Chemical Kinetics

Topic 7

Corrosion of Titanic *wreck*

$2Fe(s) + 3/2O_2(g) + H_2O \rightarrow Fe_2O_3.H_2O(s)$

Casón shipwreck

$2Na(s) + 2H_2O \rightarrow 2NaOH(aq) + H_2(g)$

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.

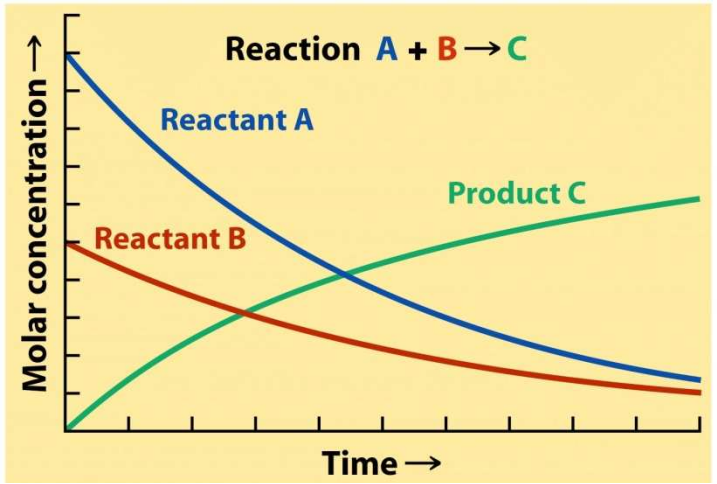
Reaction mechanism $\Rightarrow$ the detailed sequence of simple or elemental steps that a reactants follow as they transform into products.

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 substance A when time changes from *t* to *t+dt*. Rates can not be negative so a negative sign must be added 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): $rate = k[A]^{n_1}[B]^{n_2}\cdots[N]^{n_N}$

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

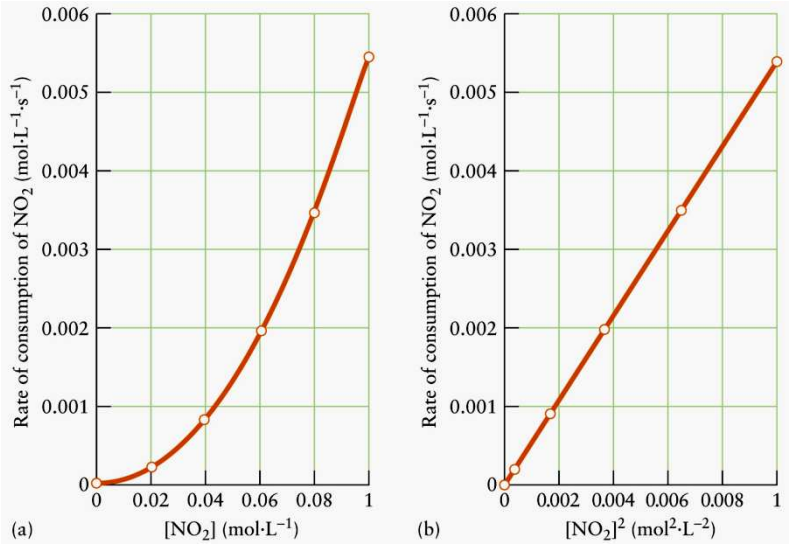
Units of k: **$(concentration)^{1-n}\ (time)^{-1}$**

But the rate law must be determined experimentally

Example: $2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$

Rate of consumption $NO_2 = k\ [NO_2]^2$

¿units of k?



Integrated reaction rate laws

FIRST ORDER REACTIONS

A → Products

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

Rate law ⇒ $-d[A]/dt = k[A]$

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

Integration limits:

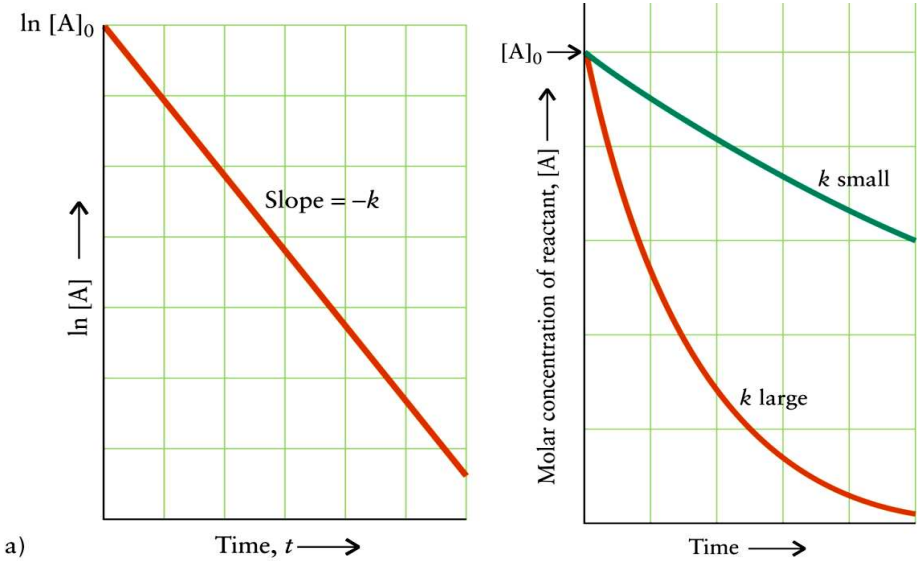
$t=0 \rightarrow [A] = [A]_0$

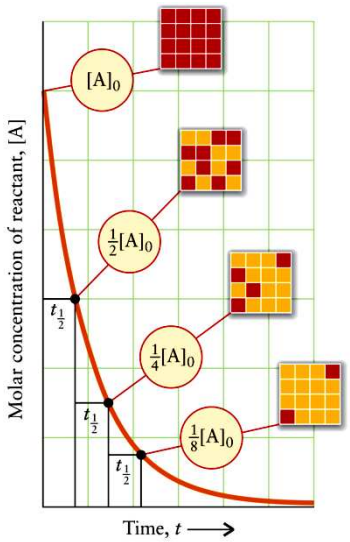
$t=t \rightarrow [A] = [A]_t$

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

Time needed to consume half of the original reactant.

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





SECOND ORDER REACTIONS

Integrated reaction rate laws

A → Products

Rate law ⇒ $-d[A]/dt = k[A]^2$

Integrated rate law

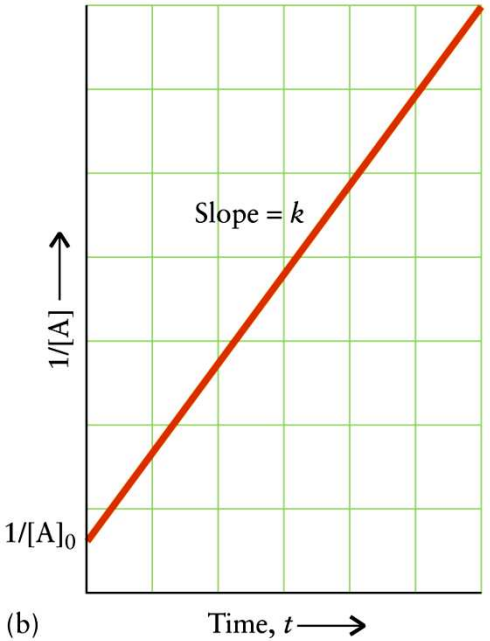
$$-\int_{[A]=[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_{t=t_0}^{t} kdt; \qquad \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

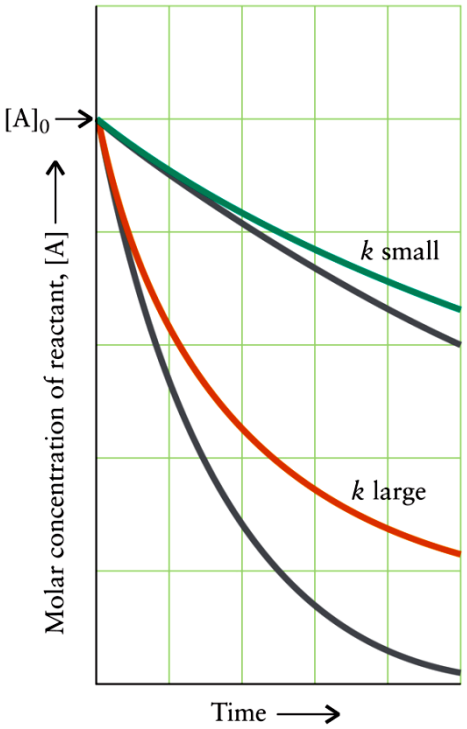
Integration limits:

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

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

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





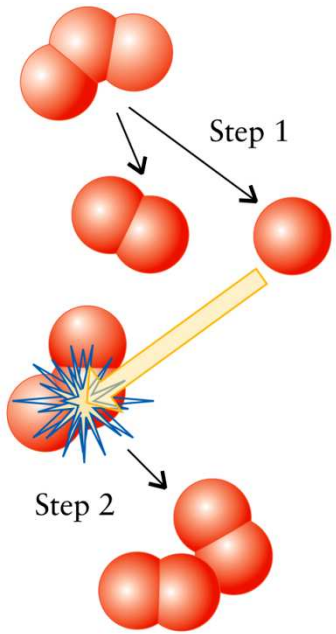
Reaction Mechanism

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

Chemical process $\Rightarrow \sum$ 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

$$O_3 \rightarrow O_2 + O$$
$$O + O_3 \rightarrow 2\ O_2$$

$$2\ O_3 \rightarrow 3\ O_2$$

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

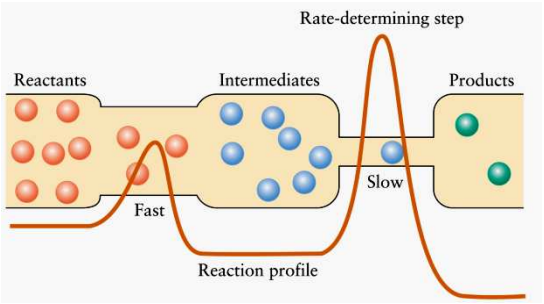
Example: decomposition of N_2O_5 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

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

Step 1: slow equilibrium process $N_2O_5 \leftrightarrow NO_2 + NO_3$

Step 2: quick process $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$

Step 3: slow process $NO + NO_3 \rightarrow 2NO_2$



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

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

Rate constants and equilibrium constants (reversible processes)

$$NO\ (g) + O_3\ (g) \underset{k_i}{\overset{k_d}{\rightleftharpoons}} NO_2\ (g) + O_2\ (g)$$ **elemental process**

Rate of direct reaction = $v_d = k_d[NO][O_3]$
Rate of reverse reaction = $v_i = k_i[NO_2][O_2]$

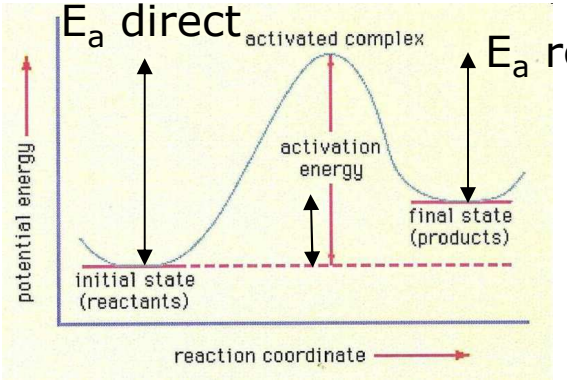
If you leave the reaction to reach chemical equilibrium, the rate for the direct process will be identical to the rate of the reverse process. Under these conditions, $v_d = v_i$

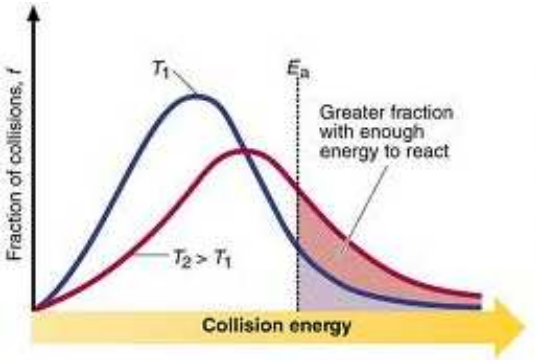
$$K = \frac{k_d}{k_i} = \left(\frac{[NO_2][O_2]}{[NO][O_3]} \right)_{eq}$$

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

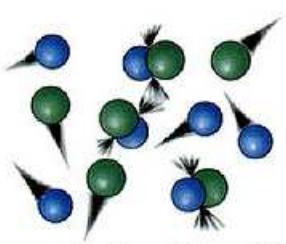
Collision Theory for reactions in the gas phase.

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

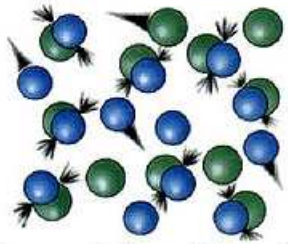




$E_{a,direct} - E_{a,reverse} = \Delta E$
Internal energy variation



Low concentration = Few collisions



High concentration = More collisions

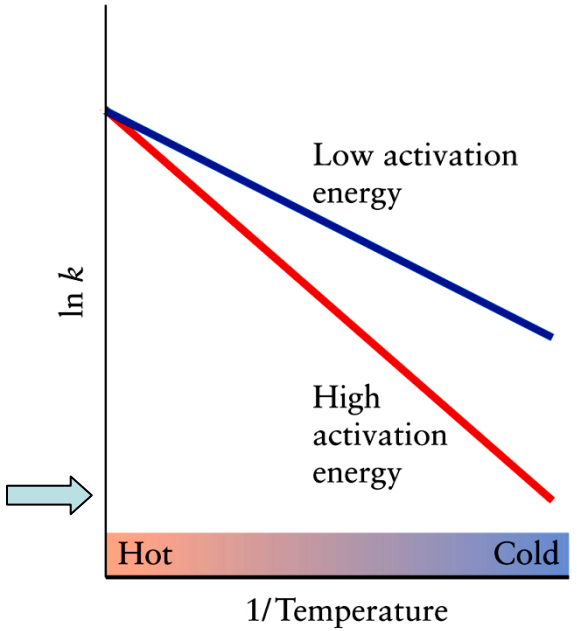
Temperature effect on reaction rate.

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
Ea = activation energy

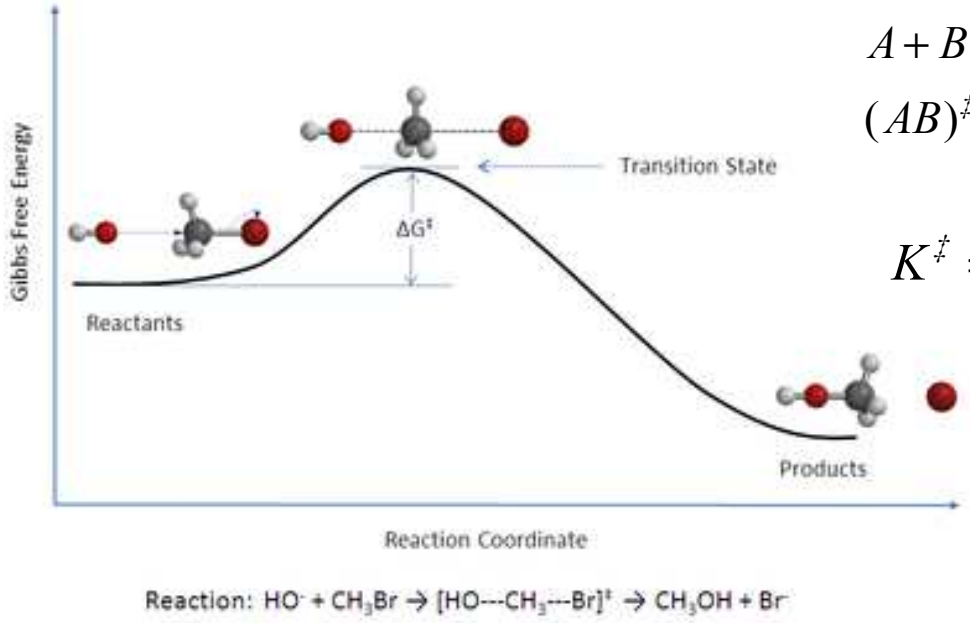
$$ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$



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

Transition State theory.

1. Activated complexes are called Transition States, TS, (AB)‡.
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.



$$A + B \Leftrightarrow (AB)^{\ddagger}$$

$$(AB)^{\ddagger} \xrightarrow{k_1} C + D$$

An equilibrium constant can be defined for the TS

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

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

Recalling the relationship between K and free energy

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

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

Catalysis: speeding up of chemical reactions

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

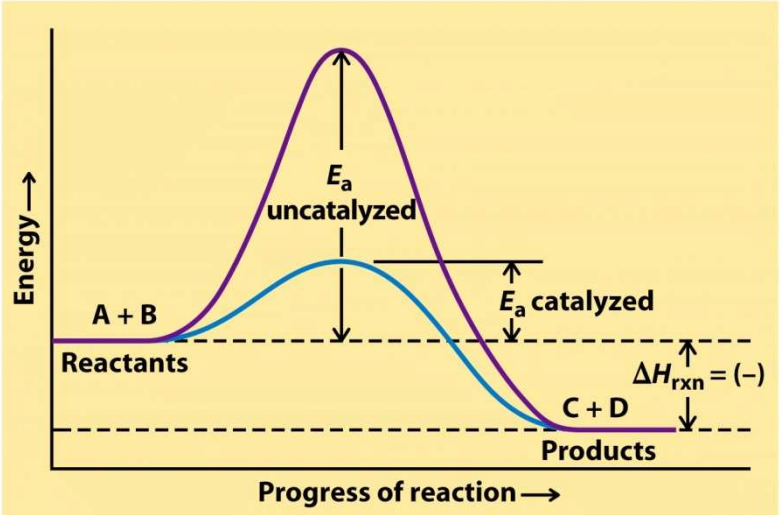
Catalysts provide an alternative pathway for the reaction that decreases activation energy E_a.

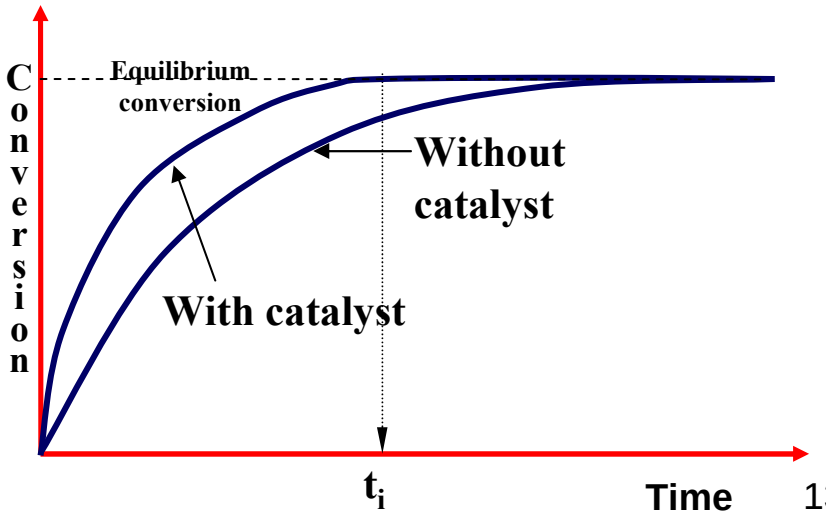
Catalysts do not modify reaction thermodynamics (equilibrium constants, reaction enthalpy), only modifies kinetic constant

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.





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).

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

Types:

- Reactants transform into products only in the presence of catalyst:
  $A + C \rightarrow B + C$ K_1
- Two pathways for transformation of reactants: with and without catalyst:
  $A + C \rightarrow B + C$ $K_1 >> K_2$
  $A \rightarrow B$ K_2
- An intermediate compound is formed with the catalyst that regenerates the catalyst if decomposed:
  $A + C \rightarrow AC \rightarrow B + C$ K_1
- Auto-catalysis $\Rightarrow$ some of the reactants or products act as catalyst
  $A \rightarrow B + C$ K_2
  $A+C \rightarrow B + C$ $K_1 >> K_2$

Heterogeneous catalysis

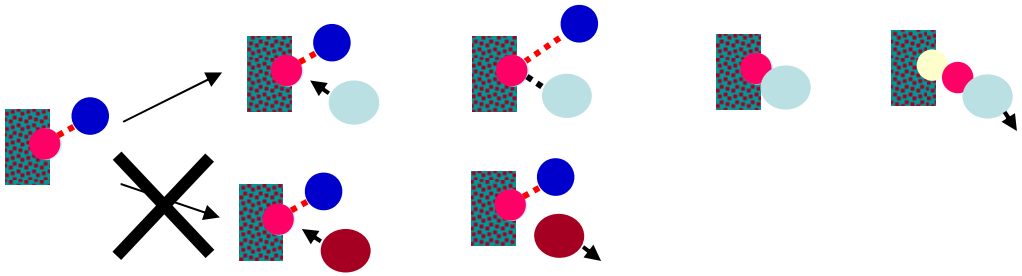
- Catalyst and reactants are in different phases
- It is more specific
- Reaction rate depends on the accessible surface of catalyst: external surface and internal surface within the pores must be accessible to reactants.

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

$$\frac{\sum P_i}{W_{cat}} \text{ ó } \frac{\sum P_i}{V_{cat}}$$

Selectivity: ability to orient formation of specific products



$$\frac{P_i}{\sum P_i}$$

Design of heterogeneous catalysts

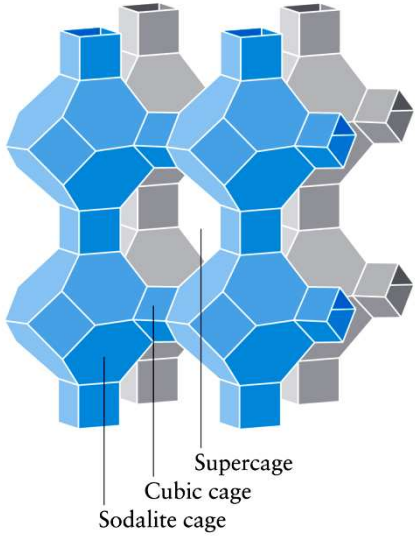
Materials with very high specific surface (typically 100-1000 m^2/g) (is a material property of solids which measures the total surface area per unit of mass)

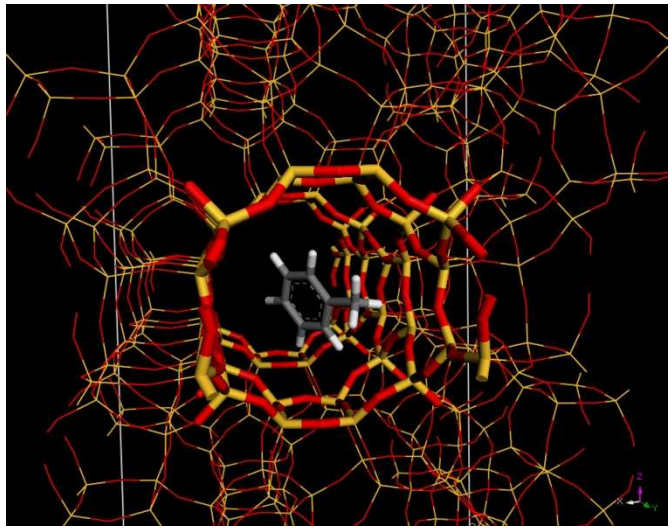
- Porous support (Ex. alumina, silicates…). To consider:

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

- **Supported active centers** (Ex. metals). To consider:

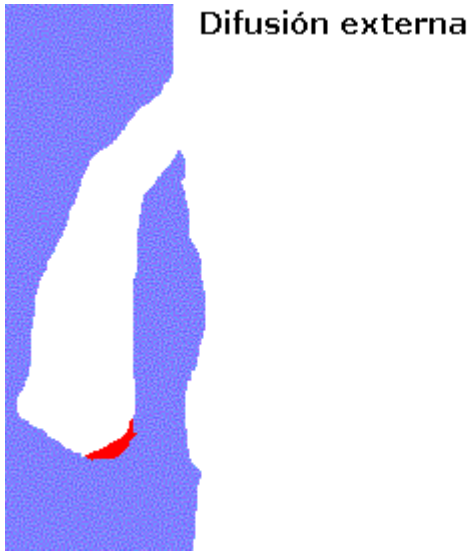
- Stability and resistance to poisoning
- Dispersion degree over the support
- Interaction with the support

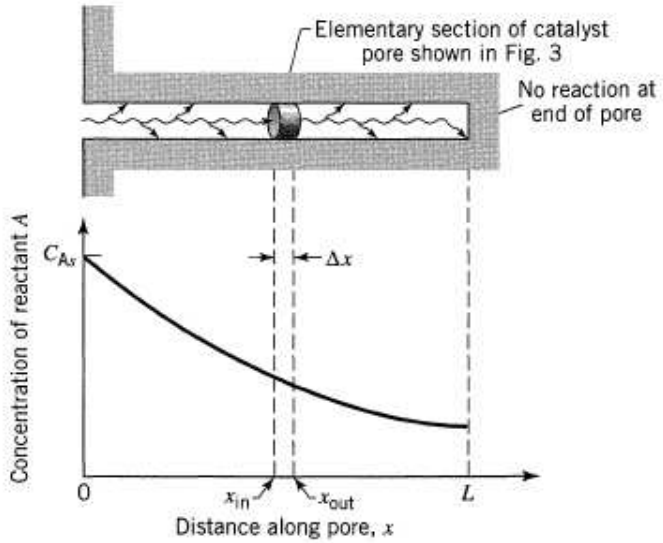


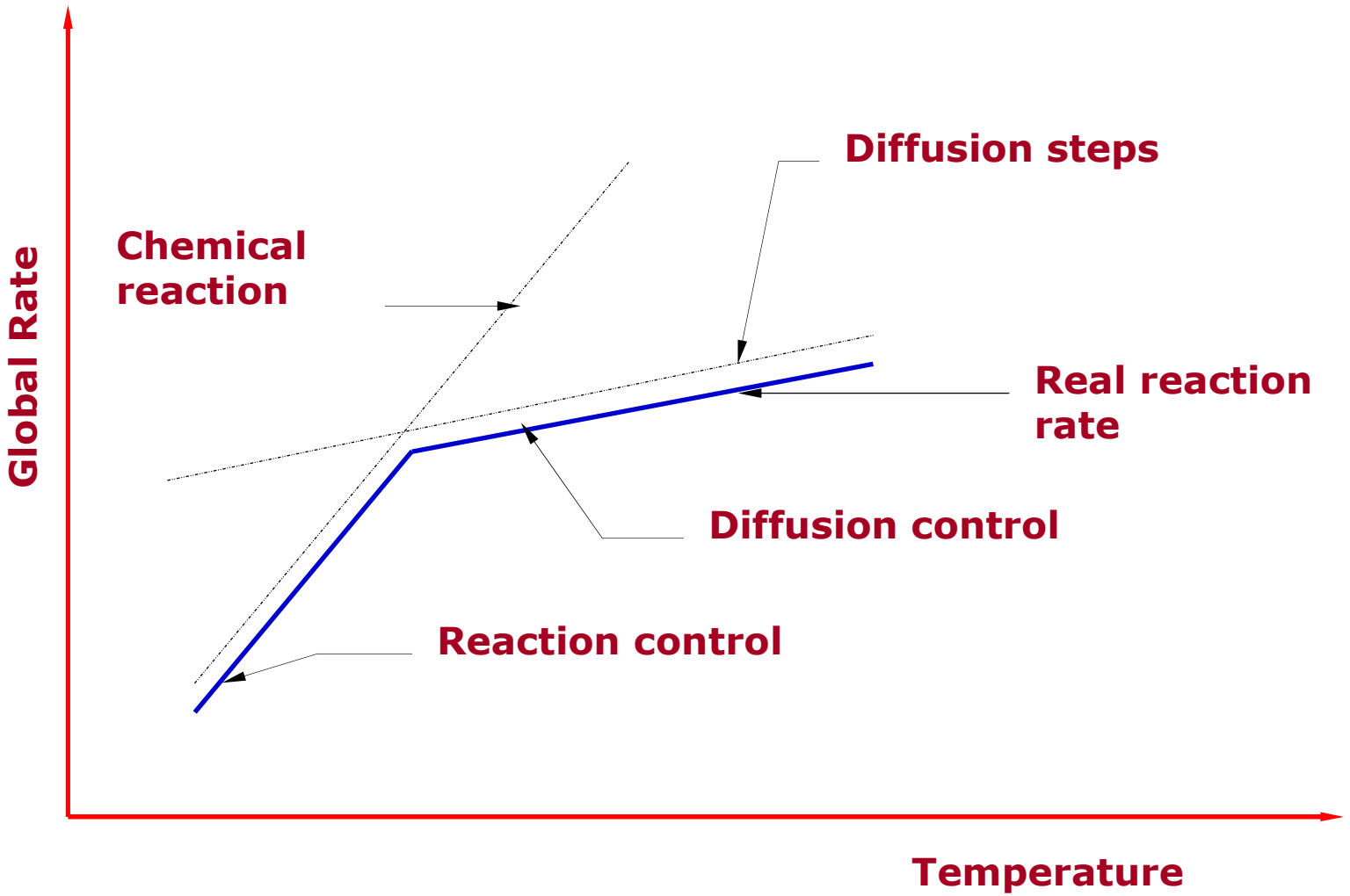


Steps of heterogeneous catalysis

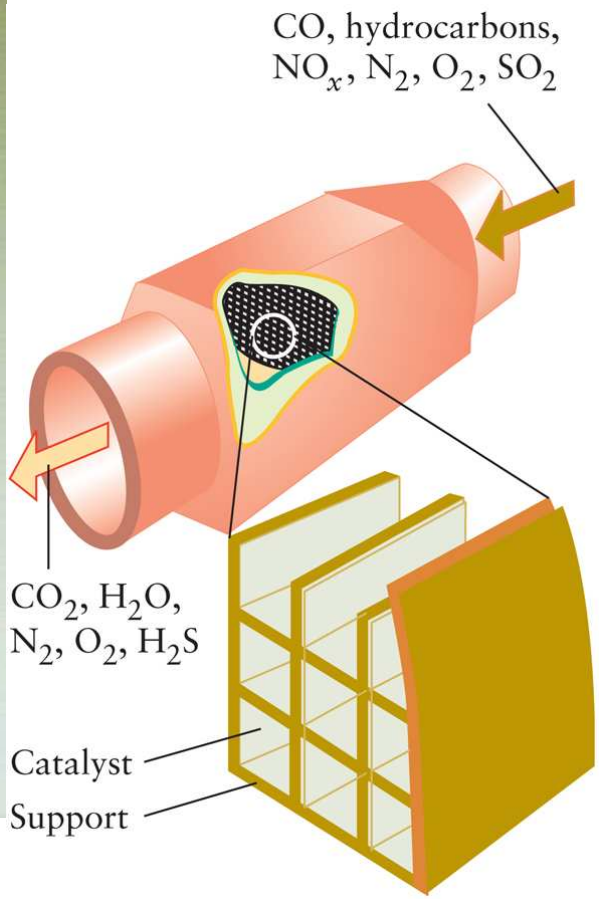
1.- **External diffusion** of reactants from the bulk to the catalyst surface.
2.- **Internal diffusion** through the catalyst pores.
3.- **Adsorption** of reactants over the surface of catalyst.
4.- **Chemical transformation** of adsorbed species over the catalyst surface
5.- **Desorption** of products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






Global Rate
Chemical reaction
Diffusion steps
Real reaction rate
Diffusion control
Reaction control
Temperature

EXAMPLES: CATALYTIC CONVERTER



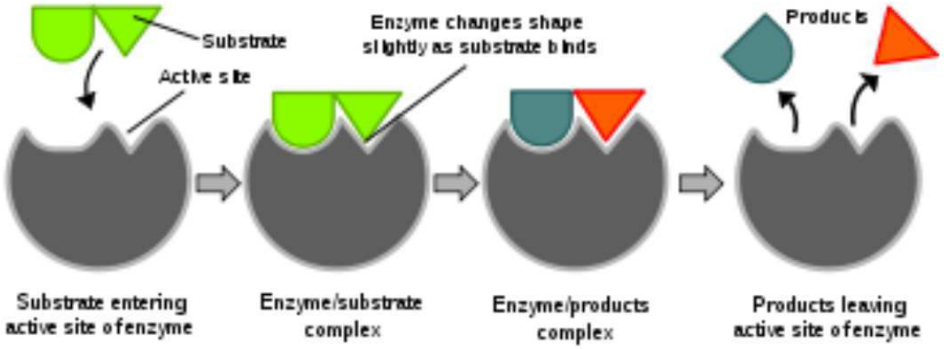
$2\ NO_x \rightarrow x0_2 + N_2$

$2\ CO + O_2 \rightarrow 2\ CO_2$

$2\ C_xH_y + (2x+y/2)\ O_2 \rightarrow 2x\ CO_2 + y\ H_2O$

ENZYMATIC CATALYSIS

- Enzymes are biological catalysts produced by living organisms. Commonly proteins
- They generally increase reaction rate by a factor ~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:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \qquad ES \xrightarrow{k_2} E + P$$

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

$$V = \frac{dP}{dt} = k_2[ES]$$

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

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

MICHAELIS –MENTEN Kinetics (Cont)

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:

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

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] >>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