quad (1)$$

If  $a = b$  i.e.  $A$  and  $B$  are present in equimolar amounts,

$$dx/dt = k(a-x)^2 = k(b-x)^2$$

Integration of (1) yields (by the method of partial functions).

$$k = [1/t(a-b)] \ln [b(a-x)/a(b-x)]$$

The rate constant depends upon the units employed to express concentrations.

The units of  $k$  are  $\text{con}^{-1} \text{ time}^{-1}$ . If the concentration is moles/litre,  $k$  will be  $(\text{moles/litre})^{-1} \text{ sec}^{-1}$

$$k = 1/t (x/a(a-x))$$

When  $x$  is  $a/2$ ,

$t_{0.5} = 1/ka$ , the time is inversely proportional to initial concentration, in sharp difference with the first order reactions. For any other fraction, a similar relation exists.

## Examples

The decomposition of HI is a second order reaction. However, the study of this reaction is difficult since the reaction is reversible.

One reaction that is second order is  $\text{H}_2 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_6$ .

The reaction can be studied by determining the pressure at various times.

Reaction of isobutyl bromide and sodium ethoxide is second order.



**Saponification of an ester is a second order reaction.**



This is different from the acid hydrolysis since both reactants are present in similar amounts.

The reaction can be studied by a number of methods. The first method is by conductance measurements. The replacement of OH<sup>-</sup> ions by CH<sub>3</sub>COO<sup>-</sup> ions will change the conductance of the solution. This change can be correlated with the extent of the reaction. In the second, definite quantities of the reaction mixture are withdrawn at intervals and the amount of alkali left out is determined. If the initial concentrations of alkali and ester are known, the rate constant can be determined.

Rate can also be treated graphically.

$$t = [2.030/k(a-b)] \log b/a + [2.303/k(a-b)] \log a-x/b-x$$

Plot of t against log [a-x/b-x] will give a straight line with slope [2.303/k(a-b)]

Reactions of alkyl iodides with tertiary amines is also second order.



# Third order reactions



$$-dC/dt = kC^3$$

$$k = 1/(2t) (1/C^2 - 1/C_0^2)$$

$$= 1/(2t) [(1/(a-x)^2 - 1/a^2)]$$

$$\text{Unit } \text{con}^{-2} \text{ time}^{-1}$$

For order n, k is  $\text{conc.}^{n-1} \text{ time}^{-1}$

For completing half of the reaction,

$$k = 1/(2t) 3/a^2$$

$$t_{0.5} = 3/(2ka^2)$$

Time to complete a fraction is inversely proportional to the square of the initial concentration.

There are five gas phase reactions which are definitively third order. These are the termolecular reactions involving two molecules of nitric oxide and one molecule of  $\text{Cl}_2$ ,  $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{O}_2$  or  $\text{Br}_2$ .



For reactions of the type,



If  $x$  is the amount of B reacted after time  $t$ ,

$$\frac{dx}{dt} = k (a - 2x)^2 (b - x)$$

$$k = \frac{1}{t(2b-a)^2} \left[ \frac{(2b-a)^2 2x}{a(a-2x)} + \ln \left[ \frac{b(a-2x)}{a(b-x)} \right] \right]$$

Although a number of third order reactions in solution are reported, none of them is proven.

Complications and how to solve them

## 1. Pseudo Order

An expression for second order reaction



Can be written as,

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

And the integration,

$$\int -1/A^2 dA = kdt$$

$$1/A_t - 1/A_o = kt$$

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 or  $B_0 \approx B_t$ .

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.

## 2. Reactions occur in stages

Third order reactions are hard to occur.

Higher order reactions (more than three) are very rare, may not even occur.

### INTERMEDIATE

Reasons: Geometry, orientation,...

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.

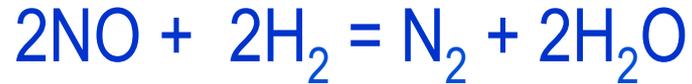
Concept of intermediate

Valid in solutions also

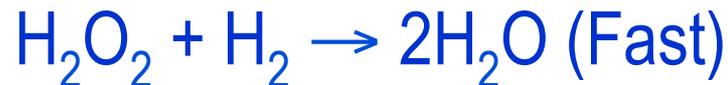
Reactions may happen in steps!

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.

How do you find slowest step? Mechanism.

Check out..

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.

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.

**Summary: Reactions can be tested.**

### 3. 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.

# Time to complete a definite fraction of the reaction

For a reaction of order  $n$ , the time to complete half the Reaction,  $t_{0.5} = \text{constant} * 1/c_0^{n-1}$

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  $t_{0.5} \times c_0^{n-1}$  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.

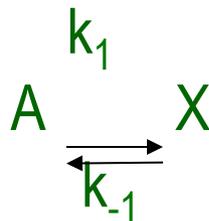
Take log and subtract

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

$dc_1/dt$  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.

## 4. 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

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

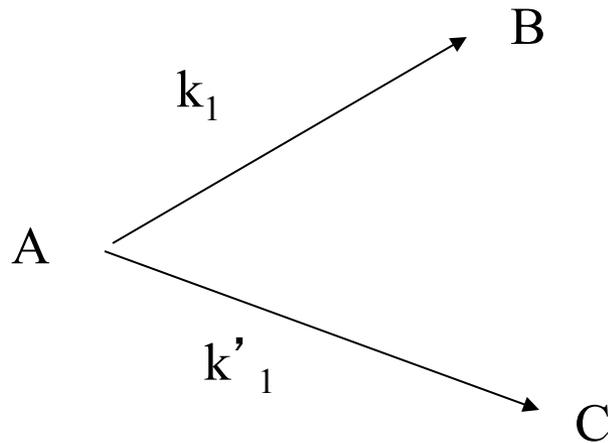
which is the same as Eq. (4)

## RATE EQUATIONS FOR OPPOSING REACTIONS

Stoichiometric equation	Rate equation	Integrated rate equation
$A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1}x$	
$A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1}(x + x_0)$	$x_e/a_0 \ln x_e/x_e - x = k_1t$
$2A \rightleftharpoons X$	$dx/dt = k_1(a_0 - x) - k_{-1}x/2$	
$A \rightleftharpoons 2X$	$dx/dt = k_1(a_0 - x/2) - k_{-1}x$	
$A \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x) - k_{-1}x^2$	$x_e/(2a_0 - x_e) \ln a_0x_e + x(a_0 - x_e)/a_0(x_e - x) = k_1t$
$A + B \rightleftharpoons X$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}x$	$x_e/(a_0^2 - x_e^2) \ln x_e(a_0^2 - xx_e)/a_0^2(x_e - x) = k_1t$
$A + B \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}x^2$	$X_e/2a_0(a_0 - x_e) \ln x(a_0 - 2x_e) + a_0x_e/a_0(x_e - x)$
$2A \rightleftharpoons X + Y$	$dx/dt = k_1(a_0 - x)^2 - k_{-1}(x/2)^2$	

## 5. 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 side or parallel reactions. To calculate the overall rate, the rate of the side reactions should be taken into account. Consider a reaction,

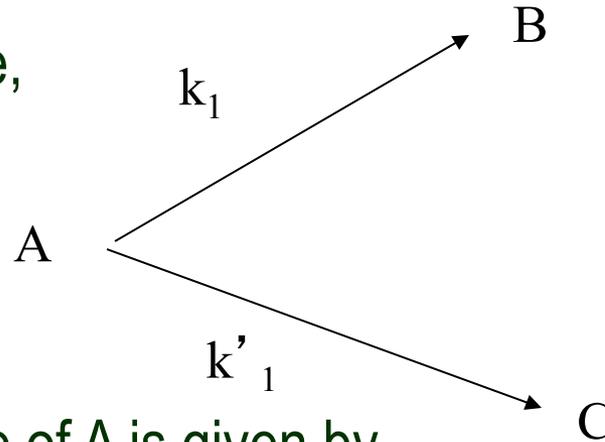


The rates these two reactions are,

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

and

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



The overall rate of disappearance of A is given by

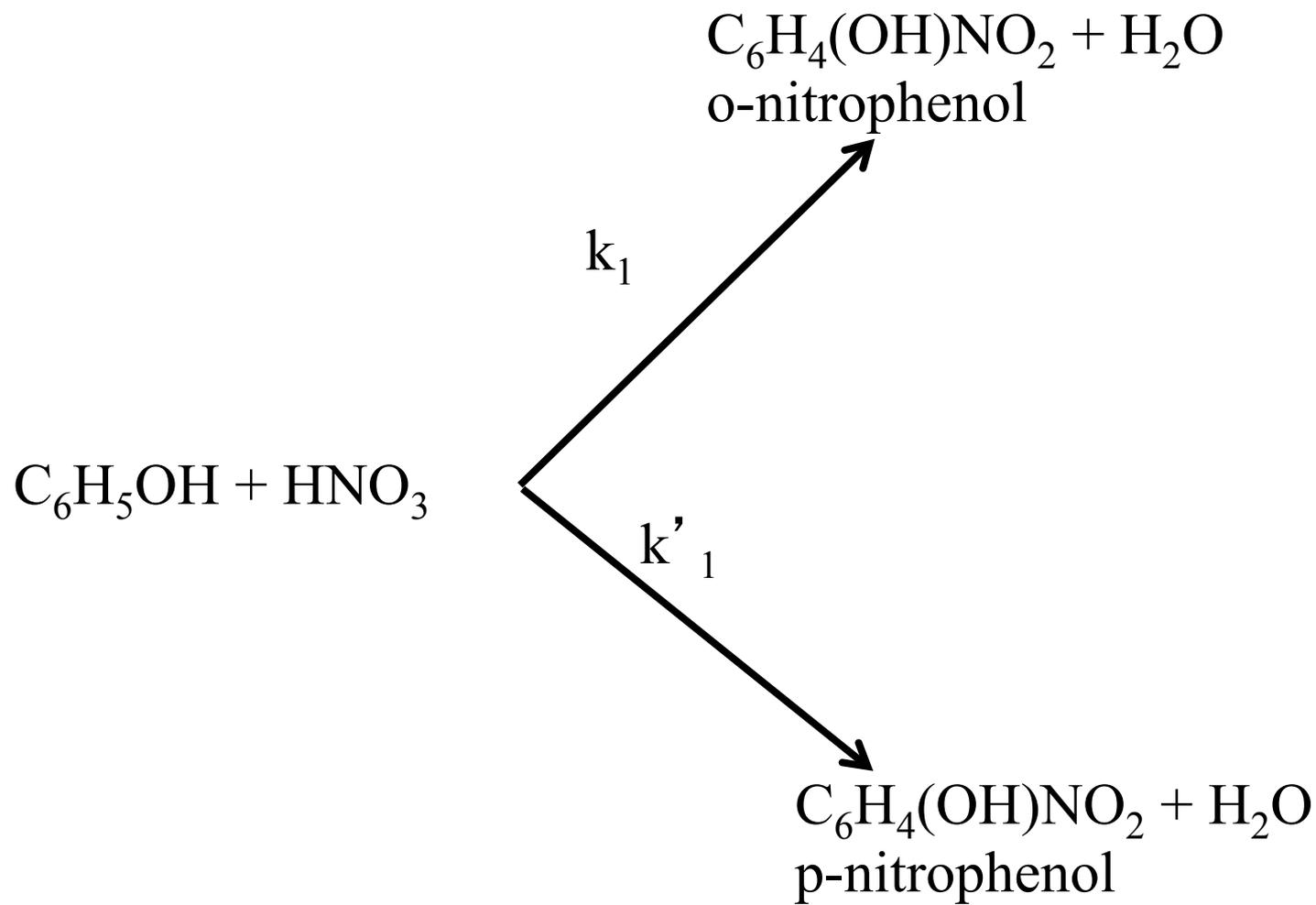
$$\begin{aligned} -d[A]/dt &= k_1[A] + k'_1[A] \\ &= [k_1 + k'_1][A] \end{aligned} \quad (1)$$

The ratio of the two rates is given as

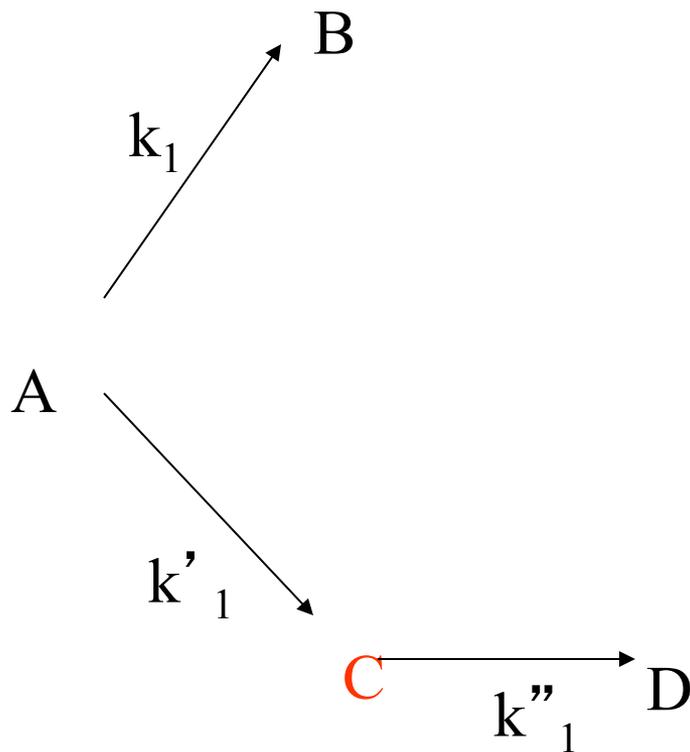
$$d[B]/dt / d[C]/dt = k_1/k'_1 \quad (2)$$

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.