Chemical kinetic

Study of the rate of chemical reactions

- Measurements of reactions rates
- How to predict reaction rates
- Determine reaction mechanisms

$$\mathbf{a\,A + b\,B \longrightarrow g\,G + h\,H}$$

General Reaction Rate

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{g}\frac{\Delta[G]}{\Delta t} = \frac{1}{h}\frac{\Delta[H]}{\Delta t}$$

Chemical kinetic

General Reaction Rate

$$aA + bB \longrightarrow gG + hH$$

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t}$$

Expressed from consumption of reagents

$$\text{Rate} = \frac{1}{g}\frac{\Delta[G]}{\Delta t} = \frac{1}{h}\frac{\Delta[H]}{\Delta t}$$

Expressed from production of products

Chemical kinetic

Study of the rate of chemical reactions

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

t / s	$[H_2O_2]$ / M	Δ t	Δ $[H_2O_2]$	Rate / M s^{-1}
0	2.32			
		200	0.31	1.550E-03
200	2.01			
		200	0.29	1.450E-03
400	1.72			
		200	0.23	1.150E-03
600	1.49			
		200	0.19	9.500E-04
800	1.30			
		400	0.32	8.000E-04
1200	0.98			
		400	0.25	6.250E-04
1600	0.73			
		400	0.19	4.750E-04
2000	0.54			
		400	0.15	3.750E-04
2400	0.39			
		400	0.11	2.750E-04
2800	0.28			

Average Rate

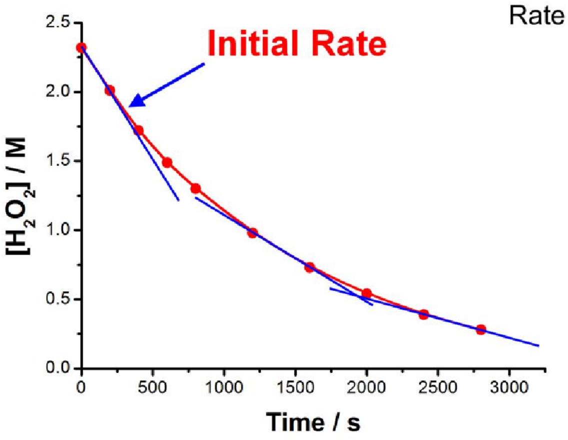
$$\text{Rate} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

$$\text{Rate} = \frac{1}{1/2}\,\frac{\Delta[O_2]}{\Delta t}$$

Chemical kinetic

Study of the rate of chemical reactions

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$$



Initial Rate

Instantaneous Rate

$$\text{Rate} = \lim_{\Delta t \to 0}\left(-\frac{\Delta[H_2O_2]}{\Delta t}\right) = -\frac{d[H_2O_2]}{dt}$$

Slope of the tangent

Chemical kinetic

Effect of concentration: the Rate Law

$$a\,A + b\,B \longrightarrow g\,G + h\,H$$

$$\boxed{\mathrm{Rate} = k\,[A]^m[B]^n}$$ **Rate Law**

k: Kinetic constant

m and n: Partial reaction order with respect to the reagents

$m + n$: Overall reaction order

m and n are small numbers:

- Positive, negative or zero
- Integer or fractional
- NO CONNECTION with stoichiometric coefficients!!!
- Must be determined experimentally.

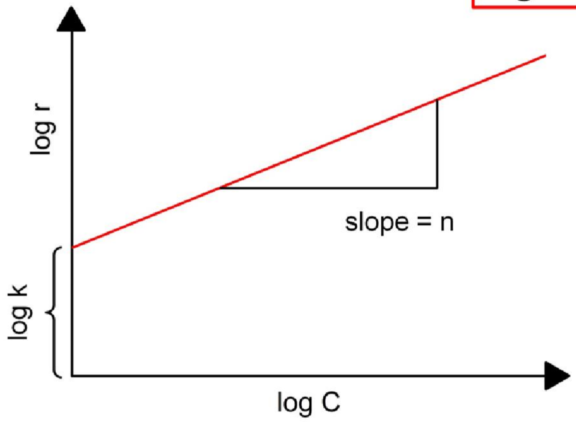
Chemical kinetic

Partial reaction order

In the case of a reaction with a only one reagent, for a nth reaction order:

$$r = -\frac{dC}{dt} = k\,C^n$$

$$\boxed{\log r = \log k + n \log C}$$

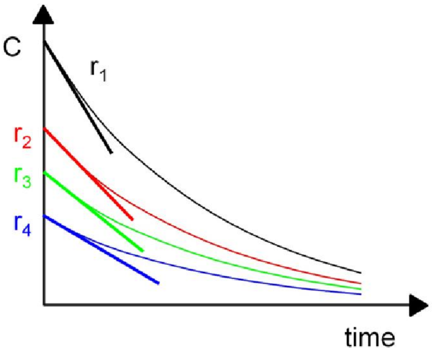


Chemical kinetic

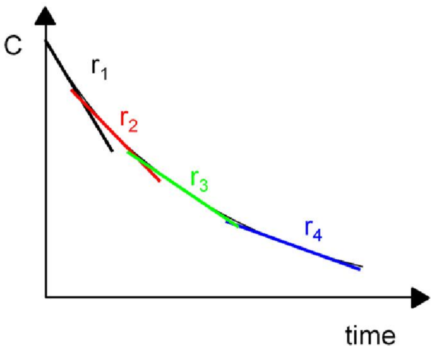
Partial reaction order

The graph can be obtained in 2 ways:

Measuring initial rate for different concentrations:



Measuring the instantaneous rate at different reaction time:



Chemical kinetic

Partial reaction order

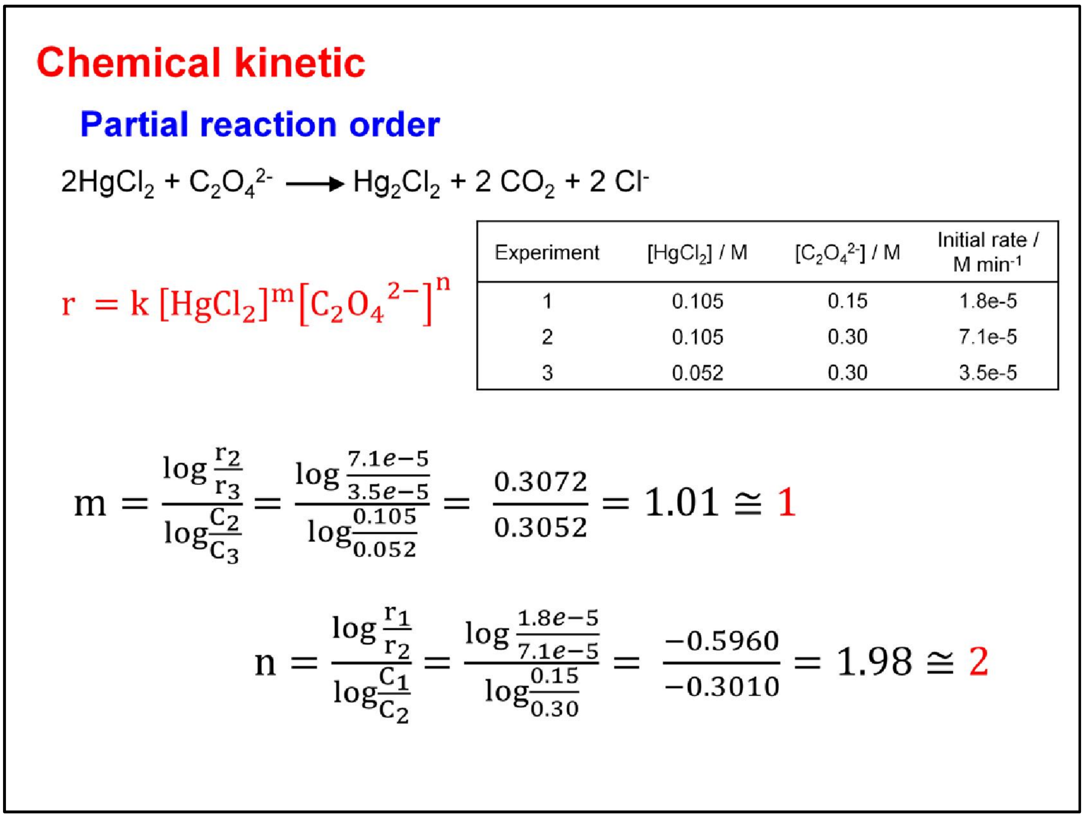
In the case of a reaction with more than one reagent, the reaction rate is determined changing the concentration of the specific reagent maintaining constant all the other:

$$\mathrm{r} = \mathrm{k}\,\mathrm{C}^{\mathrm{n}}$$

$$\frac{\mathrm{r}_1}{\mathrm{r}_2} = \left(\frac{\mathrm{C}_1}{\mathrm{C}_2}\right)^{\mathrm{n}}$$

$$\log\frac{\mathrm{r}_1}{\mathrm{r}_2} = \mathrm{n}\log\frac{\mathrm{C}_1}{\mathrm{C}_2}$$

$$\boxed{\mathrm{n} = \frac{\log\frac{\mathrm{r}_1}{\mathrm{r}_2}}{\log\frac{\mathrm{C}_1}{\mathrm{C}_2}}}$$



Chemical kinetic

Partial reaction order

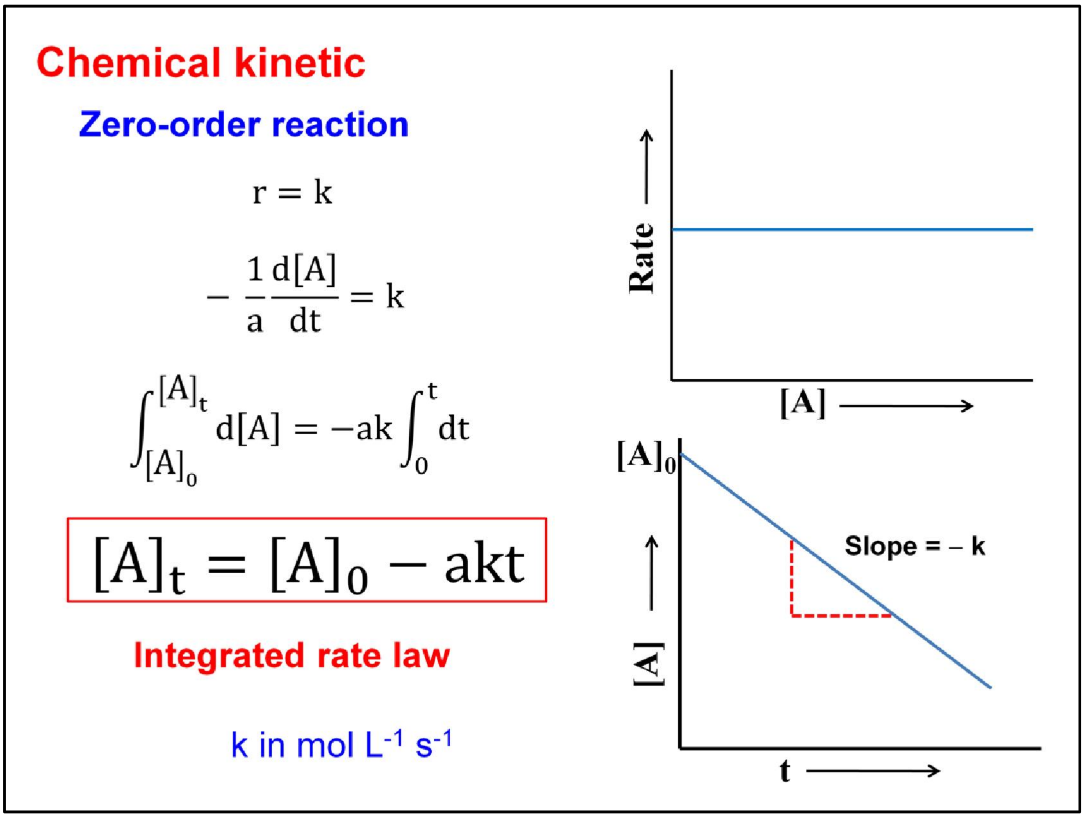
$2HgCl_2 + C_2O_4^{2-} \longrightarrow Hg_2Cl_2 + 2\,CO_2 + 2\,Cl^-$

$$r = k\,[HgCl_2]^m[C_2O_4{}^{2-}]^n$$

Experiment	$[HgCl_2]$ / M	$[C_2O_4^{2-}]$ / M	Initial rate / M min^{-1}
1	0.105	0.15	1.8e-5
2	0.105	0.30	7.1e-5
3	0.052	0.30	3.5e-5

$$m = \frac{\log\frac{r_2}{r_3}}{\log\frac{C_2}{C_3}} = \frac{\log\frac{7.1e-5}{3.5e-5}}{\log\frac{0.105}{0.052}} = \frac{0.3072}{0.3052} = 1.01 \cong 1$$

$$n = \frac{\log\frac{r_1}{r_2}}{\log\frac{C_1}{C_2}} = \frac{\log\frac{1.8e-5}{7.1e-5}}{\log\frac{0.15}{0.30}} = \frac{-0.5960}{-0.3010} = 1.98 \cong 2$$



Chemical kinetic

Zero-order reaction

$$r = k$$

$$-\frac{1}{a}\frac{d[A]}{dt} = k$$

$$\int_{[A]_0}^{[A]_t} d[A] = -ak\int_0^t dt$$

$$\boxed{[A]_t = [A]_0 - akt}$$

Integrated rate law

k in mol L^{-1} s^{-1}

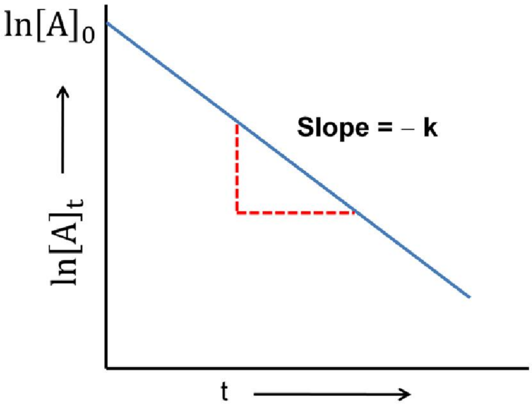
Chemical kinetic

First-order reaction

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A]$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -ak\int_0^t dt$$

$$\boxed{\ln\frac{[A]_t}{[A]_0} = -akt}$$



k in s^{-1}

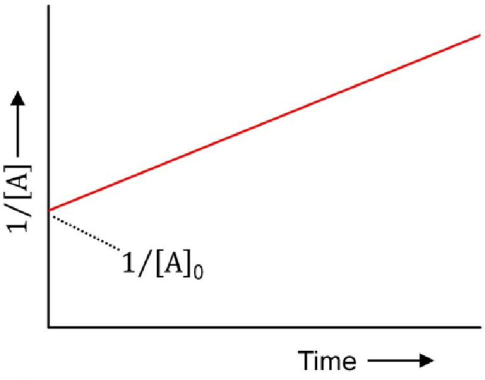
Chemical kinetic

Second-order reaction

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A]^2$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -ak\int_0^t dt$$

$$\boxed{\frac{1}{[A]_t} = akt + \frac{1}{[A]_0}}$$



k in L mol^{-1} s^{-1}

Chemical kinetic

Half-time

For a reaction the half-life $t_{1/2}$ of a particular reactant is defined as the time required to **reduce the concentration to half of its initial value**.

Order	**Half-time $t_{1/2}$**
0	$\frac{[\mathrm{A}]_0}{2\mathrm{ak}}$
1	$\frac{0.693}{\mathrm{ak}}$
2	$\frac{1}{\mathrm{ak}[\mathrm{A}]_0}$

Chemical kinetic

Factors Affecting the Rate of a Reaction

1. Concentration of the reactants

2. Nature of reactants
- Physical state
- Surface area
- Molecular nature

- ❖ Rate of reactions with reactants in
  gaseous phase > solution phase > solid phase

- ❖ Larger the surface area, larger is the area of contact hence faster is the rate of the reaction

Chemical kinetic

Molecular nature of the reactant

More is the structural similarity between the reactant and the product ⇒ faster is the reaction (Not always)

Lesser the rearrangement of bonds needed in the reaction ⇒ faster is the reaction

$NO + \frac{1}{2} O_2 \rightarrow NO_2$ ……………….(1)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ ……………….(2)

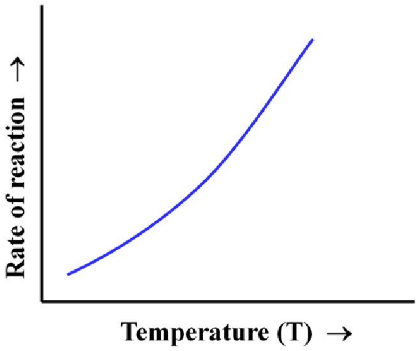
Chemical kinetic

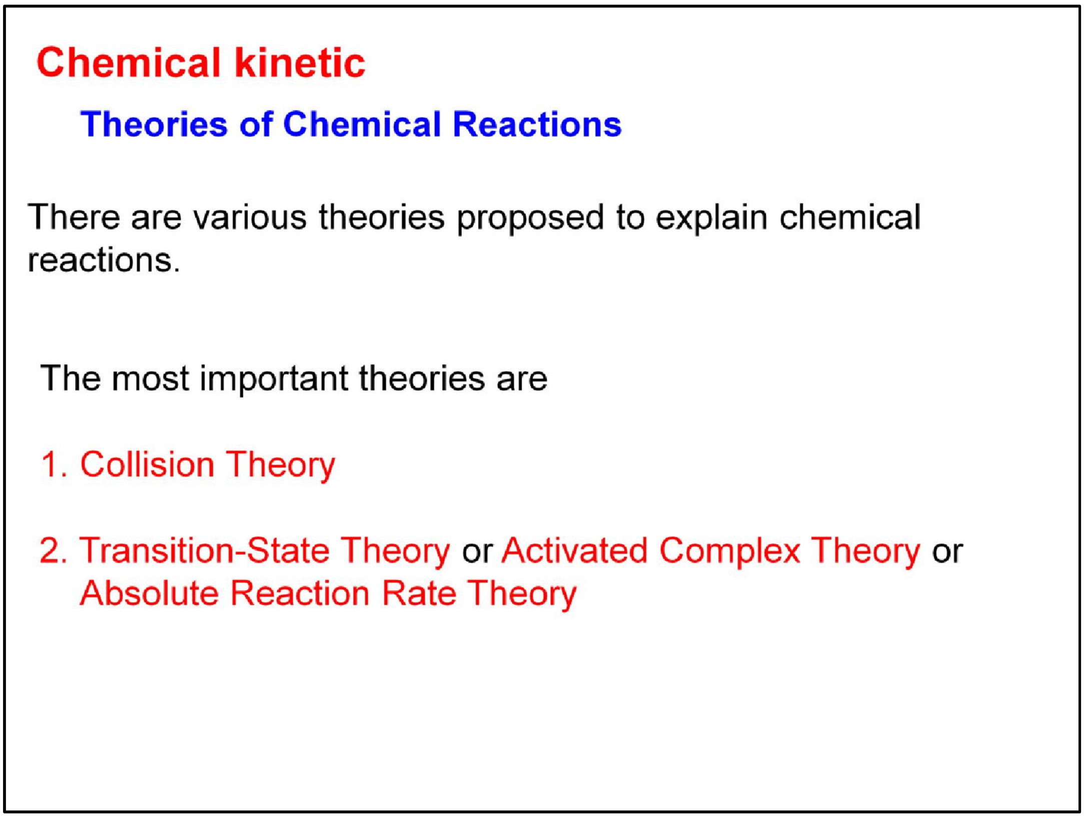
Effect of temperature

Temperature has a marked effect on the reactions

(i) Can initiate a reaction

(ii) Increases the rate of the reaction





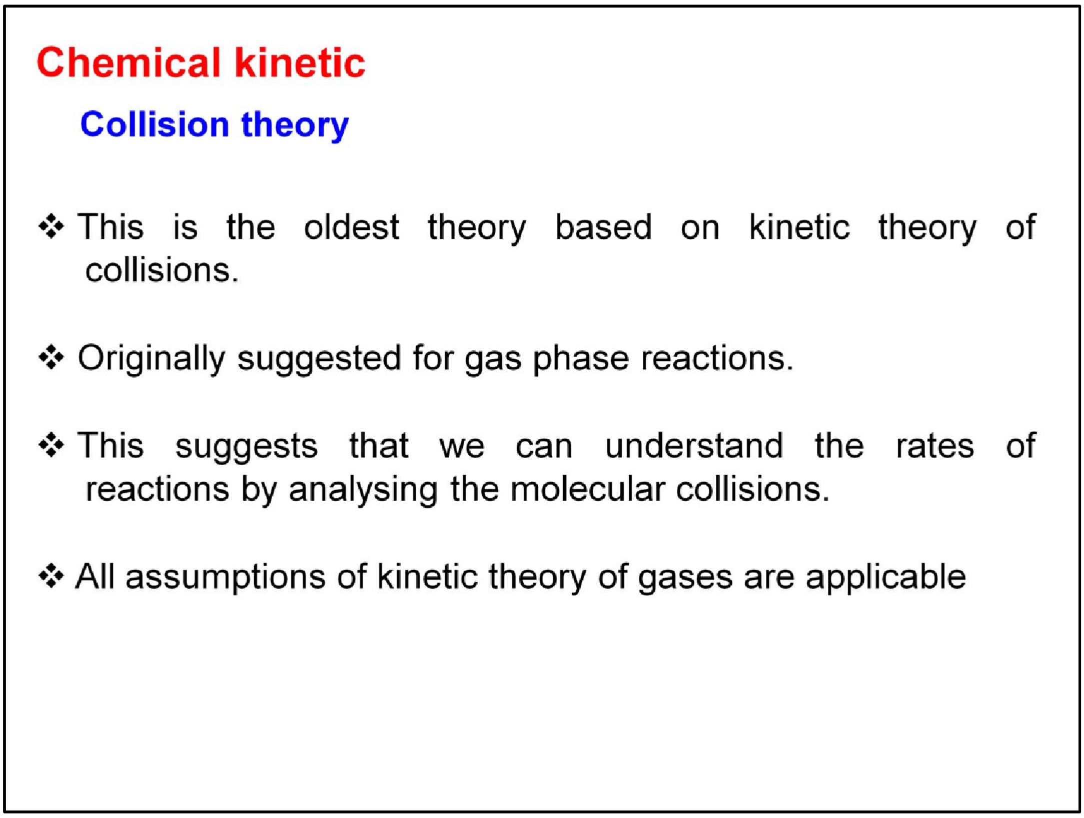
Chemical kinetic

Theories of Chemical Reactions

There are various theories proposed to explain chemical reactions.

The most important theories are

1. Collision Theory
2. Transition-State Theory or Activated Complex Theory or Absolute Reaction Rate Theory



Chemical kinetic

Collision theory

- This is the oldest theory based on kinetic theory of collisions.
- Originally suggested for gas phase reactions.
- This suggests that we can understand the rates of reactions by analysing the molecular collisions.
- All assumptions of kinetic theory of gases are applicable

Chemical kinetic

Collision theory - Assumptions

- The molecules/atoms are hard spheres
- The molecular motions are explained by classical mechanics or Newtonian mechanics
- The size of the molecules is negligible as compared to the typical distance between them
- Due to the kinetic energy of molecules, they move around and collide with each other
- The molecular collisions are perfectly elastic *i.e.* energy is conserved

Chemical kinetic

Collision theory

The velocity of the molecules is distributed according to Maxwell distribution.

The mean velocity of a molecule is given as

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi\, m}}$$

k_B Boltzmann constant,
T Temperature,
m mass of a molecule

Considering collision between two types of molecules A and B of mass m_A and m_B then the mean relative velocity is given by

$$\bar{u}_{rel} = \sqrt{\frac{8k_B T}{\pi\, \mu}} \qquad \text{Where} \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

Chemical kinetic

Collision theory

The rate of the reaction can be calculated from the rate at which the reactant molecules are colliding

So the collision rate or collision number (number of collisions per unit volume per unit time) is expressed as

$$Z_{AB} = N_A N_B \pi (r_A + r_B)^2 \bar{u}_{rel}$$

$$\boxed{Z_{AB} = N_A N_B \sigma \sqrt{\frac{8k_B T}{\pi \mu}}}$$

$$\sigma = \pi (r_A + r_B)^2 = \text{Collision cross section}$$

Chemical kinetic

Collision theory

The collision between A and B will result in a reaction provided the energy of the collision is sufficient to overcome the energy barrier E_a (effective collision).

According to Boltzmann distribution the fraction of collisions with energy of E_a is proportional to $e^{-Ea/RT}$

So the number of effective collisions per unit volume per unit time = number of product molecules formed per unit volume per unit time

$$Z_{AB}\, e^{-E_a/RT}$$

Number of moles of product formed per unit volume per unit time

$$\boxed{\left(Z_{AB}\, e^{-E_a/RT}\right)/N}$$

Chemical kinetic

Collision theory

The rate expressed in moles/unit volume/unit time is

$$r = \left(Z_{AB}\, e^{-E_a/RT}\right)/N$$

$$\boxed{r = \frac{1}{N}\, N_A N_B \sigma \sqrt{\frac{8k_B T}{\pi\, \mu}}\; e^{-E_a/RT}}$$

If the reaction is first order w.r.t. both A and B

A + B → P

r = k [A] [B]

$$\boxed{r = k\, \frac{N_A}{N}\, \frac{N_B}{N}}$$

$$\frac{N_A}{N} = [A], \qquad \frac{N_B}{N} = [B]$$

Chemical kinetic

Collision theory

Comparing the two equations we get

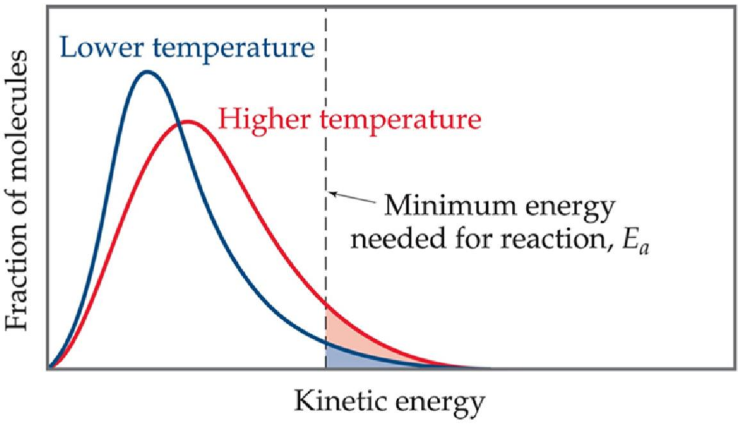
$$\boxed{k = N\sigma \sqrt{\frac{8k_BT}{\pi\,\mu}}\; e^{-E_a/RT}}$$

‘k’ is the bimolecular rate constant or second order rate constant

Chemical kinetic

Collision theory – Effect of temperature

The velocity of the molecules is distributed according to Maxwell distribution.



Increasing T, the fraction of molecules having at least Ea increases, accelerating the reaction.

Chemical kinetic

Arrhenius equation

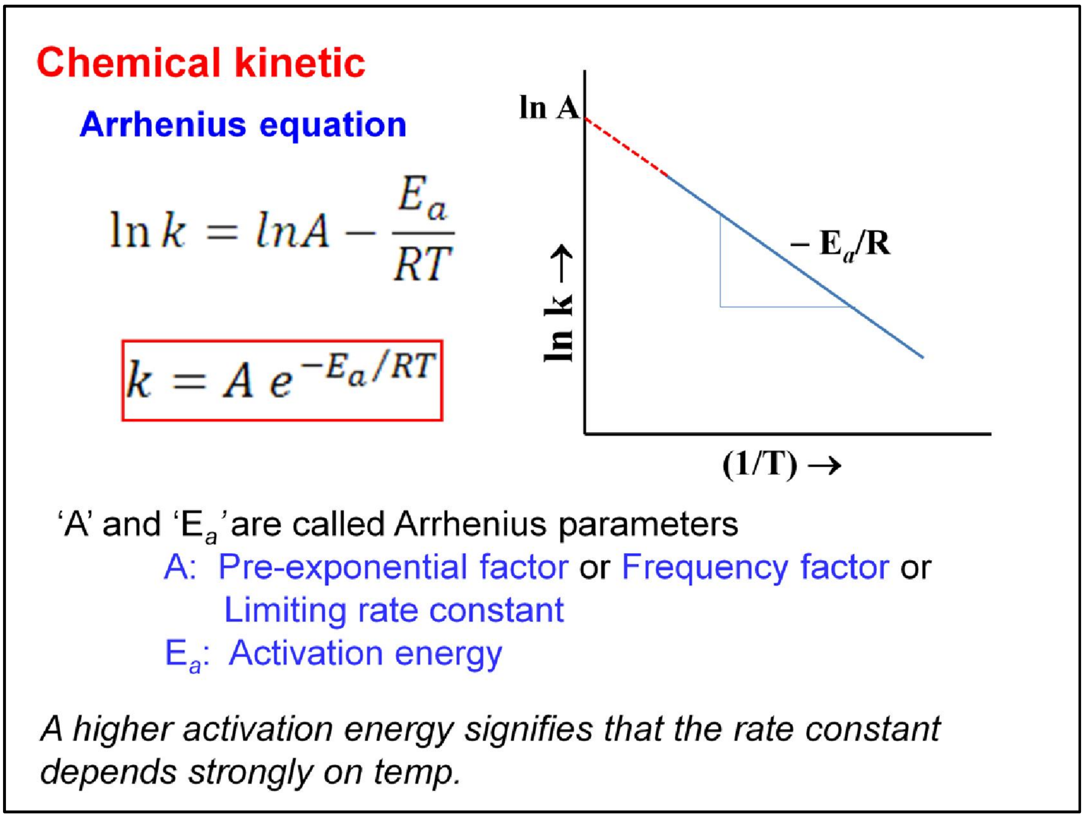
The equation:

$$\boxed{k = N\sigma \sqrt{\frac{8k_B T}{\pi\,\mu}}\; e^{-E_a/RT}}$$

$$\boxed{k = A\, e^{-E_a/RT}}$$

Arrhenius equation

with $$\boxed{A = N\sigma \sqrt{\frac{8k_B T}{\pi\,\mu}}}$$



Chemical kinetic

Arrhenius equation

$$\ln k = lnA - \frac{E_a}{RT}$$

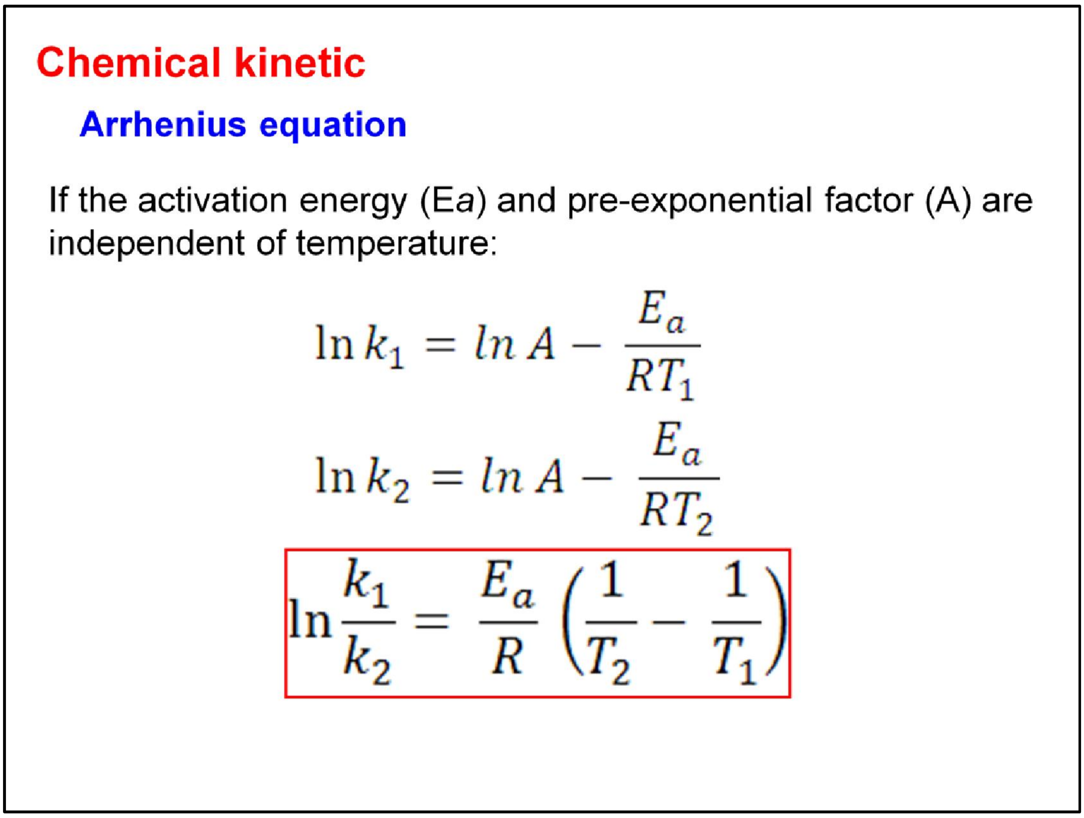
$$\boxed{k = A\, e^{-E_a/RT}}$$

'A' and 'E_a' are called Arrhenius parameters

A: Pre-exponential factor or Frequency factor or Limiting rate constant

E_a: Activation energy

A higher activation energy signifies that the rate constant depends strongly on temp.



Chemical kinetic

Arrhenius equation

If the activation energy (E*a*) and pre-exponential factor (A) are independent of temperature:

$$\ln k_1 = ln\,A - \frac{E_a}{RT_1}$$

$$\ln k_2 = ln\,A - \frac{E_a}{RT_2}$$

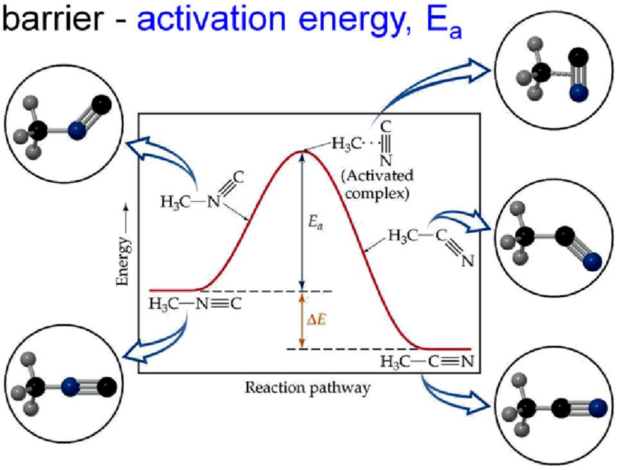
$$\boxed{\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Chemical kinetic

Activation energy

Molecules need a minimum amount of energy to react.

Visualized as an energy barrier - activation energy, E_a

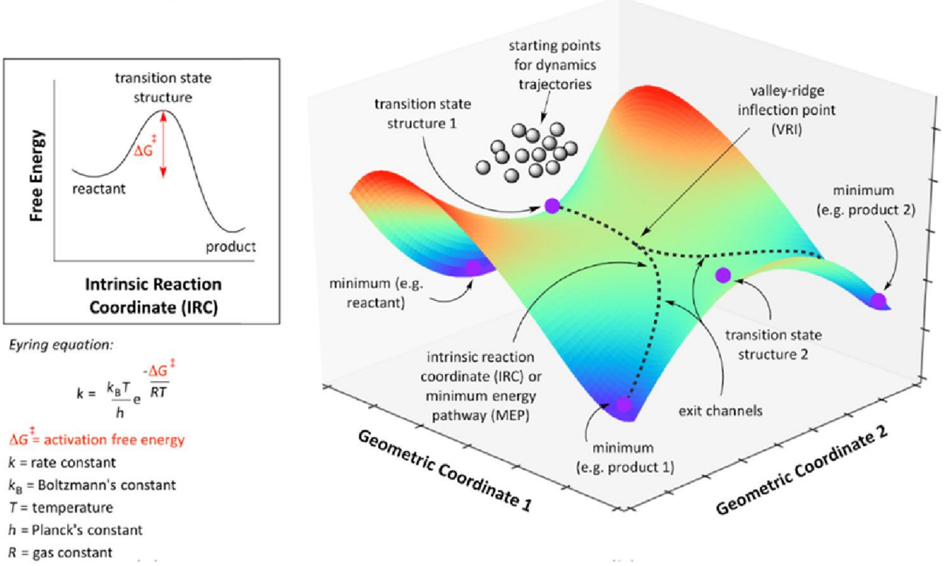


The lower the Activation barrier, the faster the reaction

Chemical kinetic

Reaction coordinate

It’s a pathway within a 3D space.



Eyring equation:

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

$\Delta G^{\ddagger}$ = activation free energy

k = rate constant

k_B = Boltzmann's constant

T = temperature

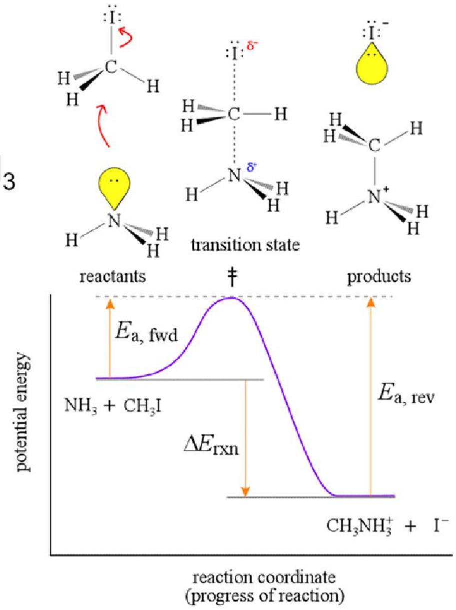
h = Planck's constant

R = gas constant

Chemical kinetic

Reaction coordinate

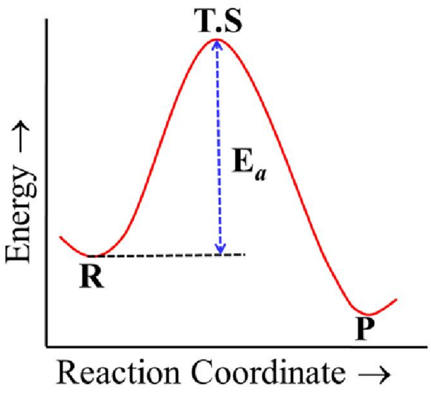
Substitution of CH_3I with NH_3

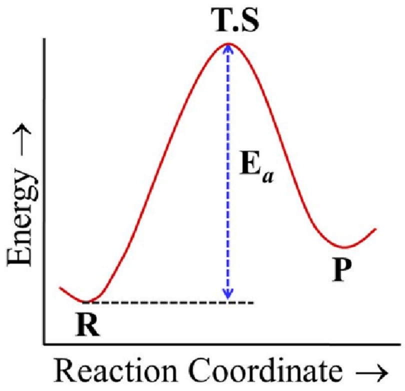


Chemical kinetic

Transition-state Theory

The reactants form some sort of complex with a structure somewhere between the reactant and the product and called as Transition-state or Activated complex





Chemical kinetic

Transition-state Theory - Assumptions

- The reactants A and B and the activated complex ($AB^{\#}$) in the T. S. are in quasi-equilibrium with each other and characterized by the pseudo-equilibrium constant ($K^{\#}$)
- The rate of the product formation is influenced by the rate of decomposition of the activated complex. The concentration of the activated complex that are becoming product can be calculated using equilibrium theory
- Molecules that have passed through activated complex configuration in the direction of product can't turn back and form reactant
- The energy distribution among the reactant molecules is in accordance with the Maxwell distribution.
- The activated complex has one special vibrational degree freedom associated with the mode of product formation along the reaction coordinate *i.e.* it has been converted to a translational degree of freedom along the reaction coordinate

Chemical kinetic

Transition-state Theory

Let’s consider a simple bimolecular reaction

$$A + B \overset{K^{\#}}{\rightleftharpoons} AB^{\neq} \overset{k^{\#}}{\rightarrow} products$$

Rate of the reaction = $k^{\#}$ [$AB^{\#}$]

In $AB^{\#}$ one of the vib. degree of freedom = translational degree of freedom which is responsible for the product formation

The rate at which the activated complex moves across the energy barrier is proportional to the vibrational frequency ‘ν’

Chemical kinetic

Transition-state Theory

The rate constant ($k^{\#}$) is related to the vibration frequency (ν) as $k^{\#} = \kappa\ \nu$ where κ **= kappa = transmission coefficient** and $0 < \kappa \leq 1$

For convenience the value of κ is taken = 1 and we know

$k_B T = h\nu$

$$Rate = \left(\frac{k_B T}{h}\right)[AB^{\neq}]$$

$$K^{\neq} = \frac{[AB^{\neq}]}{[A][B]}$$

$$[AB^{\neq}] = K^{\neq}[A][B]$$

$$Rate = \left(\frac{k_B T}{h}\right)[AB^{\neq}] \qquad \boxed{Rate = \left(\frac{k_B T}{h}\right) K^{\neq}[A][B]}$$

Chemical kinetic

Transition-state Theory

Considering the rate law for the reaction:

$$A + B \overset{k_2}{\rightarrow} Products$$

$$\boxed{Rate = k_2 [A][B]}$$

Comparing the above two equations:

$$\boxed{k_2 = bimolecular\ rate\ constant = \left(\frac{k_B T}{h}\right) K^{\neq}}$$

$$\boxed{k_2 = k^{\neq} K^{\neq}}$$

Chemical kinetic

Transition-state Theory

The equilibrium constant $K^{\#}$ can be expressed in terms of standard Gibbs free energy change of activation $(\Delta^{\neq} G^{o})$

$$\Delta^{\neq} G^{o} = -RT\, lnK^{\neq} \qquad \Delta^{\neq} G^{o} = \Delta^{\neq} H^{o} - T\Delta^{\neq} S^{o}$$

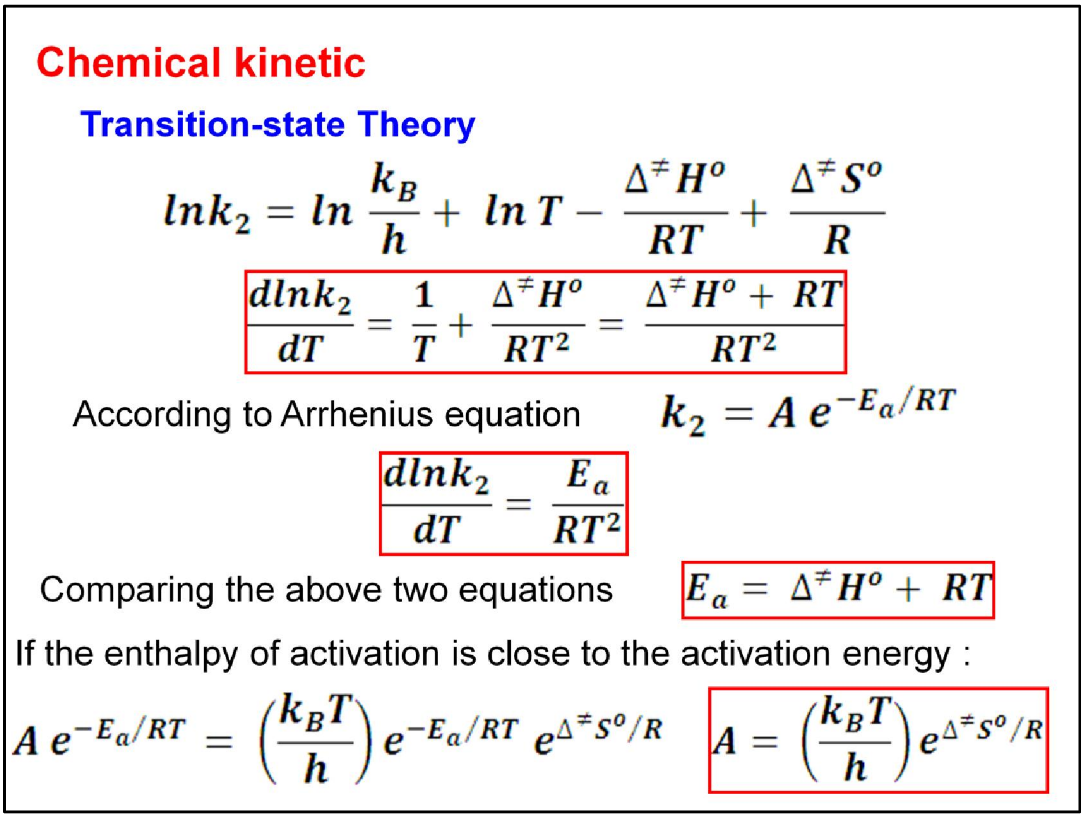
$$K^{\neq} = e^{-\Delta^{\neq} G^{o}/RT} = e^{-\Delta^{\neq} H^{o}/RT}\, e^{\Delta^{\neq} S^{o}/R}$$

$$k_2 = k^{\neq} e^{-\Delta^{\neq} H^{o}/RT}\, e^{\Delta^{\neq} S^{o}/R}$$

$$\boxed{k_2 = \left(\frac{k_B T}{h}\right) e^{-\Delta^{\neq} H^{o}/RT}\, e^{\Delta^{\neq} S^{o}/R}}$$

Eyring Equation

$$\Delta^{\neq} S^{o} = entropy\ of\ activation$$
$$\Delta^{\neq} H^{o} = enthalpy\ of\ activation$$



Chemical kinetic

Transition-state Theory

$$lnk_2 = ln\,\frac{k_B}{h} + \,ln\,T - \frac{\Delta^{\neq} H^o}{RT} + \frac{\Delta^{\neq} S^o}{R}$$

$$\boxed{\frac{dlnk_2}{dT} = \frac{1}{T} + \frac{\Delta^{\neq} H^o}{RT^2} = \frac{\Delta^{\neq} H^o + \,RT}{RT^2}}$$

According to Arrhenius equation $k_2 = A\,e^{-E_a/RT}$

$$\boxed{\frac{dlnk_2}{dT} = \frac{E_a}{RT^2}}$$

Comparing the above two equations $\boxed{E_a = \,\Delta^{\neq} H^o + \,RT}$

If the enthalpy of activation is close to the activation energy :

$$A\,e^{-E_a/RT} = \left(\frac{k_B T}{h}\right) e^{-E_a/RT}\,\,e^{\Delta^{\neq} S^o/R} \qquad \boxed{A = \left(\frac{k_B T}{h}\right) e^{\Delta^{\neq} S^o/R}}$$

Chemical kinetic

Mechanisms of reaction

A reaction mechanism is a sequence of elementary reactions (called “steps”) involved in the conversion of reactants to products.

For each elementary step:

$$\boxed{\mathrm{Rate} = k\,[A]^a[B]^b}$$

Where a and b are the stoichiometric coefficients in the step.

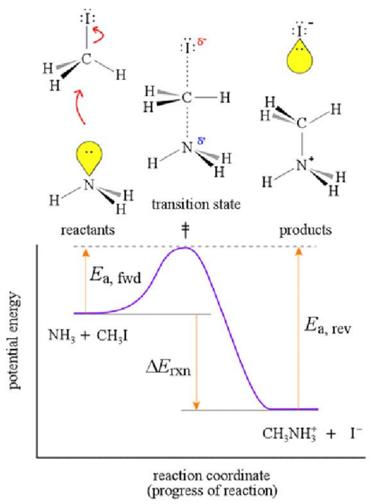
a + b = MOLECULARITY of the step.

Rate determining step: the **slowest step** in a chemical reaction determines the kinetics for the entire reaction. Steps that are **faster than the slow step are “invisible.”**

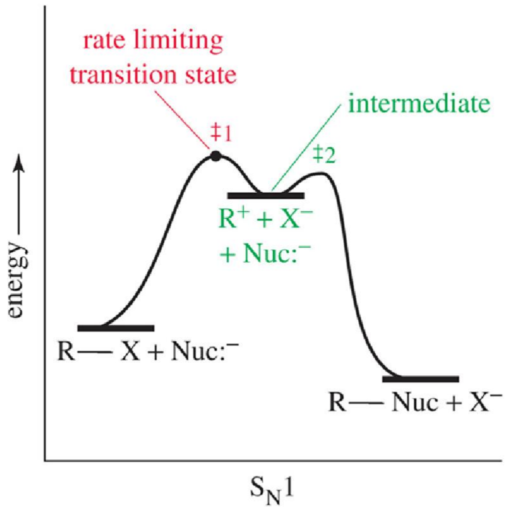
Chemical kinetic

Mechanisms of reaction

1 single step



More than one step



Chemical kinetic

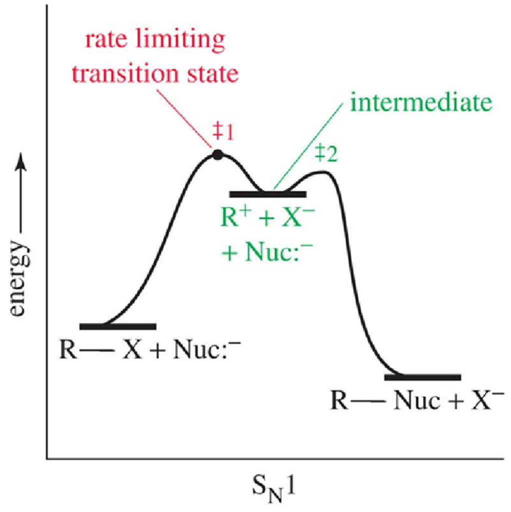
Mechanisms of reaction

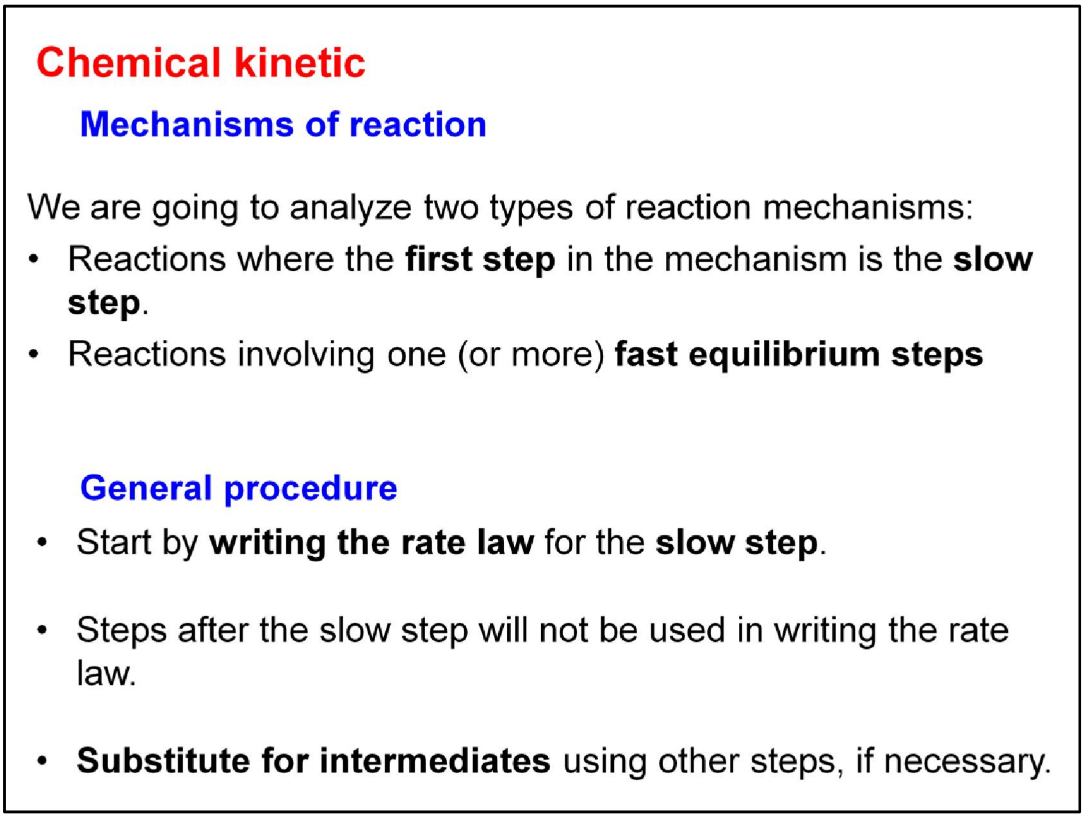
Reaction intermediates can be detected experimentally and sometimes isolated.

R.D.S. is the step with the higher E_a.

No more than two molecules are involved in each elementary step!!!

More than one step





Chemical kinetic

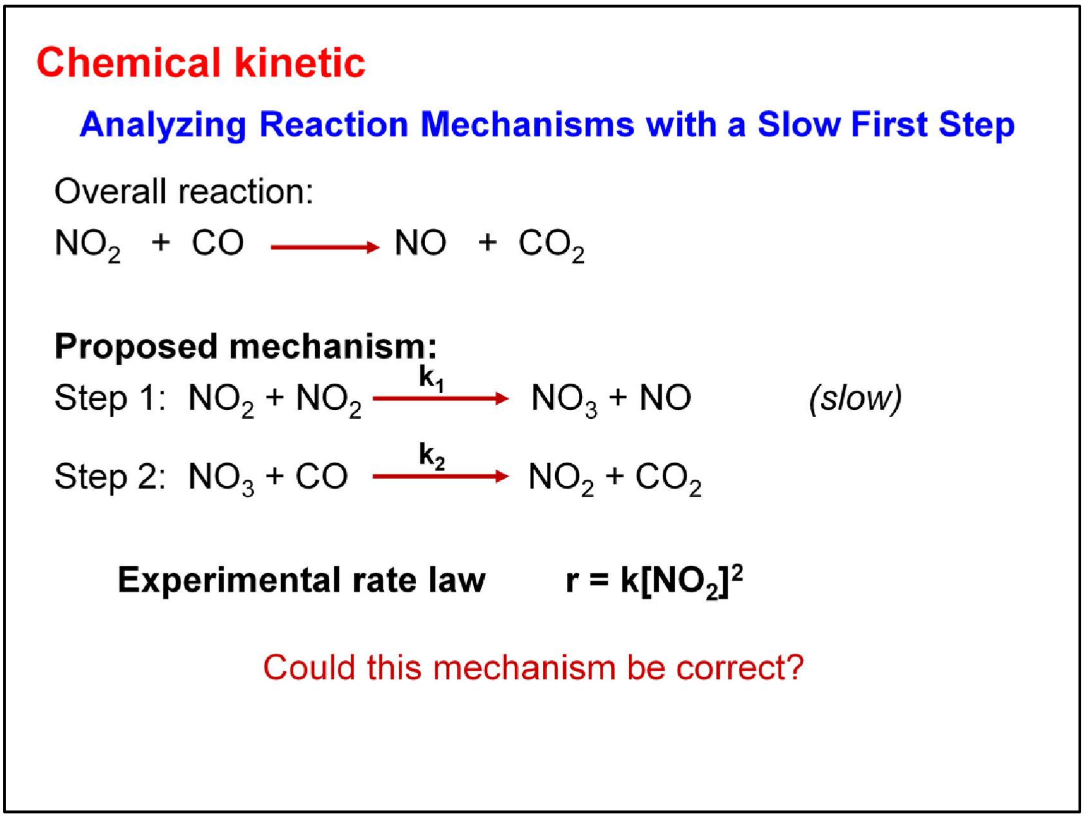
Mechanisms of reaction

We are going to analyze two types of reaction mechanisms:

- Reactions where the **first step** in the mechanism is the **slow step**.
- Reactions involving one (or more) **fast equilibrium steps**

General procedure

- Start by **writing the rate law** for the **slow step**.
- Steps after the slow step will not be used in writing the rate law.
- **Substitute for intermediates** using other steps, if necessary.



Chemical kinetic

Analyzing Reaction Mechanisms with a Slow First Step

Overall reaction:

$$NO_2 + CO \longrightarrow NO + CO_2$$

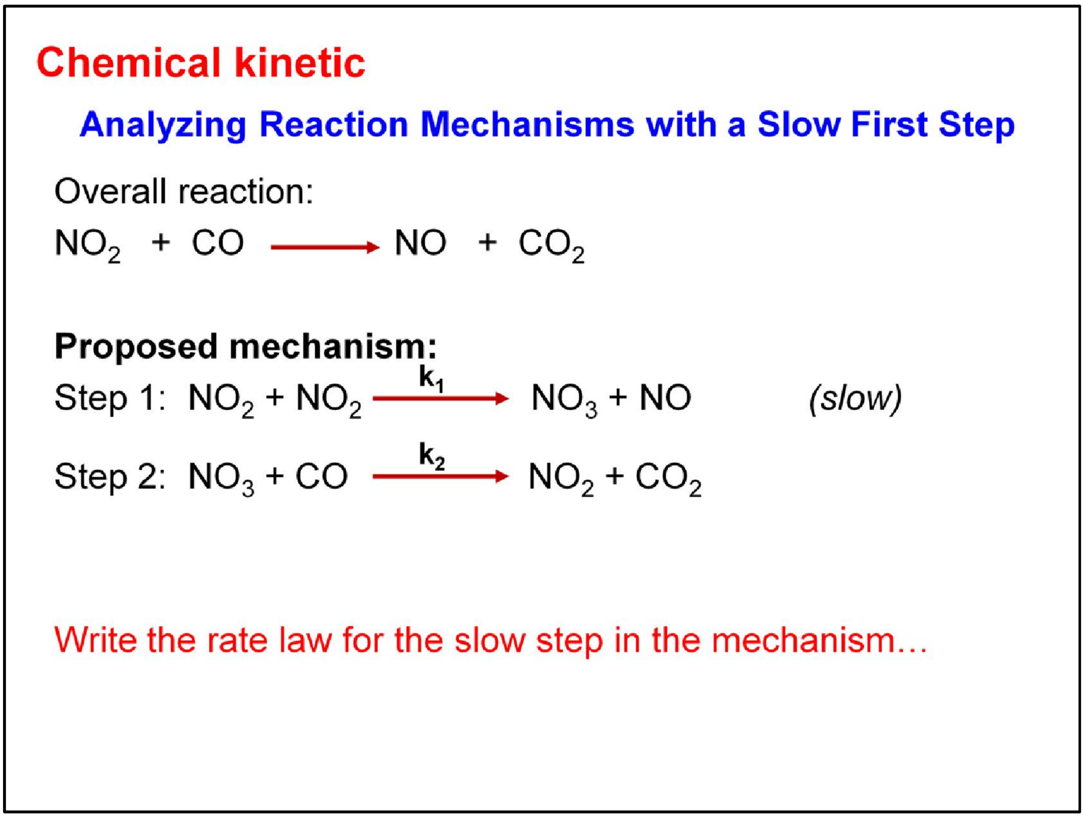
Proposed mechanism:

Step 1: $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$ *(slow)*

Step 2: $NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$

Experimental rate law $\mathbf{r = k[NO_2]^2}$

Could this mechanism be correct?



Chemical kinetic

Analyzing Reaction Mechanisms with a Slow First Step

Overall reaction:

$NO_2 + CO \longrightarrow NO + CO_2$

Proposed mechanism:

Step 1: $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$ *(slow)*

Step 2: $NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$

Write the rate law for the slow step in the mechanism…

Chemical kinetic

Analyzing Reaction Mechanisms with a Slow First Step

Overall reaction:

$NO_2 + CO \longrightarrow NO + CO_2$

Proposed mechanism:

Step 1: $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$ *(slow)*

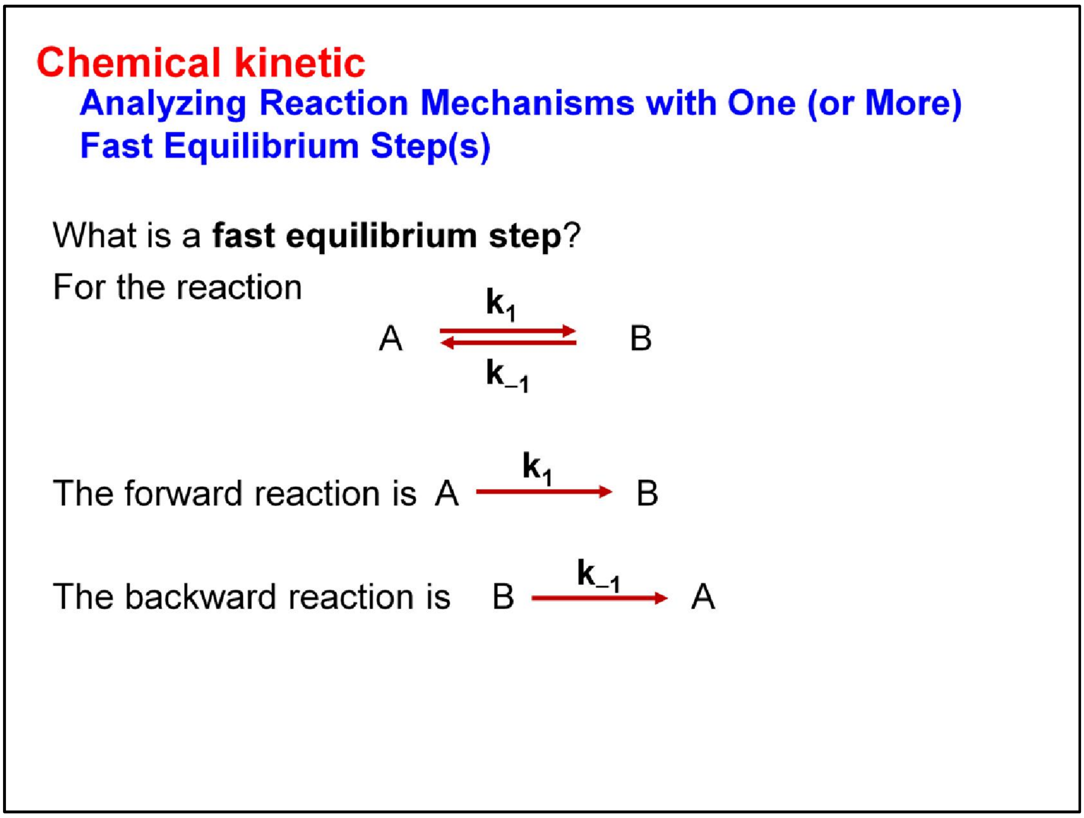
Step 2: $NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$

Rate law derived from mechanism: Rate = $k_1[NO_2]\,[NO_2]$

or…. **$r = k_1[NO_2]^2$**

Does it match the observed rate law?

Yes! We're done. The mechanism may be correct.



Chemical kinetic

Analyzing Reaction Mechanisms with One (or More) Fast Equilibrium Step(s)

What is a **fast equilibrium step**?

For the reaction

$$\mathrm{A} \underset{\mathbf{k_{-1}}}{\overset{\mathbf{k_1}}{\rightleftharpoons}} \mathrm{B}$$

The forward reaction is $\mathrm{A} \xrightarrow{\mathbf{k_1}} \mathrm{B}$

The backward reaction is $\mathrm{B} \xrightarrow{\mathbf{k_{-1}}} \mathrm{A}$

Chemical kinetic

Analyzing Reaction Mechanisms with One (or More) Fast Equilibrium Step(s)

For the reaction

$$A \underset{\mathbf{k_{-1}}}{\overset{\mathbf{k_1}}{\rightleftharpoons}} B$$

The rate law for the forward reaction is $r = k_1[A]$

The rate law for the backward reaction is $r = k_{-1}[B]$

Chemical kinetic

Analyzing Reaction Mechanisms with One (or More) Fast Equilibrium Step(s)

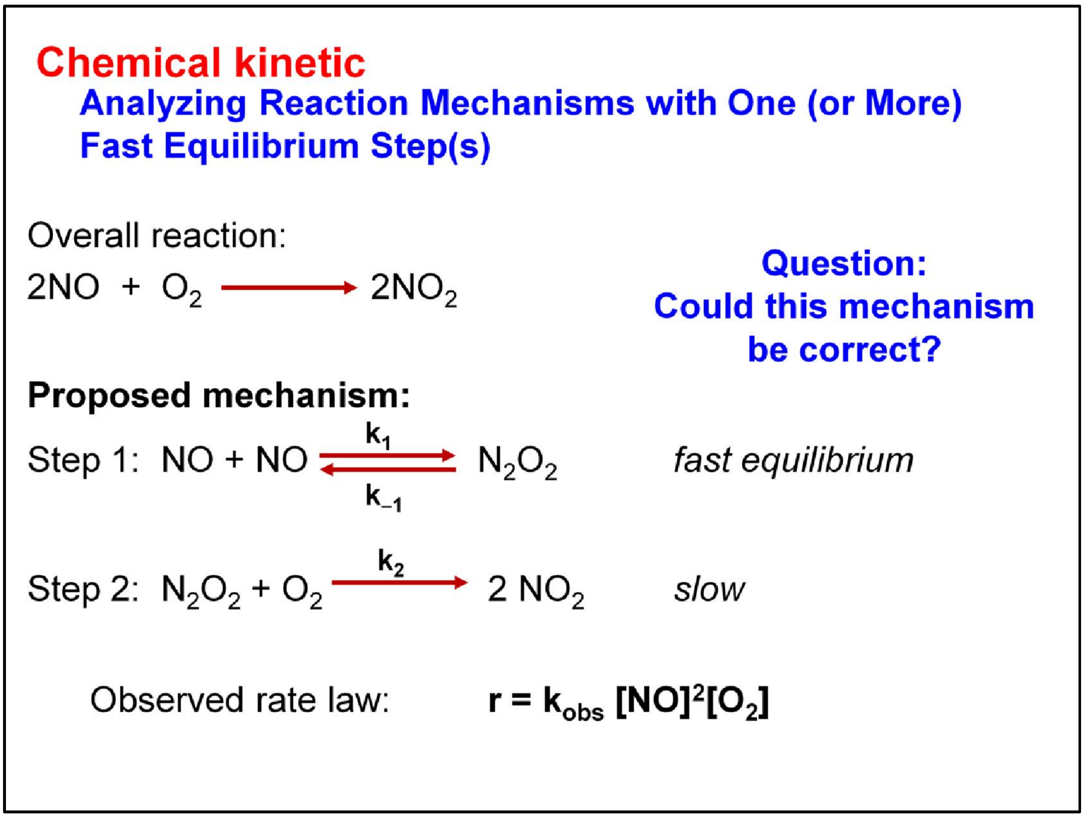
For the reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

The forward reaction rate is equal to the backward rate at equilibrium, so set them equal to each other.

$$k_1[A] = k_{-1}[B]$$

rate of fwd rxn = rate of back rxn



Chemical kinetic

Analyzing Reaction Mechanisms with One (or More) Fast Equilibrium Step(s)

Overall reaction:

$2\mathrm{NO} + \mathrm{O_2} \longrightarrow 2\mathrm{NO_2}$

Question:
Could this mechanism be correct?

Proposed mechanism:

Step 1: $\mathrm{NO} + \mathrm{NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2}$ *fast equilibrium*

Step 2: $\mathrm{N_2O_2} + \mathrm{O_2} \xrightarrow{k_2} 2\,\mathrm{NO_2}$ *slow*

Observed rate law: $\mathbf{r = k_{obs}\,[NO]^2[O_2]}$

Chemical kinetic

Analyzing Reaction Mechanisms with One (or More) Fast Equilibrium Step(s)

Proposed mechanism:

Step 1: $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ *fast equilibrium*

Step 2: $N_2O_2 + O_2 \xrightarrow{k_2} 2\ NO_2$ *slow*

Write the rate law for the slow step:

$r = k_2\ [N_2O_2][O_2]$

There is an intermediate in the rate law… not allowed!

Chemical kinetic

Analyzing Reaction Mechanisms with One (or More) Fast Equilibrium Step(s)

Proposed mechanism:

Step 1: $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ *fast equilibrium*

Step 2: $N_2O_2 + O_2 \xrightarrow{k_2} 2\ NO_2$ *slow*

Use the fast equilibrium step to substitute for the intermediate. Write the forward rate equal to the backward rate:

$$k_1[NO][NO] = k_{-1}[N_2O_2]$$

rate of fwd rxn = rate of back rxn

Chemical kinetic

Analyzing Reaction Mechanisms with One (or More) Fast Equilibrium Step(s)

Proposed mechanism:

Step 1: $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ *fast equilibrium*

Step 2: $N_2O_2 + O_2 \xrightarrow{k_2} 2\ NO_2$ *slow*

Solve for the intermediate **$[N_2O_2]$** by dividing both sides by k_{-1}

$$[\mathbf{N_2O_2}] = \left(\frac{\mathbf{k_1[NO]^2}}{\mathbf{k_{-1}}}\right)$$

Plug this quantity into the rate law for $[N_2O_2]$

Chemical kinetic

Analyzing Reaction Mechanisms with One (or More) Fast Equilibrium Step(s)

Proposed mechanism:

Step 1: $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ *fast equilibrium*

Step 2: $N_2O_2 + O_2 \xrightarrow{k_2} 2\,NO_2$ *slow*

Rate law for slow step: $r = k_2\,[N_2O_2][O_2]$

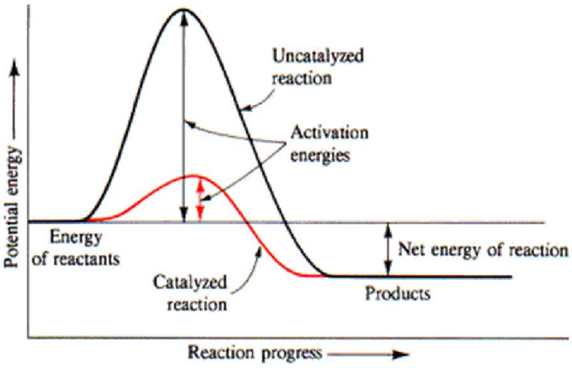
Substitute… $r = \frac{k_2 k_1}{k_{-1}}[NO]^2[O_2]$

Observed rate law: $\mathbf{r = k_{obs}\,[NO]^2[O_2]}$

Chemical kinetic

Catalysis

A catalyst is a substance that modify the reaction mechanism, accelerating the reaction but without comparing in the chemical equation.



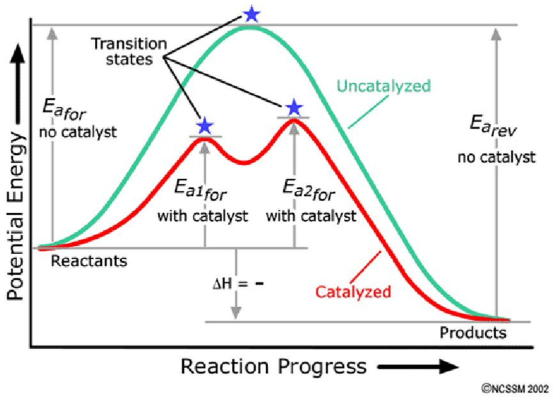
The presence of a catalyst opens a new reaction pathway, characterized by a lower E_a.

Chemical kinetic

Catalysis

Usually, several reactions steps are present with the formation of different intermediates.

The overall reaction rate is determined by the slowest step.



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Chemical kinetic

Type of catalysis

Homogeneus catalysis

Catalyst and reactants are in the same phase (gaseous or liquid)

Heterogeneous catalysis

Catalyst and reactants are in different phase (gaseous/solid or liquid/solid)

Enzymatic catalysis

Catalyst is an enzyme (macromolecules made by amino acids)