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LECTURE- CHEMICAL KINETICS

## Experimental Techniques for Measuring the Rates of Chemical Reactions

- (a) The rates of chemical reactions are measured by using techniques that monitor the concentrations of species present in the reaction mixture.
- (b) Examples of experimental techniques include real-time and quenching procedures, flow and stopped-flow techniques, and flash photolysis.

### (a) Monitoring the progress of a reaction

A reaction in which at least one component is a gas might result in an overall change in pressure in a system of constant volume, so its progress may be followed by recording the variation of pressure with time.

**Problem 1:** Predict how the total pressure varies during the gas-phase decomposition  $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  in a constant-volume container.

**Answer** Let the initial pressure be  $p_0$  and the initial amount of  $\text{N}_2\text{O}_5$  molecules present be  $n$ . When a fraction  $\alpha$  of the  $\text{N}_2\text{O}_5$  molecules has decomposed, the amounts of the components in the reaction mixture are:

	$\text{N}_2\text{O}_5$	$\text{NO}_2$	$\text{O}_2$	Total
Amount:	$n(1 - \alpha)$	$2\alpha n$	$1/2\alpha n$	$n(1 + 3/2\alpha)$

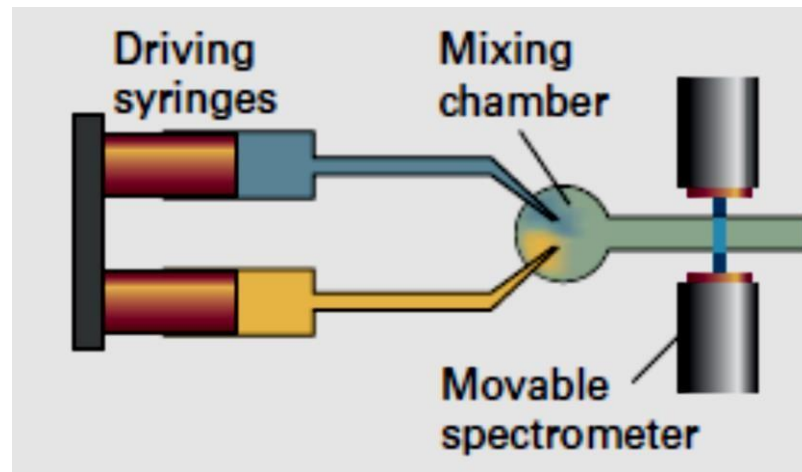
When  $\alpha = 0$  the pressure is  $p_0$ , so at any stage the total pressure is  $p = (1 + 3/2\alpha)p_0$

When the reaction is complete, the pressure will have risen to  $5/2$  times its initial value.

## Application of the techniques

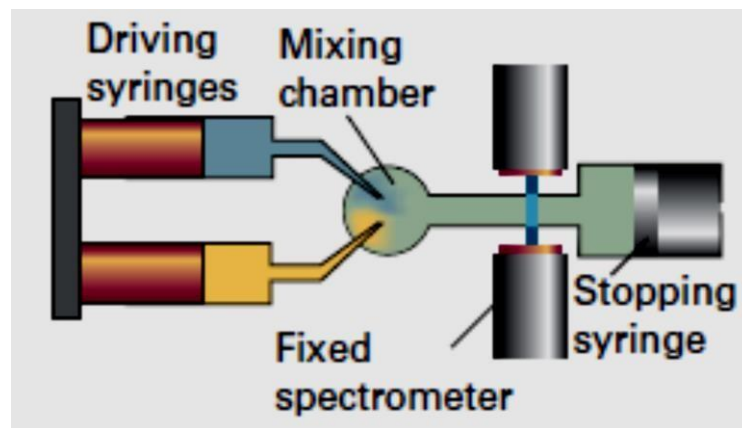
In a **real-time analysis** the composition of the system is analysed while the reaction is in progress. Either a small sample is withdrawn or the bulk solution is monitored.

In the **flow method** the reactants are mixed as they flow together in a chamber (Fig. 1). The reaction continues as the thoroughly mixed solutions flow through the outlet tube, and observation of the composition at different positions along the tube is equivalent to the observation of the reaction mixture at different times after mixing. The disadvantage of conventional flow techniques is that a large volume of reactant solution is necessary. This makes the study of fast reactions particularly difficult because to spread the reaction over a length of tube the flow must be rapid



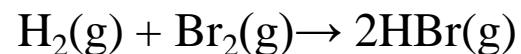
**Fig.1:** The arrangement used in the flow technique for studying reaction rates. The reactants are injected into the mixing chamber at a steady rate. The location of the spectrometer corresponds to different times after initiation.

This disadvantage is avoided by the **stopped-flow technique**, in which the reagents are mixed very quickly in a small chamber fitted with a syringe instead of an outlet tube (Fig. 2). The flow ceases when the plunger of the syringe reaches a stop, and the reaction continues in the mixed solutions. Observations, commonly using spectroscopic techniques such as ultraviolet–visible absorption, circular dichroism, and fluorescence emission, are made on the sample as a function of time. The technique allows for the study of reactions that occur on the millisecond to second timescale.



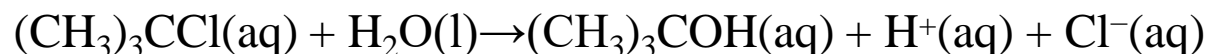
**Fig 2:** In the stopped-flow technique the reagents are driven quickly into the mixing chamber by the driving syringes and then the time dependence of the concentrations is monitored.

- Spectrophotometry, the measurement of absorption of radiation in a particular spectral region, is especially useful when one substance in the reaction mixture has a strong characteristic absorption in a conveniently accessible region of the electromagnetic spectrum. For example, the progress of the reaction



can be followed by measuring the absorption of visible light by bromine.

- A reaction that changes the number or type of ions present in a solution may be followed by monitoring the electrical conductivity of the solution. The replacement of neutral molecules by ionic products can result in dramatic changes in the conductivity, as in the reaction



- If hydrogen ions are produced or consumed, the reaction may be followed by monitoring the pH of the solution.
- Other methods of determining composition include emission spectroscopy, mass spectrometry, gas chromatography, nuclear magnetic resonance, and electron paramagnetic resonance (for reactions involving radicals or paramagnetic d-metal ions).

Very fast reactions can be studied by **flash photolysis**, in which the sample is exposed to a brief flash of light that initiates the reaction and then the contents of the reaction chamber are monitored.

In contrast to real-time analysis, **quenching methods** are based on stopping, or quenching, the reaction after it has been allowed to proceed for a certain time.

In the **chemical quench flow method**, the reactants are mixed in much the same way as in the flow method but the reaction is quenched by another reagent, such as solution of acid or base, after the mixture has travelled along a fixed length of the outlet tube. Different reaction times can be selected by varying the flow rate along the outlet tube. Once the reaction has been quenched, the solution may be examined by ‘slow’ techniques, such as gel electrophoresis, mass spectrometry, and chromatography.

In the **freeze quench method**, the reaction is quenched by cooling the mixture within milliseconds and the concentrations of reactants, intermediates, and products are measured spectroscopically.

# The Rates of Reactions

Reaction rates depend on the composition and the temperature of the reaction mixture.

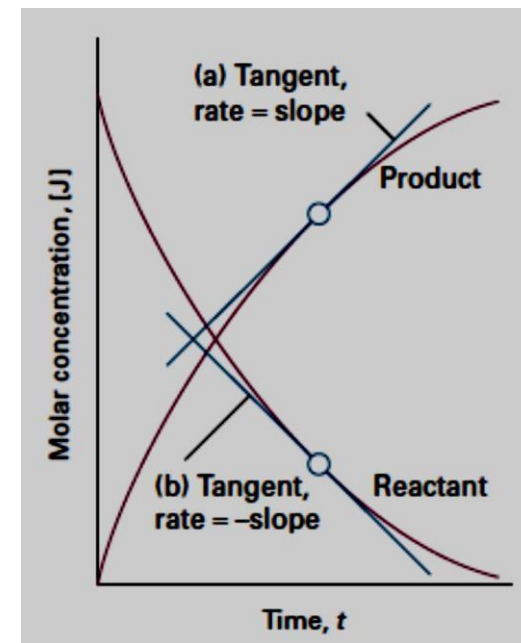
## (a) The definition of rate

Consider a reaction of the form  $A + 2 B \rightarrow 3 C + D$ ,

The instantaneous **rate of consumption** of one of the reactants at a given time is  $d[R]/dt$ , where R is A or B. This rate is a positive quantity. The **rate of formation** of one of the products (C or D, which we denote P) is  $d[P]/dt$ .

It follows from the stoichiometry for the reaction  $A + 2 B \rightarrow 3 C + D$  that

$$d[D]/dt = 1/3 d[C]/dt = -d[A]/dt = -1/2 d[B]/dt$$



**Fig. 3.** The definition of (instantaneous) rate as the slope of the tangent drawn to the curve showing the variation of concentration with time. For negative slopes, the sign is changed when reporting the rate, so all reaction rates are positive

If the rate of formation of NO in the reaction  $2 \text{NOBr(g)} \rightarrow 2 \text{NO(g)} + \text{Br}_2\text{(g)}$  is reported as  $0.16 \text{ mmol dm}^{-3} \text{ s}^{-1}$ , we use  $v_{\text{NO}} = +2$  to report that  $v = 0.080 \text{ mmol dm}^{-3} \text{ s}^{-1}$ . Because  $v_{\text{NOBr}} = -2$  it follows that  $d[\text{NOBr}]/dt = -0.16 \text{ mmol dm}^{-3} \text{ s}^{-1}$ . The rate of consumption of NOBr is therefore  $0.16 \text{ mmol dm}^{-3} \text{ s}^{-1}$ , or  $9.6 \times 10^{16} \text{ molecules cm}^{-3} \text{ s}^{-1}$ .

**Problem 1:** The rate of change of molar concentration of  $\text{CH}_3$  radicals in the reaction  $2 \text{CH}_3\text{(g)} \rightarrow \text{CH}_3\text{CH}_3\text{(g)}$  was reported as  $d[\text{CH}_3]/dt = -1.2 \text{ mol dm}^{-3} \text{ s}^{-1}$  under particular conditions. What is (a) the rate of reaction and (b) the rate of formation of  $\text{CH}_3\text{CH}_3$ ?

Ans: (a)  $0.6 \text{ mol dm}^{-3} \text{ s}^{-1}$  (b)  $0.6 \text{ mol dm}^{-3} \text{ s}^{-1}$

### (b) Rate laws and rate constants

The rate of reaction is often found to be proportional to the concentrations of the reactants raised to a power. For example, the rate of a reaction may be proportional to the molar concentrations of two reactants A and B, so we write

$$v = k_r[\text{A}][\text{B}] \longrightarrow (1)$$

with each concentration raised to the first power. The coefficient  $k_r$  is called the **rate constant** for the reaction.



A rate law of a reaction is an equation that expresses the rate of reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction at some time:

$$v = f([A], [B], \dots) \longrightarrow (2)$$

For homogeneous gas-phase reactions, it is more convenient to express the rate law in terms of partial pressures. In this case, we write

$$v = f(p_A, p_B, \dots) \longrightarrow (3)$$

The rate constant for the reaction  $\text{O}(\text{g}) + \text{O}_3(\text{g}) \rightarrow 2 \text{O}_2(\text{g})$  is  $8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. To express this rate constant in  $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , we make use of

$$1 \text{ cm} = 10^{-2} \text{ m} = 10^{-2} \times 10 \text{ dm} = 10^{-1} \text{ dm}$$

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ molecules, so } 1 \text{ molecule} = 1 \text{ mol} / 6.023 \times 10^{23}$$

It follows that

$$k_r = 8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$= 8.0 \times 10^{-15} (10^{-1} \text{ dm})^3 (1 \text{ mol} / 6.023 \times 10^{23}) \text{ s}^{-1}$$

$$= 8.0 \times 10^{-15} \times 10^{-3} \times 6.022 \times 10^{23} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 4.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

**Problem 2:** A reaction has a rate law of the form  $k_r[A]_2[B]$ . What are the units of the rate constant if the reaction rate is measured in  $\text{mol dm}^{-3} \text{s}^{-1}$ ? Ans:  $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$

With concentrations expressed in  $\text{mol dm}^{-3}$ , then the units of  $k_r$  will be  **$\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$**   
because  $\text{mol dm}^{-3} \text{s}^{-1} = k_r (\text{mol dm}^{-3})^2 \times (\text{mol dm}^{-3})$  {cancel out the similar terms on both sides}

### (c) Reaction order

Many reactions are found to have rate laws of the form

$$v = k_r[A]^a[B]^b \longrightarrow (4)$$

The power to which the concentration of a species (a product or a reactant) is raised in a rate law of this kind is the **order** of the reaction with respect to that species. A reaction with the rate law in eqn 1 is **first-order** in A and first-order in B.

The rate law in eqn 1 is therefore second-order overall.

The **overall order** of a reaction with a rate law like that in eqn 4 is the sum of the individual orders,  $a + b + \dots$

A reaction need not have an integral order, and many gas-phase reactions do not.

For example, a reaction having the rate law

$$v = k[A]^{1/2}[B] \longrightarrow (5)$$

is half-order in A, first-order in B, and order overall **3/2** (Ans: 3/2)

Some reactions obey a **zero-order rate law**, and therefore have a rate that is independent of the concentration of the reactant. Thus, the catalytic decomposition of phosphine ( $\text{PH}_3$ ) on hot tungsten at high pressures has the rate law

$$v = k_r \longrightarrow (6)$$

Zero-order reactions are also found for a number of enzyme reactions when there is a large excess of reactant relative to the enzyme, and the amount of enzyme present governs the rate, not the amount of reactant.

#### (d) The determination of the rate law

**i. Isolation method** in which the concentrations of all the reactants except one are in large excess. If B is in large excess, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law might be  $v = k_r[\text{A}][\text{B}]$ , we can approximate  $[\text{B}]$  by  $[\text{B}]_0$ , its initial value, and write

$$v = k_r'[\text{A}] \qquad k_r' = k_r[\text{B}]_0 \longrightarrow (7)$$

which has the form of a first-order rate law. Because the true rate law has been forced into first-order form by assuming that the concentration of B is constant, eqn 7 is called a **pseudofirst-order rate law**. The dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn (by having all the other substances present in large excess), and so constructing a picture of the overall rate law.

ii. In the **method of initial rates**, which is often used in conjunction with the isolation method, the rate is measured at the beginning of the reaction for several different initial concentrations of reactants. We shall suppose that the rate law for a reaction with A isolated is  $v = k_r' [A]^a$ ; then its initial rate,  $v_0$ , is given by the initial values of the concentration of A, and we write  $v_0 = k_r' [A]^a$ . Taking (common) logarithms gives:

$$\log v_0 = \log k_r' + a \log [A]_0 \longrightarrow (8)$$

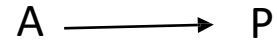
**(a) The instantaneous rate of a reaction is the slope of the tangent to the graph of concentration against time.**

**(b) A rate law is an expression for the reaction rate in terms of the concentrations of the species that occur in the overall chemical reaction.**

**(c) For a rate law of the form  $V = k_r[A]^a[B]^b \dots$ , the rate constant is  $k_r$ , the order with respect to A is  $a$ , and the overall order is  $a + b + \dots$**

**(d) The isolation method and the method of initial rates are often used in the determination of rate laws.**

## Integrated rate law



$$d[A]/dt = -k_r[A] \longrightarrow (9)$$

- we can rearrange eqn 9 into

- $d[A]/[A] = -k_r dt$

- This expression can be integrated directly because  $k_r$  is a constant independent of  $t$ . Initially (at  $t = 0$ ) the concentration of A is  $[A]_o$ , and at a later time  $t$  it is  $[A]$ , so we make these values the limits of the integrals and write

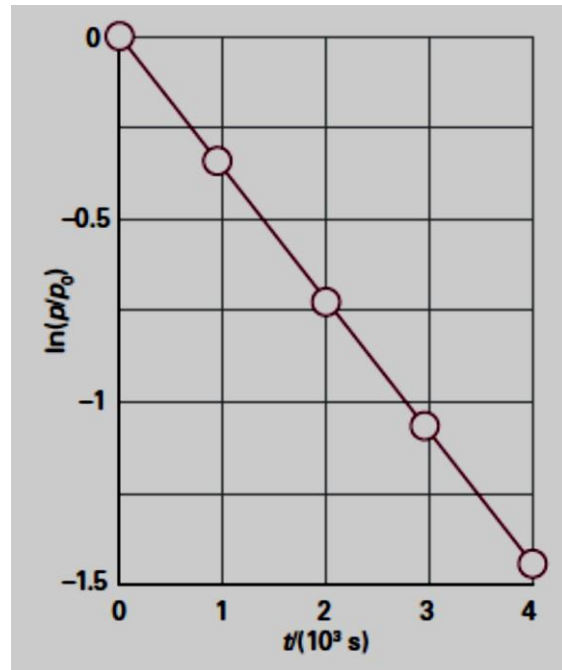
$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -k_r \int_0^t dt \longrightarrow (10)$$

$$\ln \left( \frac{[A]}{[A]_o} \right) = -k_r t \longrightarrow (11a)$$

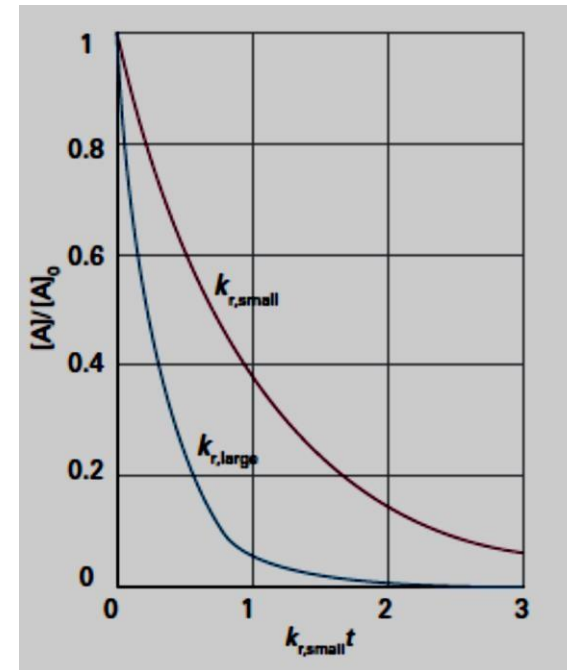
$$[A] = [A]_o e^{-k_r t} \longrightarrow (11b)$$

where  $[A]_o$  is the initial concentration of A (at  $t = 0$ ).

- Equation 11a shows that, if  $\ln([A]/[A]_0)$  is plotted against  $t$ , then a first-order reaction will give a straight line of slope  $-k_r$ .
- The eqn 11b shows that in a first order reaction the reactant concentration decreases exponentially with time with a rate determined by  $k_r$ .



**Fig. 4** The determination of the rate constant of a first-order reaction: a straight line is obtained when  $\ln[A]/[A]_0$  (or, as here,  $\ln p/p_0$ ) is plotted against  $t$ ; the slope gives  $k_r$ .



**Fig. 5.** The exponential decay of the reactant in a first-order reaction.

### (b) Half-lives and time constants

**Half-life**,  $t_{1/2}$ , of a substance is the time taken for the concentration of a reactant to fall to half its initial value. The time for  $[A]$  to decrease from  $[A]_o$  to  $1/2[A]_o$  in a first-order reaction is given by eqn 11 as

$$k_r t_{1/2} = -\left(\frac{\frac{[A]_o}{2}}{[A]_o}\right) = -\ln(1/2) = \ln 2$$

Hence,

$$t_{1/2} = \ln 2 / k_r = 0.693 / k_r$$

Half-life of a  
first-order reaction

→ (12)

**Time constant**,  $\tau$  (tau), the time required for the concentration of a reactant to fall to  $1/e$  of its initial value.

$$k_r \tau = -\ln\left(\frac{\frac{[A]_o}{e}}{[A]_o}\right) = -\ln\left(\frac{1}{e}\right) = 1$$

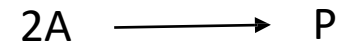
Therefore,

$$\tau = 1 / k_r$$

Time constant of a  
first-order reaction

→ (13)

**(c) Second-order reactions**



$$\frac{d[A]}{dt} = -k_r[A]^2 \longrightarrow (14)$$

$$\frac{d[A]}{[A]^2} = -k_r dt$$

The concentration of A is  $[A]_o$  at  $t = 0$  and  $[A]$  at a general time  $t$  later. Therefore,

$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = -k_r \int_0^t dt$$

$$\frac{1}{[A]} - \frac{1}{[A]_o} = k_r t \longrightarrow (15)$$

$$[A] = [A]_o / (1 + k_r t [A]_o) \longrightarrow (16)$$



It follows from equation 16 by substituting  $t = t_{1/2}$  and  $[A] = 1/2[A]_0$  that the half-life of a species A that is consumed in a second-order reaction is

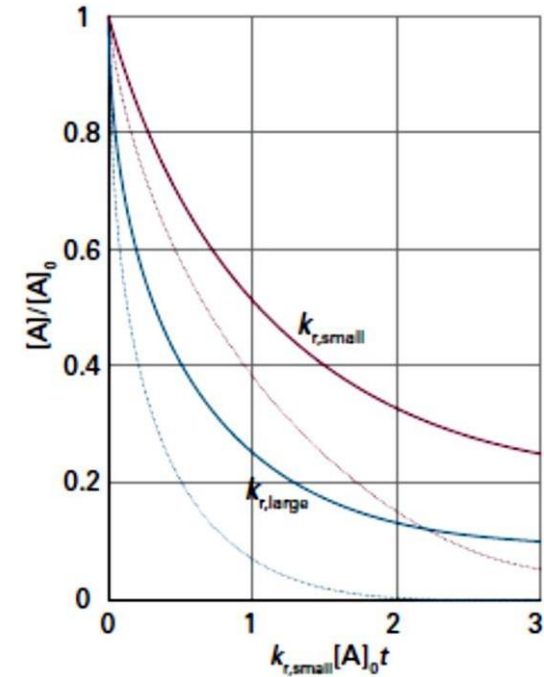
$$t_{1/2} = 1/k_r[A]_0$$

→ (17)

Half-life of a second-order reaction

In general, for an  $n$ th-order reaction (with  $n > 1$ ) of the form  $A \rightarrow \text{products}$ , the half-life is related to the rate constant and the initial concentration of A by

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k_r[A]_0^{n-1}} \rightarrow (18)$$



**Fig. 6** The variation with time of the concentration of a reactant in a second Order reaction. The grey lines are the corresponding decays in a first-order reaction with the same initial rate.

Another type of second-order reaction is one that is first-order in each of two reactants A and B:



$$\frac{d[A]}{dt} = -k_r[A][B]$$

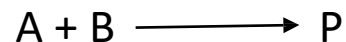
$$\ln \left( \frac{\frac{[B]}{[B]_o}}{\frac{[A]}{[A]_o}} \right) = ([B]_o - [A]_o)k_r t$$

Integrated rate law of  
a second-order reaction  
of the type  $A + B \rightarrow P$

—————→ (19)

- **An integrated rate law is an expression for the concentration of a reactant or product as a function of time.**
- **The half-life  $t_{1/2}$  of a reaction is the time it takes for the concentration of a species to fall to half its initial value.**
- **The time constant  $\tau$  is the time required for the concentration of a reactant to fall to 1/e of its initial value.**

Second-order reaction that is first-order in each of two reactants A and B:



It follows from the reaction stoichiometry that, when the concentration of A has fallen to  $[A]_o - x$ , the concentration of B will have fallen to  $[B]_o - x$ . It follows that

$$\frac{d[A]}{dt} = -k_r([A]_o - x)([B]_o - x)$$

Because  $[A] = [A]_o - x$ , it follows that  $d[A]/dt = -dx/dt$  and the rate law may be written as

$$\frac{dx}{dt} = k_r([A]_o - x)([B]_o - x)$$

The initial condition is that  $x = 0$  when  $t = 0$ ; so the integration required is

$$\int_0^x \frac{dx}{([A]_o - x)([B]_o - x)} = k_r \int_0^t dt$$

$$\int_0^x \frac{dx}{([A]_o - x)([B]_o - x)} = k_r \int_0^t dt$$

The integral on the right is simply  $k_r t$ . The integral on the left is evaluated by using the method of partial fractions in which we write

$$\frac{1}{(a-x)(b-x)} = \frac{1}{b-a} \left( \frac{1}{a-x} - \frac{1}{b-x} \right)$$

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a} \left[ \int \frac{dx}{a-x} - \int \frac{dx}{b-x} \right] = \frac{1}{b-a} \left[ \ln \left( \frac{1}{a-x} \right) - \ln \left( \frac{1}{b-x} \right) \right] + \text{constant}$$

and therefore that

$$\int_0^x \frac{dx}{([A]_o - x)([B]_o - x)} = \frac{1}{[B]_o - [A]_o} \left\{ \ln \left( \frac{[A]_o}{[A]_o - x} \right) - \ln \left( \frac{[B]_o}{[B]_o - x} \right) \right\}$$

This expression can be simplified by putting  $[A] = [A]_o - x$  and  $[B] = [B]_o - x$

$$\ln \left( \frac{[B]}{[A]} \right) = ([B]_o - [A]_o) k_r t$$

Order	Reaction	Rate law*	$t_{1/2}$	Unit of rate constant
0	$A \rightarrow P$	$v = k_r$ $k_r t = x$ for $0 \leq x \leq [A]_0$	$[A]_0 / 2k_r$	$\text{Ms}^{-1}$
1	$A \rightarrow P$	$v = k_r[A]$ $k_r t = \ln \frac{[A]_0}{[A]_0 - x}$	$(\ln 2) / k_r$	$\text{s}^{-1}$
2	$A \rightarrow P$	$v = k_r[A]^2$ $k_r t = \frac{x}{[A]_0([A]_0 - x)}$	$1 / k_r[A]_0$	$\text{Ms}^{-1}$
	$A + B \rightarrow P$	$v = k_r[A][B]$ $k_r t = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$		

\*  $x = [P]$  and  $v = dx/dt$ .

## The temperature dependence of reaction rates

The temperature dependence of the rate constant of a reaction typically follows the Arrhenius equation.

### a) The Arrhenius parameters

It is found experimentally for many reactions that a plot of  $\ln k_r$  against  $1/T$  gives a straight line. This behaviour is normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the **Arrhenius equation**

$$\ln K = \ln A - \frac{E_a}{RT} \longrightarrow (20)$$

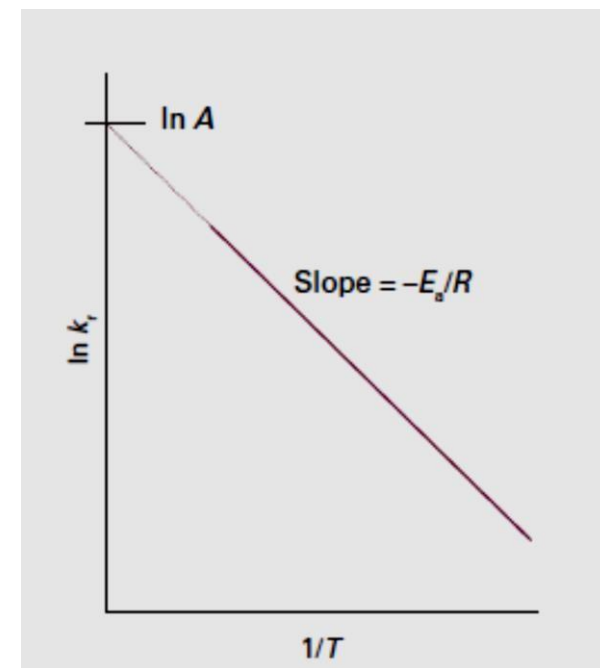
The parameter  $A$ , which corresponds to the intercept of the line at  $1/T = 0$  (at infinite temperature, Fig. 4), is called the **pre-exponential factor** or the ‘frequency factor’. The parameter  $E_a$ , which is obtained from the slope of the line ( $-E_a/R$ ), is called the **activation energy**. Collectively the two quantities are called the **Arrhenius parameters**

$$\ln K = \ln A - \frac{E_a}{RT}$$

- $E_a$  is given by the slope of the plot of  $\ln k_r$  against  $1/T$ , the higher the activation energy, the stronger the temperature dependence of the rate constant (that is, the steeper the slope). *A high activation energy signifies that the rate constant depends strongly on temperature.*
- If a reaction has zero activation energy, its rate is independent of temperature.
- In some cases the activation energy is negative, which indicates that the rate decreases as the temperature is raised indicating a complex mechanism.

$$E_a = RT^2 \left( \frac{d \ln k_r}{dt} \right) \quad \boxed{\text{Definition of the activation energy}} \longrightarrow (21)$$

- $A$  has the same units as  $k_r$ .

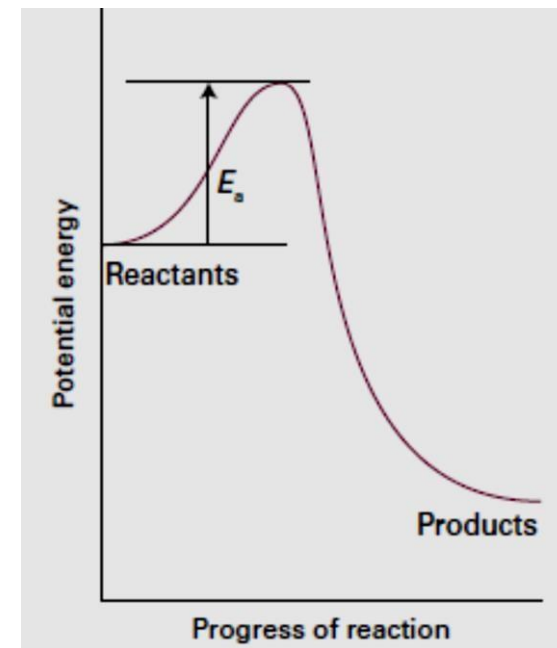


**Fig. 7:** A plot of  $\ln k_r$  against  $1/T$  is a straight line when the reaction follows the behaviour described by the Arrhenius equation. The slope gives  $-E_a/R$  and the intercept at  $1/T = 0$  gives  $\ln A$ .

## Alternative form of the Arrhenius equation

$$k_r = Ae^{-E_a/RT} \longrightarrow (22)$$

As the reaction proceeds, A and B come into contact, distort, and begin to exchange or discard atoms. The **reaction coordinate** is the collection of motions, such as changes in interatomic distances and bond angles, that are directly involved in the formation of products from reactants. The potential energy rises to a maximum and the cluster of atoms that corresponds to the maximum point is called the **activated complex**. After the maximum, the potential energy falls as the atoms rearrange in the cluster and reaches a value characteristic of the products. The peak in the potential energy profile corresponds to the activation energy  $E_a$ . The configuration corresponding to the peak in the potential energy profile is called the **transition state** of the reaction.



**Fig. 8:** A potential energy profile for an exothermic reaction. The height of the barrier between the reactants and products is the activation energy of the reaction.



- For a reaction **involving** the collision of two molecules, *the activation energy is the minimum kinetic energy that reactants must have in order to form products.*
- The fraction of collisions with a kinetic energy in excess of an energy  $E_a$  is given by the Boltzmann distribution as  $e^{-E_a/RT}$ .
- The pre-exponential factor is a measure of the rate at which collisions occur irrespective of their energy. Hence, the product of  $A$  and the exponential factor,  $e^{-E_a/RT}$ , gives the rate of *successful* collisions.

## Elementary Reactions

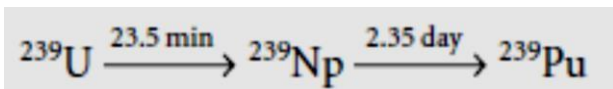
- The mechanism of reaction is the sequence of elementary steps involved in a reaction.
- The molecularity of an elementary reaction is the number of molecules coming together to react.
- An elementary unimolecular reaction has first-order kinetics; an elementary bimolecular reaction has second-order kinetics.

## Difference between molecularity and order:

- *reaction order* is an empirical quantity, and obtained from the experimental rate law;
- *molecularity* refers to an elementary reaction proposed as an individual step in a mechanism.

## Consecutive Elementary Reactions

Some reactions proceed through the formation of an intermediate (I), as in the consecutive unimolecular reactions



### (a) The variation of concentrations with time

The rate of unimolecular decomposition of A is

$$\frac{d[A]}{dt} = -k_a[A] \longrightarrow (23)$$

The intermediate I is formed from A (at a rate  $k_a[A]$ ) but decays to P (at a rate  $k_b[I]$ ). The net rate of formation of I is therefore

$$\frac{d[I]}{dt} = k_a[A] - k_b[I] \longrightarrow (24)$$

The product P is formed by the unimolecular decay of I:

$$\frac{d[P]}{dt} = k_b[I] \longrightarrow (25)$$

We suppose that initially only A is present, and that its concentration is  $[A]_0$ . The first of the rate laws, eqn 23 is an ordinary first-order decay, so we can write

$$[A] = [A]_0 e^{-k_a t} \longrightarrow (26)$$

When this equation is substituted into eqn 24, we obtain after rearrangement

$$\frac{d[I]}{dt} + k_b[I] = k_a[A]_0 e^{-k_a t} \longrightarrow (27)$$

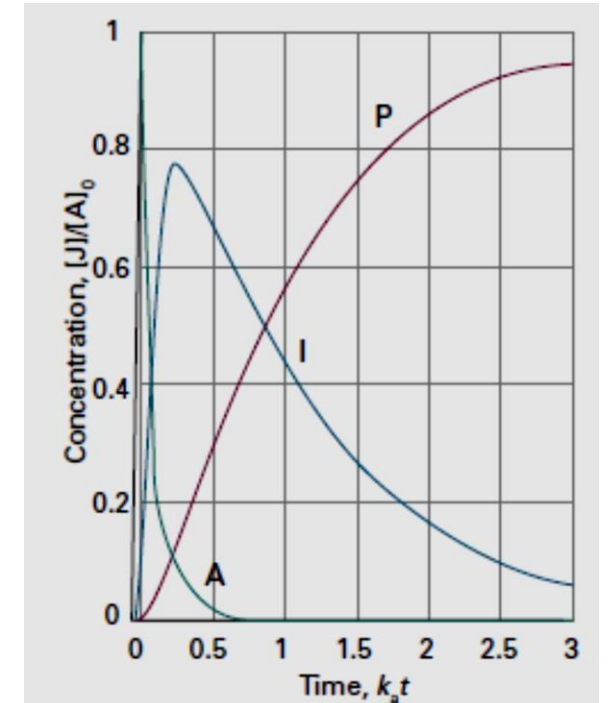
This differential equation has a standard form and, after setting  $[I]_0 = 0$ , the solution is

$$[I] = \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) [A]_0 \longrightarrow (28)$$

At all times  $[A] + [I] + [P] = [A]_0$ , so it follows that

$$P = \left\{ 1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_b - k_a} \right\} [A]_0 \longrightarrow (29)$$

The concentration of the intermediate I rises to a maximum and then falls to zero. The concentration of the product P rises from zero towards  $[A]_0$ .



**Fig. 9:** The concentrations of A, I, and P in the consecutive reaction scheme  $A \rightarrow I \rightarrow P$ .

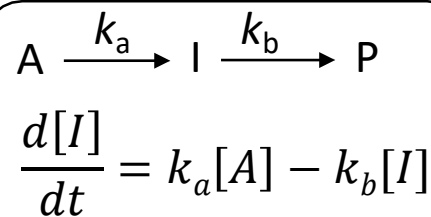
## (b) The steady-state approximation

The **steady-state approximation** (which is also widely called the **quasi-steady-state approximation**, QSSA) assumes that, after an initial **induction period**, an interval during which the concentrations of intermediates, I, rise from zero, and during the major part of the reaction, the rates of change of concentrations of all reaction intermediates are negligibly small

$$\frac{d[I]}{dt} \approx 0 \longrightarrow (30)$$

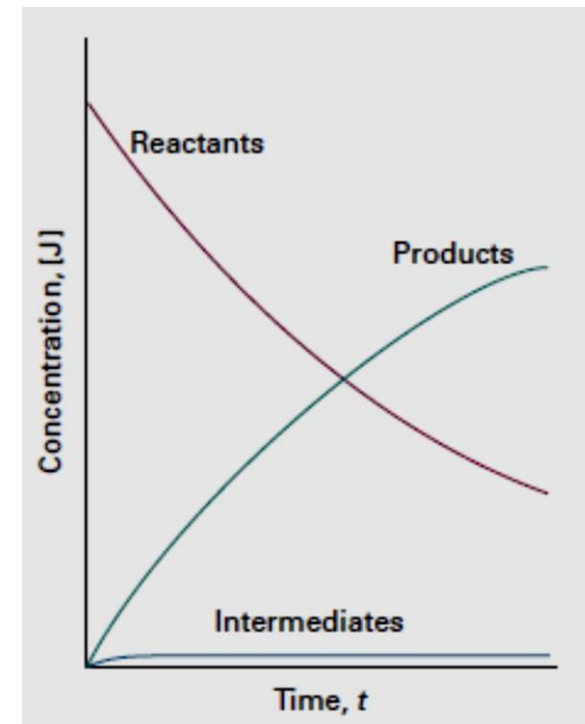
when we apply the approximation to the consecutive first-order mechanism, we set  $d[I]/dt = 0$ , which then becomes  $k_a[A] - k_b[I] \approx 0$ . Then

$$[I] \approx (k_a/k_b)[A] \longrightarrow (31)$$



On substituting this value of [I] into eqn 25, that equation becomes

$$\frac{d[P]}{dt} = k_b[I] \approx k_a[A] \longrightarrow (32) \quad \boxed{\frac{d[P]}{dt} = k_b[I]}$$



**Fig. 10:** The basis of the steady-state approximation. It is supposed that the concentrations of intermediate remain small and hardly change during the course of the reaction.

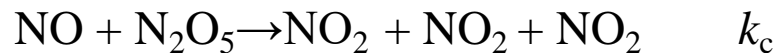
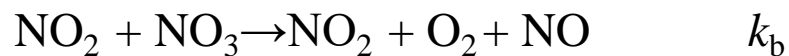
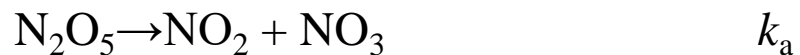
We see that P is formed by a first-order decay of A, with a rate constant  $k_a$ , the rate constant of the slower, rate-determining, step. After substituting the solution for [A], eqn , and integrating:

$$[P] = k_a[A]_o \int_0^t e^{-k_a t} dt = (1 - e^{-k_a t})[A]_o \longrightarrow (33)$$

**Problem 1:** Devise the rate law for the decomposition of  $N_2O_5$ ,



on the basis of the following mechanism:



**Answer** The intermediates are NO and NO<sub>3</sub>; the net rates of change of their concentrations are

$$\frac{d[\text{NO}]}{dt} = k_b[\text{NO}_2][\text{NO}_3] - k_c[\text{NO}][\text{N}_2\text{O}_5] \approx 0$$

$$\frac{d[\text{NO}_3]}{dt} = k_a[\text{N}_2\text{O}_5] - k'_a[\text{NO}_2][\text{NO}_3] - k_b[\text{NO}_2][\text{NO}_3] \approx 0$$

The net rate of change of concentration of N<sub>2</sub>O<sub>5</sub> is

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_a[\text{N}_2\text{O}_5] + k'_a[\text{NO}_2][\text{NO}_3] - k_c[\text{NO}][\text{N}_2\text{O}_5]$$

We use

$$k_b[\text{NO}_2][\text{NO}_3] - k_c[\text{NO}][\text{N}_2\text{O}_5] = 0$$

and

$$k_a[\text{N}_2\text{O}_5] - k'_a[\text{NO}_2][\text{NO}_3] - k_b[\text{NO}_2][\text{NO}_3] = 0$$

to write

$$[\text{NO}] = \frac{k_b[\text{NO}_2][\text{NO}_3]}{k_c[\text{N}_2\text{O}_5]}$$

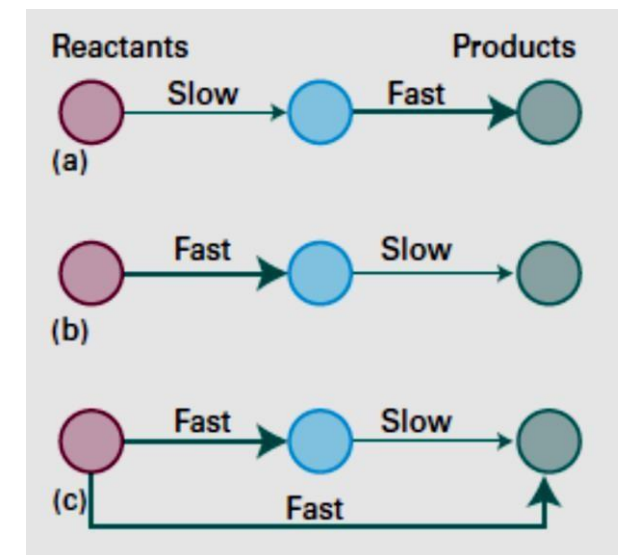
$$[\text{NO}_3] = \frac{k_a[\text{N}_2\text{O}_5]}{(k'_a + k_b)[\text{NO}_2]}$$

and then substitute these expressions into that for d[N<sub>2</sub>O<sub>5</sub>]/dt to obtain

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -\frac{2k_a k_b [\text{N}_2\text{O}_5]}{k'_a + k_b}$$

### (c) The rate-determining step

In general the **rate-determining step** is the slowest step in a mechanism and controls the overall rate of the reaction. However, the rate-determining step is not just the slowest step: it must be slow *and* be a crucial gateway for the formation of products. If a faster reaction can also lead to products, then the slowest step is irrelevant because the slow reaction can then be sidestepped.



- (a) The first step is rate-determining;  
(b) the second step is rate-determining;  
(c) although one step is slow, it is not rate-determining because there is a fast route that circumvents it.

**Problem 2:** Derive the rate law for the decomposition of ozone in the reaction  $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$  on the basis of the mechanism

