



TOPIC 6:

Chemical kinetics

Reaction rates
Reaction rate laws
Integrated reaction rate laws
Reaction mechanism
Kinetic theories
Arrhenius law
Catalysis
Enzymatic catalysis



La tumba del Titanic

<http://loincognito.files.wordpress.com/2012/04/titanic-3.jpg>

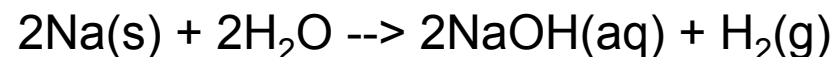
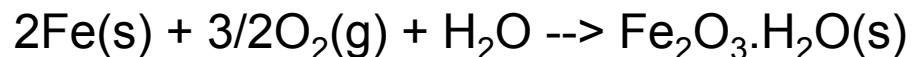
Corrosion of Titanic wreck



Fuente: Cedre



Casón
shipwreck



Two examples of the time needed for a chemical reaction to occur.
Chemical kinetics studies the rate of chemical reactions, their mechanism and the factors that influence on it.

Reaction rates

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

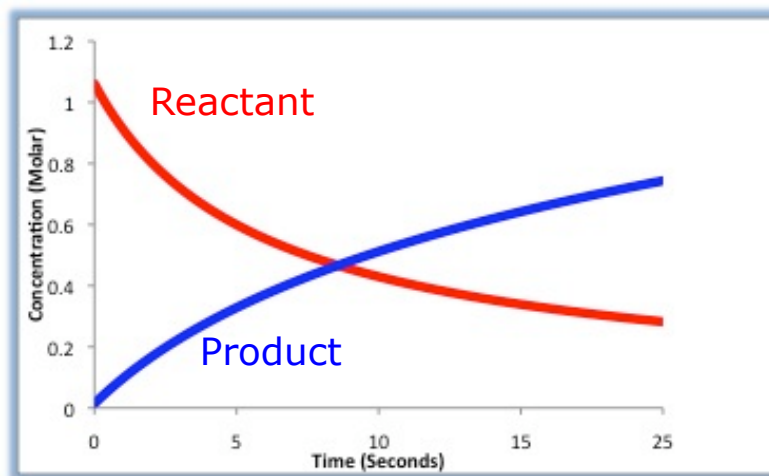
Reaction mechanism \Rightarrow the detailed sequence of simple or elemental steps that a reactants follow as they transform into products.

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

For a general reaction $aA + bB \leftrightarrow cC + dD$

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

$d[A]$ is the variation of concentration of substar A when time changes from t to $t+dt$. Rates can not be negative so a negative sign must be add to reactants rates.





Reaction rate laws

For equilibrium reactions the reaction rate must take into account both the direct transformation of reactants into products and the reverse process by which products transform into 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

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

- k is the reaction rate constant
- n_j is the reaction partial order for component j
- $n = \sum n_i$ is the global reaction order

Units of k: **(concentration)¹⁻ⁿ (time)⁻¹**

But the rate law must be determined experimentally

Example: $2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$

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

¿units of k?



Integrated reaction rate laws

FIRST ORDER REACTIONS



Rate law $\Rightarrow -d[A]/dt = k[A]$

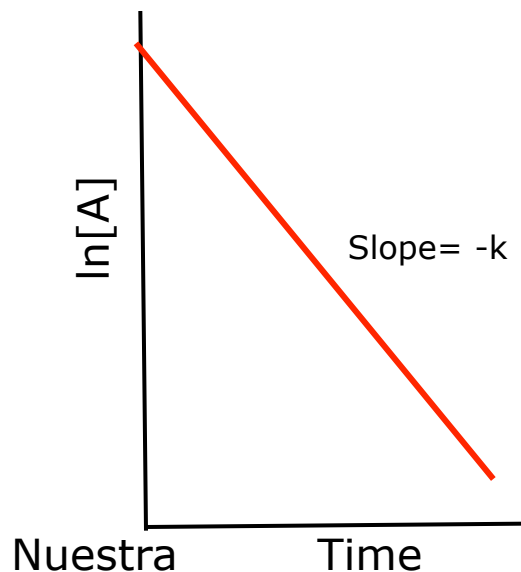
Integrated rate law

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

Integration limits:

$$t=0 \rightarrow [A] = [A]_0$$

$$t=t \rightarrow [A] = [A]_t$$

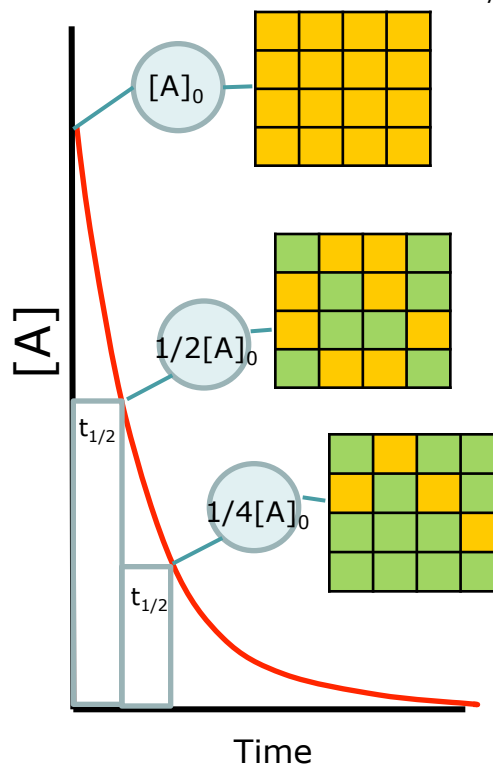


Integrated rate law: gives the time variation of the concentration of products or reactants

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

Time needed to consume half of the original reactant.

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





SECOND ORDER REACTIONS



Rate law $\Rightarrow -d[A]/dt = k[A]^2$

Integrated rate law

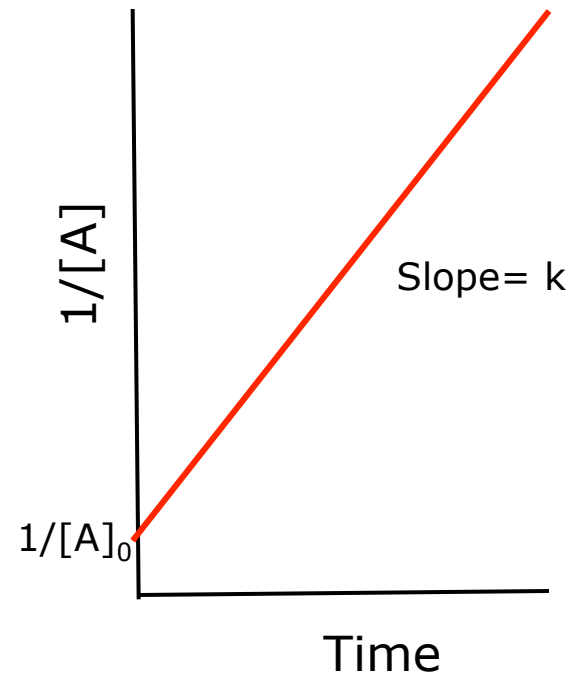
$$-\int_{[A]=[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_{t=t_0}^t k dt; \quad \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Integration limits:

$$t=0 \rightarrow [A] = [A]_0$$

$$t=t \rightarrow [A] = [A]_t$$

Reaction half life, for 2nd order reactions $\Rightarrow t_{1/2} = 1/k[A]_0$



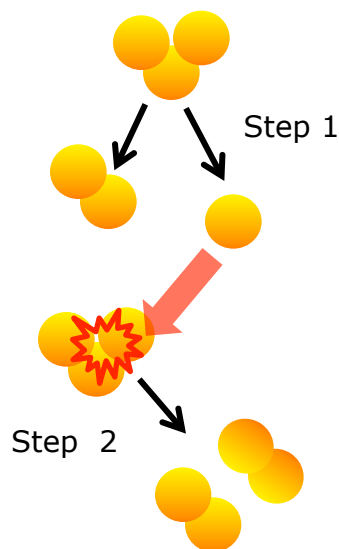
Reaction mechanism

Which is the sequence of events that transform a reactant into a product?

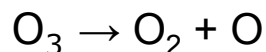
Chemical process $\Rightarrow \Sigma$ elemental processes

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

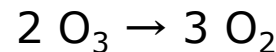
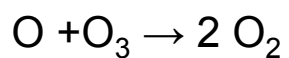
Ex: decomposition of ozone (O_3)



Unimolecular



Bimolecular



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.



Limiting step and reaction intermediate

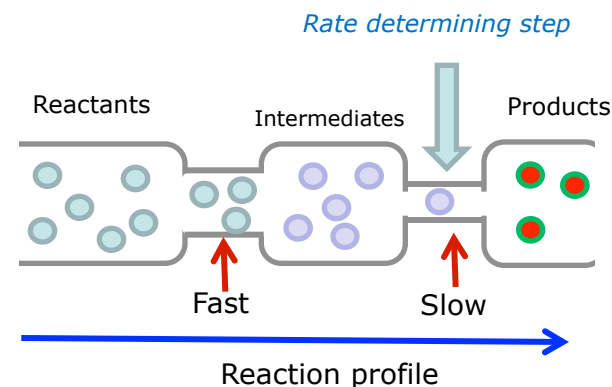
Example: decomposition of N_2O_5 $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

The experimentally determined rate law for oxygen production is $v = d[\text{O}_2]/dt = k[\text{N}_2\text{O}_5]$

Step 1: slow equilibrium process $\text{N}_2\text{O}_5 \leftrightarrow \text{NO}_2 + \text{NO}_3$

Step 2: quick process $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$

Step 3: slow process $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$

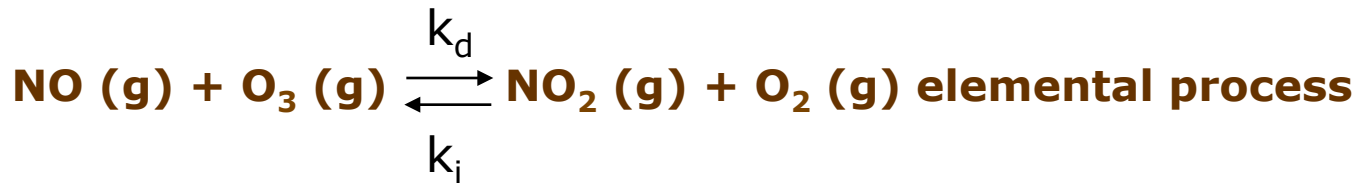


The **limiting step** is the step that controls or determines the overall reaction rate (the slowest): step 1

Nuestra

Intermediates of reaction: species that are formed from the reactants (or preceding intermediates) and react further to give the directly observed products: NO and NO_3

Rate constants and equilibrium constants (reversible processes)



Rate of direct reaction = $v_d = k_d[\text{NO}][\text{O}_3]$

Rate of reverse reaction = $v_i = k_i[\text{NO}_2][\text{O}_2]$

If you leave the reaction to reach chemical equilibrium, the rate for the direct process will be identical to the rate of the reverse process. Under these conditions, $v_d = v_i$

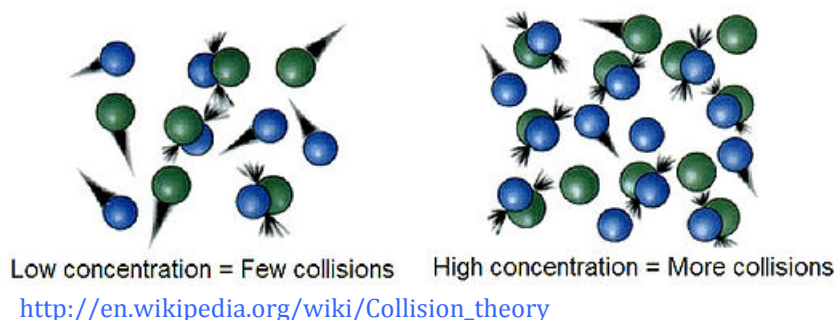
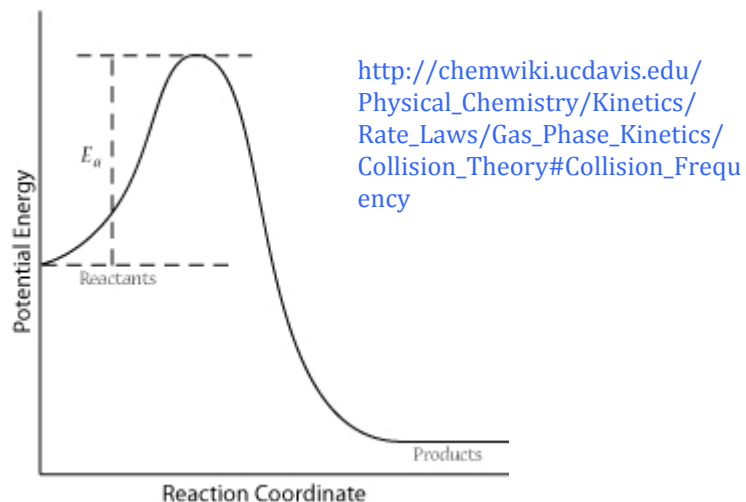
$$K = \frac{k_d}{k_i} = \left(\frac{[\text{NO}_2][\text{O}_2]}{[\text{NO}][\text{O}_3]} \right)_{eq}$$

Microscopic reversibility principle: at equilibrium, the rates of the direct and reverse elemental processes are identical. Dynamic equilibrium

Kinetic theories

Collision Theory for reactions in the gas phase.

1. For a reaction to occur the reactant particles must collide.
2. Only a certain fraction of the total collisions cause chemical change: successful collisions.
3. The successful collisions have sufficient energy (activation energy) at the moment of impact to form a high energy "activated complex".
4. Formation of the activated complex requires specific orientations of molecules in space.
5. In the activated complex existing bonds are broken and new bonds are formed.
6. Increasing the concentration of the reactants and raising the temperature bring about more collisions and therefore more successful collisions, increasing the rate of reaction



$$E_{a,\text{direct}} - E_{a,\text{reverse}} = \Delta E$$

Internal energy variation



Arrhenius law

Temperature effect on reaction rate.

From the Collisions Theory it can be derived a relation between kinetic constant and temperature known as **Arrhenius law**

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

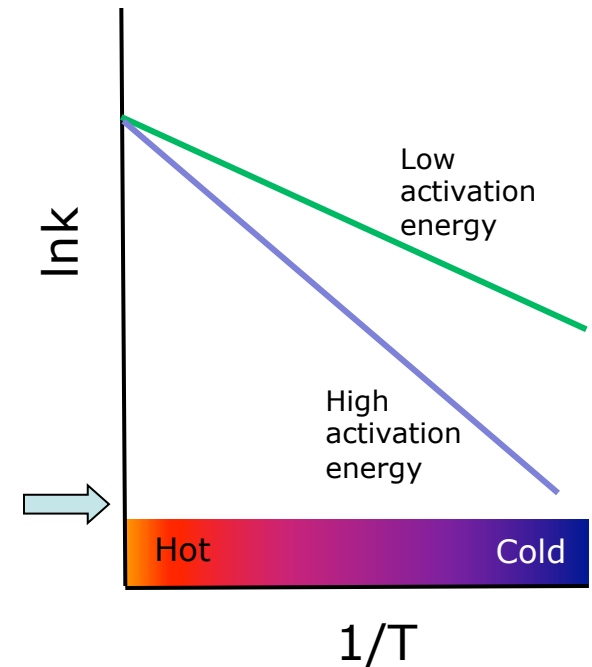
K = kinetic constant

A = pre-exponential factor

R = gas constant

E_a = activation energy

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

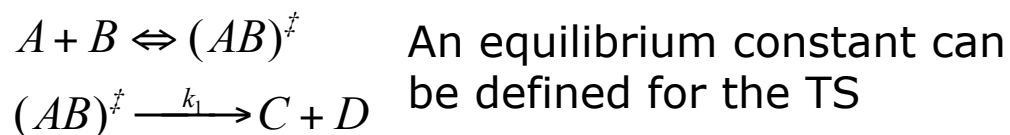
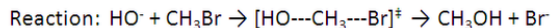
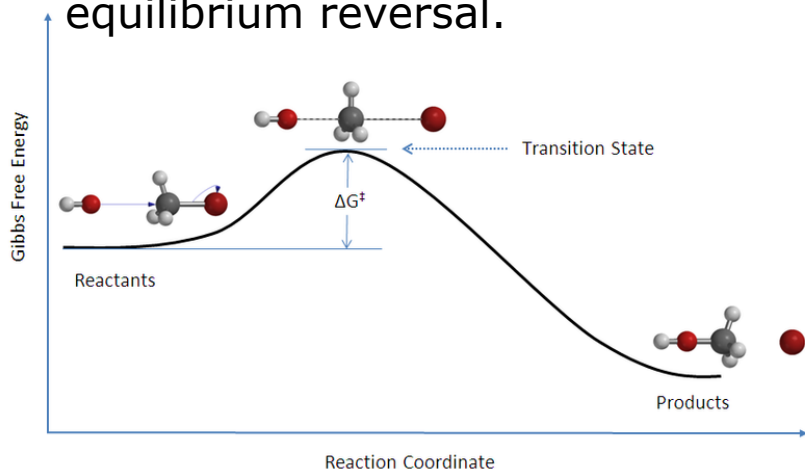


Nuestra

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

Transition State theory.

1. Activated complexes are called Transition States, TS, $(AB)^\ddagger$.
2. A TS is in a special equilibrium with reactants called "quasi-equilibrium".
3. The TS is a transient specie (short duration) with distorted bonds and angles; once formed they transform into products via k_1 or they return to reactants via equilibrium 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

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

Therefore, the **pre-exponential factor** of Arrhenius Eq. represents the **activation entropy** and the **activation energy** represents the **activation enthalpy**.

Catalysis

Catalysts are species that speed up chemical reactions without being consumed.

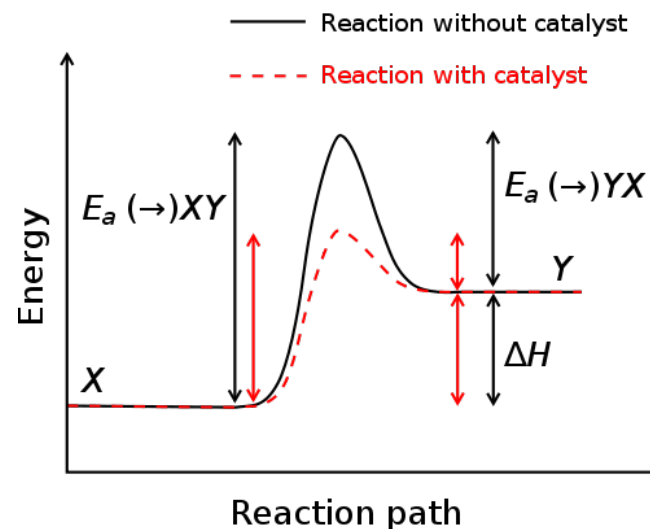
Catalysts provide an alternative pathway for the reaction that decreases activation energy E_a .

Catalysts do not modify **reaction thermodynamics** (equilibrium constants, reaction enthalpy), only modifies kinetic constant.

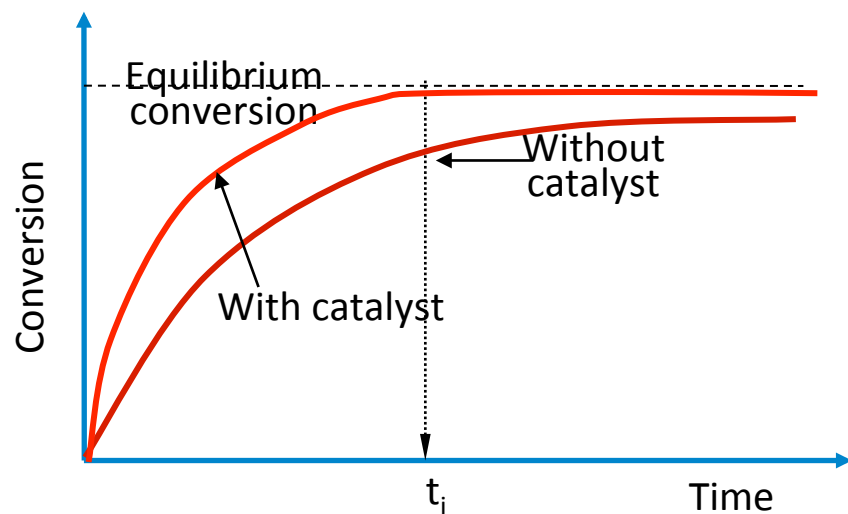
Catalysts that slow the reaction are called **negative catalysts**, or **inhibitors**.

Substances that increase the activity of catalysts are called **promoters**.

Substances that **deactivate** catalysts are called **catalytic poisons**.



http://en.wikipedia.org/wiki/File:Activation_energy.svg



Homogeneous catalysis

- Both catalyst and reactants are in the same phase (generally liquid).
- Not very specific
- Reaction rate depends on catalyst concentration: reaction rates are usually expressed as moles of consumed or produced substance per unit time and per unit volume of reactive mixture (with catalyst).

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

Types:

- 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:



- Auto-catalysis \Rightarrow some of the reactants or products act as catalyst

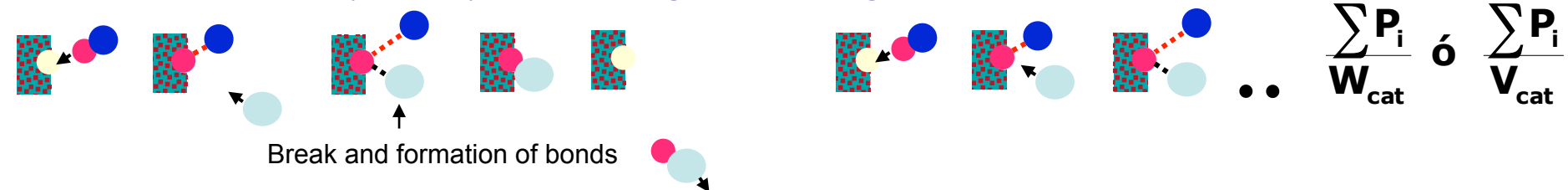


Heterogeneous catalysis

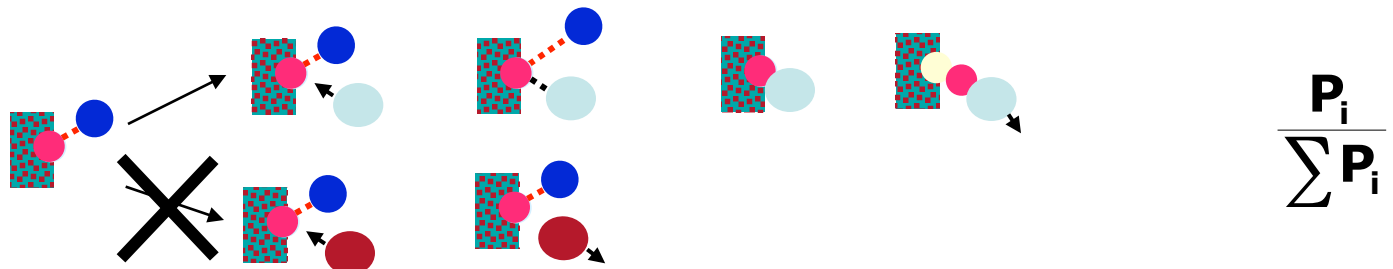
- Catalyst and reactants are in different phases
- It is more specific
- **Reaction rate depends on the accessible surface of catalyst:** external surface and internal surface within the pores must be accessible to reactants.

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

Activity: ability for breaking and forming bonds



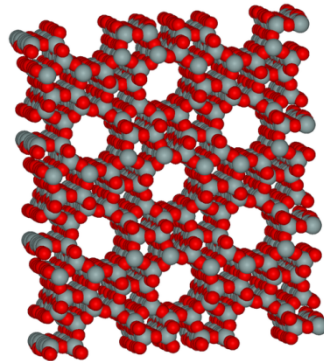
Selectivity: ability to orient formation of specific products



Design of heterogeneous catalysts

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

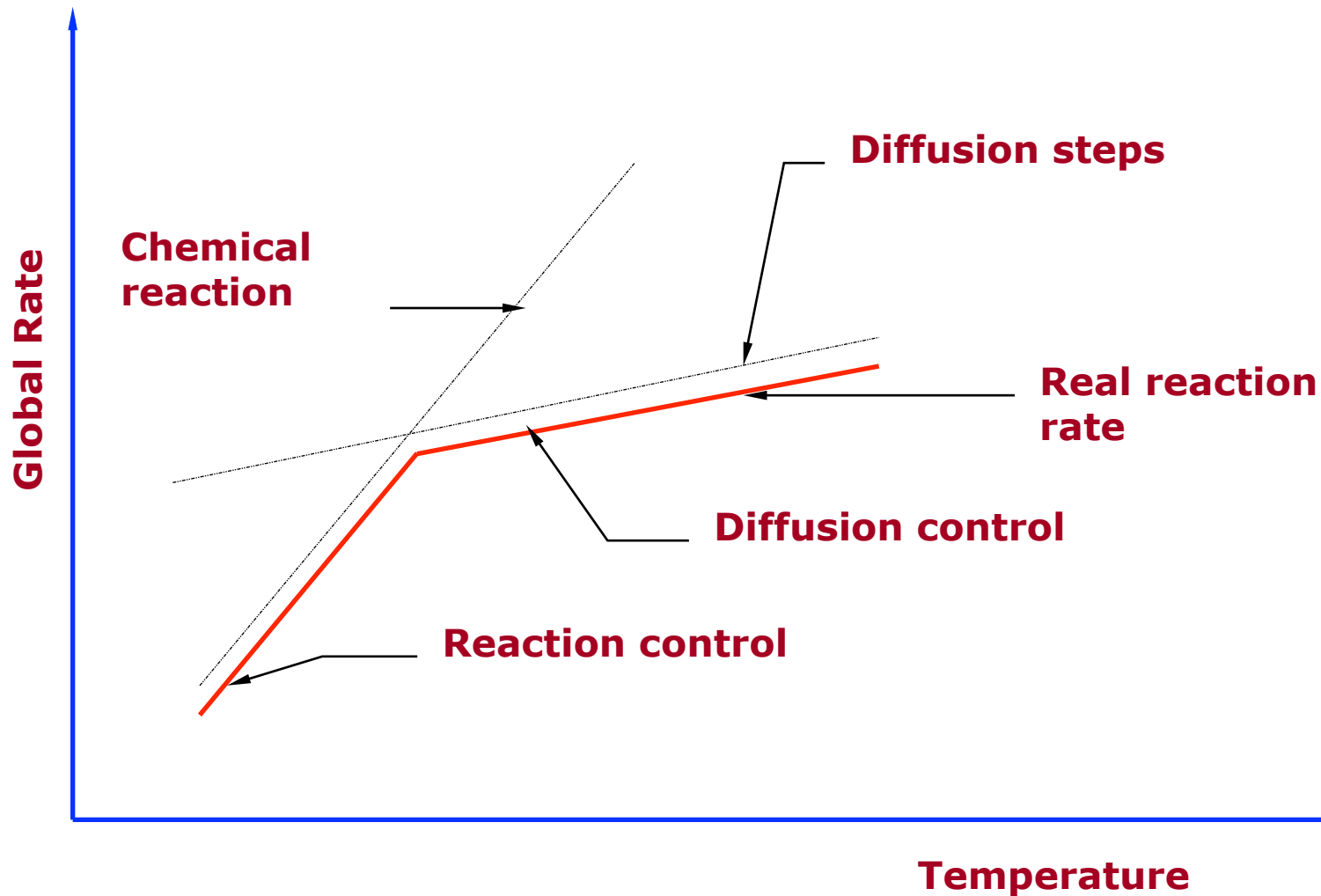
- **Porous support** (Ex. alumina, silicates...). To consider:
 - Surface area and pore size distribution
 - Mechanical strength (abrasion-erosion)
 - Geometrical factors (active center accesibility)
- **Supported active centers** (Ex. metals). To consider:
 - Stability and resistance to poisoning
 - Dispersion degree over the support
 - Interaction with the support



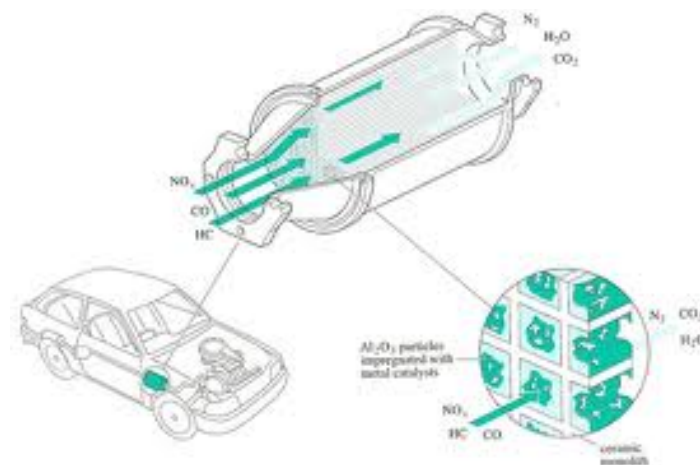
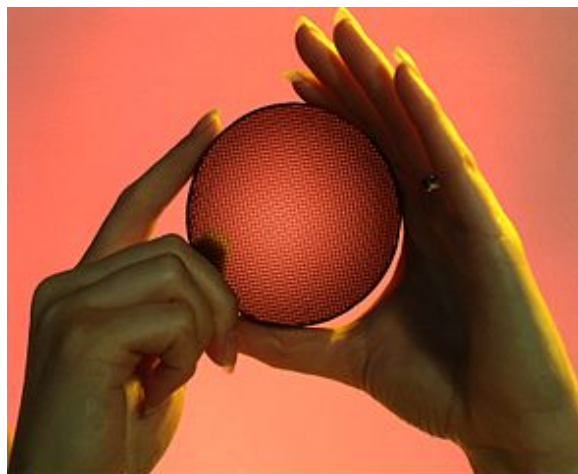


Steps of heterogeneous catalysis

- 1.- **External diffusion** of reactants from the bulk to the catalyst surface.
- 2.- **Internal diffusion** through the catalyst pores.
- 3.- **Adsorption** of reactants over the surface of catalyst.
- 4.- **Chemical transformation** of adsorbed species over the catalyst surface
- 5.- **Desorption** of products through catalyst pores.
- 6.- **Internal diffusion** through the catalyst pores.
- 7.- **External diffusion** of products from the surface of catalyst to the bulk.



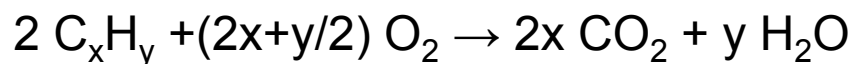
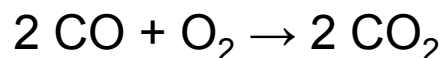
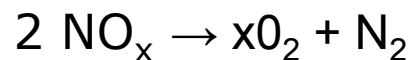
EXAMPLES: CATALYTIC CONVERTER



[http://en.wikipedia.org/wiki/
File:Low_Temperature_Oxidation_Catalyst.jpe
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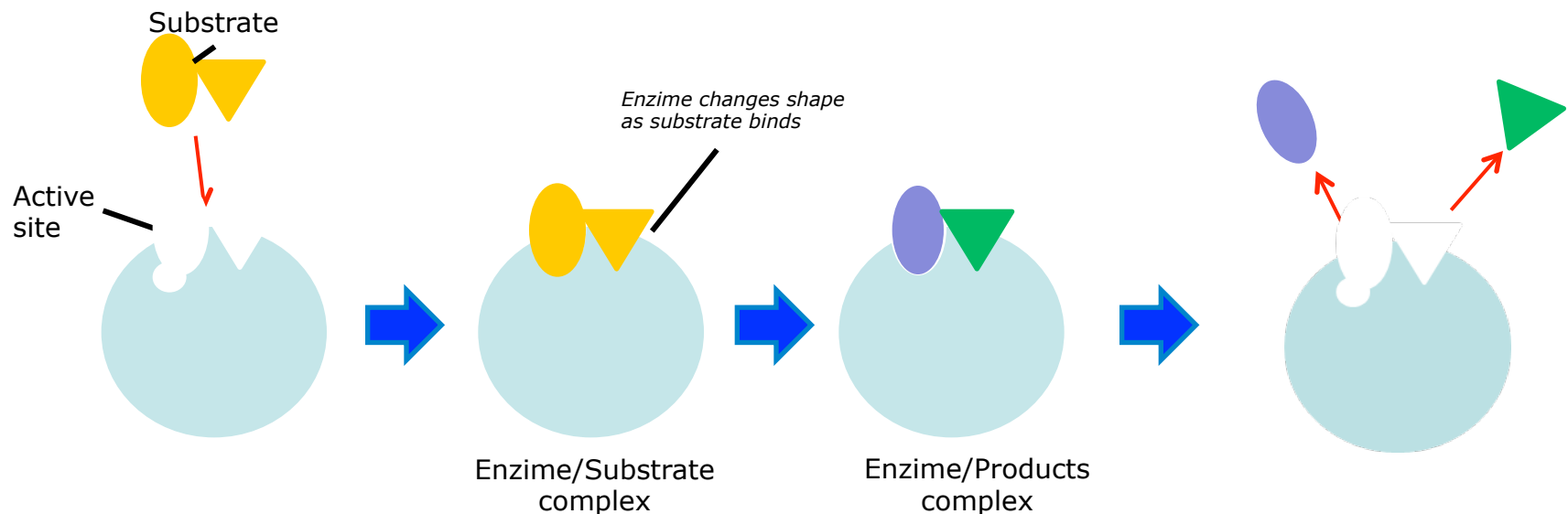
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Enzymatic catalysis

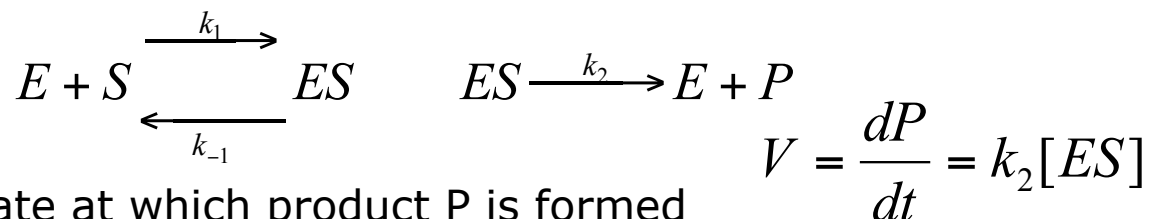
- Enzymes are **biological catalysts** produced by living organisms. Commonly **proteins**
- They generally increase reaction rate by a factor $\sim 10^6$.
- They act reducing the activation energy of biochemical reactions.
- In an enzyme-catalyzed reaction, the reactant is called **substrate**
- A common model for its action is the Induced Fit Model: the initial interaction between enzyme and substrate is relatively weak, but that these weak interactions rapidly induce conformational changes in the enzyme that strengthen binding.





MICHAELIS –MENTEN Kinetics

Let us call E the enzyme, S the substrate and P the product. Initially there is E_0 amount of free enzyme but it may react with S in an equilibrium process forming an species similar to the transition state:



Let us call dP/dt the rate at which product P is formed

The concentration of ES must be constant because if not the enzymatic reaction would not take place.

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

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

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

When both rates are equal, the concentration of ES will be constant and we have

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

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

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

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

Substitution 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 equation is called Michaelis-Menten equation. K_M is the Michaelis constant that approximately measures the affinity of the enzyme for the substrate. It is often used in its reverse form:

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

Making several experiments at constant enzyme concentration and different substrate concentrations it is possible to extract K_M and $k_2 [E]_0$.

It is interesting the limit when $[S] \gg K_M$. The rate equation is then independent of $[S]$, that is, order zero in $[S]$!! The reason is that $[S]$ is so high that all active centers in the enzyme are busy so a further increase in S has no effect on the overall rate