

Chemical Kinetics

Topic 7

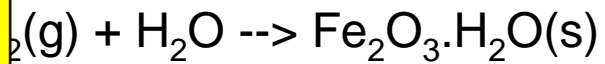
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The logo for Cartagena99 features the word "Cartagena99" in a stylized, green, cursive font. The text is set against a light blue background that resembles a stylized map of the city of Cartagena. A yellow and orange arrow-like shape points upwards from the bottom left towards the text.

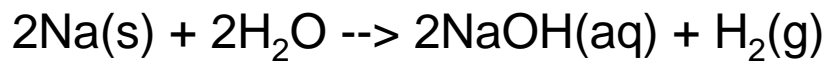
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les of the time needed for a chemical reaction to occur.
netics studies the rate of chemical reactions, their mechanism
tors that influence on it.

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Reaction rates

Rate \Rightarrow is intuitively defined as how fast or slow a reactant is consumed or how fast a product is produced.

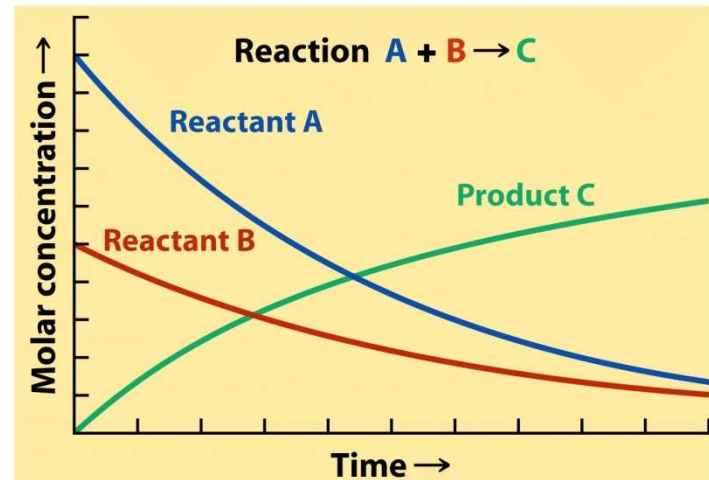
Mechanism \Rightarrow the detailed sequence of simple or elemental steps that a reaction follows as they transform into products.

Reaction rate is defined in terms of the concentration change of reactants or products.



$$\frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

The rate of variation of concentration of a reactant when time changes from t to $t+dt$. The rate must be negative so a negative sign is added to reactants rates.



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Reaction rate laws

In reactions the reaction rate must take into account both the direct process of reactants into products and the reverse process by which products reactants. This is relevant near the equilibrium. But far away from equilibrium we can consider that the direct reaction is the unique process that takes place. This will be our main hypothesis

They follow the next law (for N reactants): $rate = k[A]^{n_1} [B]^{n_2} \dots [N]^{n_N}$

Reaction rate constant

Reaction partial order for component j

the global reaction order

(concentration)¹⁻ⁿ (time)⁻¹

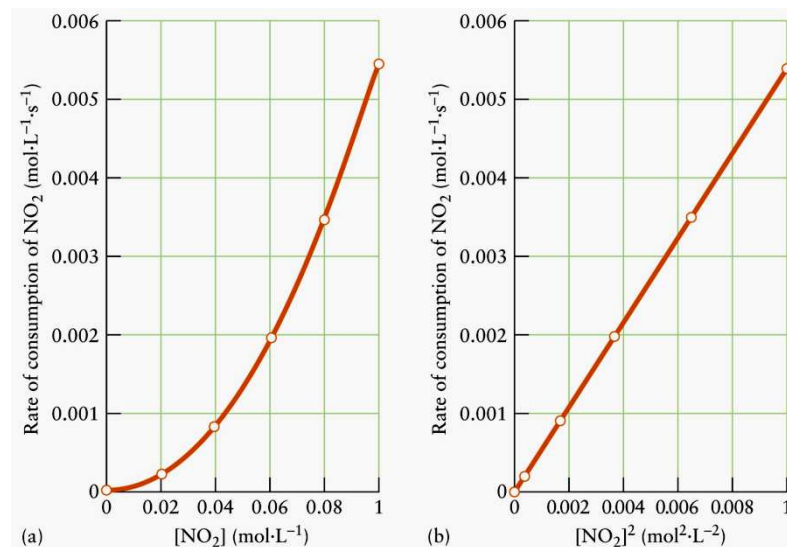
Reaction law must be determined experimentally

Example



Rate of consumption $\text{NO}_2 = k [\text{NO}_2]^2$

Units of k?



Integrated reaction rate laws

Integrated rate law: gives the time variation of products or reactants

R REACTIONS

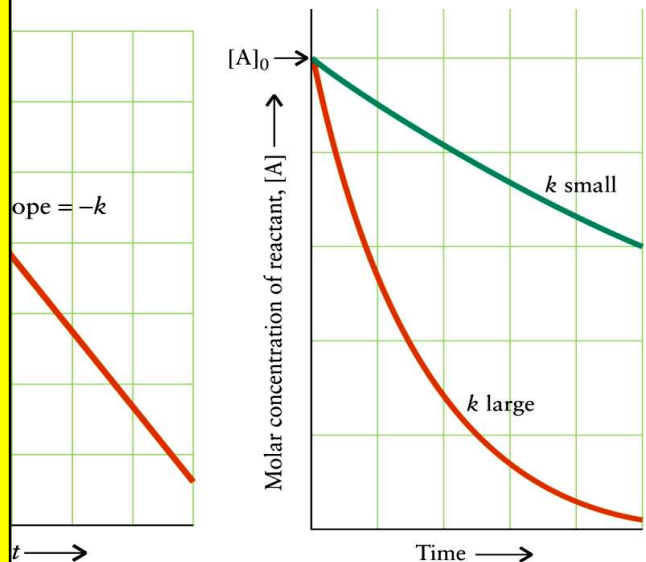
› Products

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

Integrated law
$$-\int_{[A]=[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_{t=t_0}^t k dt; \quad \ln[A] = \ln[A]_0 - kt$$

is:

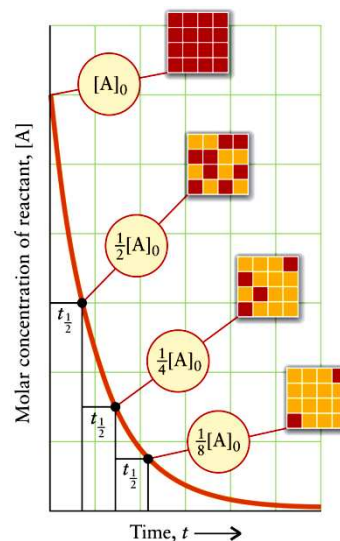
$$[A] = [A]_0 e^{-kt}$$



Reaction half life, $t_{1/2}$

Time needed to consume half of the original reactant.

First order reactions $\Rightarrow t_{1/2} = (\ln 2)/k$



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Integrated reaction rate laws

2nd ORDER REACTIONS

› Products

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

Integrating law

$$-\int_{[A]=[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_{t=0}^t k dt; \quad \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

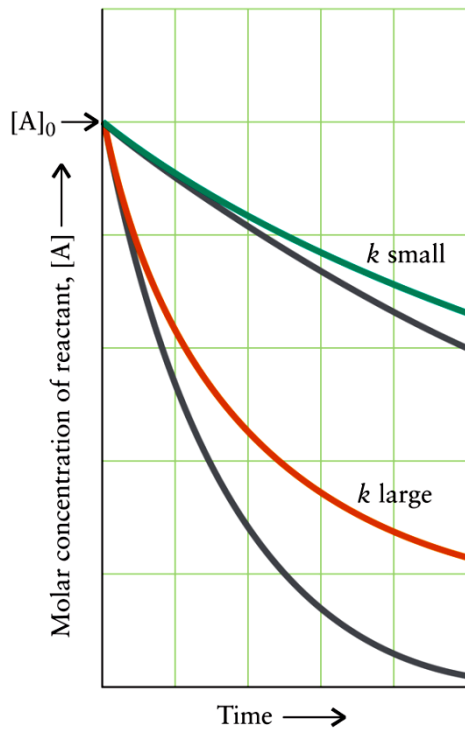
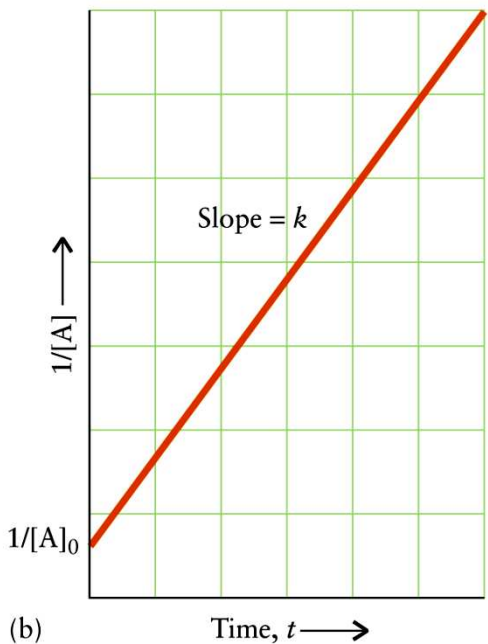
Initial conditions:

$$[A] = [A]_0$$

$$[A] = [A]_t$$

Half life, for 2nd order

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



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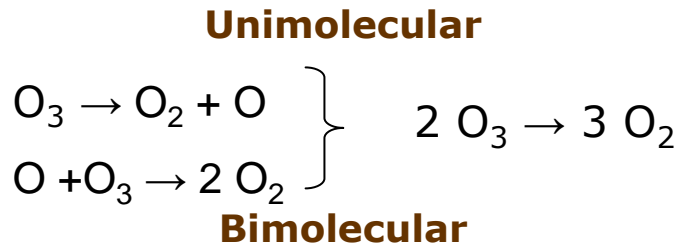
Reaction Mechanism

sequence of events that transform a reactant into a product?

Chemical process $\Rightarrow \Sigma$ elemental processes

Elemental process is the simplest reaction that takes place in a single step as a result of a collision between particles.

Ex: decomposition of ozone (O_3)



Molecularity is the number of molecules or atoms involved in an elemental process.

Reaction mechanism is the collection of **elemental processes** that are necessary for a chemical reaction to occur.

Molecularity and **reaction order** are equal in elemental processes.



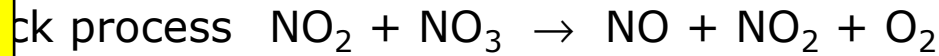
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Reaction Mechanism

and reaction intermediate

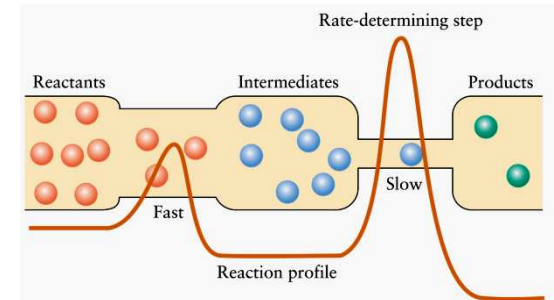


experimentally determined rate law for oxygen production is $v = d[O_2]/dt = k[N_2O_5]$



Rate-determining step is the step that controls or determines the overall reaction rate (the slowest): step 1

Species of reaction: species that are formed from the preceding intermediates) and reacts further to form the final observed products: NO and NO_3

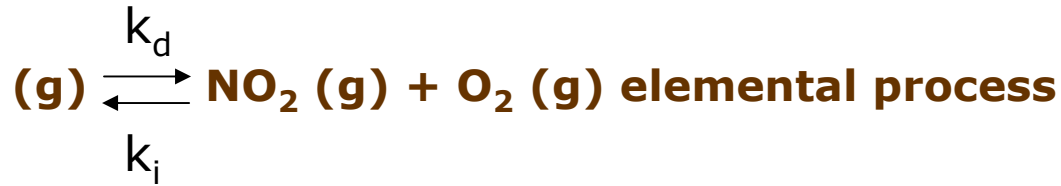


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Reaction Mechanism

nts and equilibrium constants (reversible processes)



$$\begin{aligned} \text{Direct reaction} &= v_d = k_d[\text{NO}][\text{O}_3] \\ \text{Reverse reaction} &= v_i = k_i[\text{NO}_2][\text{O}_2] \end{aligned}$$

For the reaction to reach chemical equilibrium, the rate for the forward process will be identical to the rate of the reverse process. Under these conditions, $v_d = v_i$

$$K = \frac{k_d}{k_i} = \left(\frac{[\text{NO}_2][\text{O}_2]}{[\text{NO}][\text{O}_3]} \right)_{eq}$$

Dynamic reversibility principle: at equilibrium, the rates of the direct and reverse elementary processes is identical. Dynamic equilibrium



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Kinetic theories

ory for reactions in the gas phase.

on to occur the reactant particles must collide.

ain fraction of the total collisions cause chemical change: successful

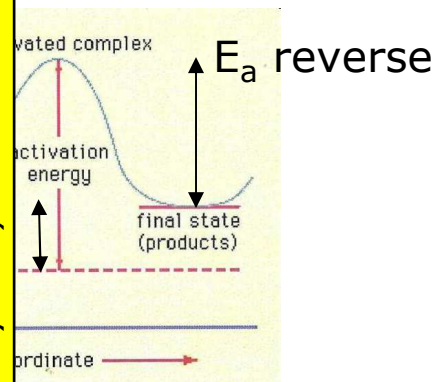
successful collisions have sufficient energy (activation energy) at the moment
to form a high energy "activated complex".

of the activated complex requires specific orientations of molecules in

activated complex existing bonds are broken and new bonds are formed.

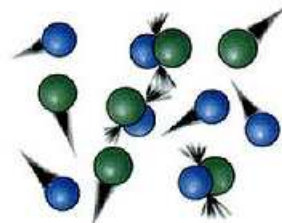
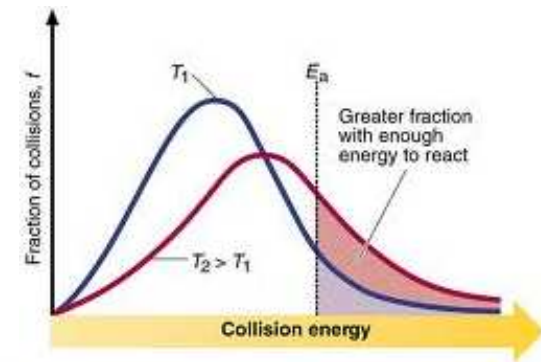
the concentration of the reactants and raising the temperature bring

collisions and therefore more successful collisions, increasing the rate

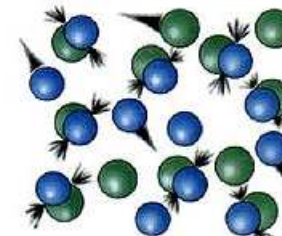


$$E_{a,reverse} = \Delta E$$

energy variation



Low concentration = Few collisions



High concentration = More collisions



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Arrhenius law

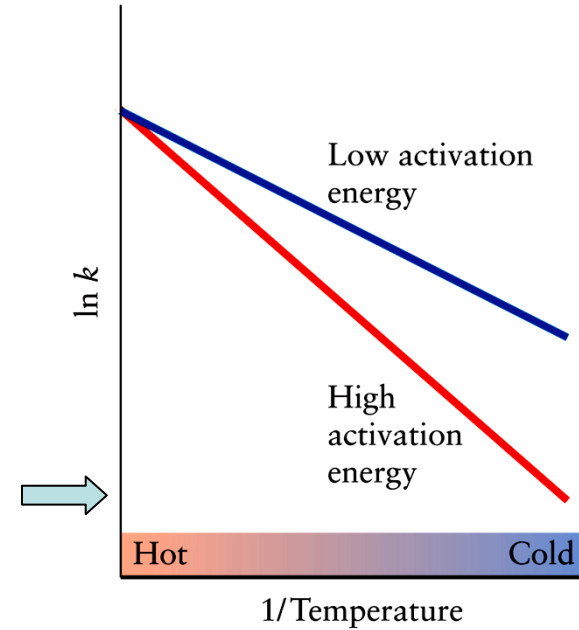
effect on reaction rate.

According to Collision Theory it can be derived a relationship between the rate constant and temperature known as the Arrhenius equation

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

ln k = ln A - $\frac{E_a}{RT}$
 A = pre-exponential factor
 E_a = activation energy

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



Activation energy is the minimum energy required for a reaction to take place. For many reactions an increase of about 10 °C in temperature, doubles the rate constant.

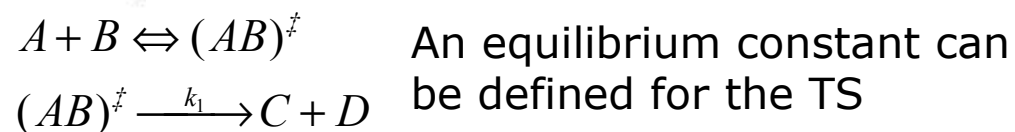
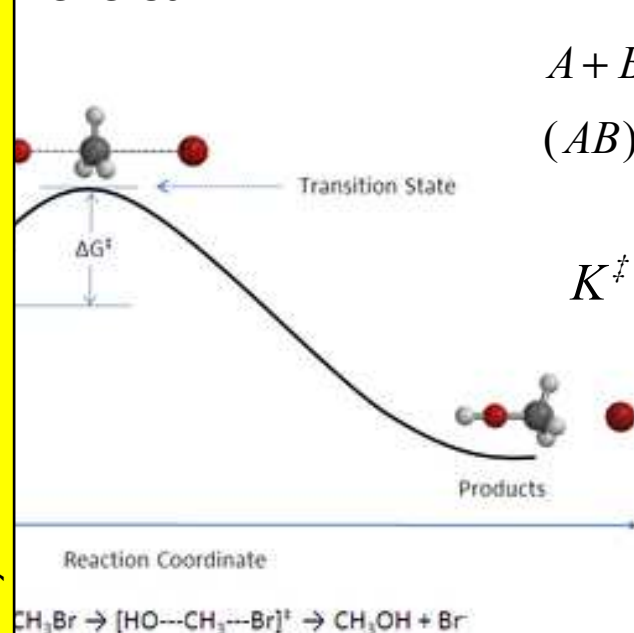


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Kinetic theories

Transition state theory.

Transition complexes are called Transition States, TS, $(AB)^\ddagger$.
 A special equilibrium with reactants called "quasi-equilibrium".
 A transient specie (short duration) with distorted bonds and angles;
 and they transform into products via k_1 or they return to reactants via reversal.



$$K^\ddagger = \frac{[(AB)^\ddagger]}{[A][B]} \quad [(AB)^\ddagger] = K^\ddagger [A][B]$$

$$\frac{d[C]}{dt} = k_1 [(AB)^\ddagger] = K^\ddagger k_1 [A][B] = k [A][B]$$

Recalling the relationship between K and free energy

$$K^\ddagger = \exp\left(-\frac{\Delta G^{0\ddagger}}{RT}\right) = \exp\left(-\frac{\Delta H^{0\ddagger}}{RT}\right) \exp\left(\frac{\Delta S^{0\ddagger}}{RT}\right)$$

The pre-exponential factor of Arrhenius Eq. represents the activation entropy.
 The activation energy represents the activation enthalpy.

Catalysis

speeding up of chemical reactions

species that speed up chemical reactions without being consumed.

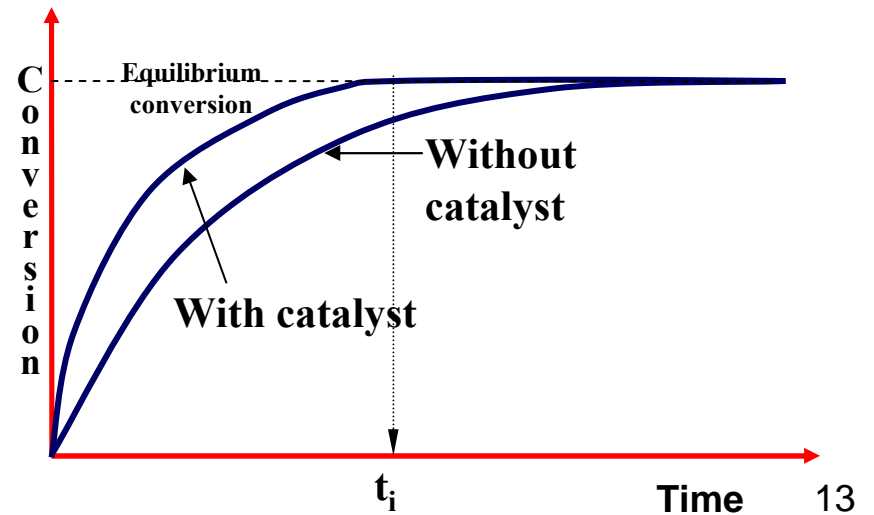
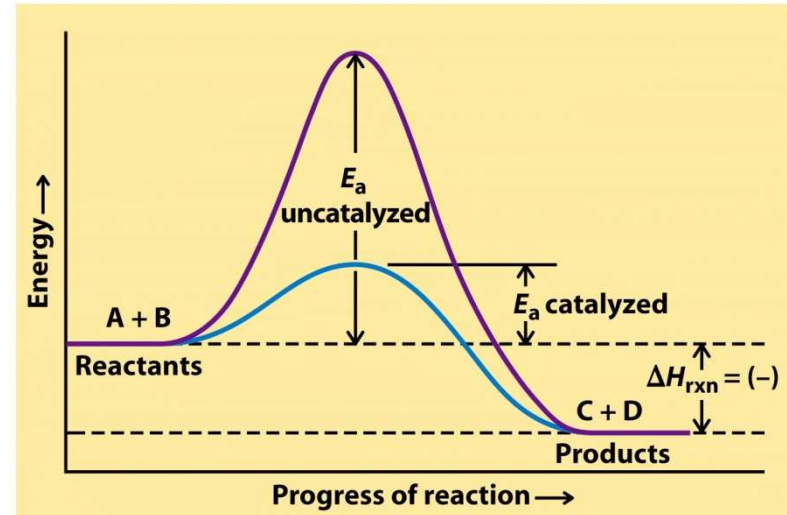
They provide an alternative pathway for a reaction that decreases activation energy

They do not modify reaction thermodynamics (equilibrium constants, enthalpy), only modifies kinetic

Substances that slow the reaction are called inhibitors, or poisons.

Substances that increase the activity of a catalyst are called promoters.

Substances that deactivate catalysts are called catalyst poisons.



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Homogeneous catalysis

Reactant and catalyst are in the same phase (generally liquid).

Specific

Rate depends on catalyst concentration: reaction rates are usually proportional to moles of consumed or produced substance per unit time and per unit volume of reactive mixture (with catalyst).

$$v = \frac{1}{\omega} \frac{\delta n}{\delta t}; \quad \omega \rightarrow \text{catalyst mass}$$

Reactants transform into products only in the presence of catalyst:



Two pathways for transformation of reactants: with and without catalyst:



An intermediate compound is formed with the catalyst that regenerates the catalyst if decomposed:



Autocatalysis \Rightarrow some of the reactants or products act as catalyst



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Homogeneous catalysis

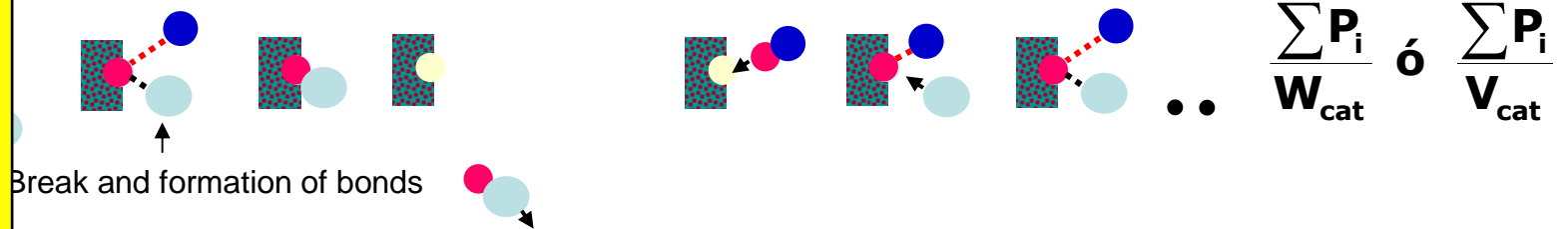
Reactants are in different phases

Specific

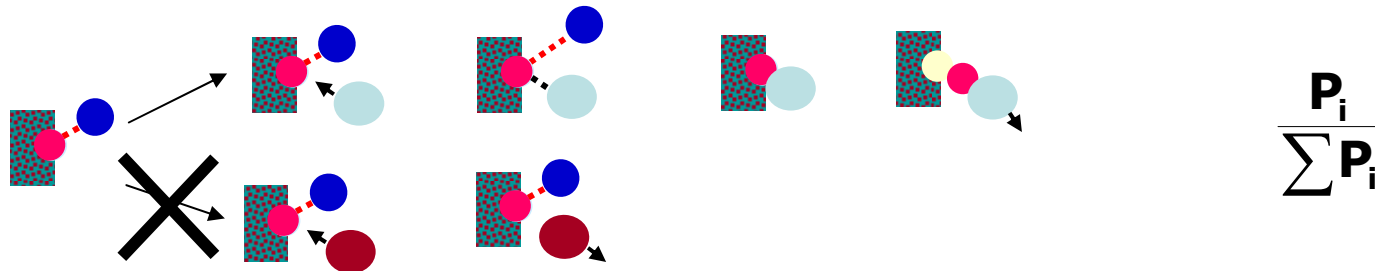
depends on the accessible surface of catalyst: external surface and internal surface within the pores must be accessible to reactants.

Active sites: specific points on the surface of the catalyst that decrease the energy of the process

Activity: ability for breaking and forming bonds



Selectivity: ability to orient formation of specific products



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Heterogeneous catalysts

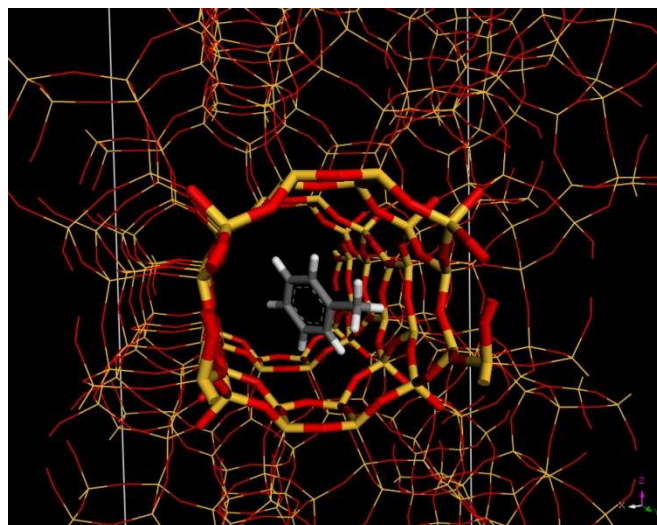
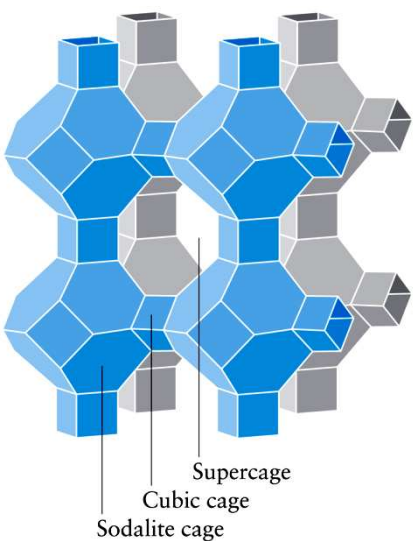
with very high specific surface (typically 100-1000 m²/g) (is a material property which measures the total surface area per unit of mass)

Support (Ex. alumina, silicates...). To consider:

- Surface area and pore size distribution
- Mechanical strength (abrasion-erosion)
- Geometrical factors (active center accessibility)

active centers (Ex. metals). To consider:

- Stability and resistance to poisoning
- Dispersion degree over the support
- Interaction with the support



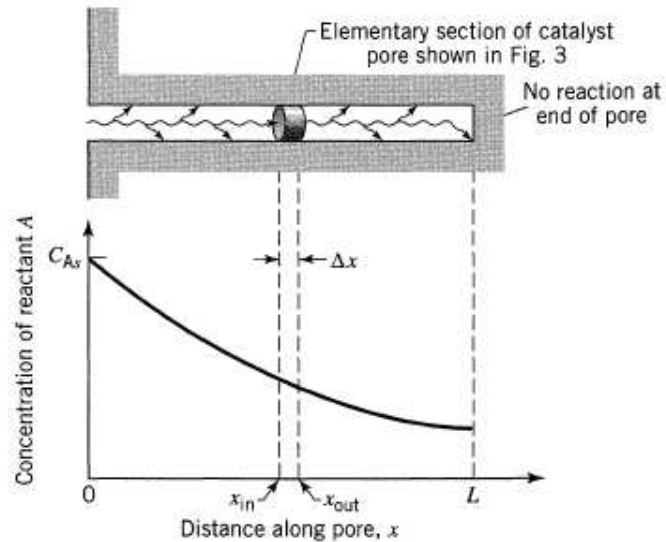
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eterogeneous catalysis

- diffusion** of reactants from the bulk to the catalyst surface.
- diffusion** through the catalyst pores.
- adsorption** of reactants over the surface of catalyst.
- transformation** of adsorbed species over the catalyst surface
- desorption** of products through catalyst pores.
- diffusion** through the catalyst pores.
- diffusion** of products from the surface of catalyst to the bulk.

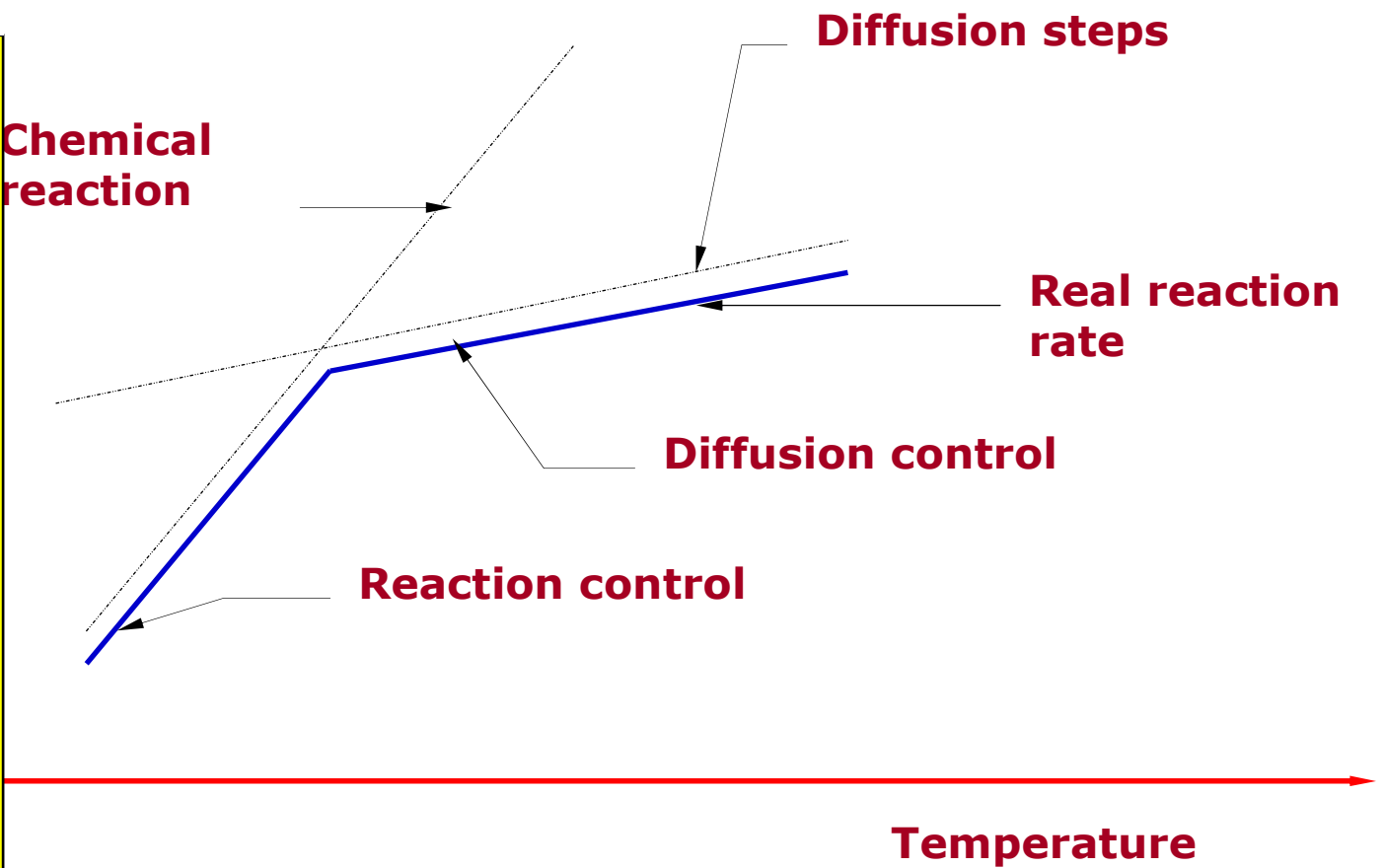
Difusión externa



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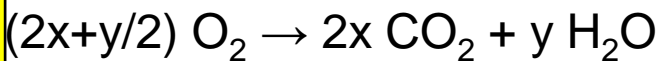
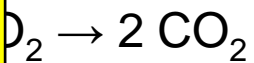
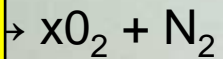
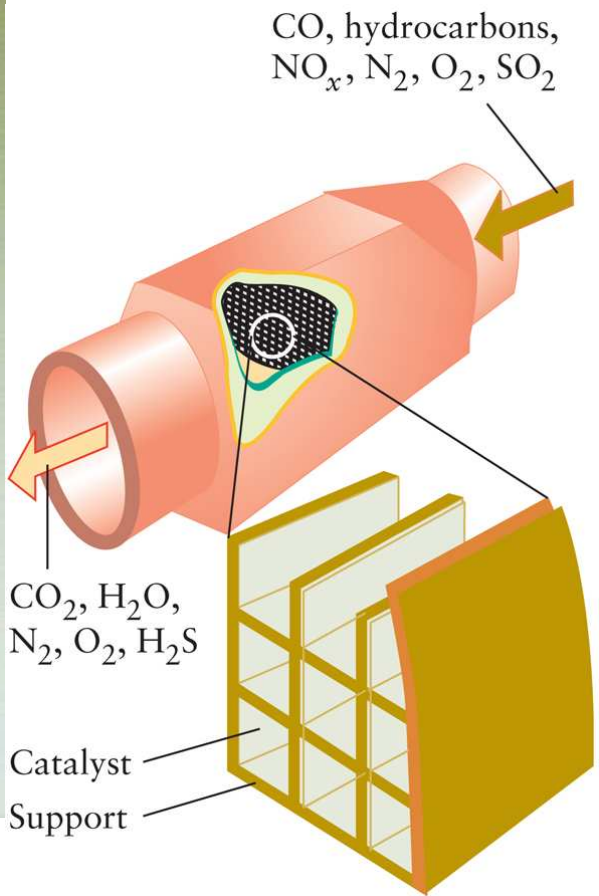
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IS: CATALYTIC CONVERTER



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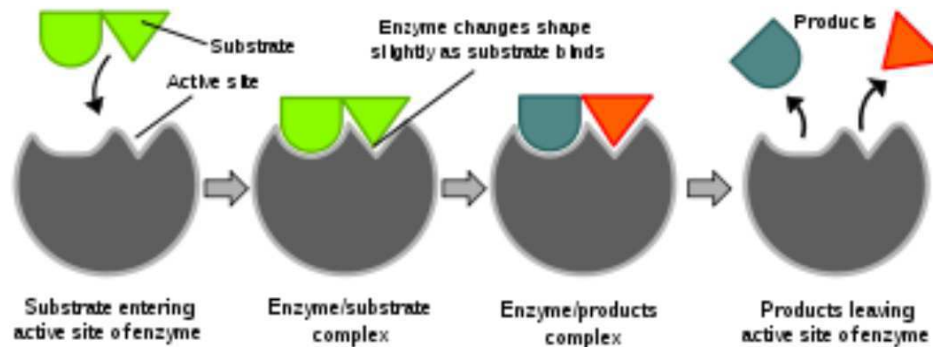
CATALYSIS

biological catalysts produced by living organisms. Commonly proteins and increase reaction rate by a factor $\sim 10^6$.

Lowering the activation energy of biochemical reactions.

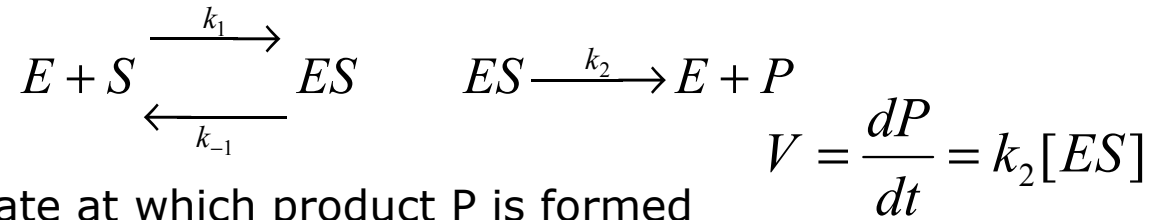
In a catalyzed reaction, the reactant is called substrate

The model for its action is the Induced Fit Model: the initial interaction between enzyme and substrate is relatively weak, but that these weak interactions cause conformational changes in the enzyme that strengthen binding.



-MENTEN Kinetics

e enzyme, S the substrate and P the product. Initially there is E_0 enzyme but it may react with S in an equilibrium process forming an enzyme-substrate complex (ES) which then goes on to the transition state:



Let the rate at which product P is formed be V . The concentration of ES must be constant because if not the enzymatic reaction would not be at equilibrium.

The appearance of ES is given by: $\frac{d[ES]}{dt} = k_1[E][S]$

There are two paths for the disappearance: via k_{-1} and via k_2 . The total rate will be:

$$-\frac{d[ES]}{dt} = k_{-1}[ES] + k_2[ES] = [ES](k_{-1} + k_2)$$

Since the rate of appearance and disappearance are equal, the concentration of ES will be constant and we have

$$k_1[E][S] = [ES](k_{-1} + k_2)$$



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-MENTEN Kinetics (Cont)

At equilibrium, the free enzyme concentration will be: $[E] = [E]_0 - [ES]$

Substitute this mass balance in the previous equation we arrive to an equation for the enzyme-substrate complex:

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

Substituting into the rate equation yields:

$$V = \frac{k_2 [E]_0 [S]}{K_M + [S]} \quad K_M = \frac{k_{-1} + k_2}{k_1}$$

This is called Michaelis-Menten equation. K_M is the Michaelis constant that roughly measures the affinity of the enzyme for the substrate. It is often used in the following form:

$$\frac{1}{V} = \frac{1}{k_2 [E]_0} + \frac{K_M}{k_2 [E]_0 [S]}$$

In linear plots (Lineweaver-Burk plots) from several experiments at constant enzyme concentration and different substrate concentrations it is possible to extract K_M and $k_2 [E]_0$.

In the high substrate limit when $[S] \gg K_M$. The rate equation is then independent of substrate concentration and is of order zero in $[S]$!! The reason is that $[S]$ is so high that all active sites of the enzyme are busy so a further increase in S has no effect on the rate.



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