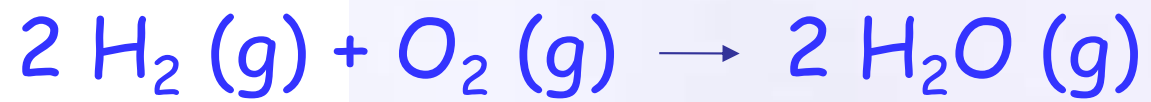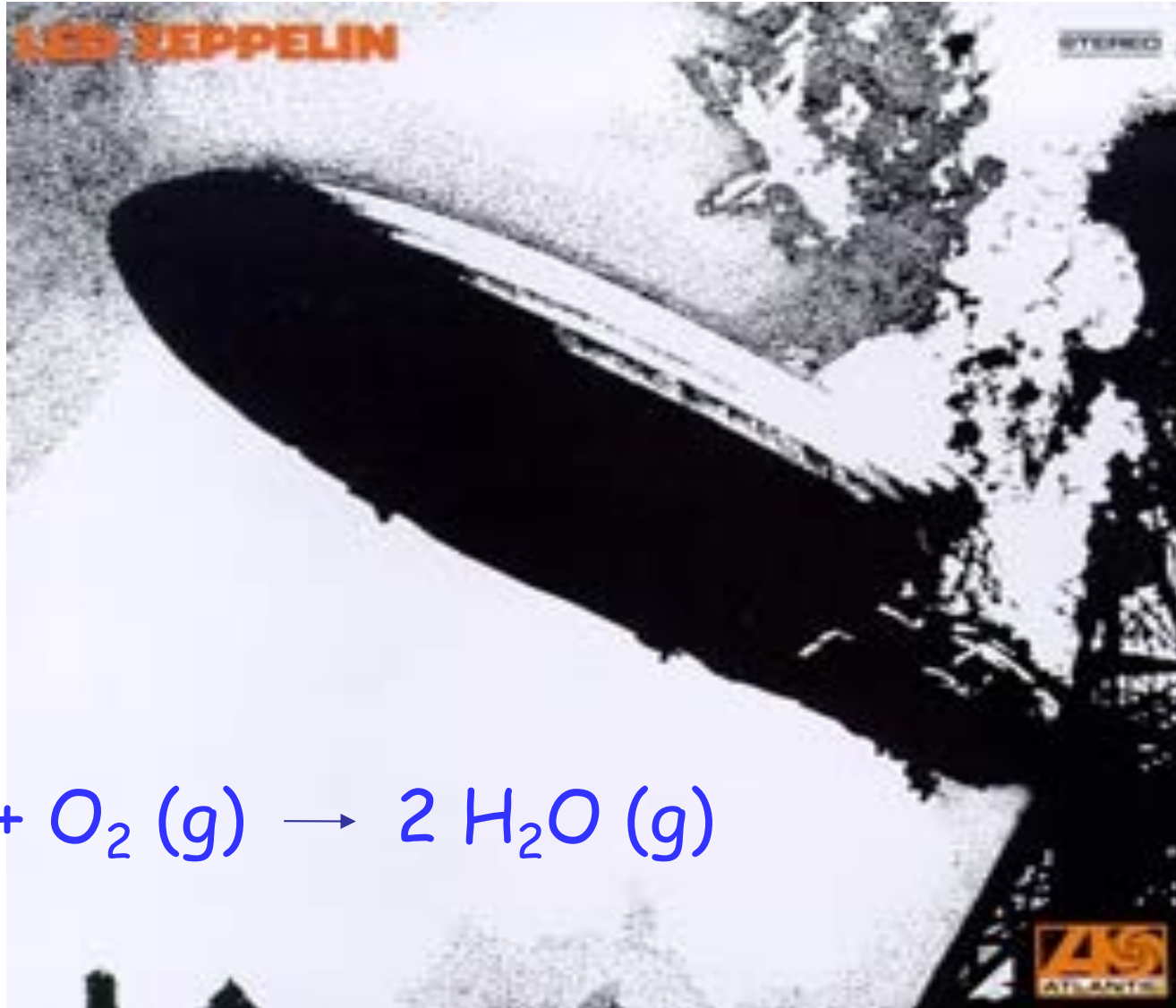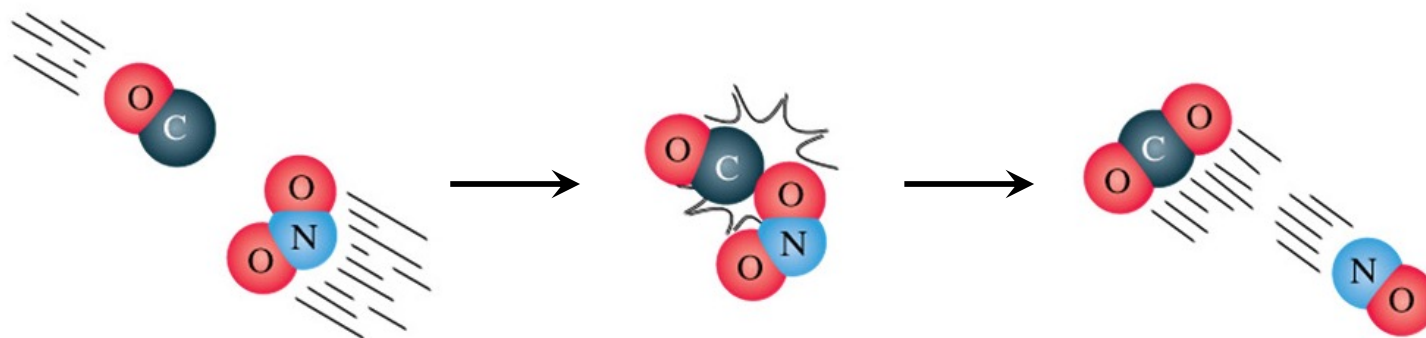# Chemical Kinetics

$$2 H_2 (g) + O_2 (g) \longrightarrow 2 H_2O (g)$$

Chemical kinetics

Unlike thermodynamics which deals with the relative stability between reactants and products in a reaction, chemical kinetics deals with the study of the rate at which a chemical reaction occurs and its dependence on various factors.

In addition to describing the dependence of a reaction rate on experimental factors, kinetics is also concerned with examining the sequence of chemical or physical processes through which the conversion between reactants and products takes place.
In this way, the study of the reaction rate aims to obtain detailed information on the interaction between molecules during the reaction.

Reaction rates

This concept is very common in several contexts
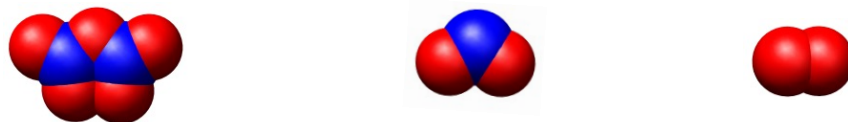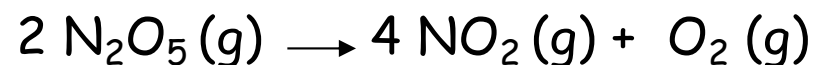

Δs

Δt

$$\text{Speed} = \frac{\text{distance}}{\text{time}} = \frac{\Delta s}{\Delta t}$$

The rate of a reaction is defined in a similar way: it corresponds to the variation of the concentration of a chemical species in the unit of time

$$\text{Reaction rate} = \frac{\text{Variation of concentration}}{\text{Time interval}}$$

Let's consider the dissociation N_2O_5 according to the following reaction

$$2\ N_2O_5\ (g) \longrightarrow 4\ NO_2\ (g) +\ O_2\ (g)$$

- The reaction course can be followed in different ways: monitoring the increqse of' O_2 or NO_2 o or the decrease of N_2O_5
- The amount of O_2 that is formed is related to the amount of N_2O_5: for one mole of O_2, 2 moles of N_2O_5 have dissociated

The rate of the re4action can be expressed, for any time interval by the ratio between the variation of N_2O_5 concentration and the time interval.

$$\text{Reaction rate} = \frac{\text{Variation of concentration of }\ N_2O_5}{\text{Time interval}} = -\ \frac{\Delta N_2O_5}{\Delta t}$$
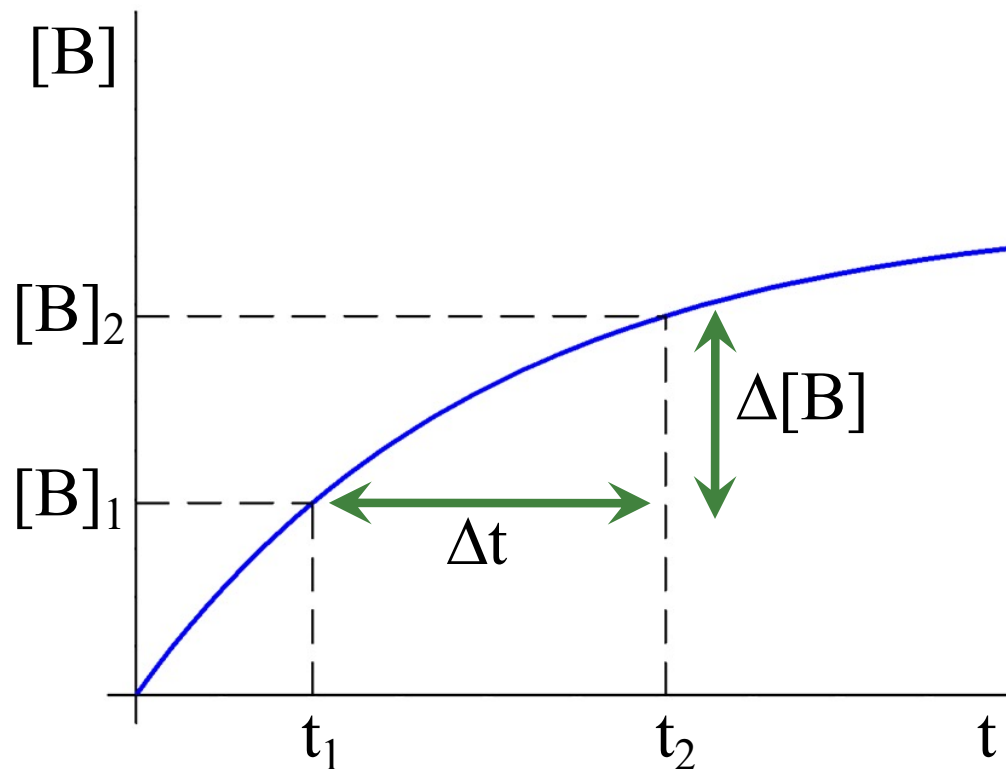
The negative "-" is due to the fact that $[N_2O_5]$ decreases over time.

IN the reaction: $A \xrightarrow{k} B$
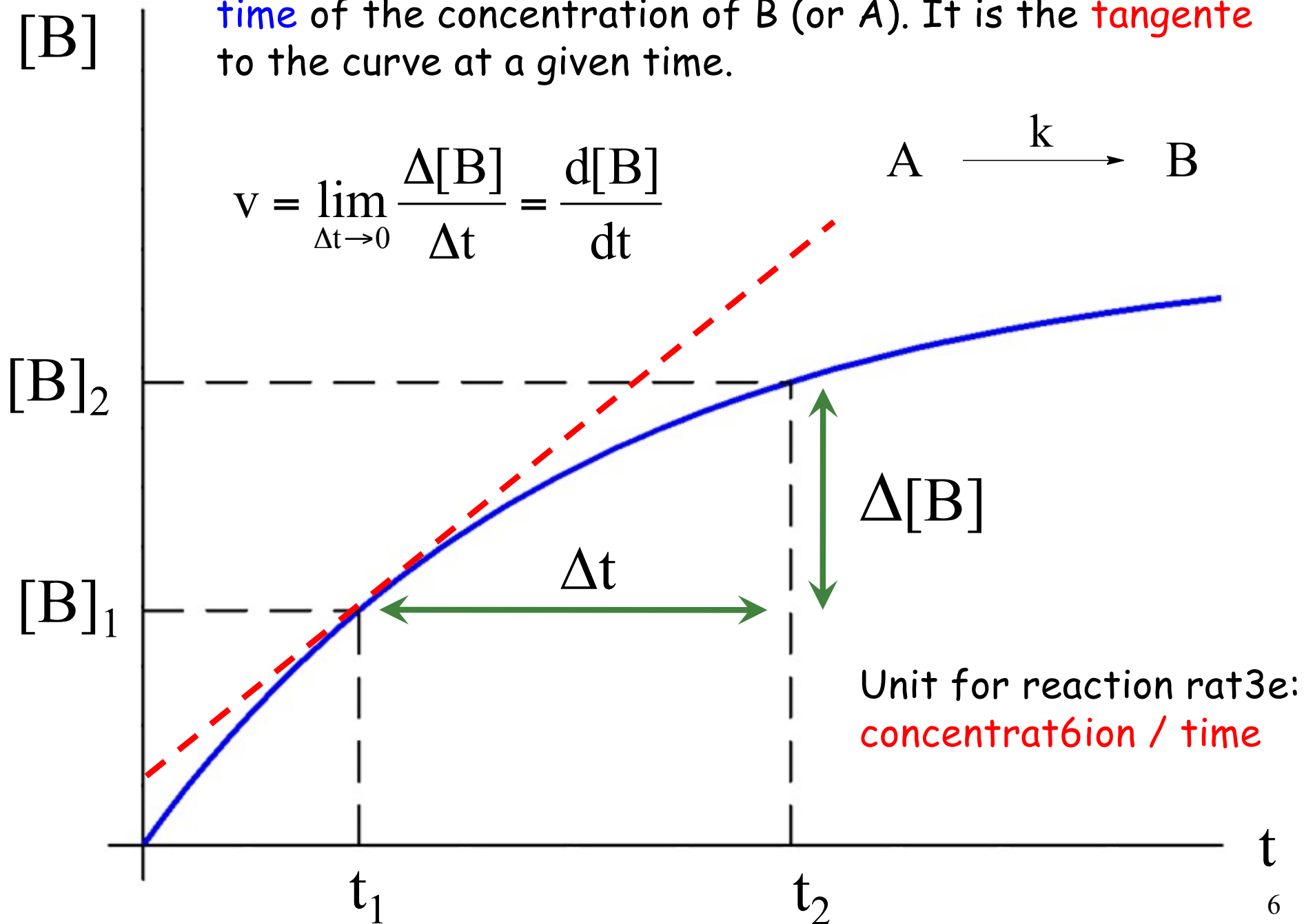
The reaction rate indicates how the concentration of reagents or prducts changer over time tempo.

Average rate

$$v = -\frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1} = \frac{[B]_2 - [B]_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$$
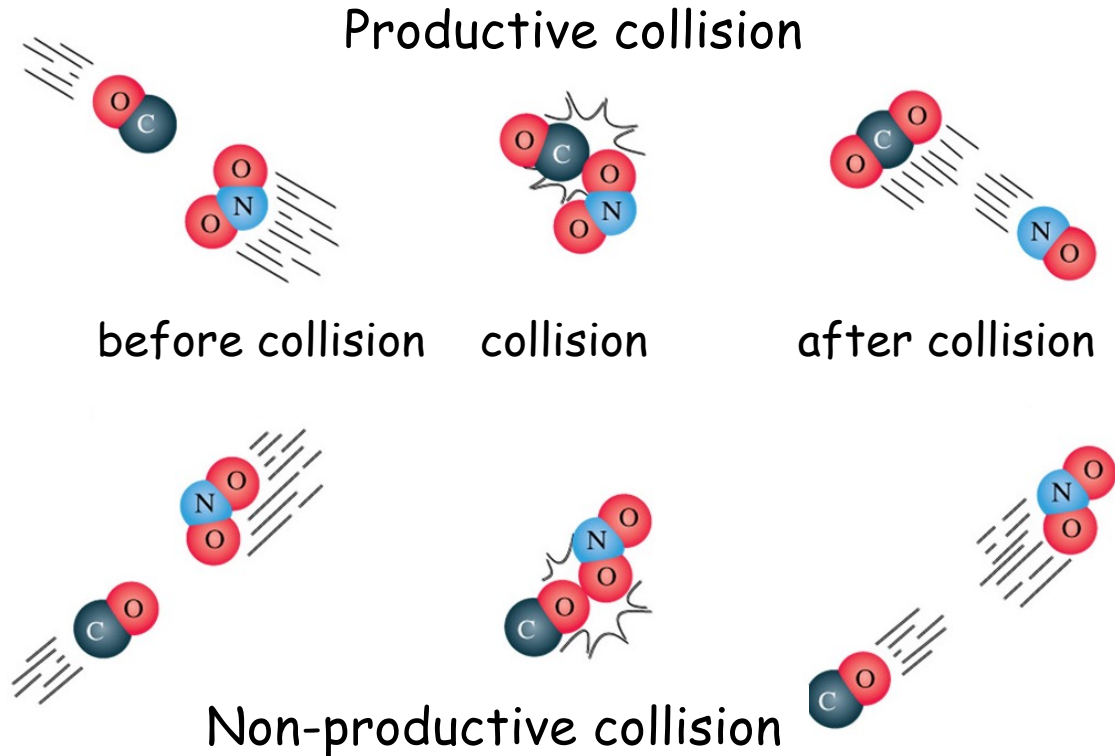
The instantaneous rate is the derivative with respect to time of the concentration of B (or A). It is the tangente to the curve at a given time.

$$v = \lim_{\Delta t \to 0} \frac{\Delta[B]}{\Delta t} = \frac{d[B]}{dt}$$

$$A \xrightarrow{\ k\ } B$$

[B]

$[B]_2$

$[B]_1$

$\Delta[B]$

Δt

Unit for reaction rat3e:
concentrat6ion / time

t_1

t_2

t

The reaction rate depends on several factors:

- the nature of the reactants
- the concentration of the reactants
- the reaction temperature
- the presence of catalysts
- the interface surface (if the reaction occurs between reagents in two different phases)

Productive collision

before collision   collision   after collision

Non-productive collision

Relationship between concentration and reaction rate

Experimental evidence shows that the the reate of a reaction depends on the concentration of the reagents. The equation correlating the rate and the concentrations is called kinetic equation or rate law kinetic equation or rate law and it has the following form:

$$a\ A + b\ B \longrightarrow c\ C + d\ D$$
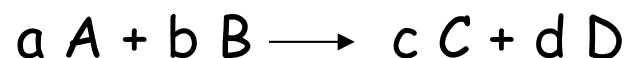
$$v = k \cdot [A]^m \cdot [B]^n$$

The product of the the concentration of reagents, raised to coefficients (i.e. m, n …, often different from the stoichiometric ones) multiplied by a constant (k). These coefficients are fothe (but not always) integer numbers and must be determined experimentally. The constant k is called specific rate constant or kinetic constant and it depends only on the r4eagents and on the temperature.

Reaction order

If the kinetic equation is known, one can define the reaction order for a given reactant as its exponent in the reaction.
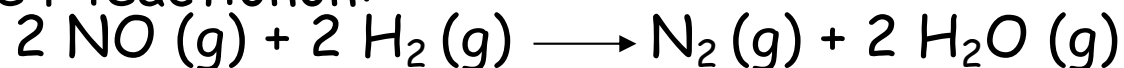
The overall reaction order is the sum of the exponents of all the species present in the reaction.
The generic reaaction: a A + b B   c C + d D
With the following kinetic equation:

$$v = k \cdot [A]^m \cdot [B]^n$$

Has an order m with respect to reagent A eand an order n with respect to reagent B and an overall reaction oredr of m+n. For example the r4eactionon:

2 NO (g) + 2 H$_2$ (g) $\longrightarrow$ N$_2$ (g) + 2 H$_2$O (g)
With kinetic equation v = k [NO]^2[H$_2$]

has second order with respect to NO, first order with respect to H$_2$ and overall thirs order. If a reagent does not appear in the kinetic reaction, the reaction has a zero order for that compound.

Experimental determination of the reaction order: method of initial rates

The relationship between concentrations and rates must be determined experimentally using the initial rates (rates measured at t=0).
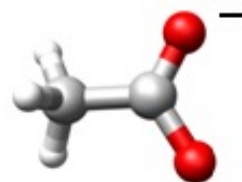Measuring initial rates is convenient because the concentrations are known and interferences by products ore other reactions is avoidedi.
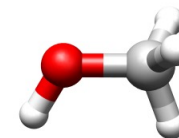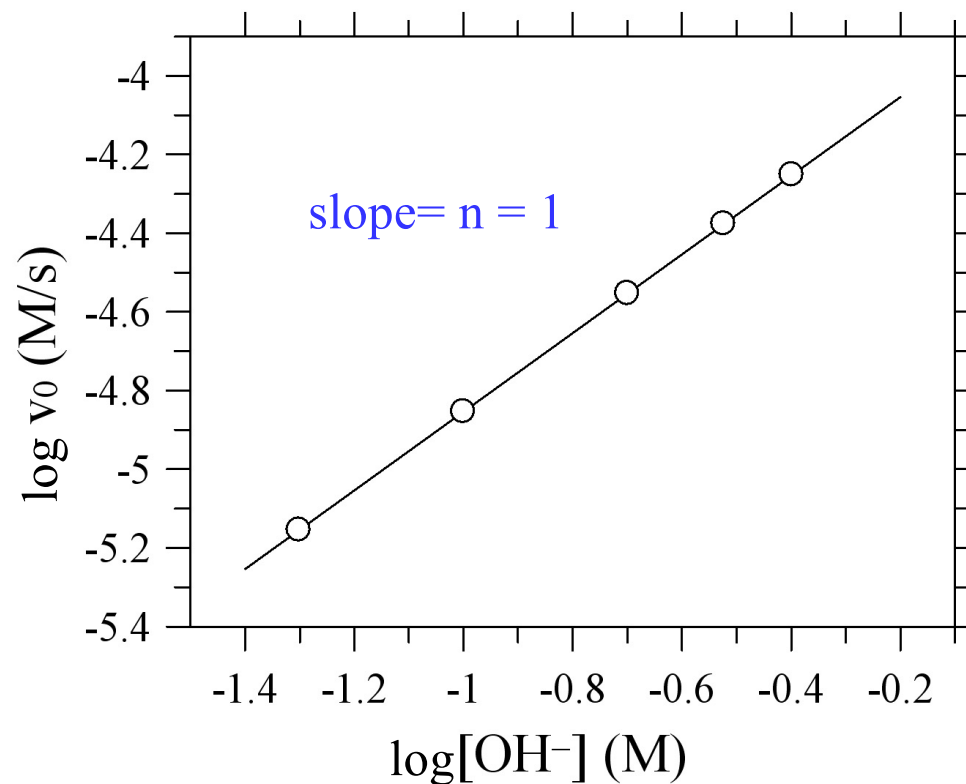
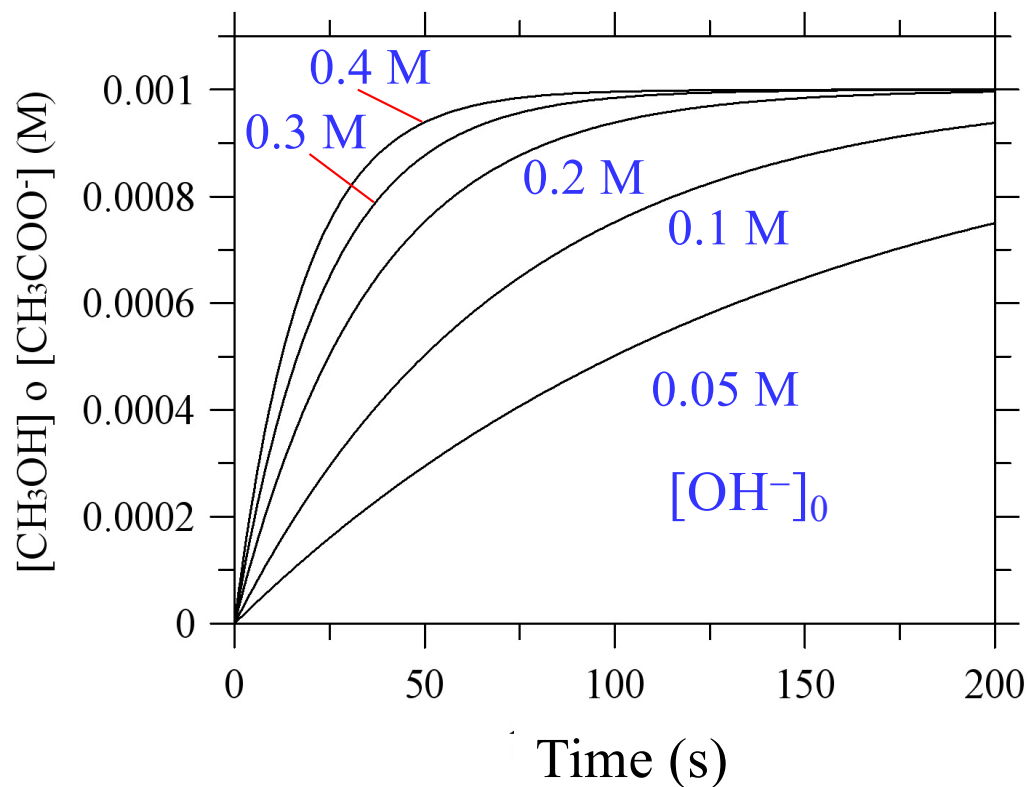$$CH_3COOCH_3 \text{ (aq)} + OH^- \text{ (aq)} \rightarrow CH_3COO^- \text{ (aq)} + CH_3OH \text{ (aq)}$$
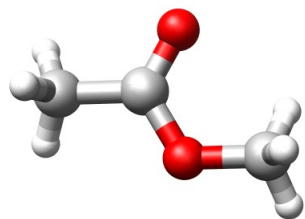
Methyl acetate   oxydril   acetate   methanol

$$v = [CH_3COOCH_3]^m \cdot [OH^-]^n$$

The reaction has order 1 for methyl acetate and order 1 for oxydril.

$$CH_3COOCH_3 \ (aq) + OH^- \ (aq) \longrightarrow CH_3COO^- \ (aq) + CH_3OH \ (aq)$$

[methyl acetate]$_0$ = 0.001 M, T = 25 °C

$$v_0 = [CH_3COOCH_3]_0^m \cdot [OH^-]_0^n$$

$$\log v_0 = m \cdot \log[CH_3COOCH_3]_0 + n \cdot \log[OH^-]_0$$

The specific rate constant k

The specific rate constant k is the proportionality constant that relates rate and concentration at a given temperature. It is a very relvant parameter because allows one to calculate the rate at any concentration value.

The units of the specific rate constant k must be consistent with other values in the equation.

$$A \xrightarrow{k} B$$

$$v = k\,[A] \quad \{k = time^{-1}\}$$

$$A + B \xrightarrow{k} C + D$$

$$v = k\,[A]\,[B] \quad \{k = concentration^{-1} \times time^{-1}\}$$
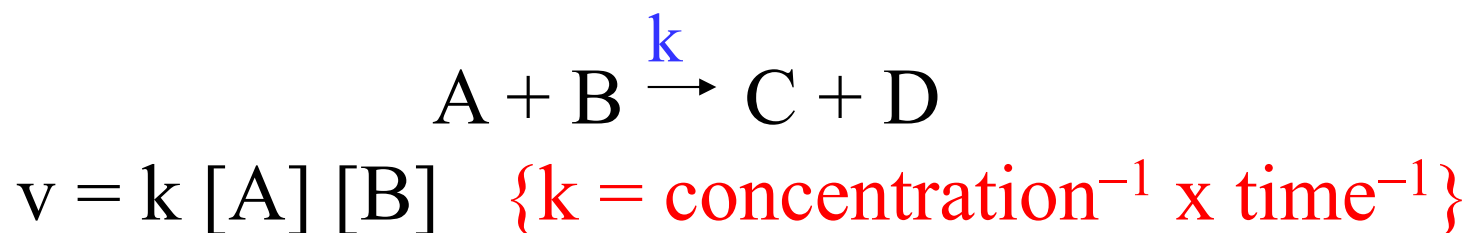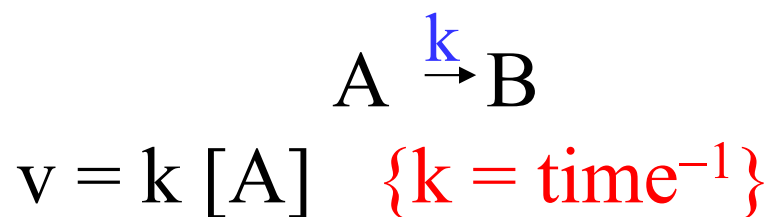
Relationship between time and concentration: integrated kinetic laws.

It can be useful to know for how long a reaction has to proceed to achieve a certain contration of a reagent or of a product or how much of a reagent or of a product we will have after a certain time.

To this purpose one has to derive an equation that relates tie and concentrations: the integrated kinetic equation.

$$CH_3COOCH_3 \text{ (aq)} + OH^- \text{ (aq)} \rightarrow CH_3COO^- \text{ (aq)} + CH_3OH \text{ (aq)}$$
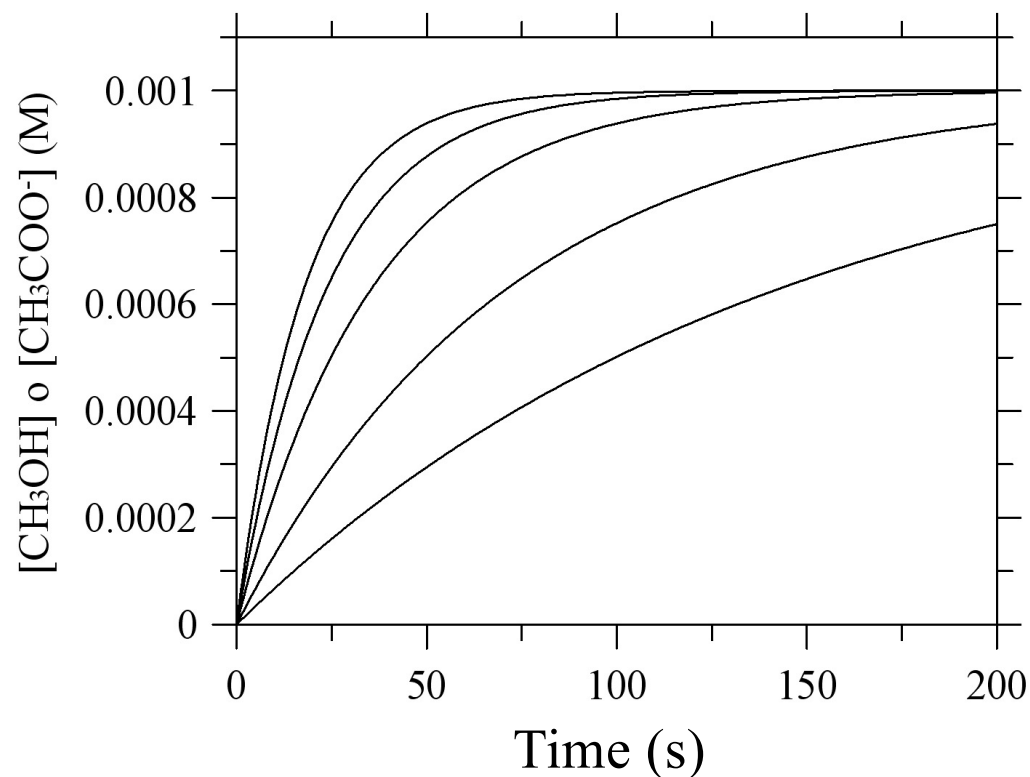
The integrated kinetic equation describes the time dependence of the formation of products and of reactants disappearance.

A → B (reaction 1° order)

$v = k[A] = -\delta[A]/\delta t$ from which $-\delta[A]/[A] = k\delta t$

The relationship between the variation of the concentration of A, $\delta[A]$, with respect to its concentration [A] is constant.

Integrating,
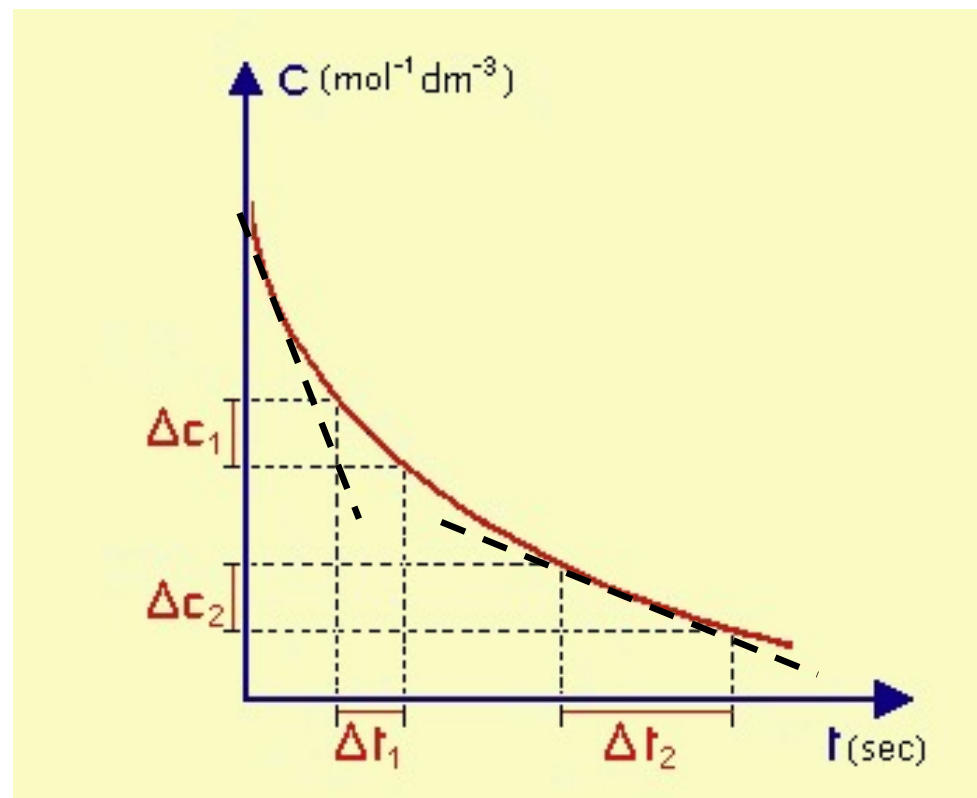$$\ln[A] = -kt + \text{cost.}$$
$$\text{if } t = 0, \quad [A] = [A]_0$$
$$\ln[A]_0 = \text{cost}$$

From which

$$\ln[A] = -kt + \ln[A]_0$$
$$[A] = [A]_0\, e^{-kt}$$

[A] decreases exponentially in time

For evaluating rates ,one often uses the **half life** ($t_{1/2}$) which is the time necessary for the the initial concentration to be halved.

Form the previous equation:
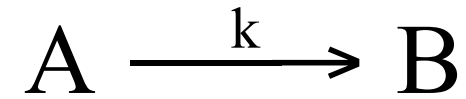
$$\ln [A]/[A]_0 = -k (t-t_0)$$

If we consider as $[A] = 1/2 [A]_0$, (that is if we want that the concetration is half of the initial one, as defined for half life), and since $t_0 = 0$ (reaction start), one has:

$$\ln \frac{[A]_0}{[A]_0/2} = -k\, t_{1/2} \qquad\qquad t_{1/2} = \ln2/k = 0.693/k$$
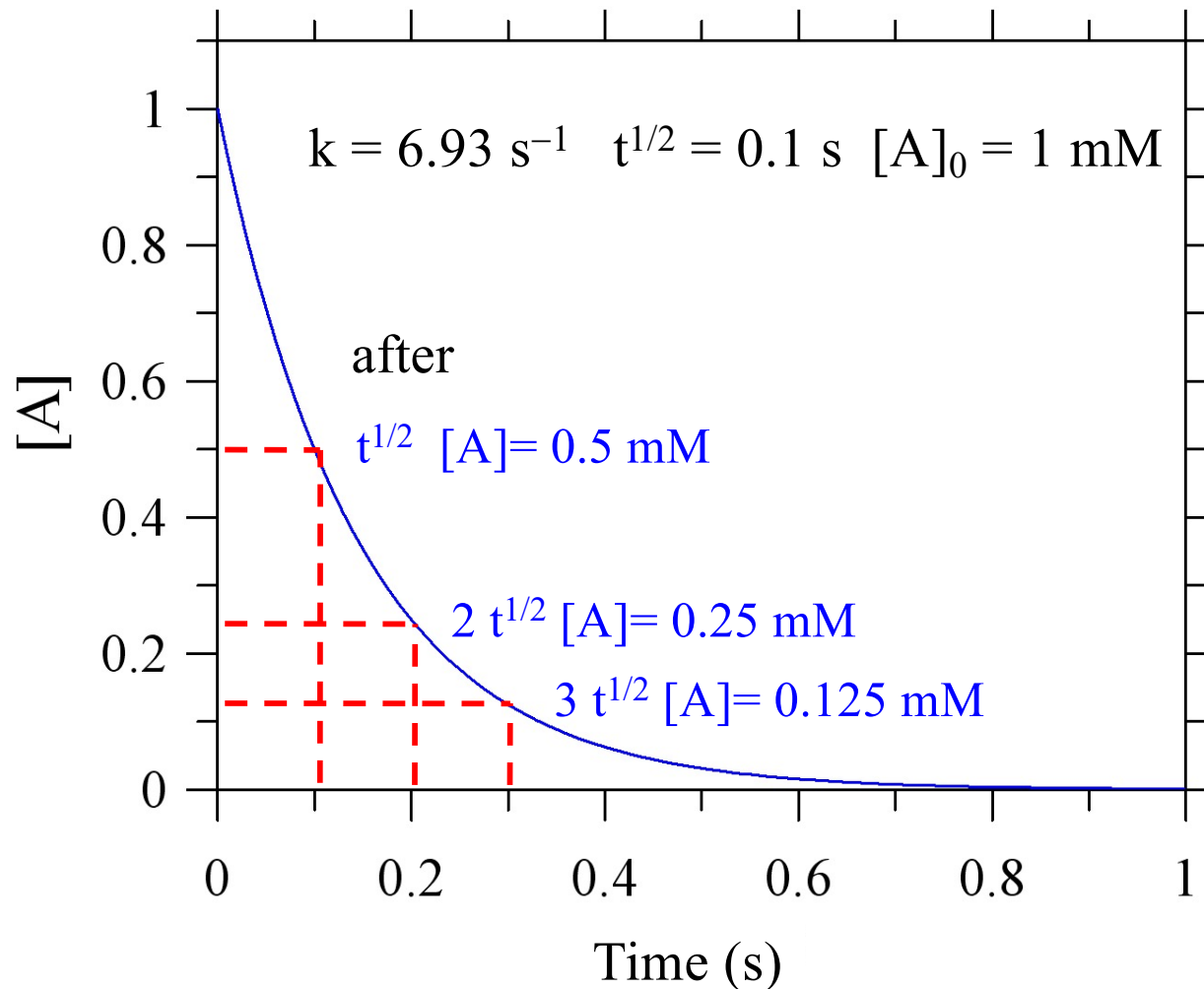
The half-life is inversely proportional to the rate constant and is independent of the concentration of the reactants

Reaction of the 1° order

$$A \xrightarrow{k} B$$

$$[A] = [A]_0 e^{-kt}$$ the time course is exponential

$k = 6.93 \text{ s}^{-1}$ $t^{1/2} = 0.1 \text{ s}$ $[A]_0 = 1 \text{ mM}$

after

$t^{1/2}$ $[A] = 0.5 \text{ mM}$

$2 t^{1/2}$ $[A] = 0.25 \text{ mM}$
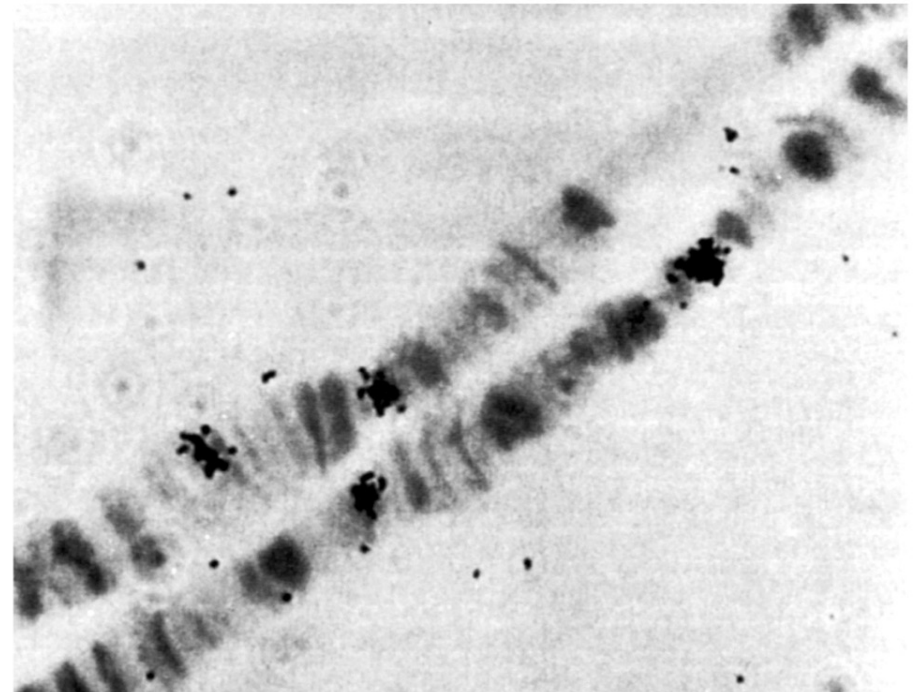
$3 t^{1/2}$ $[A] = 0.125 \text{ mM}$

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

[A]

Time (s)

16

Radiactive isotopes in biology and medicine
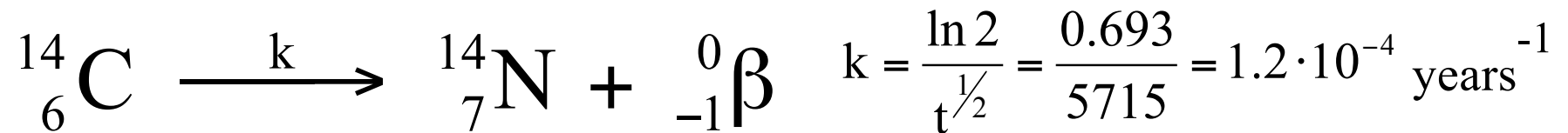
- They are used as labels or as toxic agents (radiotherapy)
- They must have half-lives of days or months
- They must not accumulate in the organism
- Their decay products must be stable

| radionuclide	Half-life ($t^{1/2}$)	tipo of radiation
^3H	12 years	β
^{14}C	5715 years	β
^{24}Na	15 hours	β
^{32}P	14 days	β
^{35}S	87 days	β
^{40}K	$1.25 \cdot 10^9$ years	β
^{45}Ca	163 days	β
^{125}I	59 days	γ
^{131}I	8 days	γ, β

Radiocarbon Dating

Carbon has three isotopes: two are stable (^{12}C and ^{13}C) nd one is radioactive (^{14}C). The latter decays with β particles (electrons) into nitrogen (^{14}N), with a half-life of 5715 years.

$$^{14}_{6}C \xrightarrow{\ k\ } \ ^{14}_{7}N + \ ^{0}_{-1}\beta \qquad k = \frac{\ln 2}{t^{1/2}} = \frac{0.693}{5715} = 1.2\cdot10^{-4} \ \text{years}^{-1}$$

The production of new ^{14}C occurs in nature in the upper layers of the troposphere and in the stratosphere, due to the capture of thermal neutrons by nitrogen atoms. The dynamic equilibrium that is established between production and radioactive decay therefore keeps the concentration of ^{14}C constant in the atmosphere (where it is present mainly linked to oxygen in the form of CO_2).

18

All living organisms that particopate to the carbon cycle constantly exchange C with the atmosphere by means of respiration (animals) or photosynthesis (plants), or they assimilate by feeding on plants or animals. Consequently, finas long as an organism is alive, the ratio between ^{14}C concentration and of other C isotopes is constant and equa to the one in the atmosphere.

Dafter death, however, the organism does not exchange C with the atmosphere. Due to decay the concentration of ^{14}C decreases exponentially according to the law:

$$^{14}_{6}C \xrightarrow{\ k\ } {}^{14}_{7}N + {}^{0}_{-1}\beta \qquad\qquad [^{14}C] = [^{14}C]_0\, e^{-kt} \qquad\qquad k = \frac{\ln 2}{t^{1/2}}$$
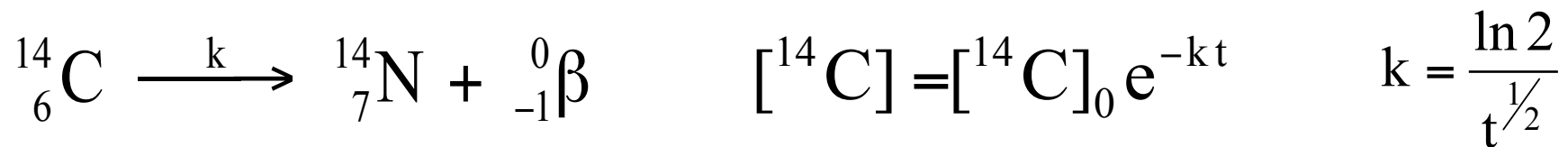
Here, $[^{14}C]_0$ is the concentration of ^{14}C at the momen t of death
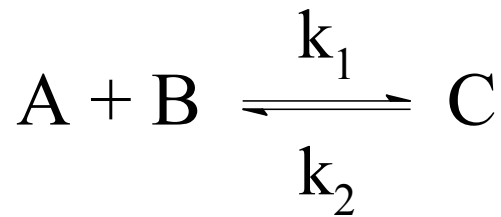
The method based on ^{14}C was validated with samples from Egypt where the date was known by independent evidence.
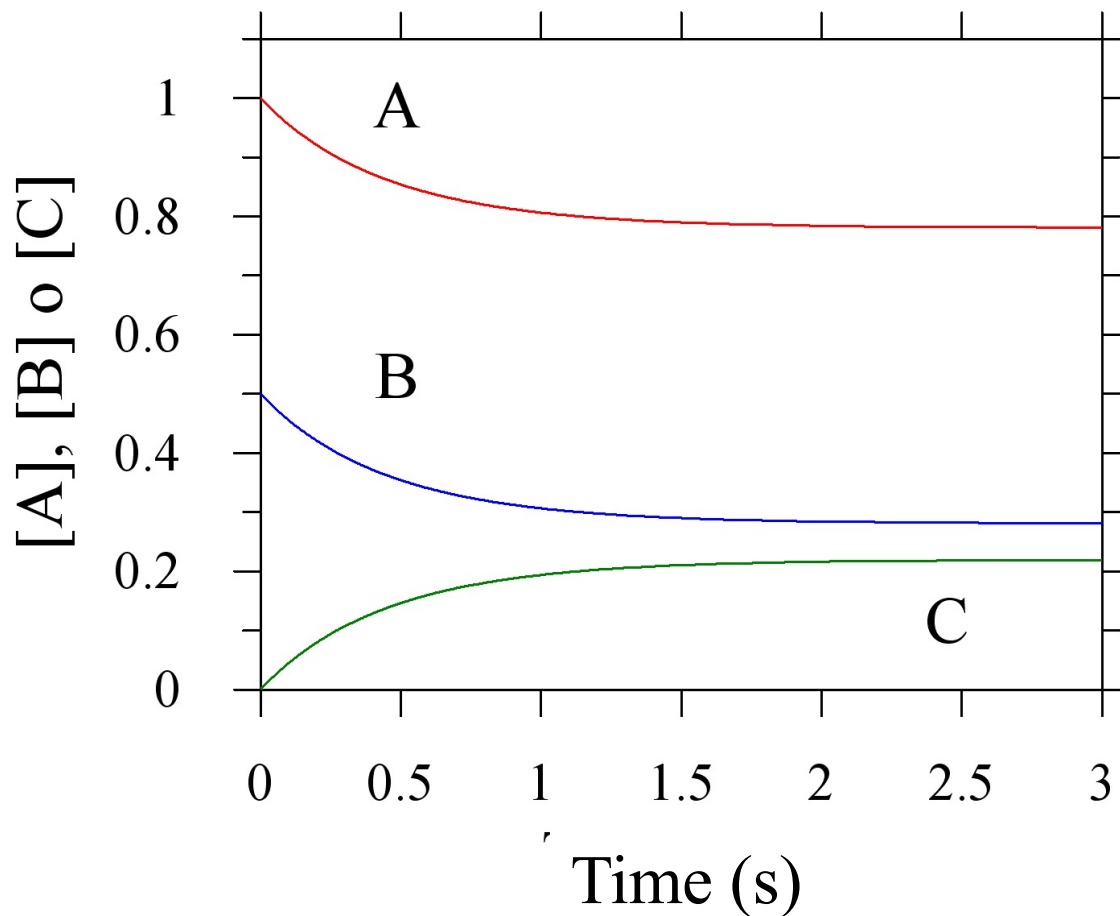
Half-life of ^{14}C = 5715 years.

$$[^{14}C] = [^{14}C]_0 \, e^{-\frac{t_{DEATH}}{t_{1/2}} \ln 2} \qquad\qquad t_{DEATH} = -\frac{t_{1/2}}{\ln 2} \ln \frac{[^{14}C]}{[^{14}C]_0}$$

Thermodynamics and kinetics: reversible reactions.

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$$

Rate of the direct reaction (v_D)

The kinetic equation is: $v = k_1 \cdot [A] \cdot [B] - k_2 \cdot [C]$

Rate of the inverse reaction (v_I)

At equilibrium $v_D = v_I$
and

$$K_{EQ} = \frac{[C]}{[A] \cdot [B]} = \frac{k_1}{k_2}$$

Reaction from a microscocopic point of view

For a reaction to take place the theory of collisions states three conditions:

1. The reactants must collide
2. The reactants must collide with energy sufficient to break the bonds involved in the reaction
3. The molecules must collide with a geometry geometry that allows atomic rerrangement and product formation.
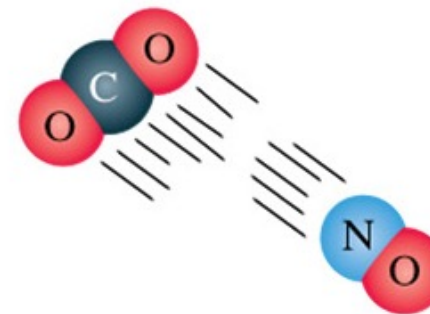
1. Molecules must collide

$$CO\ (g) + NO_2\ (g) \rightarrow CO_2\ (g) + NO\ (g)$$
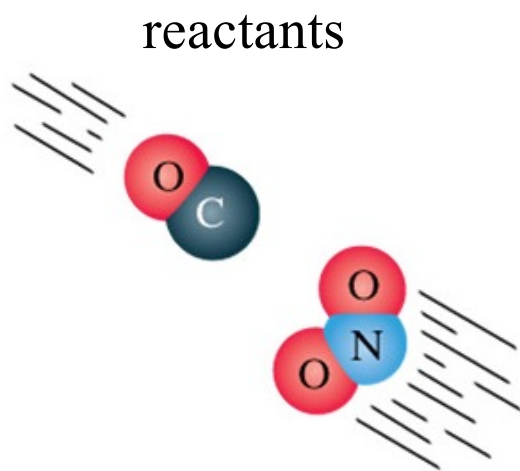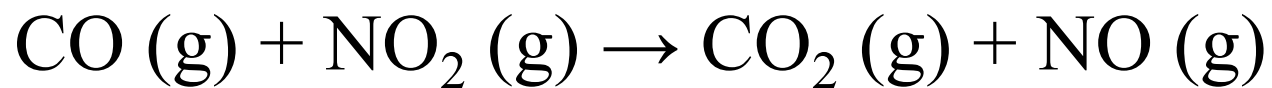
reactants

collision
complex

products

Trajectory of reagents

Recognition
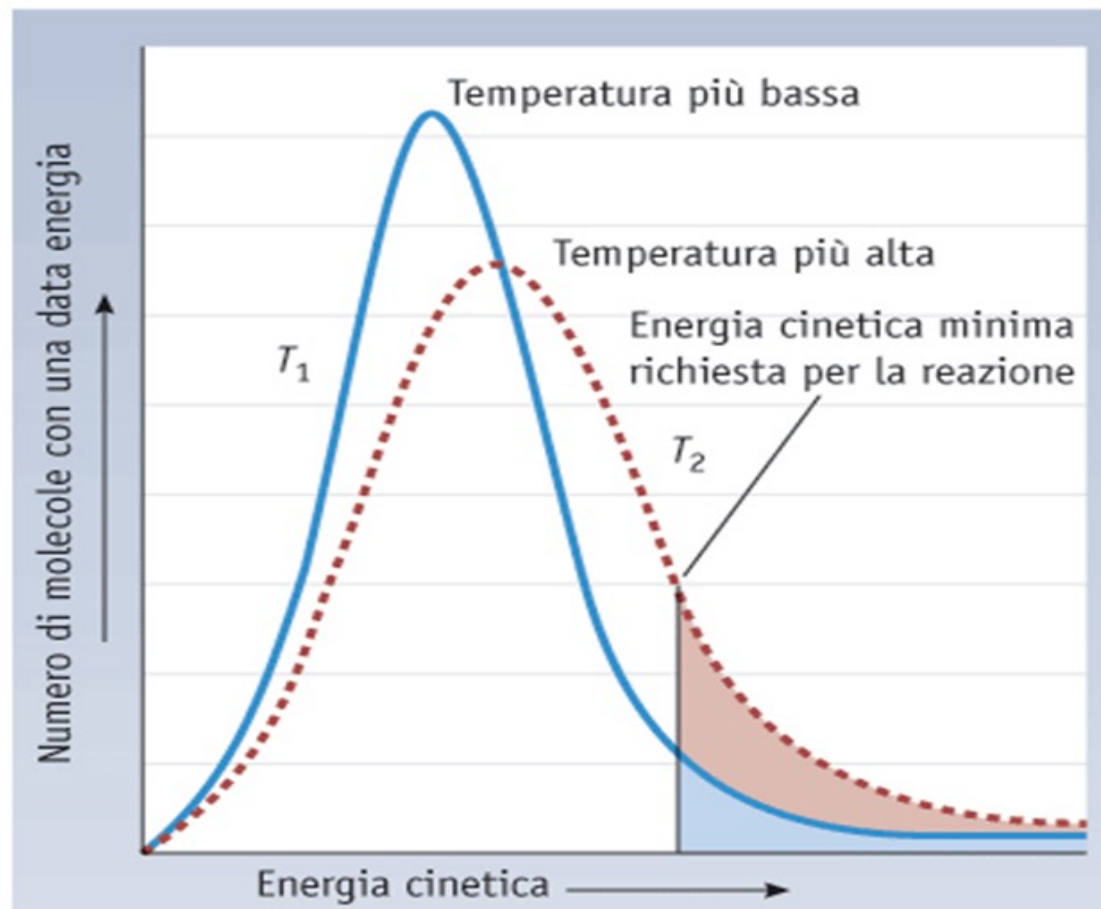
Separation of products

2. The reactants must collide with energy sufficient to break the bonds involved in the reaction

Maxwell-Boltzmann distribution

Numero di molecole con una data energia

Temperatura più bassa

Temperatura più alta

Energia cinetica minima richiesta per la reazione

T_1

T_2

Energia cinetica

The minimum kinetic energy is called activation energy E_a (the energy of the sttransition state or activated complex)

$$A + B \rightarrow C + D$$

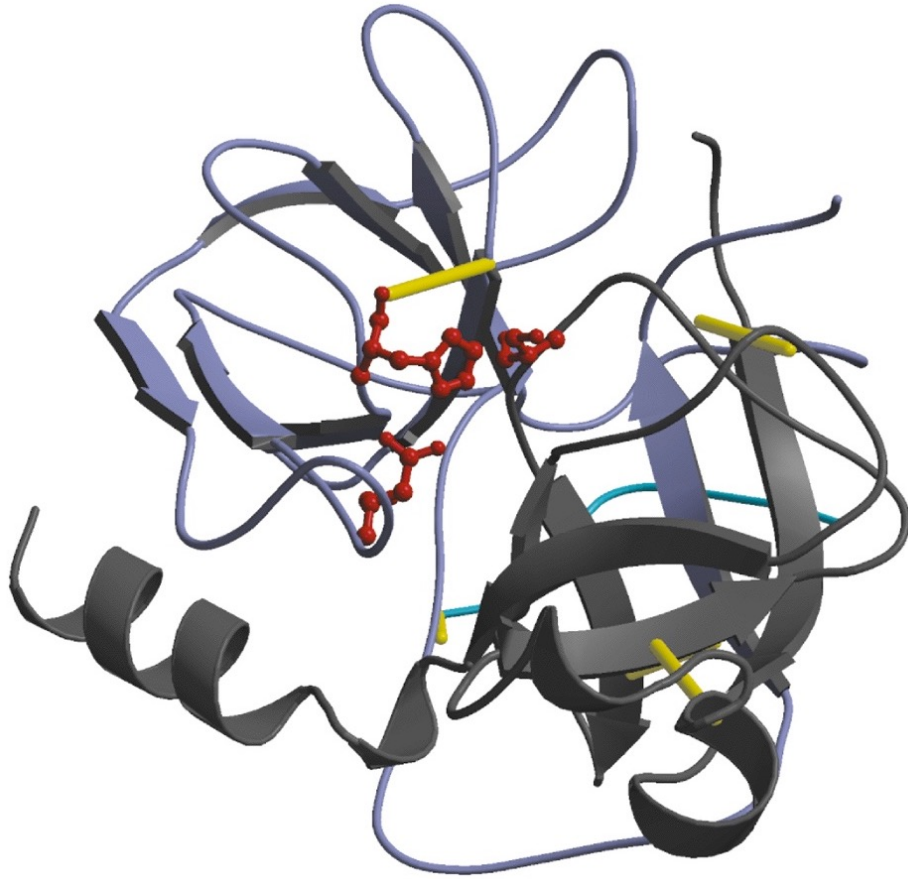complesso attivato

E_a
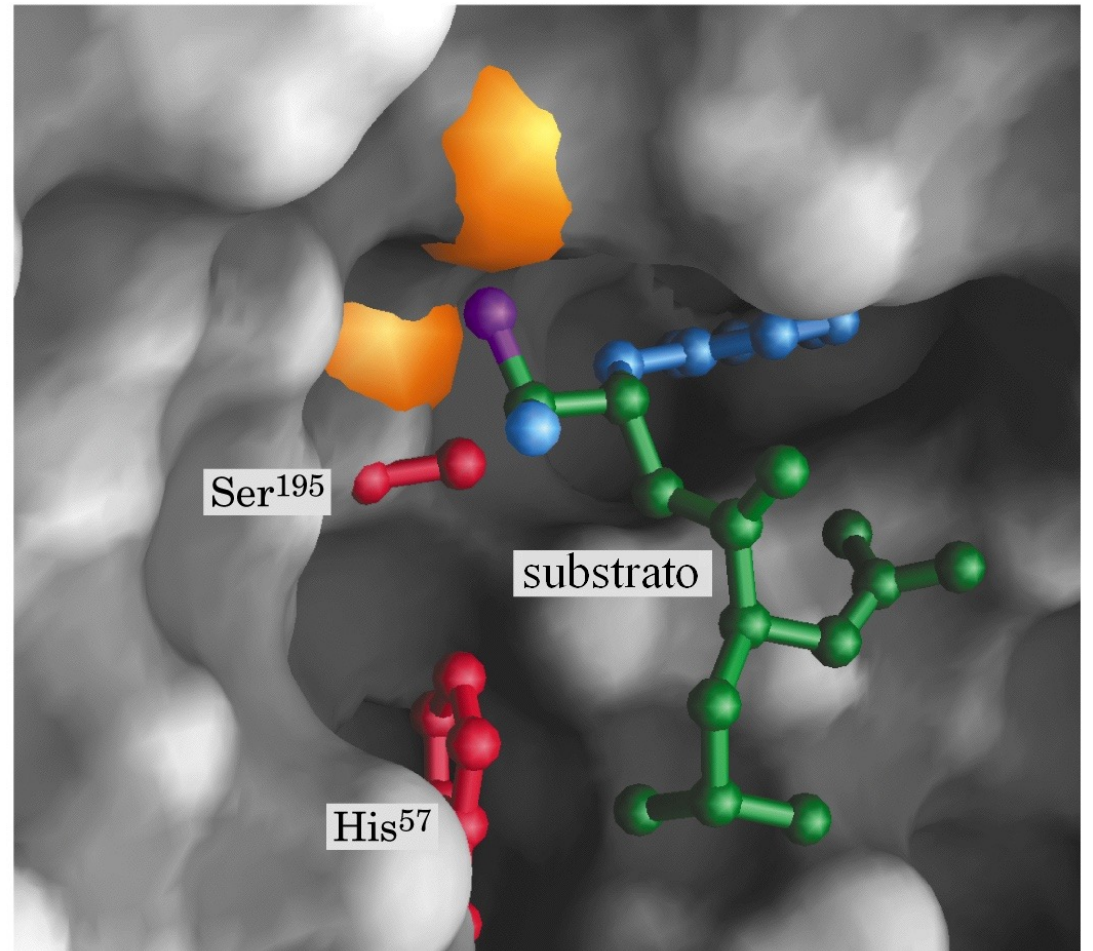
A + B

C + D

energy
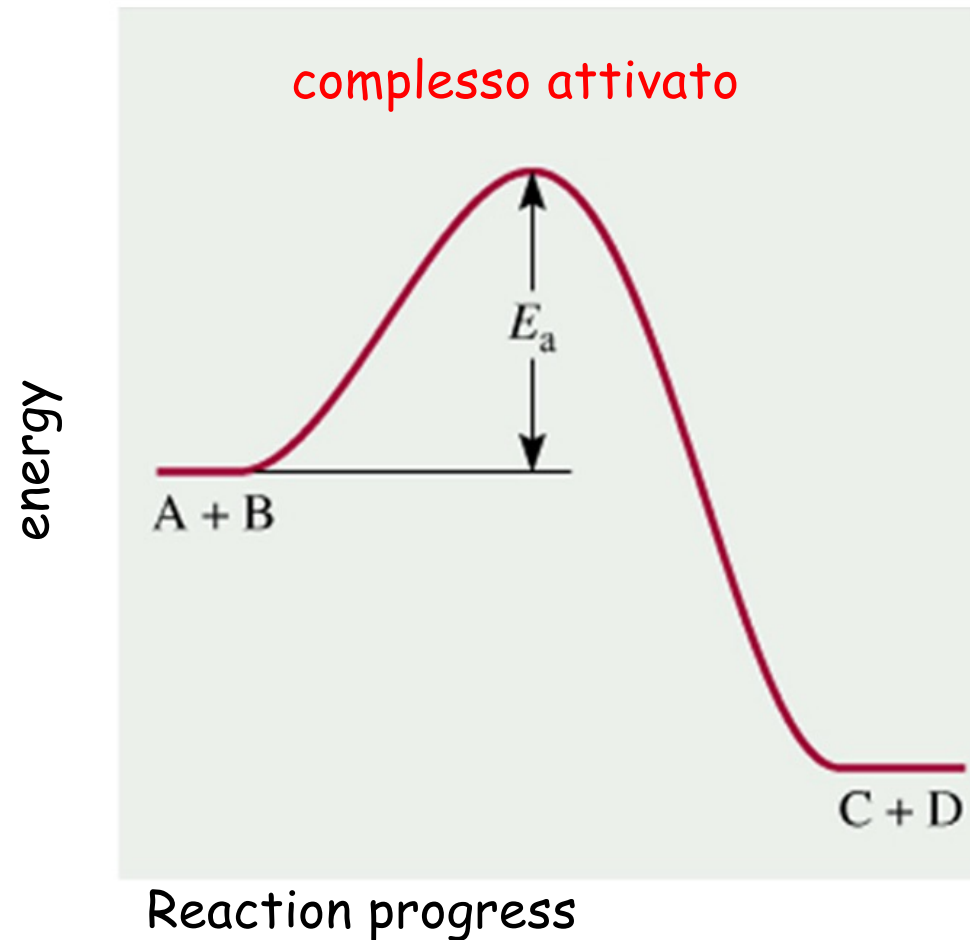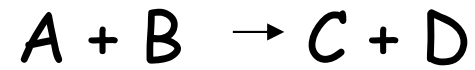
Reaction progress

Reaction progress= reaction coordinate

3. The molecules must collide with a geometry geometry that allows atomic rerrangement and product formation

Productive collision

before collision   collision   after collision

Non-productive collision
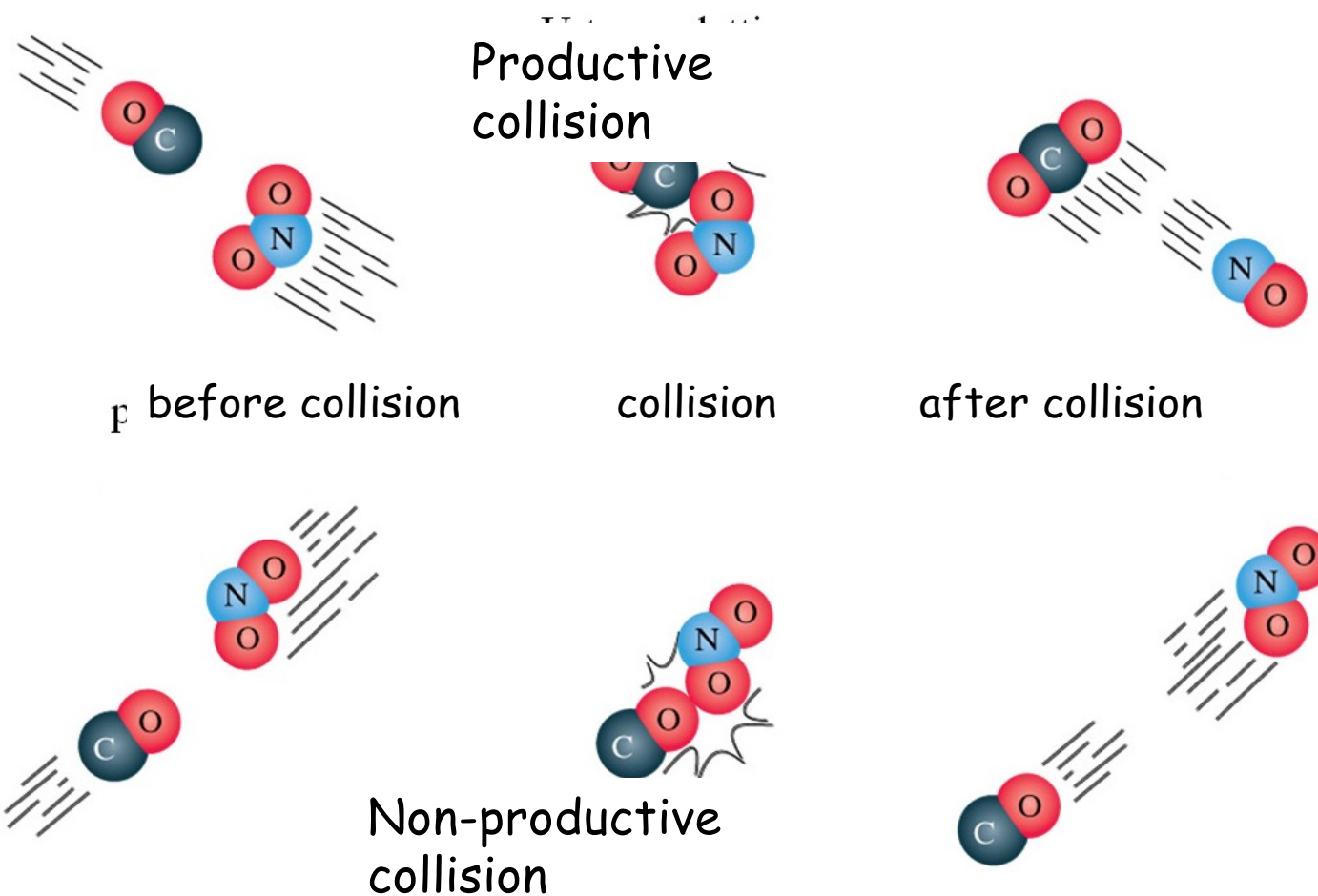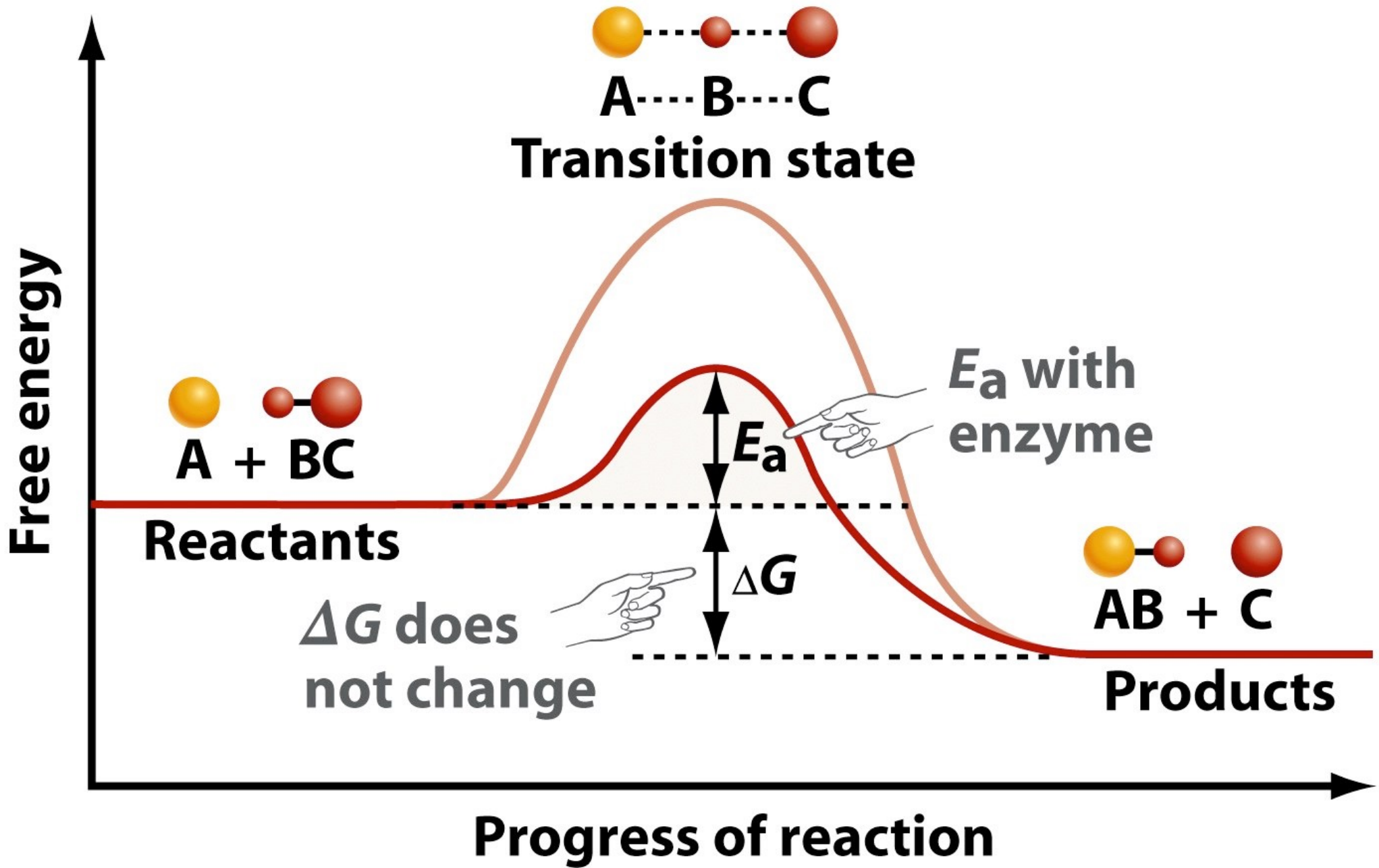
Enzymes
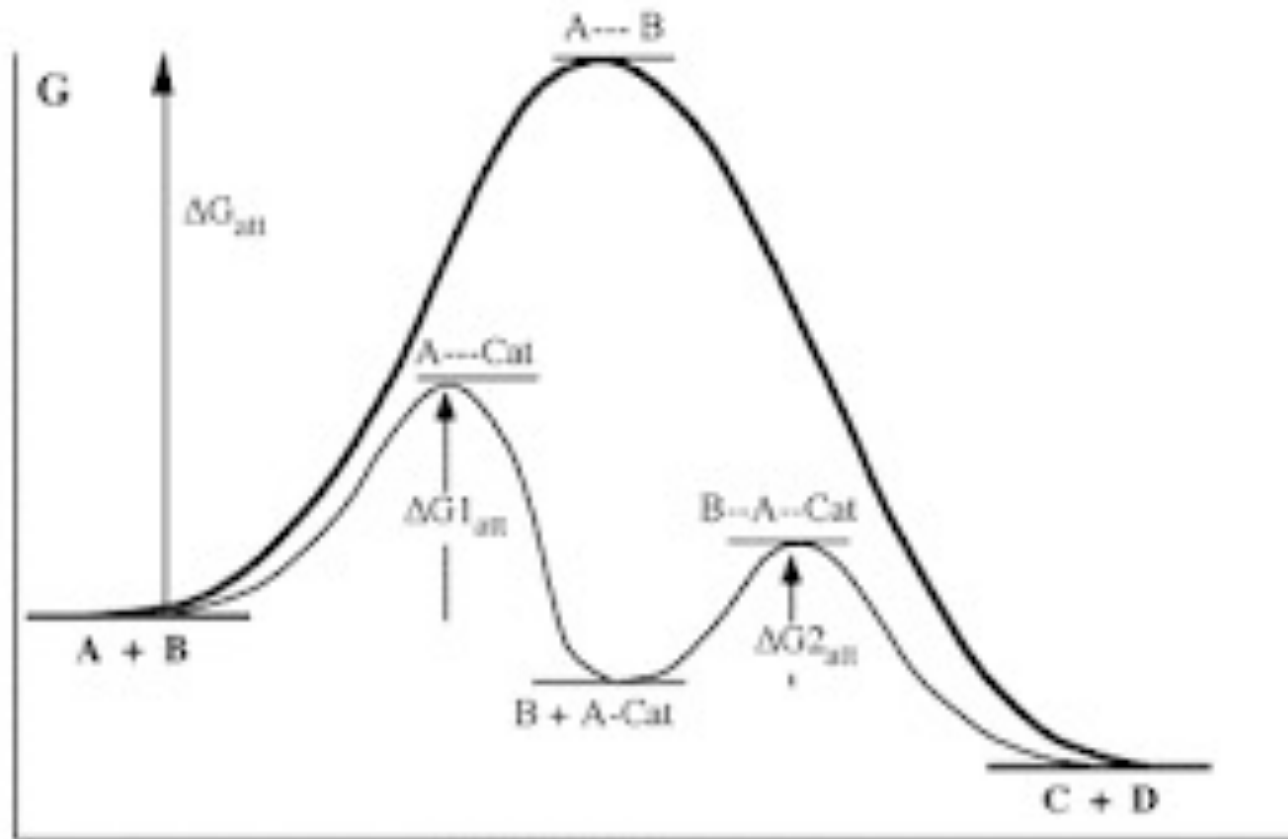

trypsin

active site

Figure 3-21   Biological Science, 2/e

Catalyzed reactions can proceed through mechanisms different from spontaneous ones (formation of intermediates).

Reaction coordinates

General properties of enzymes (and differences from non-biological catalysts)

Higher reaction rates: the rates of enzyme catlysed reaction are typically 10^6 - 10^{14} faster than those of the corresponding non-catalyzed chemical transformations and at least several orders of magnitude higher than those of the corresponding chemically catalyzed reactions.

Milder reaction conditions: reactions occur at temperature lower than 100 ° C, atmospheric pressure and pH close to 7. Conversely, chemical catalysis often requires high temperatures and pressures and extreme pH values.

High reaction specificity: enzymes have an extreme degree of specificity not comparable with the one of chemical catalysts

Regulation: lemany enzyme respond to the presence of compounds different from their substrates. This is due to allosteric regulation, civalemt modification and regulation of their biosynthesis.