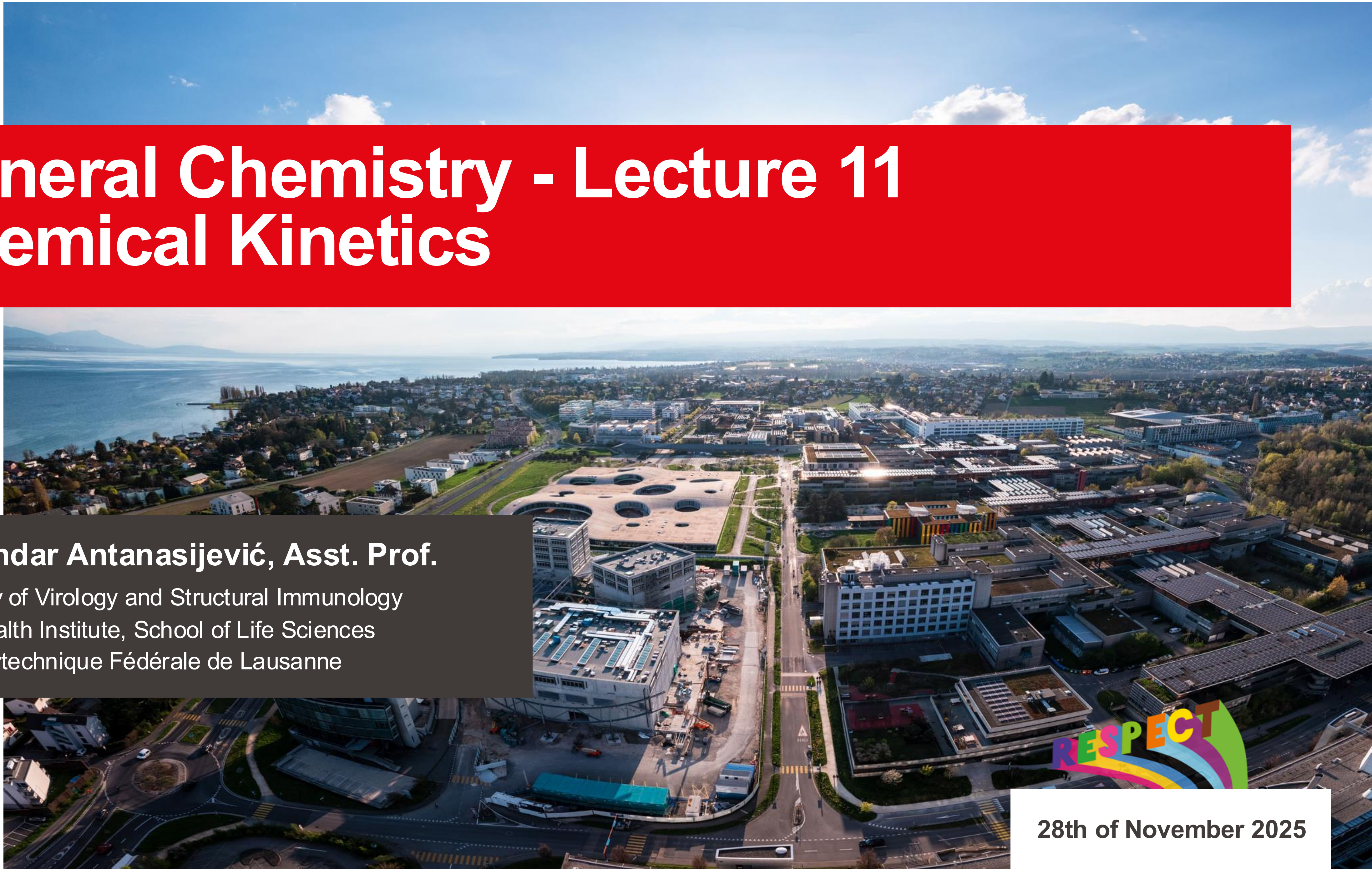
General Chemistry - Lecture 11
Chemical Kinetics



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28th of November 2025

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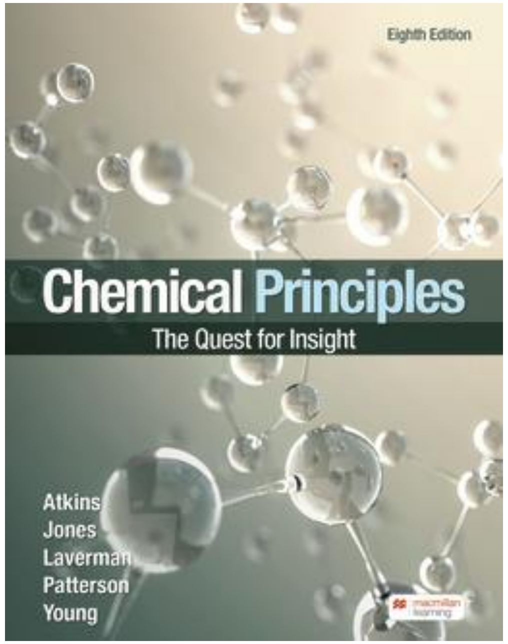
Learning Objectives

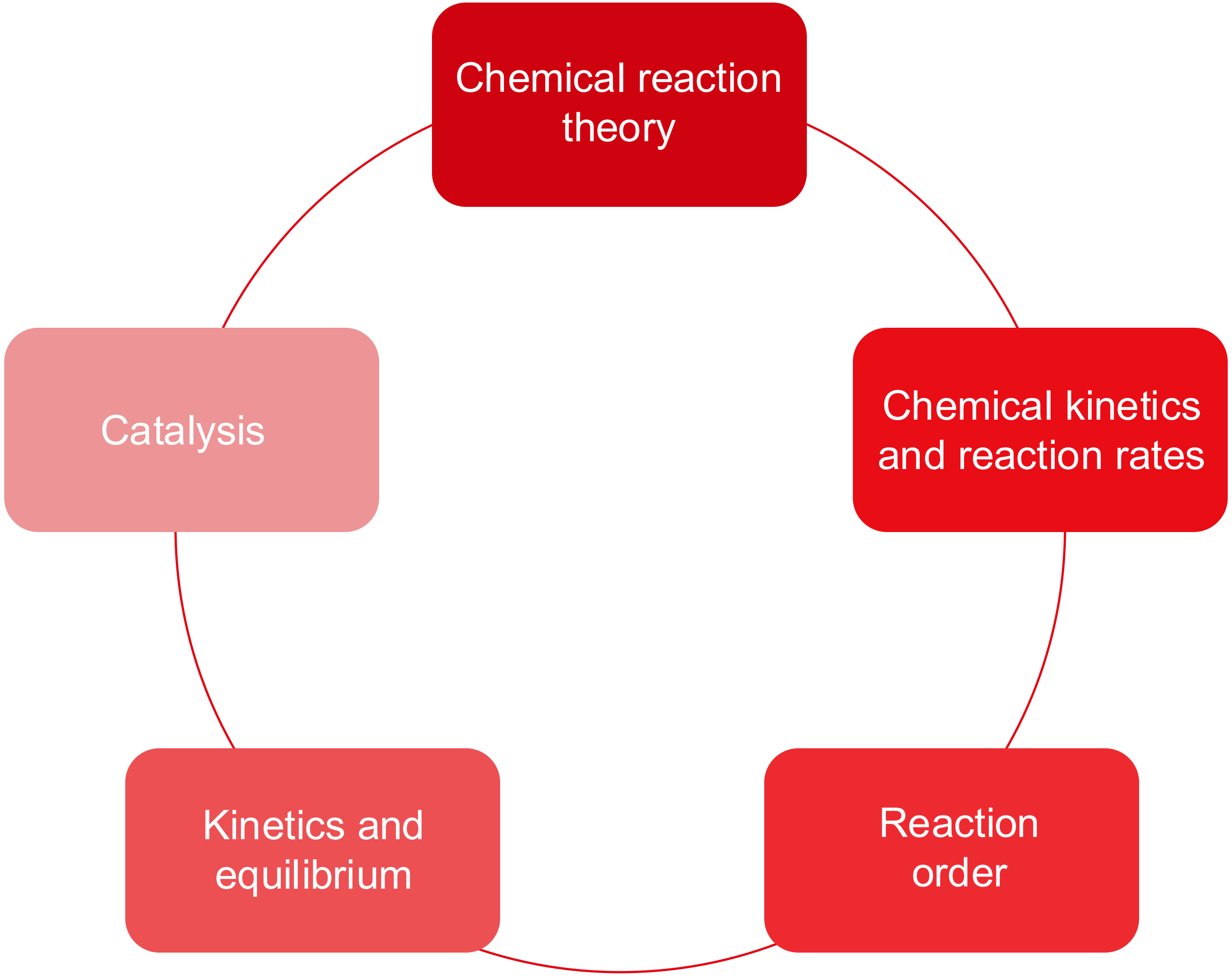
- Understanding reaction equilibrium and the meaning of Gibbs free energy
- Establishing a link between reaction equilibrium and kinetics
- Understanding reaction rates and orders
- Learning the basic concepts in catalysis
- Mastering the use of relevant equations

Reading suggestions

- Chemical Principles: The Quest of Insight
  - Chapter 7



Plan



Chemical reaction theory

Chemical kinetics and reaction rates

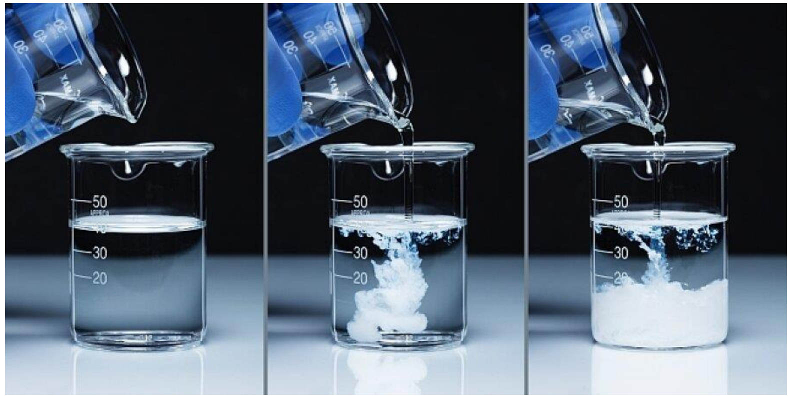
Reaction order

Kinetics and equilibrium

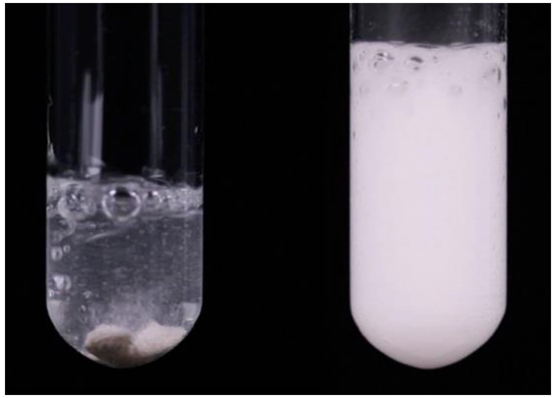
Catalysis

Different types of chemical reactions

- Depending on the nature of reactants and products as well as the underlying chemical transformation, the chemical reactions can be divided into several categories:
  - **Acid-base** (transfer of protons): $NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$
  - **Redox** (transfer of electrons): $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
  - **Precipitation** (insoluble product): $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
  - **Gas-forming** (gas-phase product): $CaCO_3(s) + 2\ HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
  - **Complexation** (ligand binding): $Ag^+(aq) + 2\ NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)$
  - **Organic transformation** (e.g., substitution): $CH_3Br(l) + OH^-(aq) \rightarrow CH_3OH(l) + Br^-(aq)$
  - **Polymerization** (molecule chains): $n\ CH_2{=}CH_2(g) \rightarrow -(CH_2-CH_2)_n-(s)$



Precipitation: AgCl(s) production

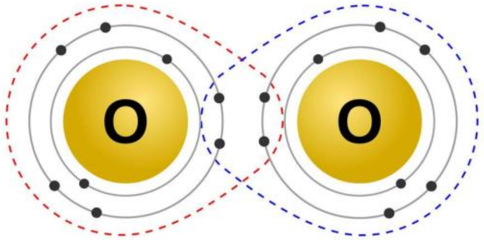


Gas forming: CO_2 production

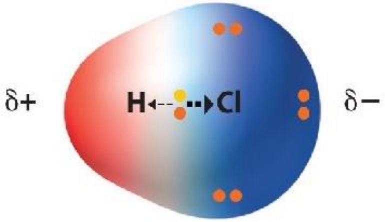
What makes chemical groups reactive

- Chemical reactivity is driven by **electrons**, their number, arrangement, and stability they confer to different bonds.
- Some common factors influencing reactivity are:
  - Stability of electron configurations in orbitals
  - Electronegativity of atoms
    - Ionic bond character
    - Electrophilic and nucleophilic groups
    - Charged groups
  - Resonance effects
  - Bond strength and bond strain
  - Intermolecular interactions

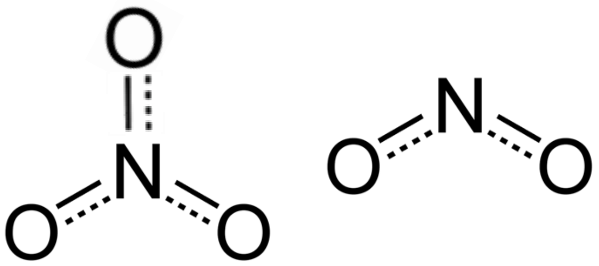
The octet rule



Ionic bond character



Resonance stabilization



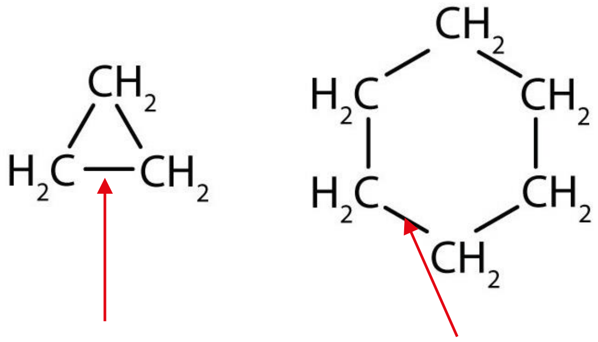
Nitrate ion

Lower local charge

Nitrite ion

Higher local charge

Same bonds - different strength



Cyclopropane

~280 kJ/mol

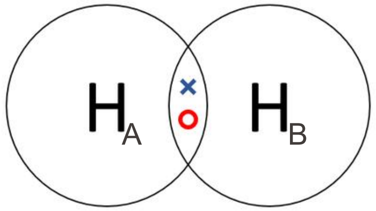
Cyclohexane

~370 kJ/mol

Molecular orbitals

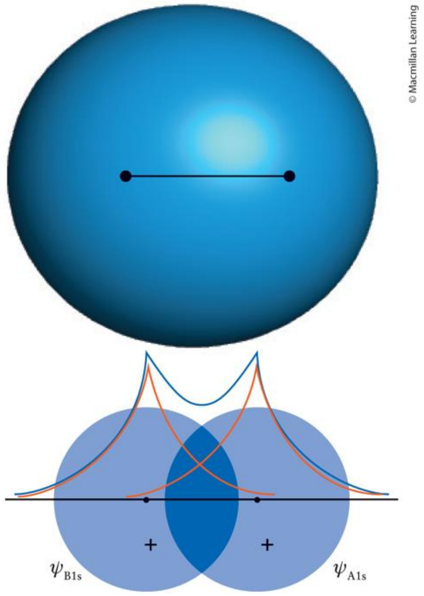
- Molecular orbitals are assembled by **combining (or hybridizing) wavefunctions** (Ψ) corresponding to atomic orbitals.
- Differences in wavefunction coupling produces unique **energy levels** in molecules

Hydrogen molecule

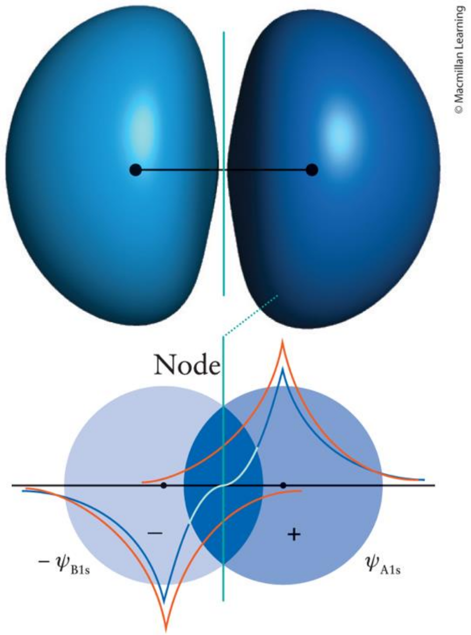


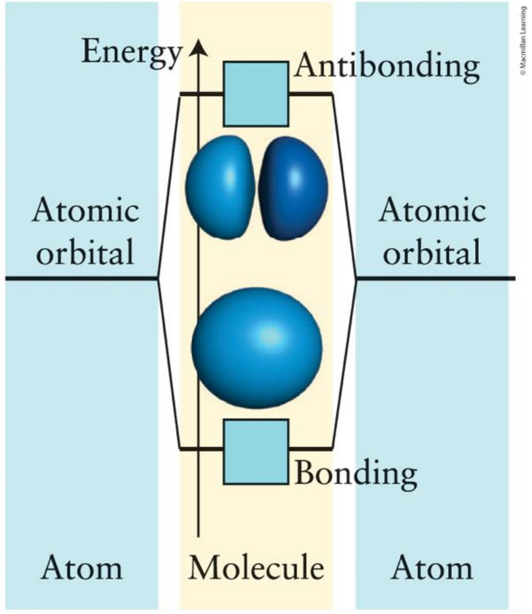
$$\psi = \psi_{\mathrm{A1s}} + \psi_{\mathrm{B1s}}$$

2 functions in phase = **Bonding**



2 functions in phase = **Antibonding**



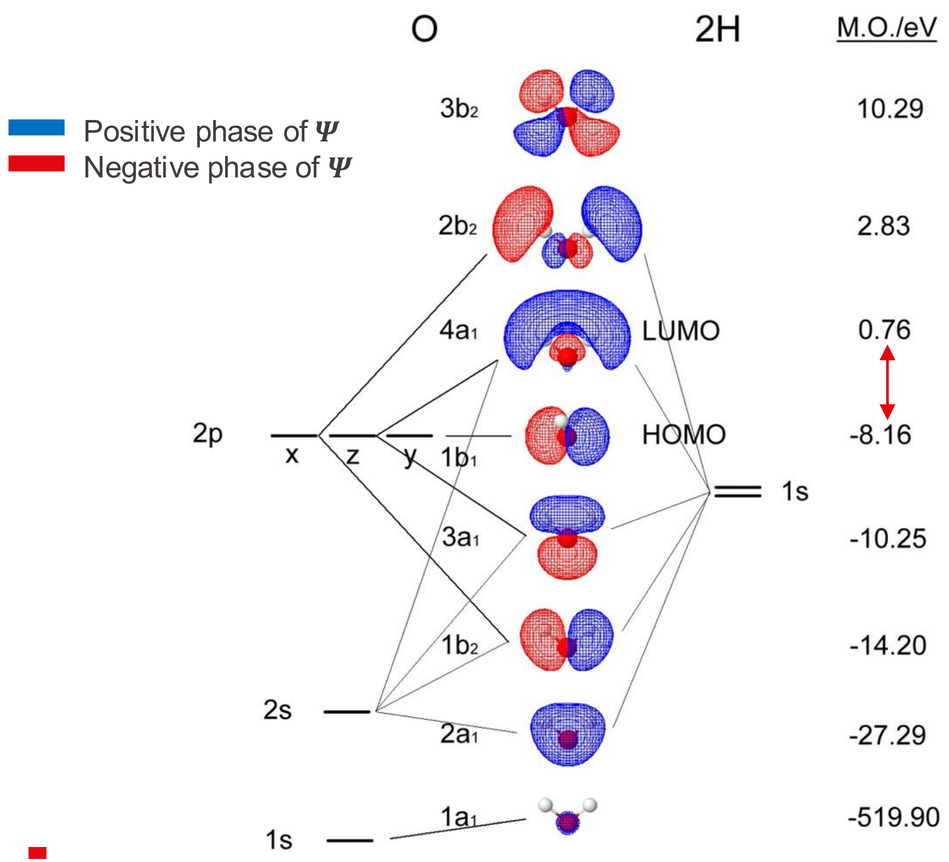


- The excitation from one molecular orbital level to another can be induced by energy introduced through external factors, such as light and molecular collisions.

Molecular orbitals - HOMO vs LUMO

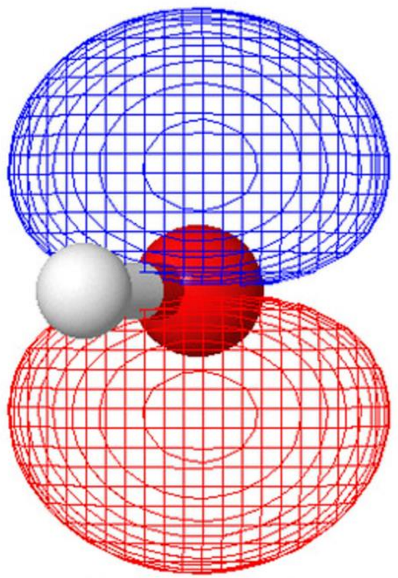
- The number of energy levels increases with the number of orbitals each atom brings (i.e., atom size) and complexity of the molecule (i.e., total number of atoms)

Water molecule



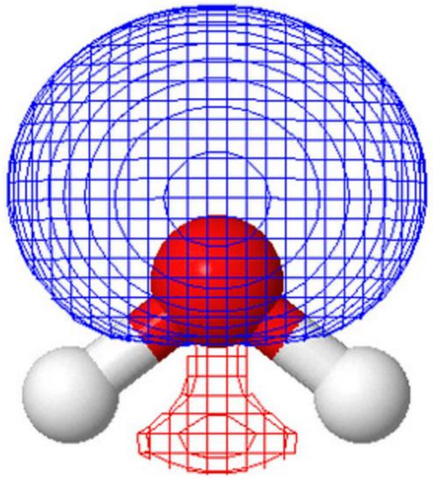
HOMO

Highest occupied molecular orbital



LUMO

Lowest unoccupied molecular orbital

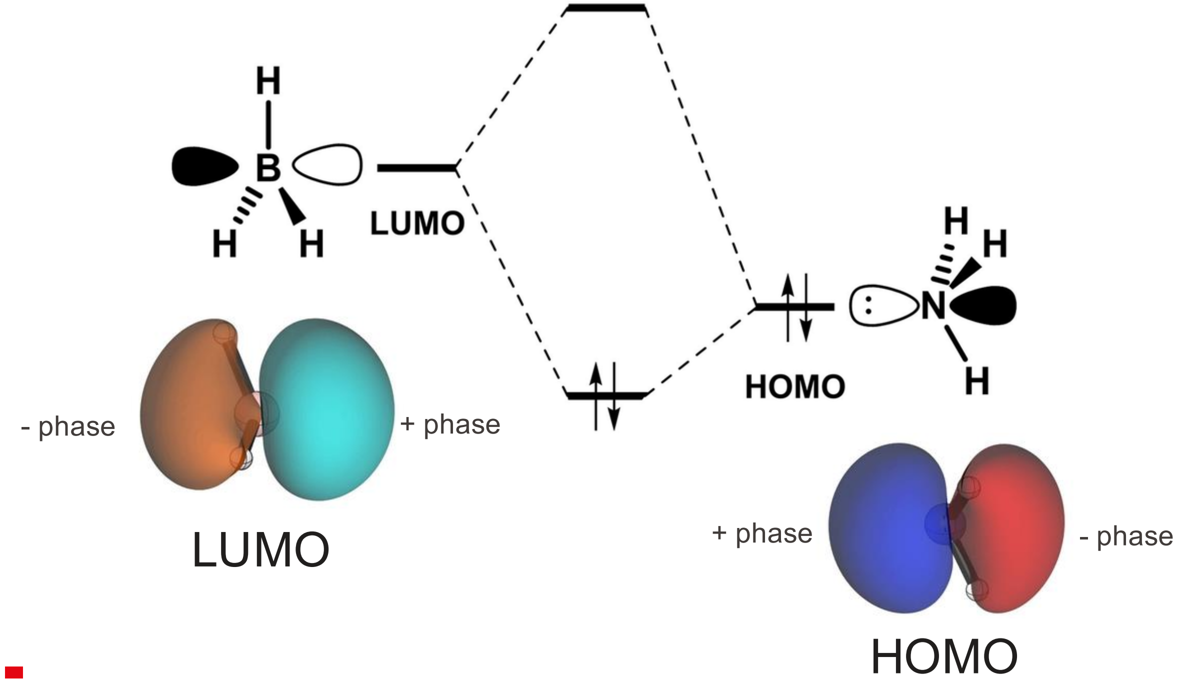


- It is the **lowest energy difference** between the ground state and the excited state.
- Electrons can only access **unoccupied** orbitals (Pauli exclusion principle)

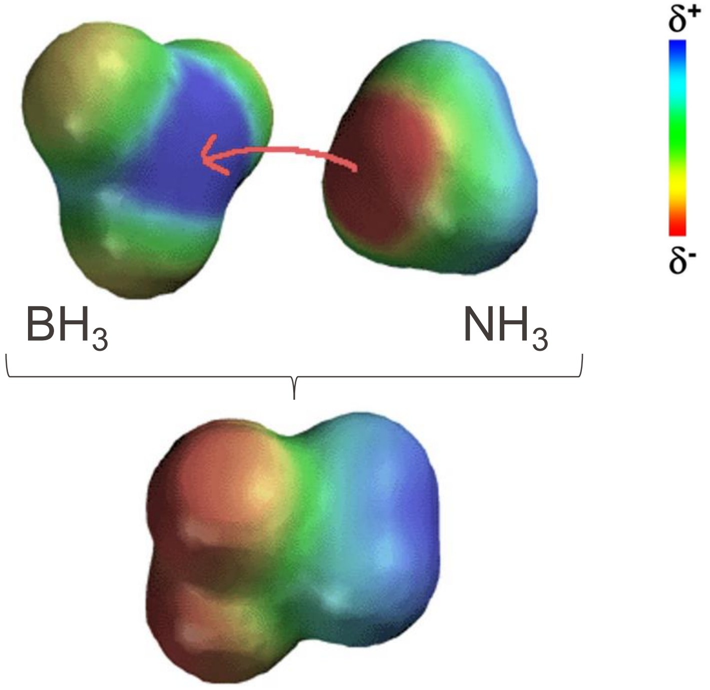
Frontier molecular orbital theory

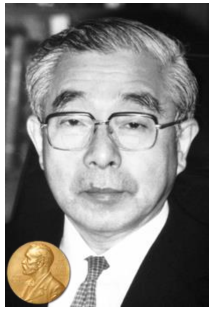
- **Frontier molecular orbital** (FMO) theory approximates reactivity through complementary HOMO-LUMO interactions between 2 chemical groups:
  - HOMO holds the most reactive valent electrons in one molecule (= **nucleophilic region**)
  - LUMO holds the most accessible empty orbital in another molecule (= **electrophilic region**)

$NH_3(g) + BH_3(g) \rightarrow H_3B{:}NH_3(s)$



Partial charge distribution:



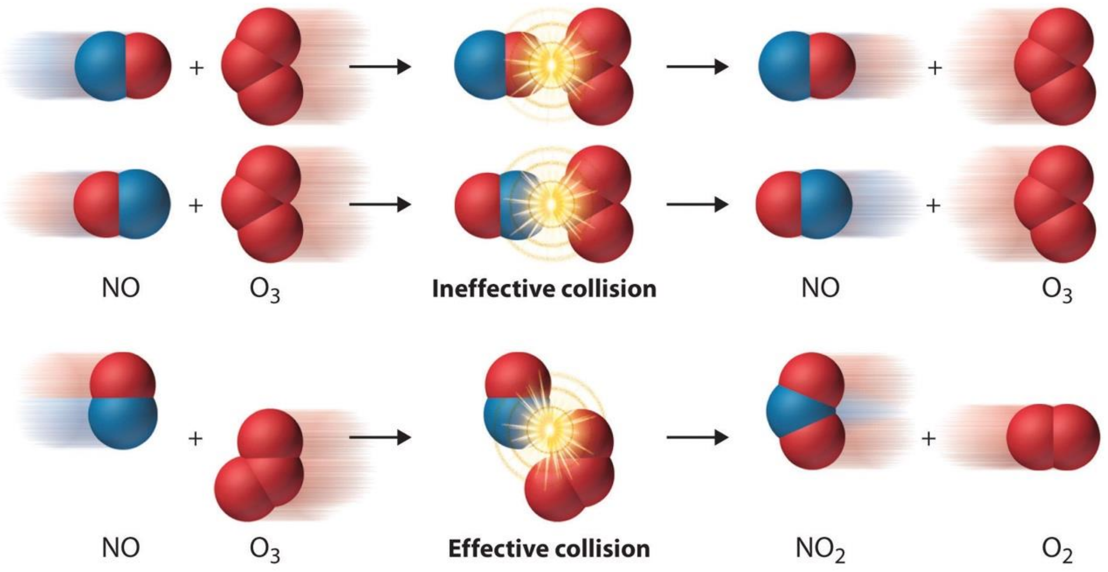


Kenichi Fukui
(1918 - 1998)

FMO advantages and limitations

- The FMO theory treats electrons as delocalized wave functions favoring HOMO-LUMO combinations as they result in **lowest combined energy** of a newly generated orbital
- It allows to understand the **formation of electron orbitals in molecules** of different complexity, while explaining their magnetic, spectroscopic and chemical properties

- However, FMO does not provide any reference to **dynamical** parameters of chemical reactions
- This includes molecular diffusion and collisions under different conditions (e.g., pressure, concentration, temperature)

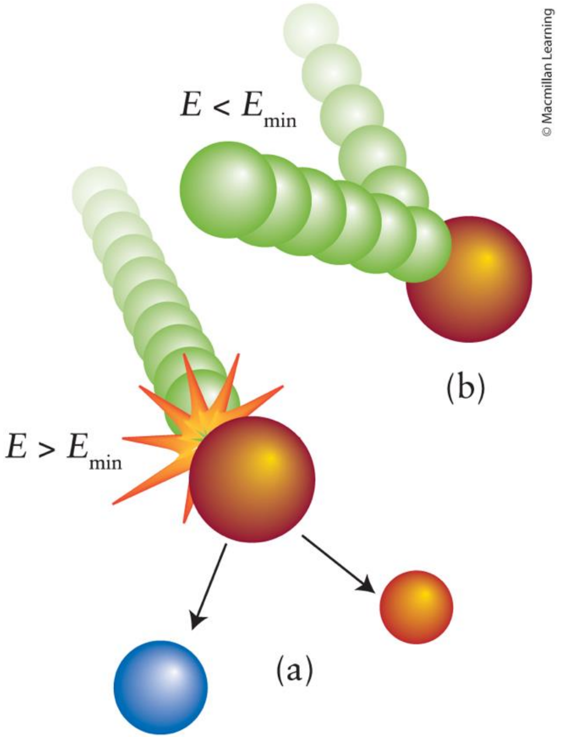


In order to react, molecules have to engage each other in a certain way

The Collision theory

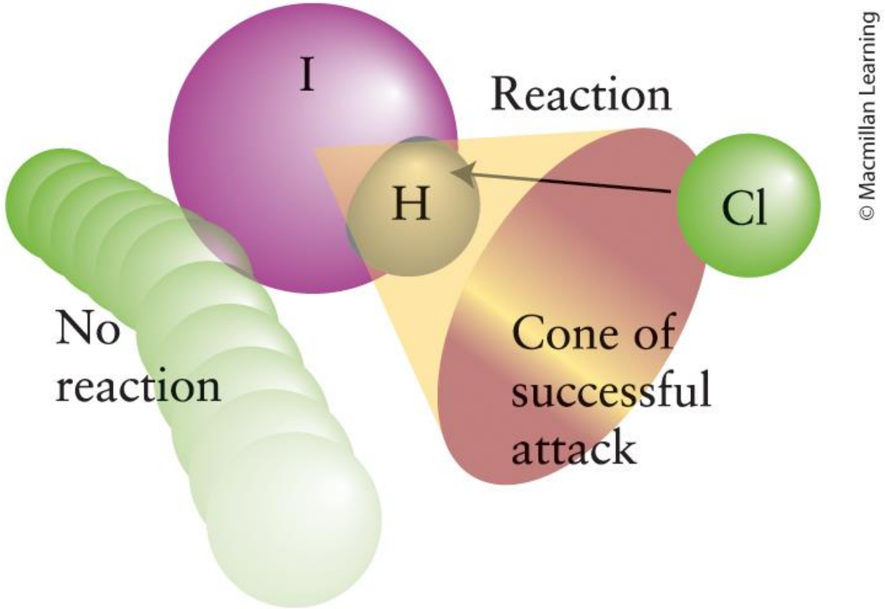
- **The collision theory** states that a chemical reaction occurs only when reacting particles collide with sufficient energy and with the correct orientation to break and form bonds.

Minimal energy requirement



E_{min} is the minimum kinetic energy required for a collision to result in products.

Geometric requirements



Steric factor (P) quantifies the probability of engaging the cone of successful attack (0-1)

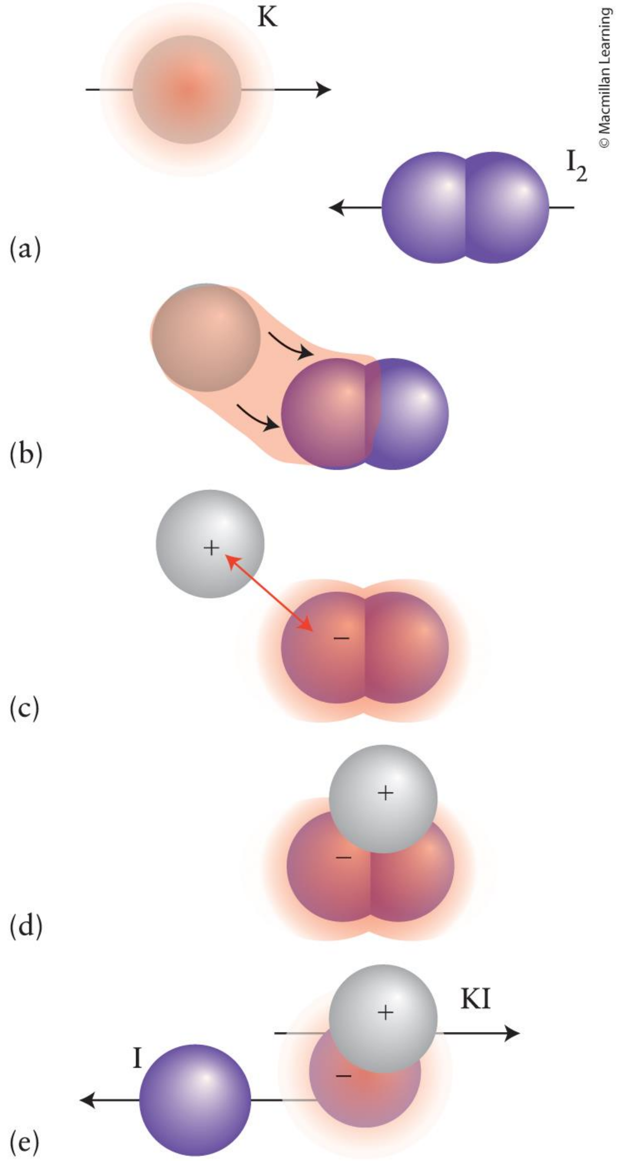
What happens during molecular collisions?

- In the **redox** reaction between K and I_2 to form KI:
  - (a) K atom approaches an I_2 molecule;
  - (b) An electron passes from the K atom to the I_2 molecule.
  - (b and c) The electron transition: $\mathrm{HOMO}_{K(4s)} \rightarrow \mathrm{LUMO}_{I2(\sigma^*)}$
  - (d) The charge difference tethers the two ions together.
  - (e) Finally, an I^- ion separates and leaves with the K^+ ion.

$$K(g) + I_2(g) \rightarrow KI(g) + I(g)$$

E_{min} ~ **1-8 kJ/mol** *Steric Factor (P)* ~ **0.9-1**

Low E_{min} and high P result in favorable reaction conditions



Collision energy and temperature

- **Boltzmann** analysis gives the distribution of kinetic energy values for molecules in gas or liquid
- P (E) is the probability for a molecule to have a kinetic energy of E:

$$P\,(E) \propto e^{-E/kBT}$$

E - Kinetic energy of a molecule
T - Temperature (K)
k_B - Boltzmann constant

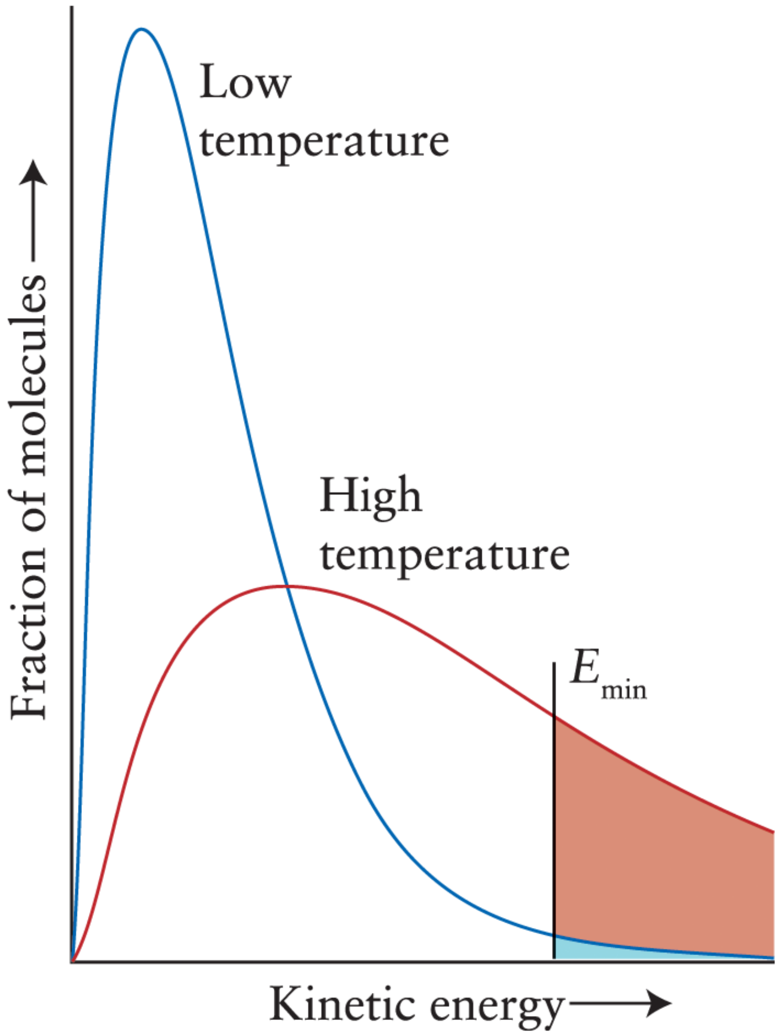
- Average kinetic energy for molecules in ideal gas:

$$E_{avg} = 3/2 \bullet k_B \bullet T \quad \rightarrow \quad E_{avg}\,(25^\circ C) = 3.7\ kJ/mol$$

$$E_{avg}\,(100^\circ C) = 4.7\ kJ/mol$$

- Higher temperature increases average kinetic energy

Boltzmann distribution



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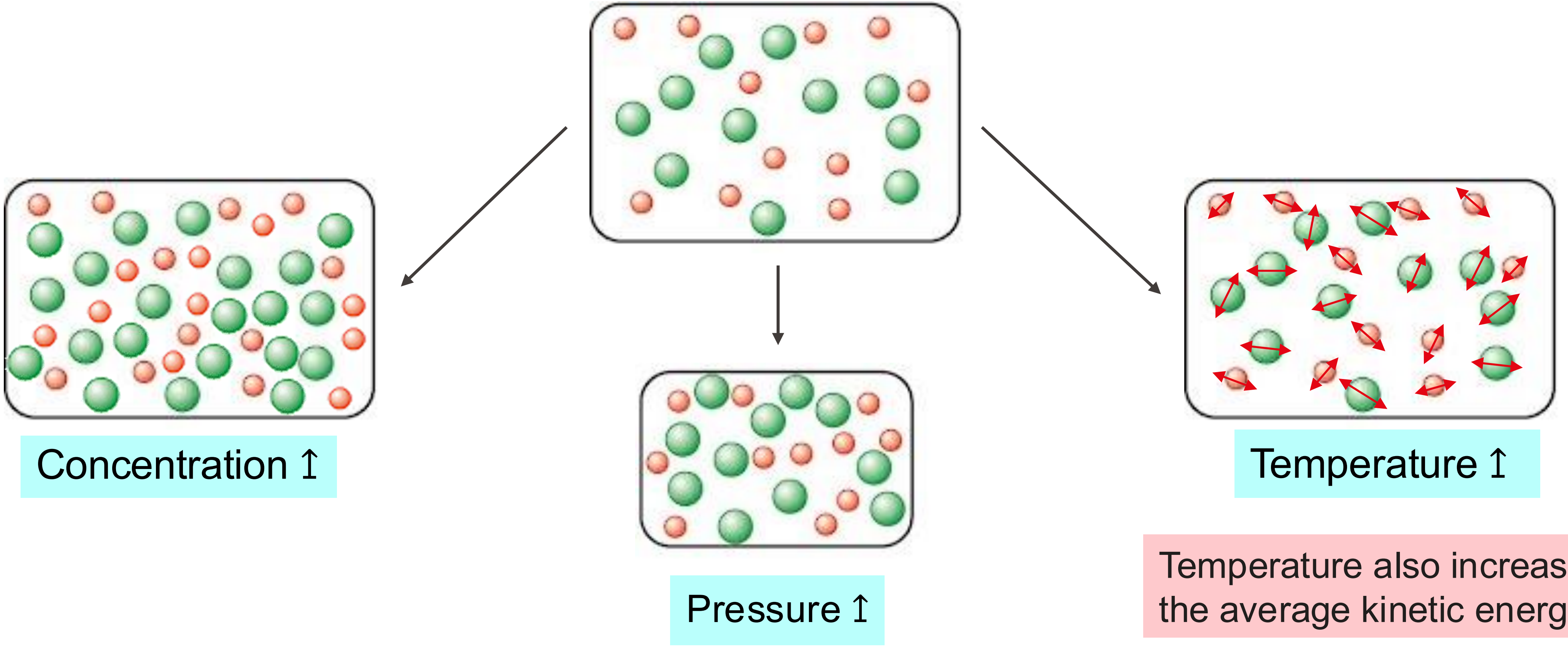
Frequency of collisions (F)

- Molecular collisions with energy > E_{min} and appropriate geometry (P) will lead to successful generation of products.
- Increasing concentration, pressure, or temperature raises the number of molecular collisions per unit of time, thereby accelerating reaction rates.



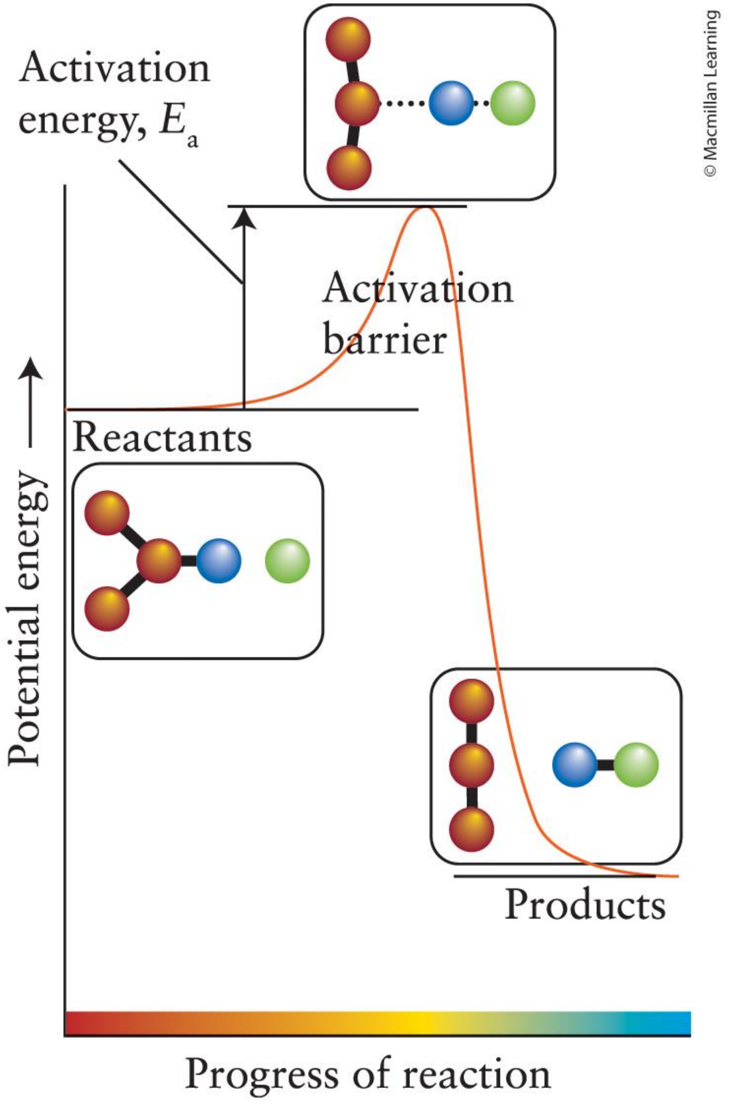
Temperature also increases the average kinetic energy

Collision energy and Transition state barrier

- Following a favorable collision, the reactions proceed through one or several steps
- During these steps the molecular bonds are being stretched and molecular orbitals disrupted
- This is reflected in an increased system energy (E_a) - a barrier that needs to be overcome
- **Activation Energy (E_a)** is one of the main determinants of the reaction rate:

Arrhenius equation: $$k_r = Ae^{-\frac{E_a}{RT}}$$

k_r - The rate constant corresponding to a chemical conversion
A - Collision frequency factor (accounting for F and P)
E_a - Activation energy (J)
T - Temperature (K)
R - Universal gas constant

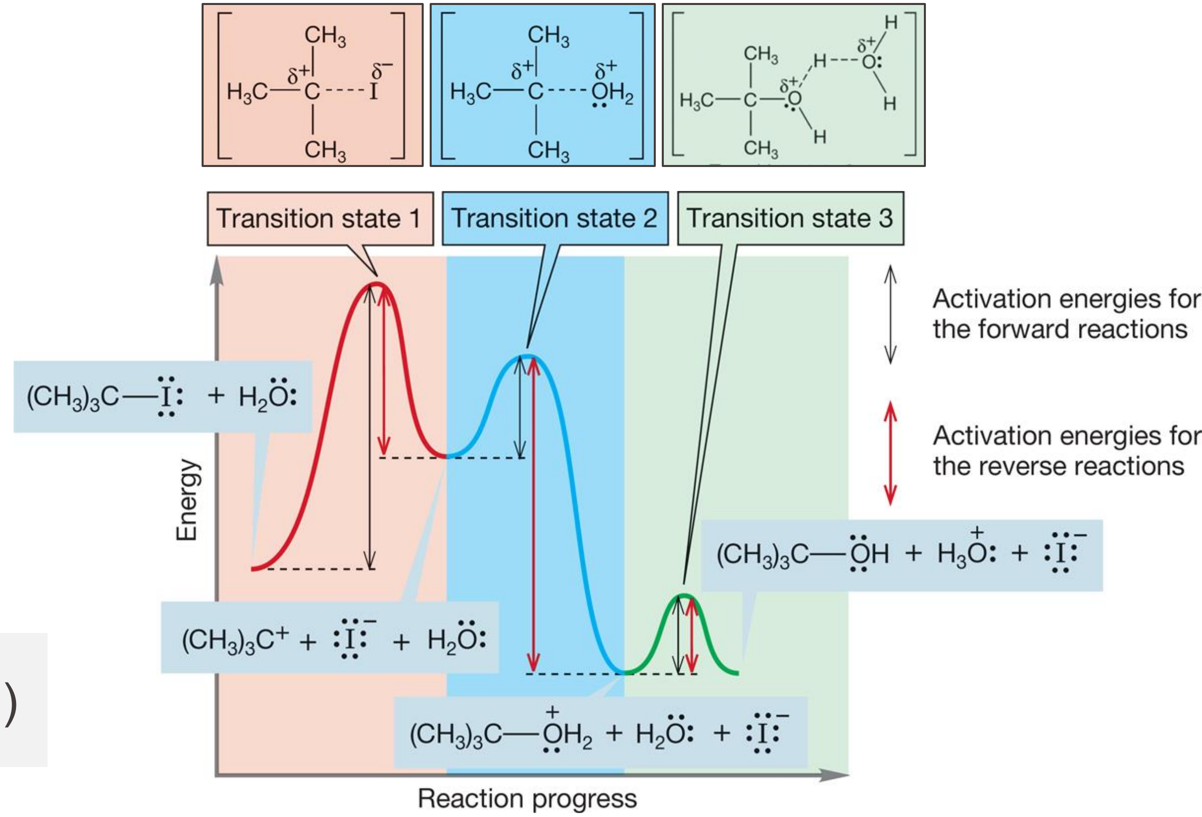


Multistep reactions have many transition states

- For **elementary** reactions, the energy from molecular collisions ($E > E_{min}$) is sufficient to overcome the E_a barrier. Hence:

$$\mathbf{E_{min} \equiv E_a}$$

- Most reactions involve intermediate steps with **several energy barriers**



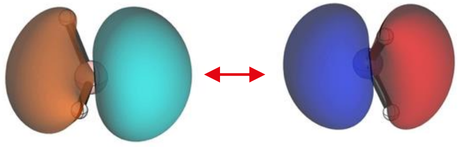
<u>Example</u>: tert-butyl-iodide conversion to alcohol

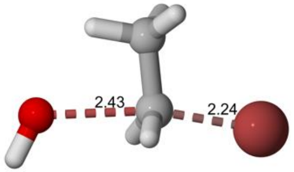
$$\mathbf{(CH_3)_3C\text{-}I}\ (aq) + \mathbf{H_2O}\ (l) \rightarrow \mathbf{(CH_3)_3C\text{-}OH}\ (aq) + \mathbf{HI}\ (aq)$$

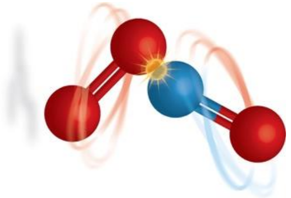
- In these cases, the additional transition energy may come from vibrational/rotational energy in the molecule, energy redistribution in intermediates, solvent interactions etc.

Combining all the concepts

- Reaction mechanisms are complex but can be approximated on the level of electrons, atoms, and molecules, allowing to make a link to macroscopic measurements







Valent Bond
FMO theories

↔

Transition-state
theory

↔

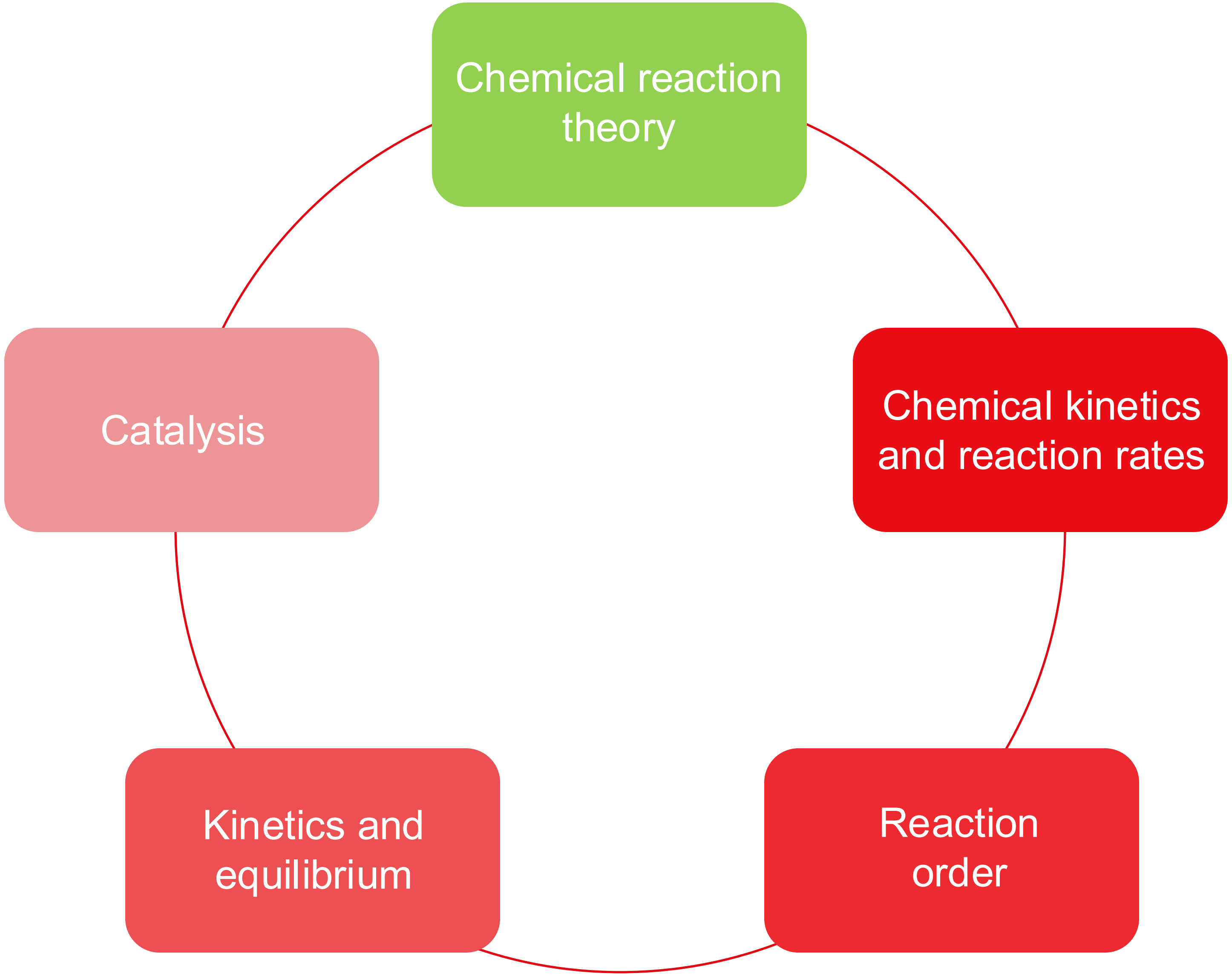
Molecular collision
theory

Explains reactivity, stereo- and regio-selectivity

Explains energy, reaction rates, transition state geometry

Effects of temperature, concentration and molecule orientation

Plan



Chemical reaction theory

Chemical kinetics and reaction rates

Reaction order

Kinetics and equilibrium

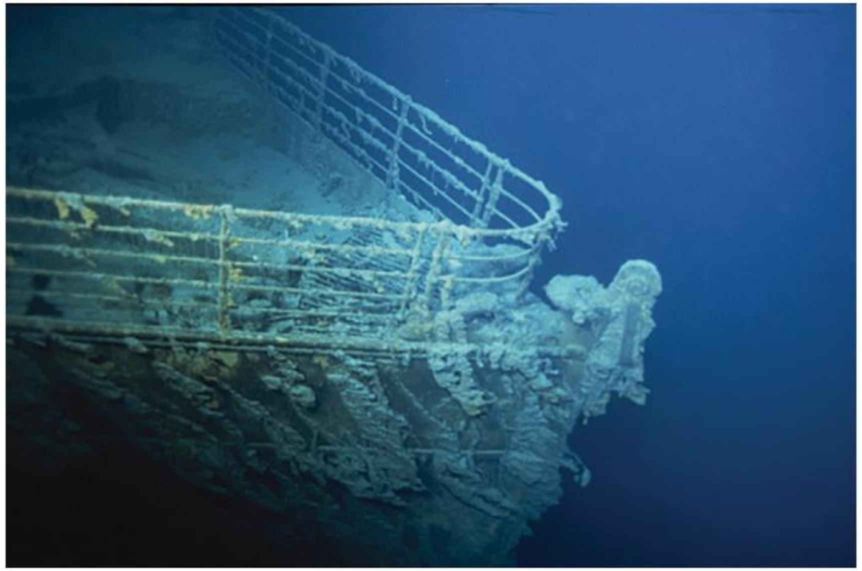
Catalysis

Chemical kinetics

- **Chemical kinetics** is the branch of chemistry that studies the rates of chemical reactions and the factors that affect them.

Sergei Butorin/Alamy.

Explosion → Very fast



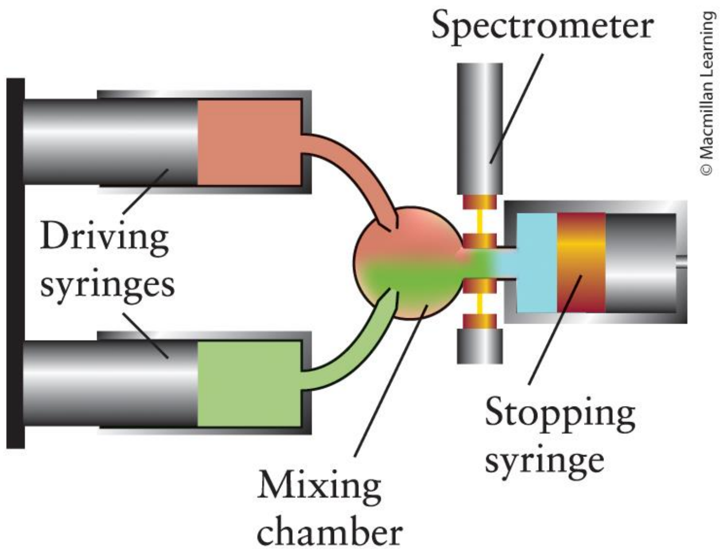
Xavier DESMIER/Getty Images.

Corrosion → Very slow

- **Thermodynamics** can tell which chemical species will be energetically favored
- **Kinetics** can tell how fast a chemical reaction will go, and how to control the rate.

Reaction rate

- **Reaction rate** is the change in concentration of a reactant or product per unit of time in a chemical reaction.
- Imagine a reaction where two gases (red and green) combine to make a product (blue):



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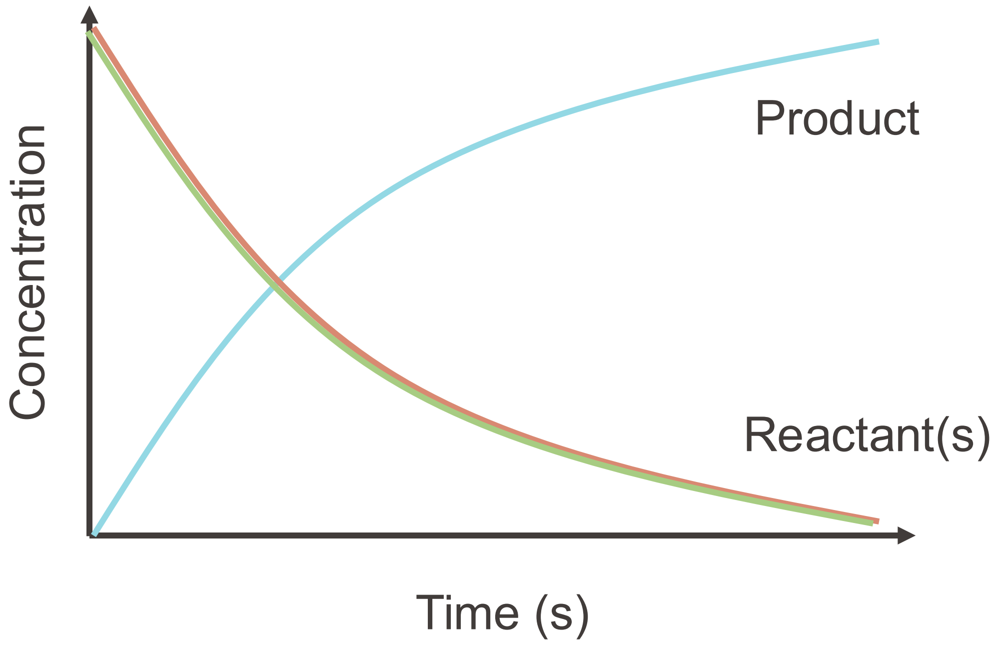
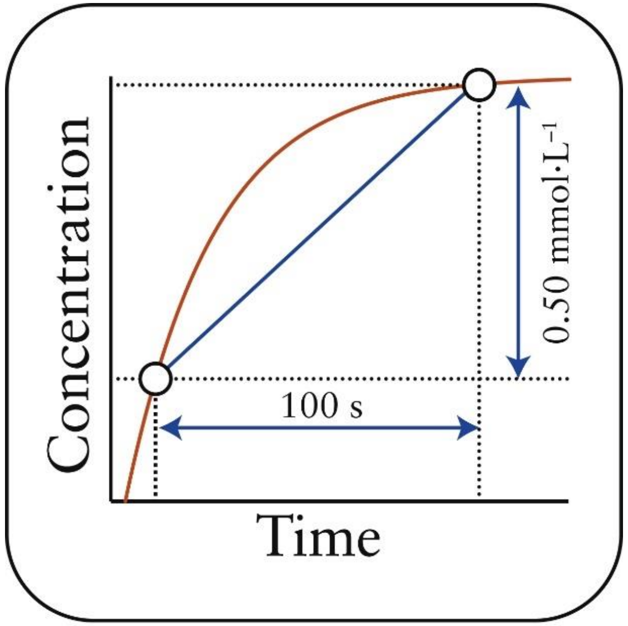


- The reactants are gradually depleted while products get generated. In addition to chemical reactivity, the rate of product generation will depend on reactant concentration.

Measuring reaction rates

- The average reaction rate under given conditions can be calculated by quantifying the change in concentration of reactants or products over time.

$$\mathbf{R} = -\frac{\Delta[\mathrm{R}]}{\Delta t} \qquad \mathbf{P} = \frac{\Delta[\mathrm{P}]}{\Delta t} = \frac{[\mathrm{P}]_{t2} - [\mathrm{P}]_{t1}}{t_2 - t_1}$$



- Reaction rate (sometimes labeled as **v**) has the units of concentration/time (e.g., M/s)

- However, the reactions may involve multiple components and different stoichiometric coefficients, which need to be accounted for:

$$\mathbf{H_2\,(g) + I_2\,(g) \rightarrow 2\;HI\,(g)}$$

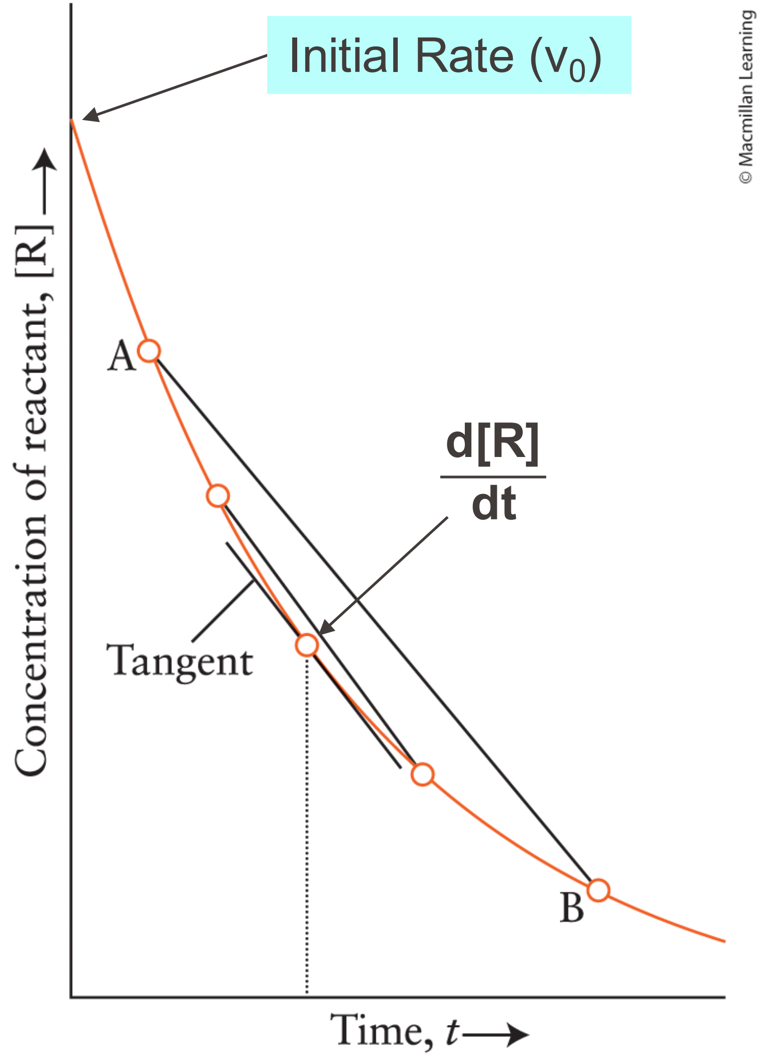
$$\boxed{\frac{1}{2}}\frac{\Delta[\mathrm{HI}]}{\Delta t} = -\frac{\Delta[\mathrm{H_2}]}{\Delta t} = -\frac{\Delta[\mathrm{I_2}]}{\Delta t}$$

Measuring reaction rates

- **Reaction rate** can be calculated at any time point by determining the value of the first derivative in the Concentration vs Time plot (slope of the tangent)
- The initial rate at **time 0** is commonly used for plots and analyses as it represents the **maximum reaction rate** under given experimental conditions
- For a general reaction at a constant volume and T:

$$\nu_A\,A + \nu_B\,B \longrightarrow \nu_M\,M + \nu_N\,N$$

$$\text{Reaction rate (v)} = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = +\frac{1}{\nu_M}\frac{d[M]}{dt} = +\frac{1}{\nu_N}\frac{d[N]}{dt} \quad (\text{mol L}^{-1}\text{s}^{-1})$$



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Reaction rate depends on reactant concentration

- Consider a general one-directional reaction at constant volume and temperature:

$$\nu_A \mathrm{A} + \nu_B \mathrm{B} \longrightarrow \nu_M \mathrm{M} + \nu_N \mathrm{N}$$

- The dependence of reaction rate on concentration can be written as follows:

$$v = k\,[A]^{\alpha}[B]^{\beta}$$

v - Reaction rate
k - Rate constant (depends on T)
[A], [B] - Concentrations of reactants
α - Reaction order of reactant A ←
β - Reaction order of reactant B ←

These are not the same as stoichiometric coefficients

- This is an **empirical rate law**, that combines reactant quantities to the overall propensity for this reaction to occur expressed through the rate constants and reaction orders.

Rate constants and temperature

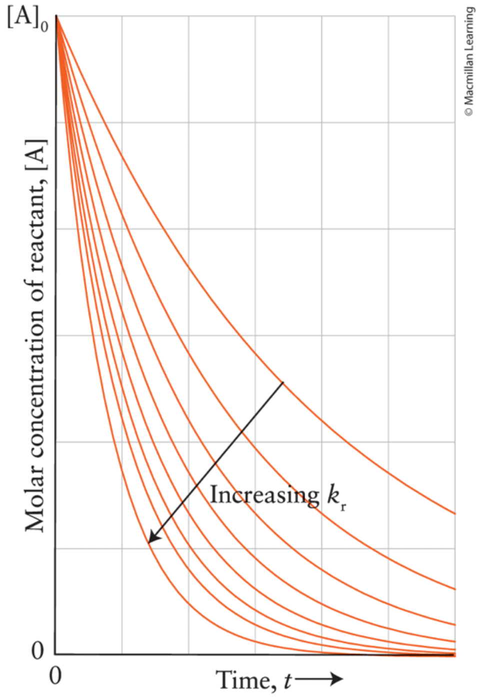
- **Rate constant** originates from the Collision and Transition-state theories and describes the probability of successful molecule collision leading to product generation
- It increases with lower E_a and higher temperature following Arrhenius equation

Arrhenius equation:

$$k_r = Ae^{-\frac{E_a}{RT}}$$

k_r - Reaction rate constant
A - Collision frequency factor
E_a - Activation energy
T - Temperature
R - Universal gas constant

Units of k depend on reaction



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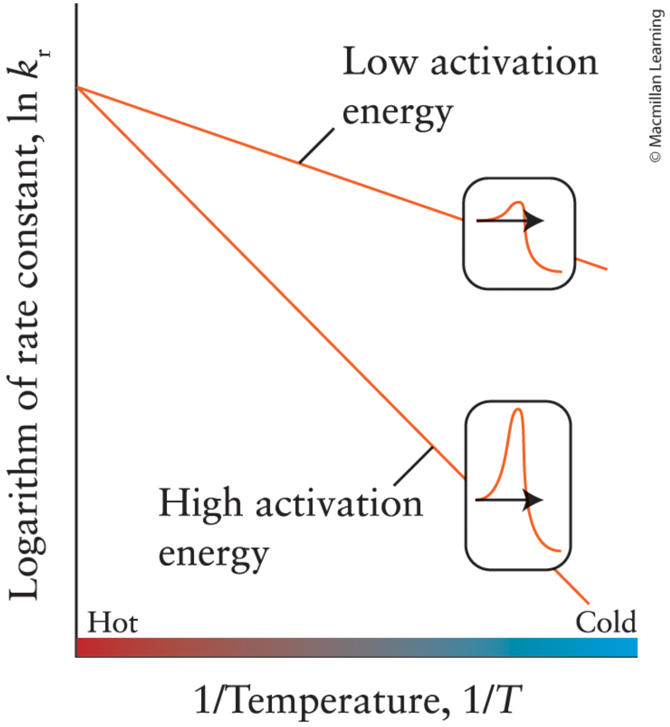
Greater k → Faster reaction



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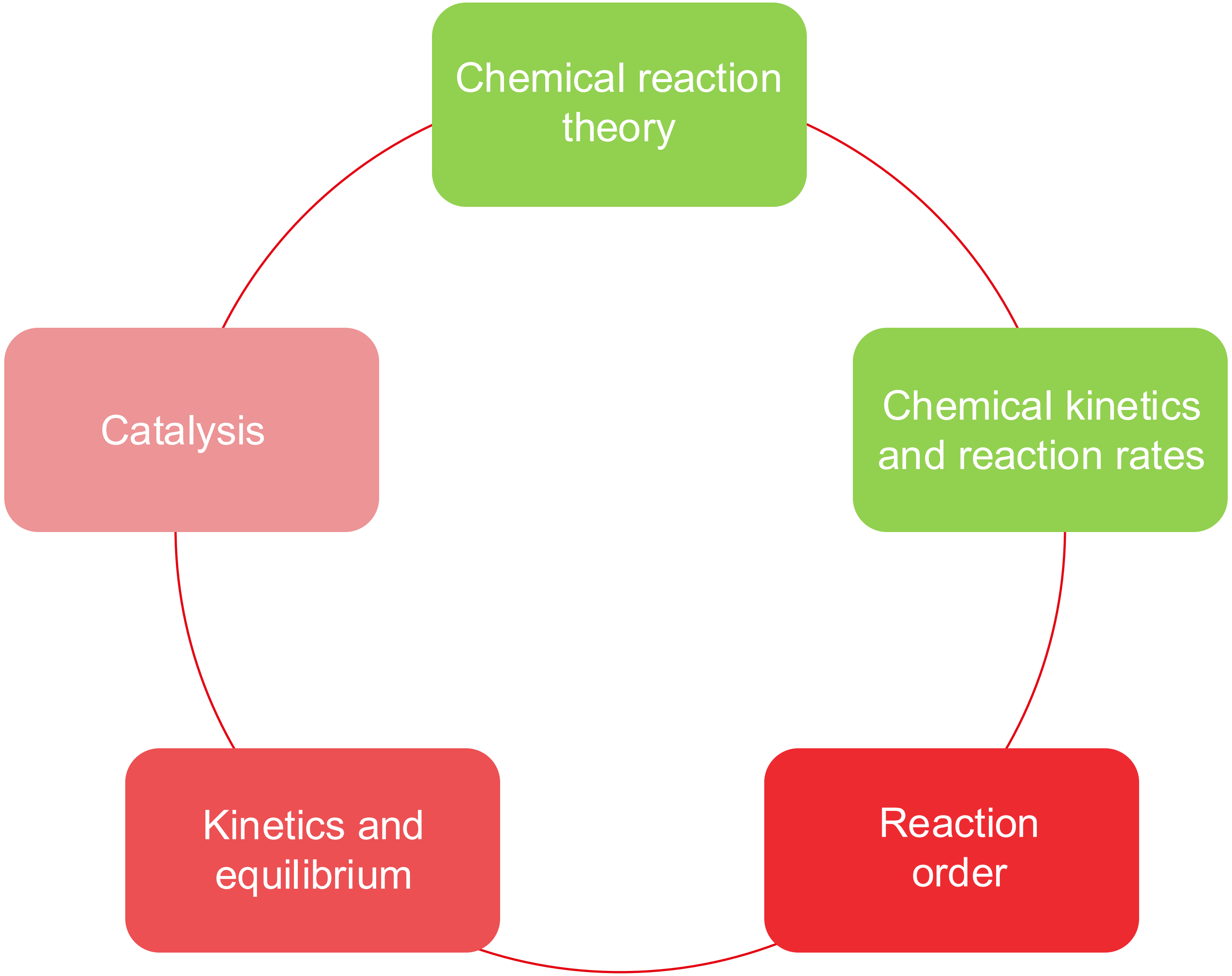
$\ln(k) = \ln(A) - E_a/R \cdot 1/T$

Plan



Chemical reaction theory

Chemical kinetics and reaction rates

Reaction order

Kinetics and equilibrium

Catalysis

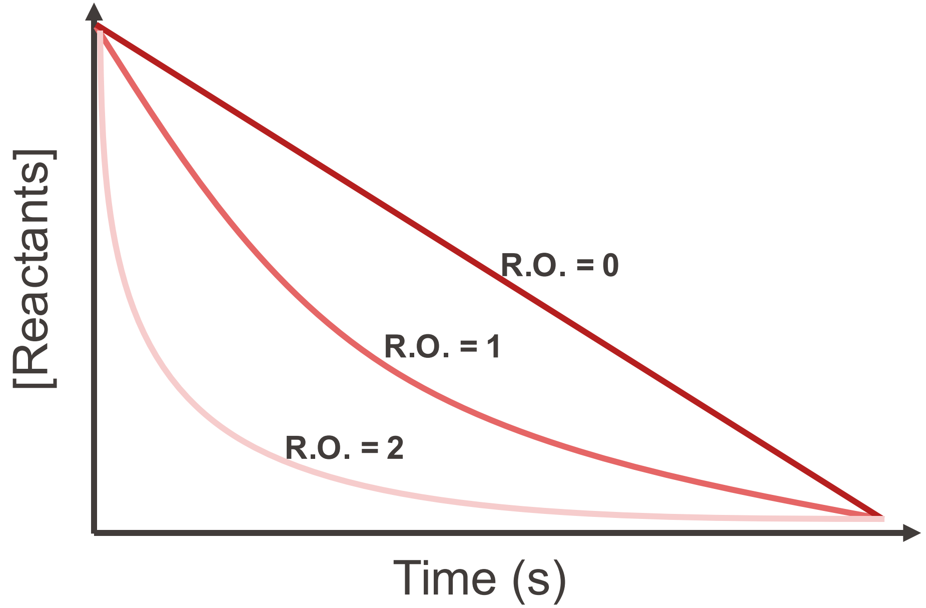
Reaction order

- The **overall reaction order** for a given chemical process is the sum of the partial reaction orders experimentally determined for each reactant.
- If we go back to the general reaction and the reaction rate expression:

$$aA + bB + cC + \ldots \rightarrow \text{Products}$$

$$v = k \bullet [A]^{\alpha} \bullet [B]^{\beta} \bullet [C]^{\gamma} \bullet \ldots$$

$$R.O. = \alpha + \beta + \gamma + \ldots$$



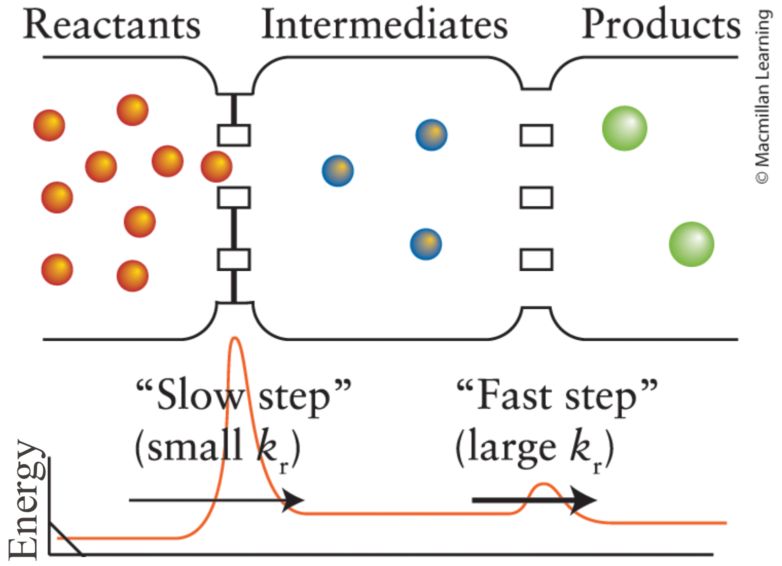
- The reaction order describes **how the reaction rate depends** on the combined effect of all **reactant concentrations**

Partial reaction orders

- **Partial reaction orders** (α and β) describe **how** the reaction rate depends on individual reactant concentrations (A and B, respectively).
- The reaction orders α and β depend on the reaction mechanism = the number and nature of **elementary** steps and, in particular, on which step is **rate-determining**.

$$\nu_A A + \nu_B B \longrightarrow \nu_M M + \nu_N N$$

$$v = k [A]^{\alpha}[B]^{\beta}$$

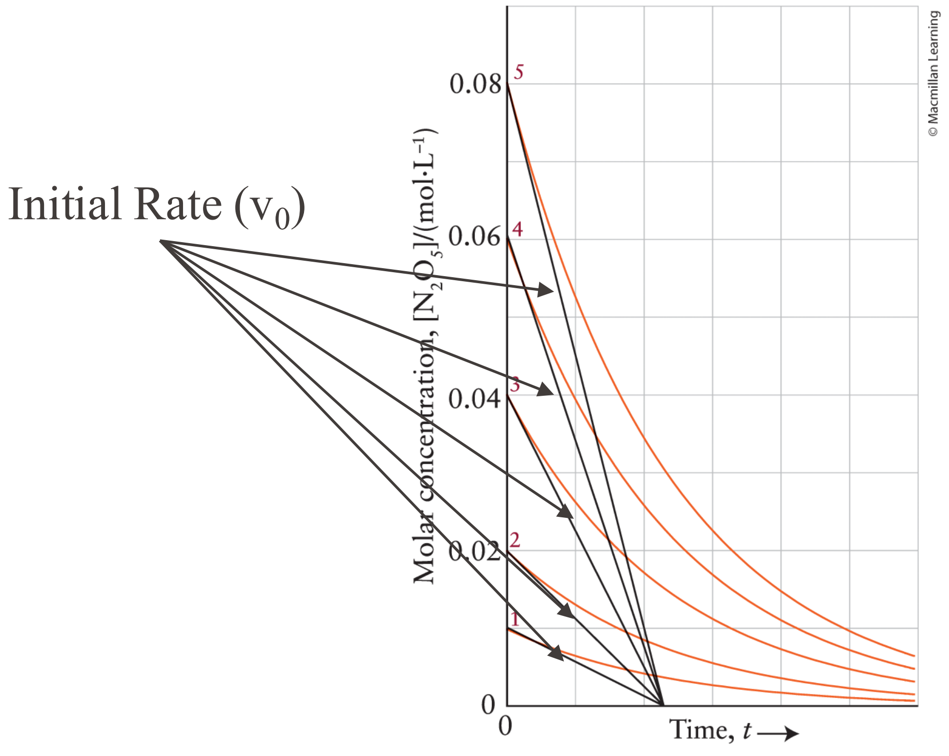


- Reaction orders (α and β) are equal to the stoichiometric coefficients (v_a and v_β) only when the reaction proceeds through a single elementary rate-determining step.

Determining partial reaction orders (1 reactant)

- Initial reaction rates (v_0) are measured across different starting concentrations $[R]_0$ of a given reactant. The v_0 vs $[R]_0$ plot is used to determine the partial reaction order for R

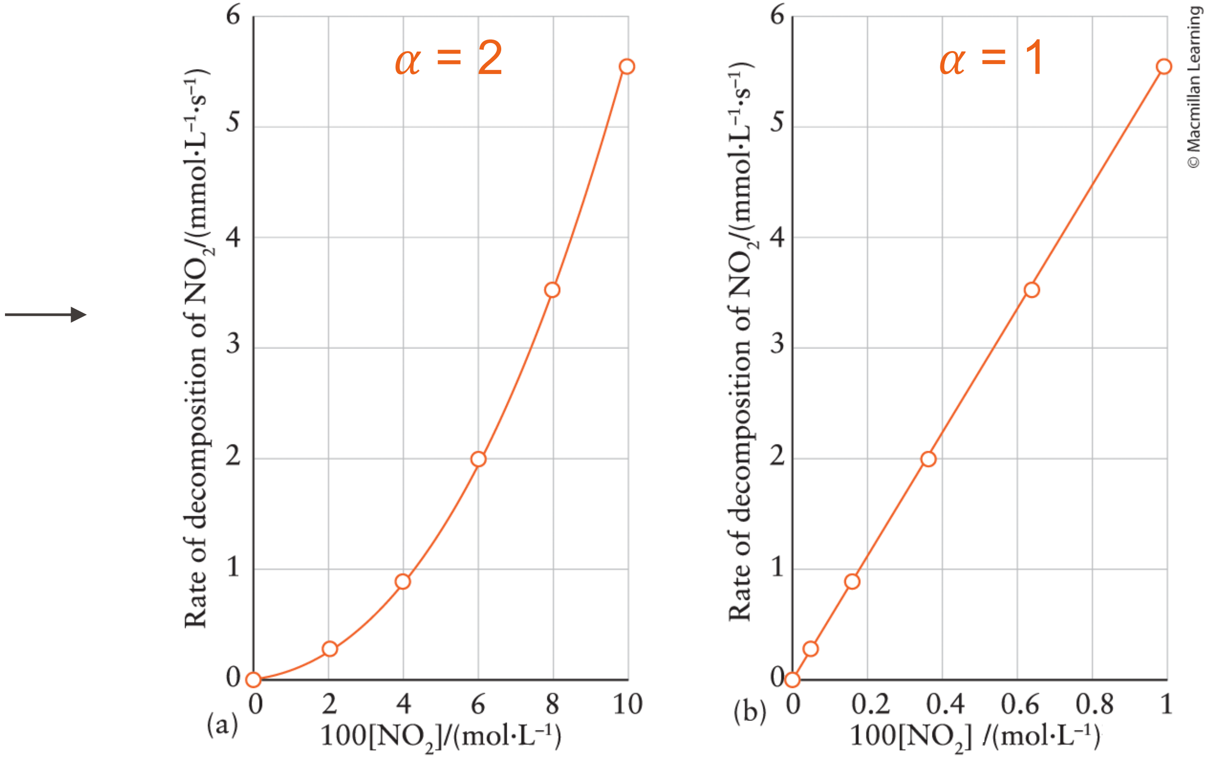
$2\ N_2O_5\,(g) \rightarrow 4\ NO_2\,(g) + O_2\,(g)$



5 reaction curves

$v_0 = k \bullet [N_2O_5]^2$

$v_0 = k \bullet [N_2O_5]^1$



Plot of initial rates (v_0) vs Initial concentrations

Determining partial reaction orders (>1 reactants)

- Higher number of reactants increases the complexity of these experiments, as there are more species that simultaneously contribute to product formation:

$$aA + bB + cC + \ldots \rightarrow \text{Products}$$

- The way to approach these experiments is to vary the concentration of one reactant and measure reaction rate, while keeping all the other reactants at a constant concentration.

$$v_0 = k[A]_0^{\alpha}[B]_0^{\beta}[C]_0^{\gamma}$$

$$v_0' = k[nA]_0^{\alpha}[B]_0^{\beta}[C]_0^{\gamma}$$

$$\frac{v_0'}{v_0} = \frac{k[nA]_0^{\alpha}[B]_0^{\beta}[C]_0^{\gamma}}{k[A]_0^{\alpha}[B]_0^{\beta}[C]_0^{\gamma}} = n^{\alpha}$$

- Example: You doubled the initial concentration of A (n=2) and the result was:

$v_0' / v_0 = 1 \rightarrow \alpha = 0$

$v_0' / v_0 = 2 \rightarrow \alpha = 1$

$v_0' / v_0 = 4 \rightarrow \alpha = 2$

$v_0' / v_0 = 8 \rightarrow \alpha = 3$

Determining partial reaction orders (>1 reactants)

- Let's evaluate the following reaction involving 2 reactants (NO and Cl_2):

$$2\ NO\ (g) + Cl_2\ (g) \rightarrow 2\ NOCl(g)$$

- The following initial rates were recorded for the corresponding starting conditions:

Condition	$[NO]_0$ (mol • L^{-1})	$[Cl_2]_0$ (mol • L^{-1})	V_0 (mol • L^{-1} • s^{-1})
1	0.0125	0.0255	$2.27 \cdot 10^{-5}$
2	0.0125	0.0510	$4.55 \cdot 10^{-5}$
3	0.0250	0.0255	$9.08 \cdot 10^{-5}$

- If $[Cl_2]_0$ increases by 2-fold the V_0 increases by 2-fold → 1st order dependence
- If $[NO]_0$ increases by 2-fold the V_0 increases by 4-fold → 2nd order dependence

$$v = k \cdot [NO]^2 \cdot [Cl_2]$$

Zero order chemical reactions

k units: mol • L^{-1} • s^{-1}

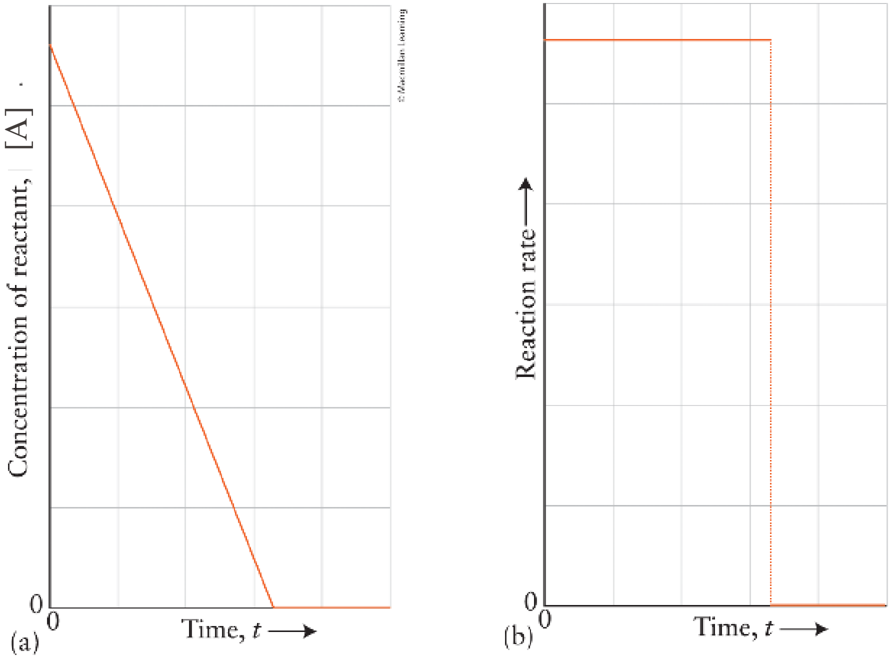
- A zero-order reaction is a reaction whose rate is independent of the concentration of the reactant(s).
- Changing the reactant concentration does not change the reaction rate.

Example: Decomposition of ammonia

$2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$

Reaction rate: $v = -\frac{d[A]}{dt} = k$

After integration: $[A] = [A]_0 - kt$



- Typically occurring in photochemical or surface-catalyzed reactions (e.g., NH3 decomp.)

First order chemical reactions

k units: s^{-1}

- A first-order reaction is a reaction whose rate depends linearly on the concentration of one reactant. These typically involve unimolecular rearrangements or decomposition

Example: Hydrogen peroxide decomposition

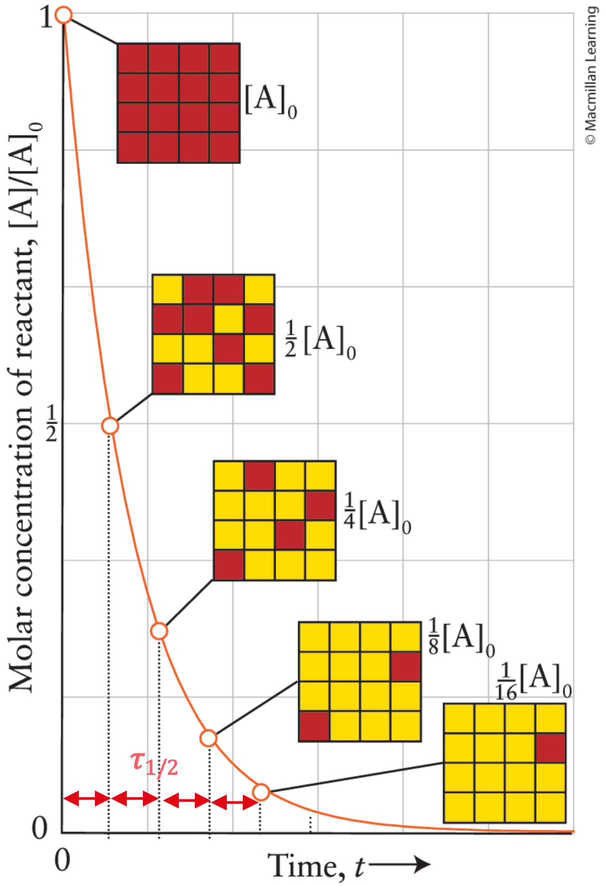
$$H_2O_2(l) \rightarrow H_2O(l) + \tfrac{1}{2} O_2(g)$$

Reaction rate: $$v = -\frac{d[A]}{dt} = k[A]$$

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

Constant

$$[A]\tau_{1/2} = \frac{1}{2}[A]_0 \longrightarrow \tau_{1/2} = \frac{\ln(2)}{k}$$



- A time of half-life ($\tau_{1/2}$) determines how quickly the concentration decreases by 50%.

Second order chemical reactions

k units: $mol^{-1} \cdot L \cdot s^{-1}$

- A second-order reaction is a reaction whose rate depends on the square of one reactant concentration or on the product of two reactant concentrations.

Example: Dinitrogen pentoxide decomposition

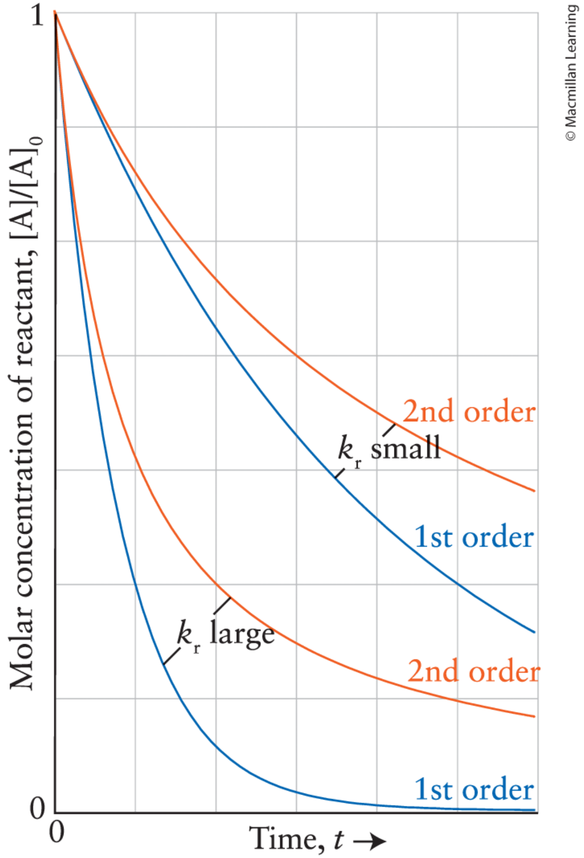
$$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$

Reaction rate: $v = -\dfrac{d[A]}{dt} = k[A]^2$

After integration: $\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$

$$\frac{1}{[A]_{\tau 1/2}} = \frac{1}{[A]_0} + k\,\tau_{1/2} \longrightarrow \tau_{1/2} = \frac{1}{k[A]_0}$$

Depends on $[A]_0$



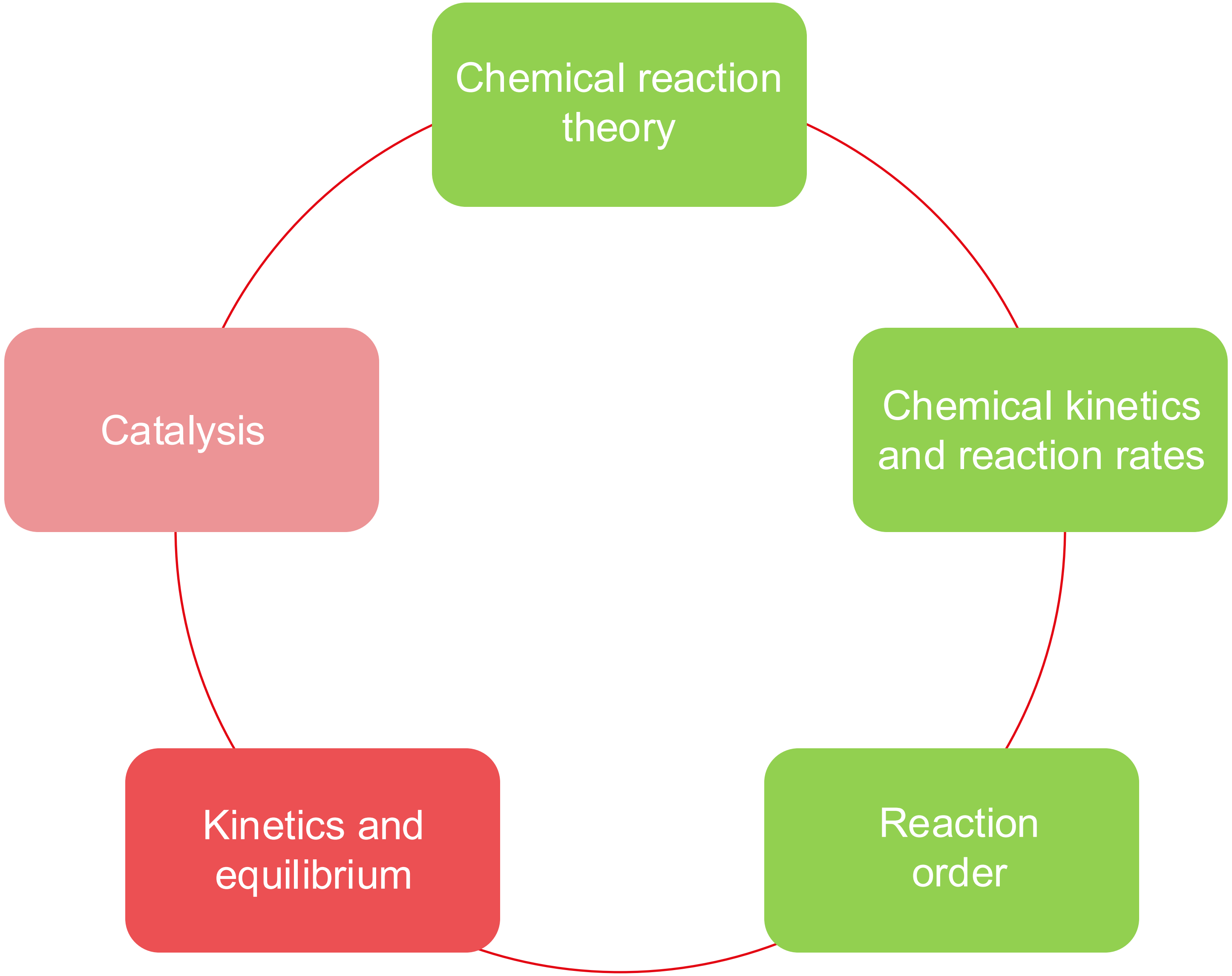
- At concentrations <1 mol/L, 2nd order reactions are slower than 1st order of equal k

Reaction order and molecularity

- **Molecularity** refers to the number of reactant molecules that participate in a single elementary step of a reaction mechanism.
- The reaction mechanism can explain the rate law as a series of **elementary reactions**
- If the reaction steps are elementary, then **the order is equal to molecularity**

Molecularity	Reaction	Reaction speed	Reaction order
Unimolecular	$A \rightarrow$ Products	$v = k\cdot[A]$	1
Bimolecular	$A + A \rightarrow$ Products	$v = k\cdot[A]^2$	2
Bimolecular	$A + B \rightarrow$ Products	$v = k\cdot[A]\cdot[B]$	2
Termolecular	$A + A + A \rightarrow$ Products	$v = k\cdot[A]^3$	3
Termolecular	$A + A + B \rightarrow$ Products	$v = k\cdot[A]^2\cdot[B]$	3
Termolecular	$A + B + C \rightarrow$ Products	$v = k\cdot[A]\cdot[B]\cdot[C]$	3

Plan



Chemical reaction theory

Chemical kinetics and reaction rates

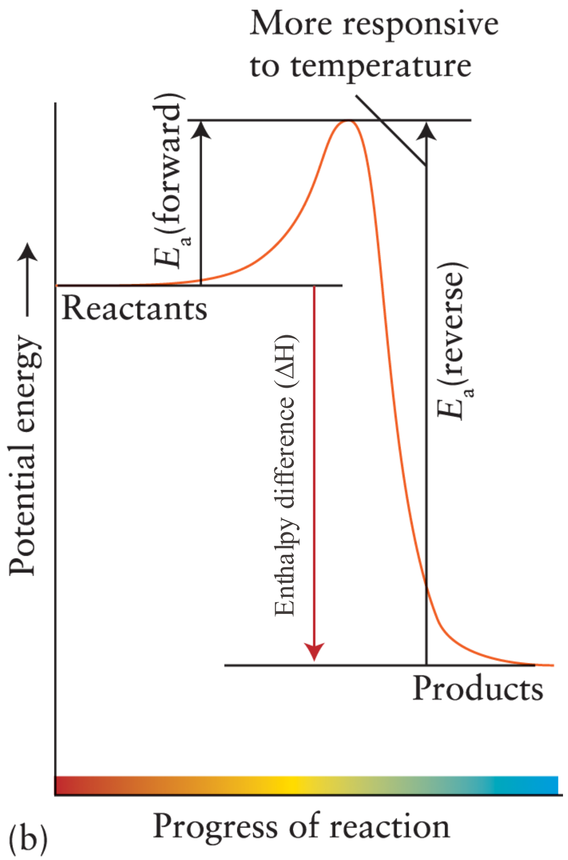
Reaction order

Kinetics and equilibrium

Catalysis

Reaction rates and reversible reactions

- From a thermodynamic standpoint, all reactions are considered reversible, and the difference in energy is what results in preference towards reactants or products



- If we imagine a reaction:

$$\textbf{Reactants} \;\underset{k_{rev}}{\overset{k_{for}}{\rightleftarrows}}\; \textbf{Products}$$

- The rate constants of the two reactions can be expressed as:

$$k_{for} = A_{for} \bullet e^{-\frac{E_a(forward)}{RT}} \qquad k_{rev} = A_{rev} \bullet e^{-\frac{E_a(reverse)}{RT}}$$

- The rates of these two reactions are:

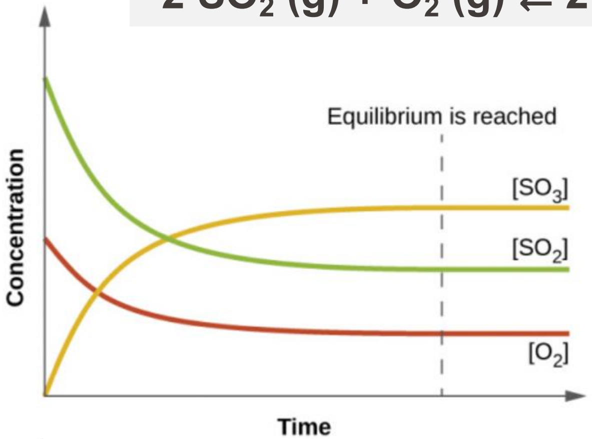
$$v_{for} = k_{for} \bullet [\text{Reactants}]^{\alpha} \qquad v_{rev} = k_{rev} \bullet [\text{Products}]^{\beta}$$

- At equal concentrations of R and P, the two reaction rates will differ due to E_a and A.

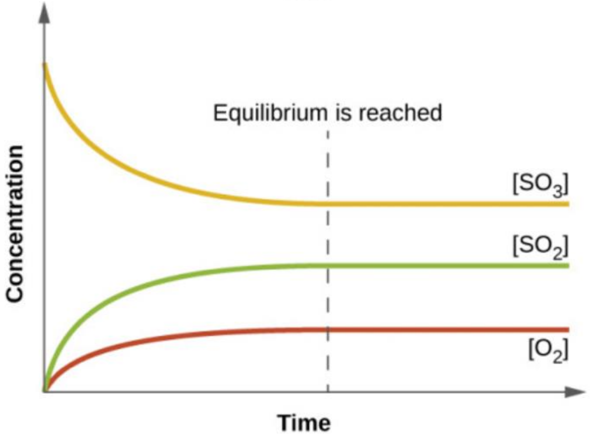
Reaction rates and chemical equilibrium

- At equilibrium, the two reaction rates will be the same, despite $k_{for} \neq k_{rev}$
- The concentrations of reactants and products will adjust such that they give equal rate of two reverse reactions and no net change in the amounts of either species.

$2\ SO_2\ (g) + O_2\ (g) \rightleftarrows 2\ SO_3\ (g)$



Start from reactants



Start from products

- ➢ At Equilibrium: $\mathbf{v_{for} = v_{rev}}$

$$k_{for} \cdot [\text{Reactants}]_{eq}^{\alpha} = k_{rev} \cdot [\text{Products}]_{eq}^{\beta}$$

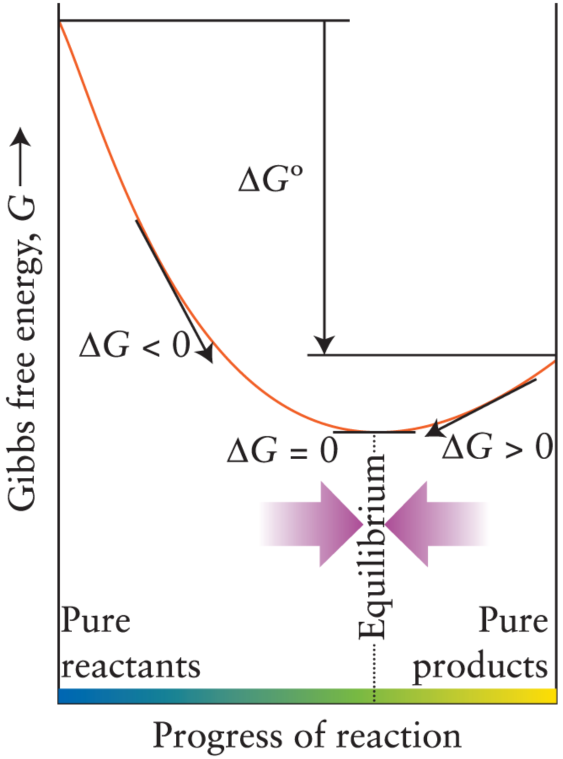
$$k_{for} / k_{rev} = [\text{Products}]_{eq}^{\beta} / [\text{Reactants}]_{eq}^{\alpha}$$

- ➢ Given that: $\mathbf{K_{eq} = [\text{Products}]_{eq}^{\beta} / [\text{Reactants}]_{eq}^{\alpha}}$

$$\boxed{K_{eq} = k_{for} / k_{rev}}$$

Thermodynamic view of equilibrium

- From the thermodynamic perspective the equilibrium is reached when the change in Gibbs free energy ΔG is 0.



$\Delta G = \Delta G^0 + RT\ ln(Q)$

The reaction quitient (Q) is the ratio of product and reactant activities

$Q = [Products]^{\beta} / [Reactants]^{\alpha}$

At Equilibrium: **$\Delta G = 0;\ Q = K_{eq}$**

$\Delta G^0 = -\ RT\ ln(K_{eq})$ ⟶ $\boxed{K_{eq} = e^{-\Delta G^0 / RT}}$

Note: For calculations of K_{eq} or Q we use activities (a_i) instead of concentrations (C_i) which are related via the following equation: $a_i = \gamma_i \frac{C_i}{C^0}$ γ_i = activity coefficient, C^0 = reference concentration

Understanding the equilibrium position

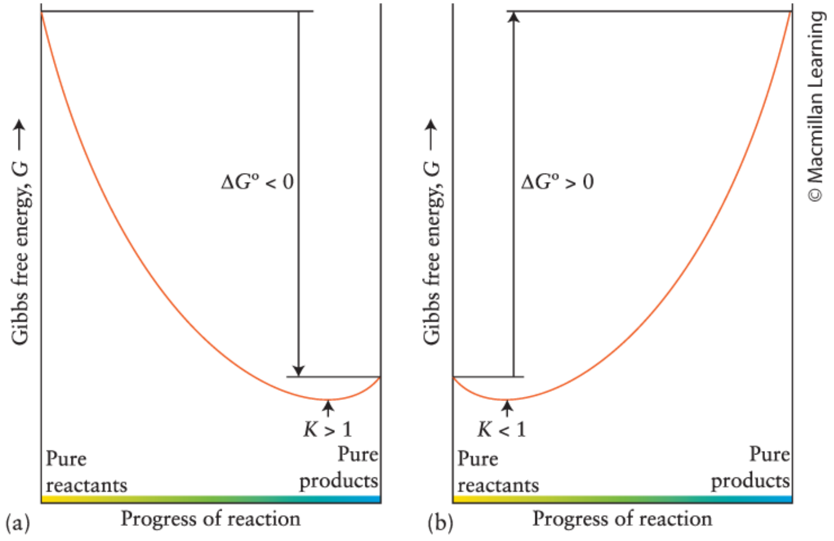
- In equilibrium the system will exhibit greater quantity of the chemical species with lower Gibbs free energy

$k_{for} > k_{rev}$

[Prod.] > [React.]

$k_{for} < k_{rev}$

[Prod.] < [React.]



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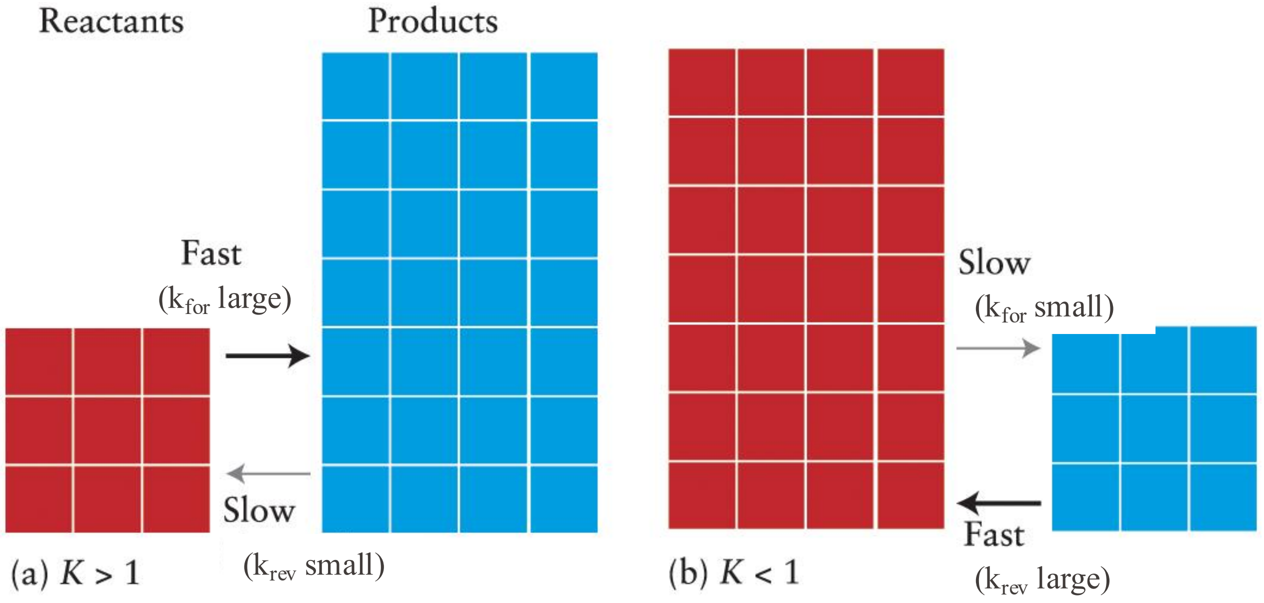
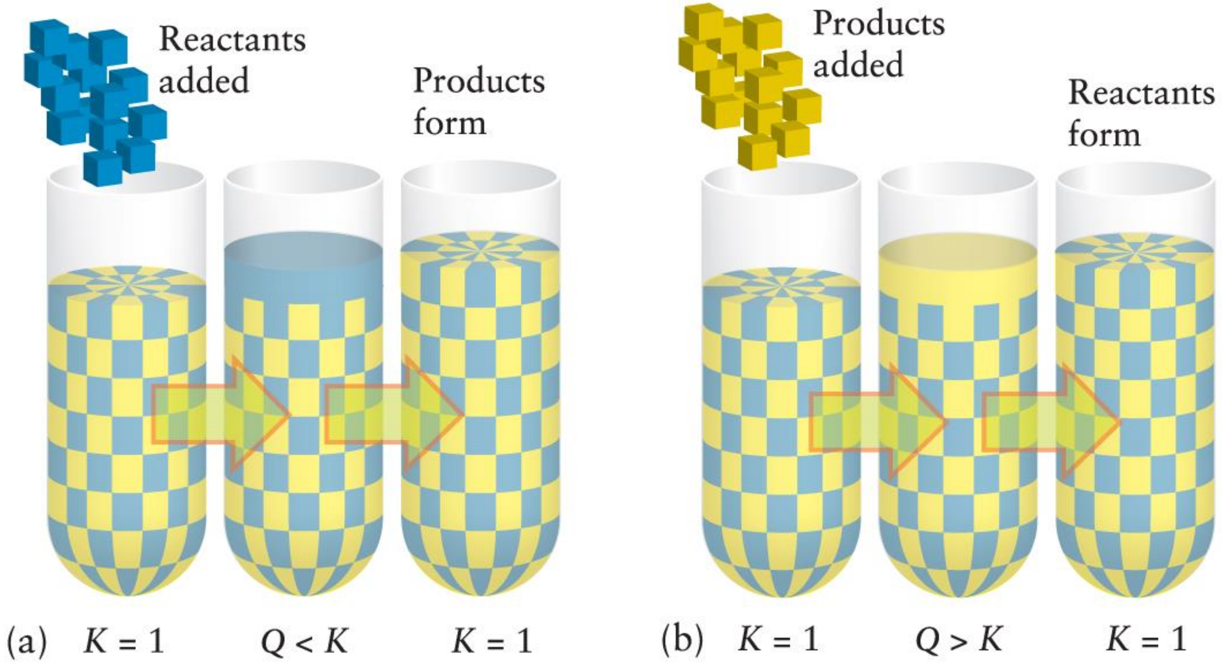
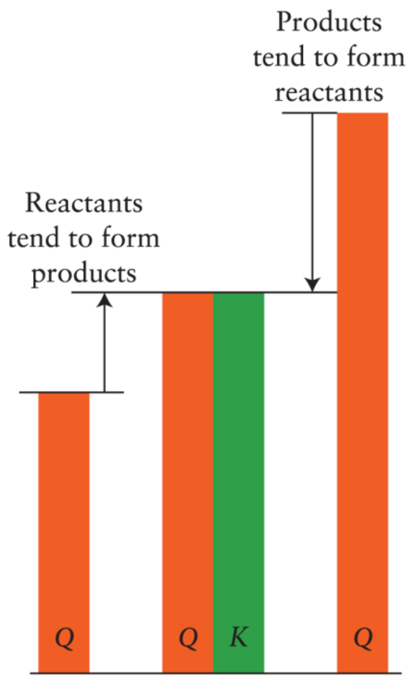


- A reaction that appears one-directional can be understood as one whose equilibrium lies extremely far to the right, such that $k_{for} >> k_{rev}$

Understanding out-of-equilibrium behaviour

- When a system in equilibrium is subjected to a change, the system will adjust its composition in the direction that counteracts the change (Le Châtelier principle)
- Thermodynamics can be applied to determine the free energy change and overall system tendency (i.e., towards reactants or products) for out-of-equilibrium chemical reactions



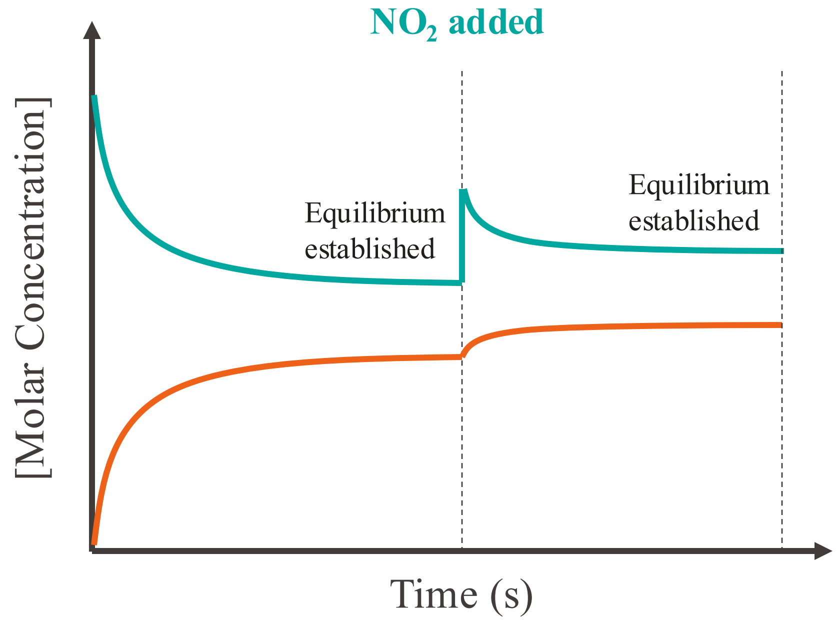


Henry Le Châtelier
(1850 - 1936)

Understanding out-of-equilibrium behaviour

- Chemical kinetics allows us to determine how quickly a disturbed system will relax back to equilibrium by incorporating the rates of the forward and reverse reactions.

$2\ NO_2\ (g) \rightleftarrows N_2O_4\ (g)$



- The partial orders for this reaction are:

2nd order for NO_2: $\text{rate}_f = k_f[\mathrm{NO_2}]^2$

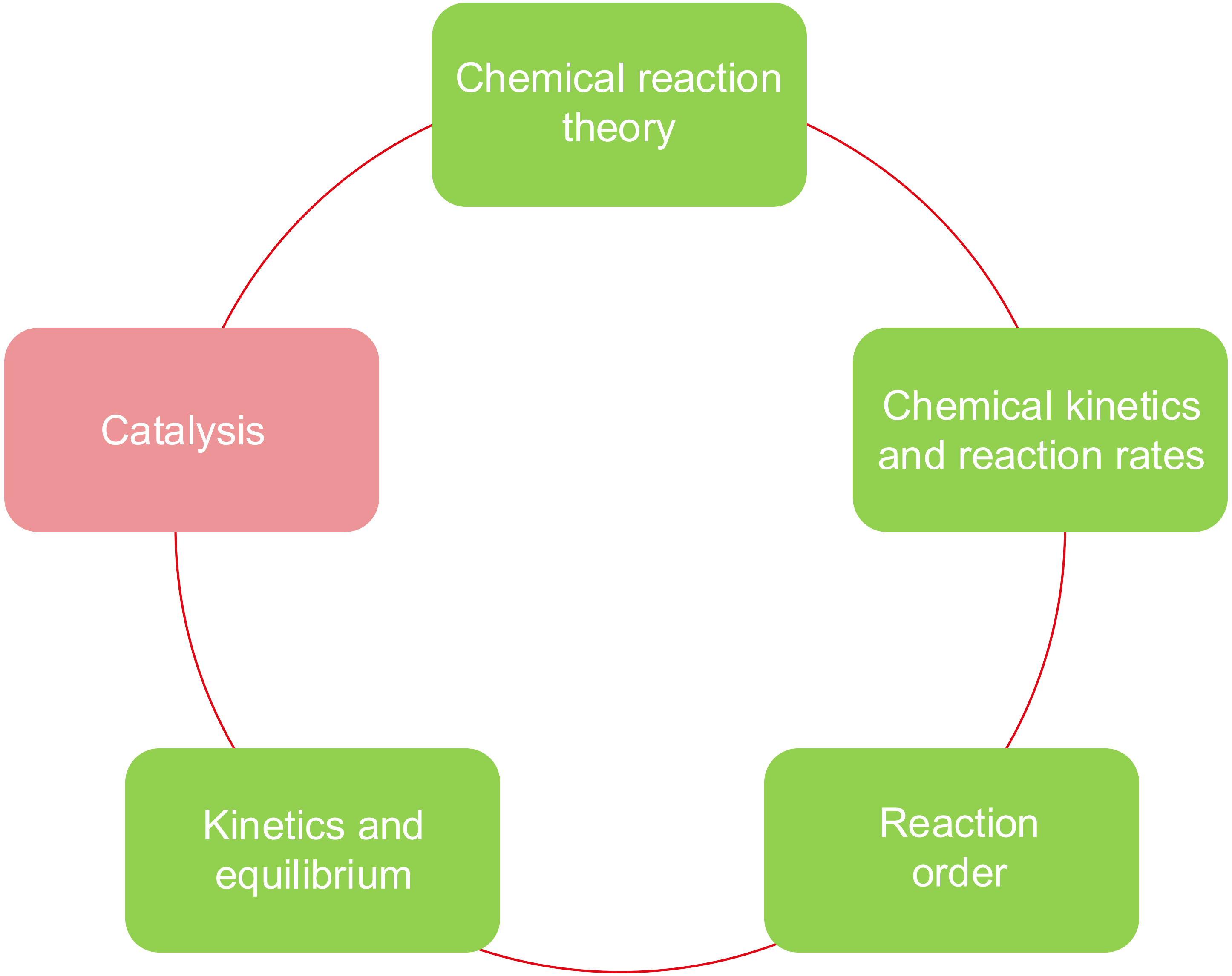
1st order for N_2O_4: $\text{rate}_r = k_r[\mathrm{N_2O_4}]$

- Following the addition of extra NO_2 the system recovers the equilibrium at a rate that is calculated as:

$$\frac{d[NO_2]}{dt} = -2k_f[NO_2]^2 + 2k_r[N_2O_4]$$

Return to equilibrium depends on both, direct and reverse, reactions

Plan



Chemical reaction theory

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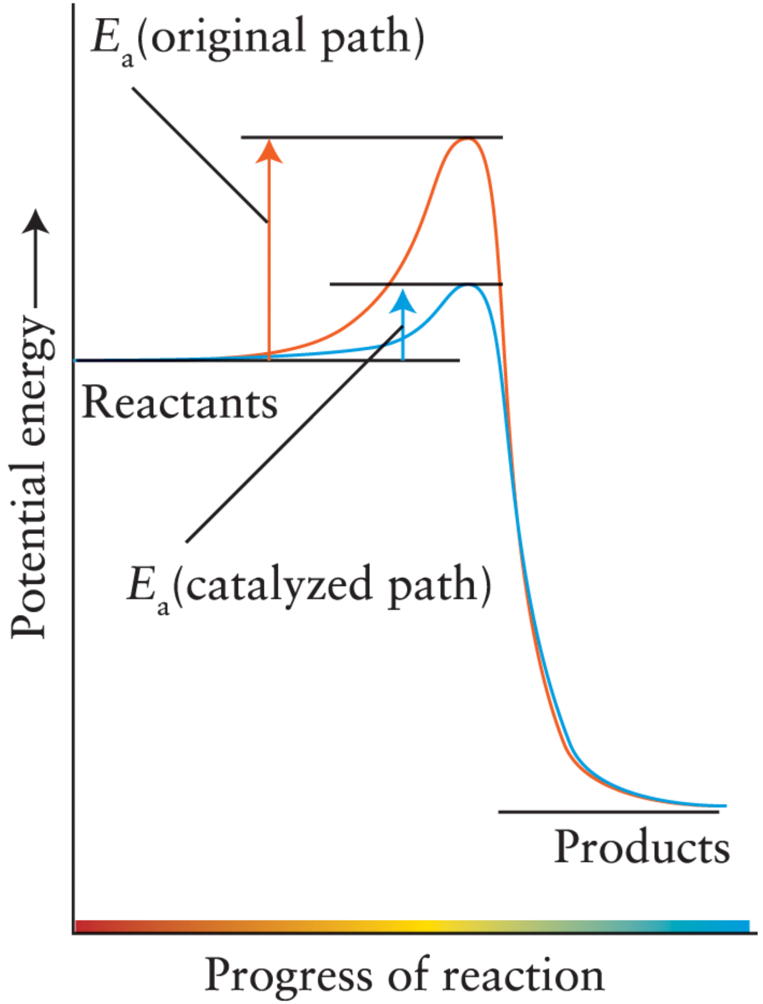
Catalysis

How catalysts work

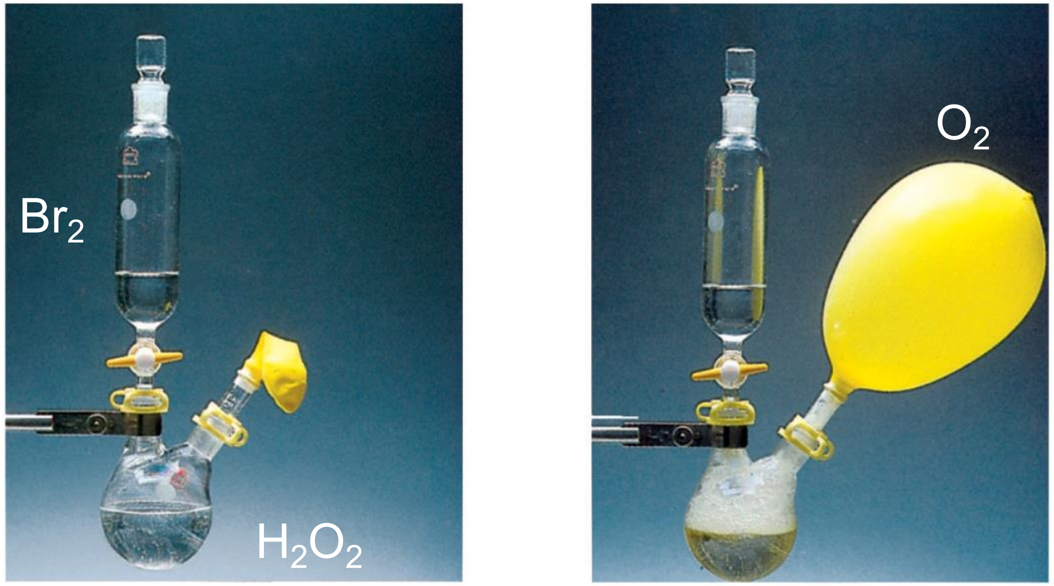


- A **catalyst** increases the reaction rate without being consumed
- The term was coined by J.J. Berzelius:
    - *κατά + λύσις = completely loosening or breaking apart*
- A catalyst works by lowering the activation energy, thereby allowing more reactant molecules to cross the energy barrier and form products.
- **Homogenous** catalysts exist in the same phase as the reactants (e.g., both soluble)
- **Heterogenous** catalysts exist in different phases compared to reactants (e.g., solid vs gas or liquid)

Examples of catalysed reactions

- Catalysts can play a role in the intermediate reaction steps, but (seemingly) do not contribute to the composition of the resulting product
- Example: Hydrogen peroxide decomposition catalyzed by Br_2,

$$2\ H_2O_2(aq) \xrightarrow{Br_2} 2\ H_2O(l) + O_2(g)$$



- ➢ H_2O_2 oxidizes bromide to HOBr

$$H_2O_2 + Br^- + H^+ \rightarrow HOBr + H_2O$$

- ➢ HOBr reacts efficiently with H_2O_2 producing O_2

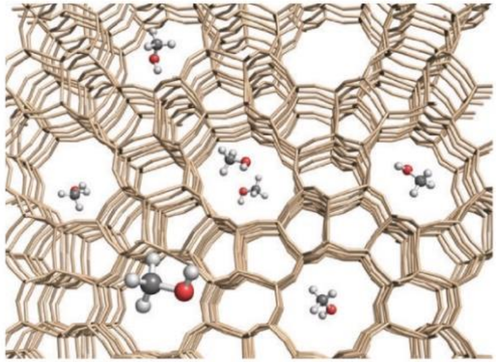
$$HOBr + H_2O_2 \rightarrow Br^- + O^2 + H_2O + H^+$$

- ➢ Br is reduced in the process but is converted back to original form via follow-up reactions.

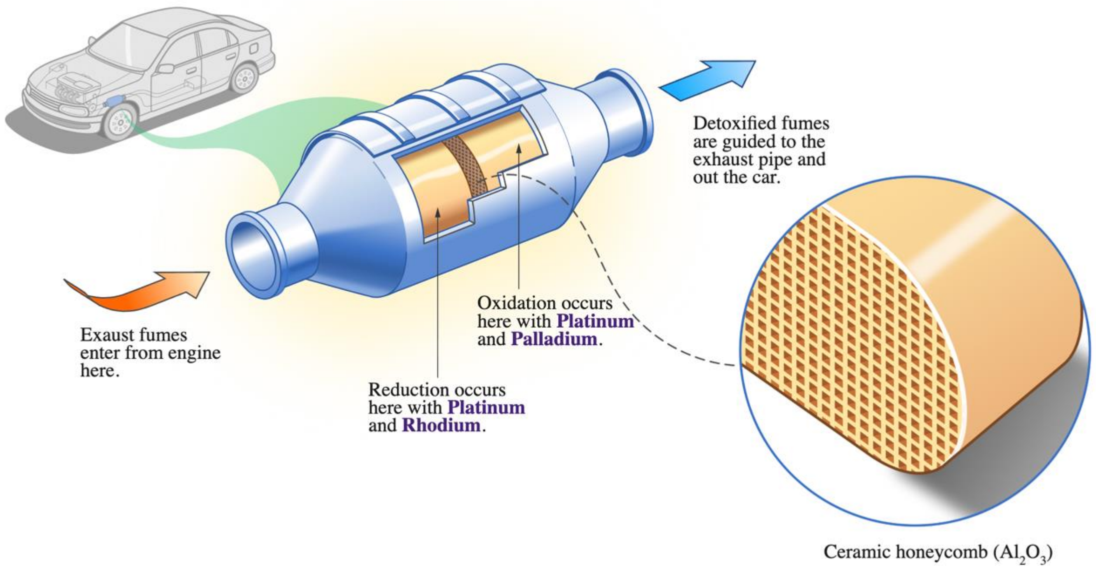
- Acid–base and redox processes are among the most common mechanisms in catalysis.

Industrial catalysts

- Industrial catalysis is the use of catalysts **to accelerate and control chemical reactions on a large scale**, enabling efficient and selective production of different materials.
- Microporous catalysts are an important class of **heterogeneous** catalysts widely used in industrial processes, including catalytic converters in automobiles.



Zeolite mesh
(SiO_4 + AlO_4)



Catalytic converter of an automobile

- Industrial catalysts often work by either providing **electron-exchange environment** (= redox) or through **adsorption of reactant molecules** onto their surface.

Biomolecular catalysts - Enzymes

- Enzymes are biomolecules produced by living systems to catalyze metabolic reactions (i.e., to conserve and transform chemical energy) and synthesize other biomolecules
- Enzymes have extraordinary catalytic power and a high degree of specificity for their substrates, and they accelerate chemical reactions tremendously (10^5 to 10^{17}-fold).

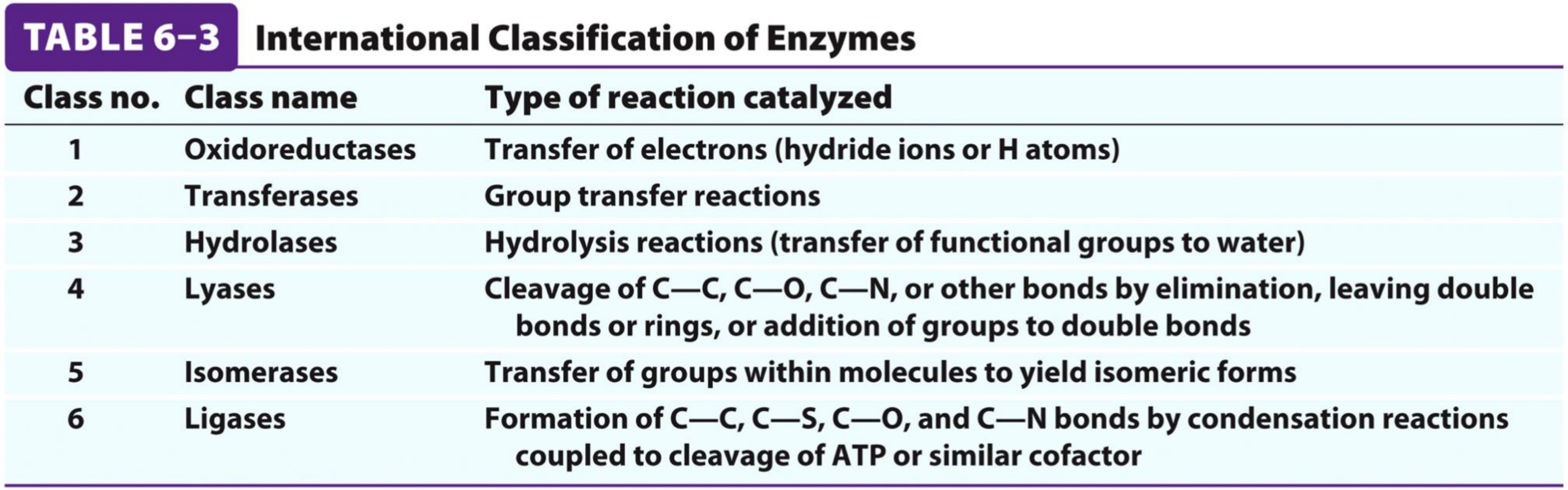
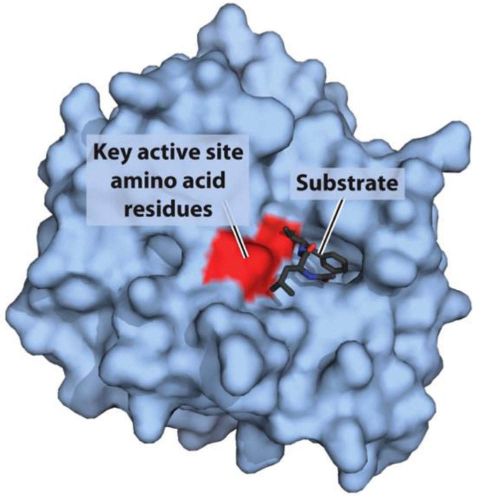


TABLE 6–3 International Classification of Enzymes

Class no.	Class name	Type of reaction catalyzed
1	Oxidoreductases	Transfer of electrons (hydride ions or H atoms)
2	Transferases	Group transfer reactions
3	Hydrolases	Hydrolysis reactions (transfer of functional groups to water)
4	Lyases	Cleavage of C—C, C—O, C—N, or other bonds by elimination, leaving double bonds or rings, or addition of groups to double bonds
5	Isomerases	Transfer of groups within molecules to yield isomeric forms
6	Ligases	Formation of C—C, C—S, C—O, and C—N bonds by condensation reactions coupled to cleavage of ATP or similar cofactor

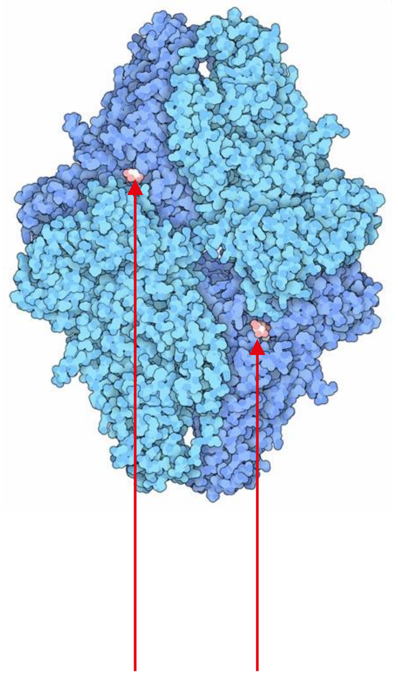


- The name enzyme comes from Greek “*énzymon*” which means “leavened with yeast”
-

Enzymatic catalysis mechanisms

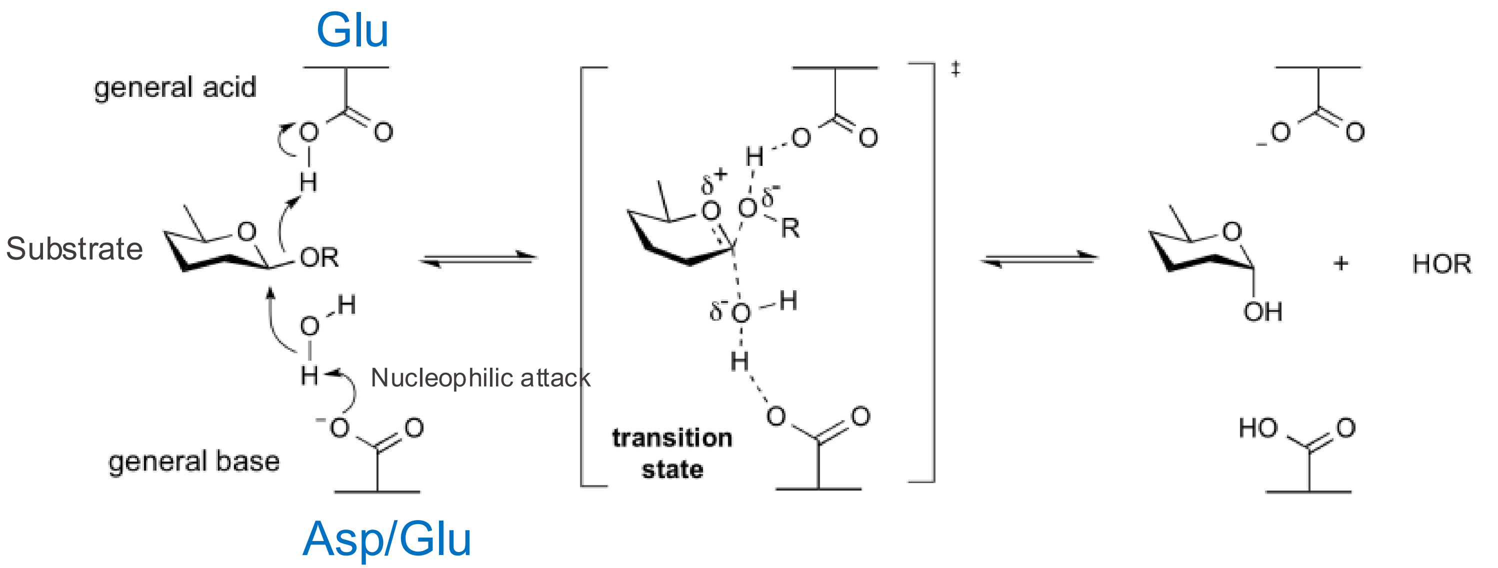
- Many enzymatic mechanisms involve transfer of protons (general acid-base catalysis) or the formation of transient covalent bonds in the active site via amino-acids or cofactors
- The geometry of enzyme active site is optimized to support (induce) the transition state of a molecule which helps to overcome the E_a barrier

β-galactosidase



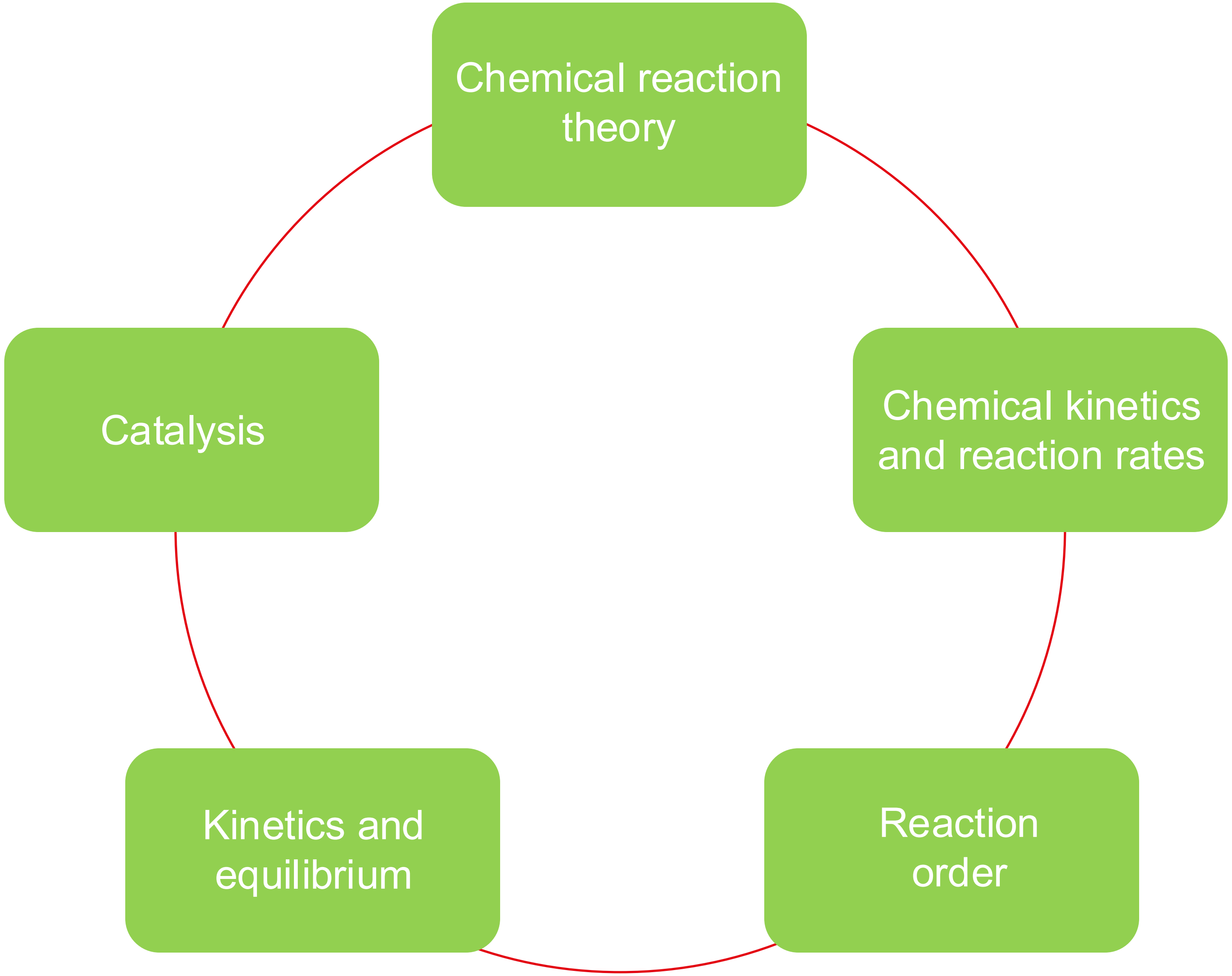
Active sites

β-galactosidase cleaves galactose from carbohydrates (e.g., lactose)



Nucleophile is a chemical group that forms bonds by donating electron pair
Electrophile forms bonds with nucleophiles by accepting electrons

Plan



Chemical reaction theory

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Catalysis

Have a beautiful day !

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