

Chemistry course
ACME Faculty, EHVE course
B.Sc. Studies, I year, I semester
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Kinetics

Reaction rate

- Reaction can take nano- or microseconds but can last hundreds of years as well. What is “time” of the reaction, if the point is to obtain equilibrium. In this context, no reaction ever finish its course, but steadily closes up to the equilibrium (asymptotic).
- Duration of reaction is not the same as reaction rate though.

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Reaction rate

- For vehicles, velocity is time derivative of the position change ($V = dS/dt$)
- For reactions, position change analog is product quantity (or substrate quantity). Thus, **reaction rate** is time derivative of the reagent’s quantity (concentration):
 $v = d[R]/dt$

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Reaction rate

- Reagent quantity can be described through concentration or fraction (percent) of the initial/final quantity/concentration value.
- In case of product, advancement of the reaction has positive value, in case of substrate – negative. We can refer to it as in case of distance to travel – one can count kilometers (percent of road) of distance left or count the distance traveled.
 $v = dc_p/dt = -dc_s/dt$

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Reaction rate

Reaction rate depends on:

- Constant characteristic for the given reaction (experimentally determined **reaction rate constant**)
- Reagents’ concentrations (both substrate and products)
- Temperature
- Catalyst presence
- Pressure (if any reagent is gaseous)
- Solvent type (applies in case of reaction taking part in solute/liquid phase)
- Size reduction/specific surface of chemical reactivity (if reaction is multiphase)
- Electromagnetic radiation (applies to photochemical reactions)

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How do reaction occur?

- In order for reaction to initiate, chaotically (randomly) moving particles have to collide. The less necessary molecules are in the given volume, the slower (as a mean) reaction advances.
- Temperature affects reaction rate, because molecules do move faster (they have more energy), so in the same period of time more collisions will take place.

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How do reaction occur?

Statistically, chance for the collision, which means being at the same time, at the same place with proper directions of movement (against each other) have only two particles (collision of three particles are just a tiny fraction of all collisions, other multi-particle collisions are almost impossible to happen). If stoichiometry requires more particles than two to take part in reaction, it means, that temporarily intermediate product will form. Intermediate collision with third particle will form the final product (or another intermediate).

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How do reaction occur?

Any collision is not enough. It has to have proper momentum – minimal temperature necessary for reaction to occur. When that minimal temperature is achieved by the system, reaction occur. Further temperature increase causes reaction rate to accelerate. Energy required for reaction initiation (minimal particle momentum resulting from temperature) is called the **activation energy**.



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How do reaction occur?

- If collision are necessary for the reaction to occur, so the more particles are colliding, the better. Thus, reaction rate depends on reagents' concentrations.
- Molecule decomposition also results from collision – with other molecule/particle or with the wall (partition) of a vessel (flask, jar, lake...).



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Reaction rate

- Typical formula for one-phase reaction rate includes reaction rate constant (k), which is characteristic for a given reaction in a given temperature: $v = k [A]^x [B]^y$
- Above formula includes reagents' concentrations as well – substrates, products or even catalysts.
- In case of products (if they do affect rate) it is typically negative power (so the rate can be inversely proportional to their concentration).

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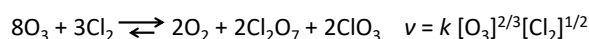
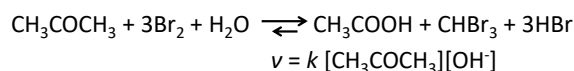
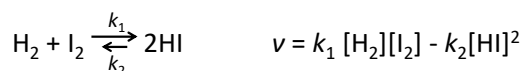
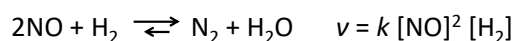
Reaction parameters

- Concentration influence on reaction rate does not have to be linear. Concentration can be present in formula with exponent other than one, fractional as well.
- All exponents (and presence of given reagent's concentration in formula at all), reaction rate constant and effect of other parameters are determined experimentally. Unfortunately, there is no general method for anticipating which parameter and in what way influences reaction rate (although it is often possible to predict with good probability).

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Concentration vs reaction rate

Examples of reactions and their reaction rate formulae:



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Temperature vs reaction rate

- Reaction rate increases with temperature for almost every reaction: $k = f(t)$
- Increase of reaction rate with temperature is exponential – as a rule of a thumb (numerous exceptions) for **every 10 °C/K** process rate increases **2-4x**, and that increase is called **temperature coefficient (Θ)**:
$$\Theta = k_{T+10}/k_T = k_T/k_{T-10} \approx 3 \pm 1$$
- Θ is characteristic for every reaction and can be constant only for certain temperature range (*e.g.* above minimum for reaction initiation or below maximum temperature of reagents' stability)

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Temperature vs reaction rate

Most of reactions are subject to this rule, but there are exceptions, *e.g.* sudden rate increase above certain temperature or $\Theta > 10$ for broad range of temperatures...

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Catalysis

Catalyst is a substance that increases reaction rate by its presence only. It is not consumed during process. Often catalyst is enabling reaction to initiate (*e.g.* without catalyst reaction rate is too slow to measure it). Influence of catalyst is hard to calculate, because it is often working through changing mechanism of reaction (reaction path). Those “new” reactions are faster than original one (will have different reaction rate constant).

- Catalyst X flowchart:

Reaction without catalyst: $A + B \rightarrow AB$

With catalyst: $A + X \rightarrow AX$ $AX + B \rightarrow AB + X$

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Catalyst

- Most often catalyst is working through essential decrease of process activation energy.
- Usually reaction is taking place only on catalyst surface, so chemists tend to expand it as much as possible to increase contact surface. It is achieved through size reduction (nano- or microparticles), deposition of catalyst on grids, 3D structures, surface development (*e.g.* catalyst deposition on activated charcoal or molecular sieves) and so on.

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Catalyst

- Popular example is automotive catalyst – promoting combustion of compounds unburned in engine, *e.g.* NO_x , hydrocarbons, CO, *etc.*
- Catalyst is often the cheapest alternative to heating (heating has its limits and it costs much). Catalyst allows for process initiation temperature to drop and/or accelerates reaction rate at the given temperature by several fold. It can also work through a significant temperature coefficient increase.

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Catalyst

- Catalysts are essential for modern chemical industry, in terms of tonnage they are most important in fertilizers industry and petrochemistry, but in pharmaceuticals industry as well.
- Catalysts are usually made of noble metals (platinum, palladium, iridium, ruthenium, rhodium), rare earth metals (yttrium, scandium), less frequently other metals (gold, silver, nickel, tin, titanium) or compounds and alloys of noble metals (*e.g.* Bi_3Ir , Pt-Ru, Pt-Pd, Pd/Ni). Of course anything can be a catalyst potentially. Organic compounds as well (especially in organisms – enzymes, proteins, *etc.*).

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Future belongs to catalysis!

- Catalysts are fundamental for many devices. For instance, fuel cells are still not used widespread, because their most important part is platinum catalyst. Most efficient fuel cells (hydrogen) have efficiency of ca. 0.7 W from 1 mg of platinum, so ca. 1.5 g Pt/kW. It means, that just the raw material costs ca. 100 \$/kW (let alone its processing and catalyst forming, other components cost and assembly). It matters due to scale of production, which is in gigawatts.
- Thus, alternatives from cheap materials are sought for. Alternative has to be at least economically better (*i.e.* increase of power divided by catalyst cost in case of alternatives use would be higher than in case of platinum).

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Future belongs to catalysis!

- Economy is important especially in nitric industry (fertilizers) – catalysts are **poisoned**, so they have to be regenerated, otherwise their efficiency is decreasing (faster and faster).
- In big factory it may be tons of platinum (palladium) annually in form of dust deposited on grids (pellets).

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Inhibitors

- Substances that decrease reaction rate or even disable the process by their sole presence are called **inhibitors**. Many medicines (their active substances) are working through inhibition of reaction between proteins/enzymes/bacteria and so on.
- Also inhibitors of corrosion are popular – those are substances protecting steel constructions by **inhibition** (blocking/disabling) of typical corrosive reactions.
- They can also work through catalyst poisoning.

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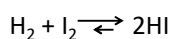
Mechanism of reaction

- **Mechanism of reaction** is a path, that substrates (and possible intermediates) have to go through to become products (and vice-versa – these are usually dynamic equilibria).
- Mechanism can be **simple**, that is when reaction occurs in a **single step**.
- Mechanism is **complex**, if there are **multiple steps**.
- **Intermediate product** is the one that forms temporarily (especially unstable one) and forms just to react further until the final product is obtained.

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Mechanism of reaction

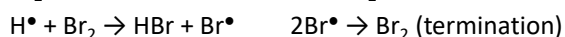
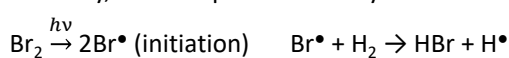
For instance iodine reaction with hydrogen is simple:



Reaction of bromine with hydrogen is complex:



In reality, it is a sequence of many reactions:



Br^\bullet i H^\bullet radicals are intermediate products.

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Mechanism of reaction

- Mechanism is hard to predict, so each one is investigated experimentally.
 - **Alignment of the particles** that collide also matters – if one reacting molecule is big, like $\text{CH}_3\text{CH}_2\text{OH}$, it matters, if the other molecule will hit carbon from CH_3 group, the middle one or oxygen atom. Successful reaction depends on that, *e.g.* alcohol oxidation to acid.

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Mechanism of reaction vs reaction rate

- Multi-step reactions are not necessarily slower than one-step ones. The only limit of reaction rate of the multi-step reaction is the **rate determining step** – step that is the slowest one.
- Unfortunately, as it is with mechanism prediction, it is not possible to predict (with good probability), which step will be the slowest (of course after mechanism investigation and steps identification, it is possible to measure their rates).

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Particle energy

- Energy of the particle is the sum of its kinetic energy (velocity, $E = mv^2/2$) and energy of its bonds.
- Energy of the particle does not change upon collision, but it can lead to conversion of kinetic energy part into bonds' energy or vice versa.
- Bonds' energies in different compounds are different - above conversion always takes place during reaction.
- Kinetic energy of particle is closely related to temperature – if molecules are accelerating then temperature is increasing and vice versa (in solid state movement is represented by vibration in crystal lattice node).

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Exo- vs Endo-

- Reaction is exothermic if temperature in reaction mixture is increasing due to its progress, because kinetic energy is increasing in a system (and products' energy of bonds is smaller than that of substrates).
- After **endothermic** reaction temperature decreases, because kinetic energy is decreasing (changes into products' energy of bonds).

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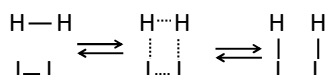
Exo- vs Endo-

- In order to keep the reaction rate, it needs to be cooled down (exergonic) or heat (endergonic).
- Too high temperature can cause decomposition of substrates/products or boil out solvent (lack of proper contact between substrates).
- Too low temperature is slowing down the reaction (or it is not initiated at all).

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Activated complex

Why do reactions occur can be often explained with **activated complex** theory. When molecules collide, they form in a moment of collision temporary unstable molecule (lifetime below 10^{-12} s), which is consisting of substrates and can decompose back into substrates or can split in new way (and form products), *e.g.*:



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Activated complex

- Forming activated complex needs minimal energy – that is what we call activation energy.
- Intermediate state between substrates and products is a state in which “old” bonds still exist (although weakened) and “new” bonds are already forming.
- That explains, why activation energy of reactions is smaller than sum of broken bonds' energies.
- Reaction rate constant depends on concentration and rate at which activated complex transforms into product.

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Catalysis once again

Collisions between chaotically moving particles are frequent, but effective ones are relatively rare (so there is a place for improvement). Catalysts “catch” one of substrates and form temporary bond with it (complex). Such complex has lower reaction activation energy (than raw substrate). It waits until “hit” by second substrate. That way two reactions occur instead of one, but both are faster and occur easier than one without catalyst.

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Chemical equilibrium and invertibility

- Theoretically all reactions are reversible, *i.e.* reaction direction can be reversed under certain conditions.
- In reality, reaction is assumed to be irreversible, if it occurs with 100% yield in respect to one of substrates, *i.e.* substrate is depleted.
- „Depletion” of reagent can also happen if product is precipitating or it escapes as a vapor (so it cannot take part in reverse reaction).

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Chemical equilibrium

- Final state after reaction is a result of equilibrium state – what substrates to products ratio is approached by reaction.
- Reactions that are assumed to be “one-way” (irreversible) are those, in which dynamic equilibrium approaches products-only state. Such reaction can be noted with \rightarrow sign, instead of equilibrium sign.

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Chemical equilibrium

Equilibrium in reaction occurs when reactions in both directions have certain rates. *E.g.* when reaction towards “right” has much higher rate, then reaction goes “to the end”. When rates are close to each other, concentrations of both substrates and products can be similar (it is another thing is, how long it takes to establish that equilibrium).

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Chemical equilibrium

In order for equilibrium caused by similar reactions’ rates (both toward “left” and “right”) to establish, no “escape” of products can occur. It means that there can be no mass exchange between environment and reaction mixture. Reaction mixture has to be single-phase (homogeneous) (solution or gas mixture).

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Chemical equilibrium

- With progress of reaction, rate of reaction in one direction decreases and in other direction increases, until both rates equalize – that is when equilibrium is obtained. It is a dynamic equilibrium, *i.e.* both reactions are still ongoing, though at the same rate.
- Point, at which equilibrium is established is described by **equilibrium constant**.

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Equilibrium constant

Reagents' concentrations at equilibrium are described with a following formula:

$$K_c = [P_1]^{x_1} \cdot [P_2]^{x_2} \cdot \dots \cdot [S_1]^{-x_3} \cdot [S_2]^{-x_4} \cdot \dots$$

where K_c – equilibrium constant;

S - substrates; P - products;

Index exponents x are stoichiometric coefficients of reaction equation;

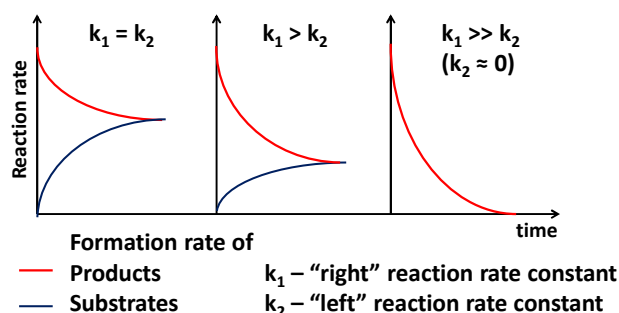
Thus for $2H_2 + O_2 \rightarrow 2H_2O$ reaction:

$$K_c = [H_2O]^2 \cdot [H_2]^{-2} \cdot [O_2]^{-1}$$

Value of K_c is determined experimentally and characteristic for the given reaction (at the given temperature).

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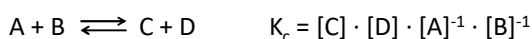
State of chemical equilibrium



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Le Chatelier's principle (pol. contrariness rule)

- Le Chatelier's principle states, that if equilibrium would be unbalanced (disturbed) then the system would tend to equilibrium by counteracting the disturbance (and to equalize reaction rates in both directions).
- E.g. if we add more of one of the substrates, then we will obtain more of product, but less than if we would add also second substrate in stoichiometric amount:



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Le Chatelier's principle

- Suppose that K_c is 1, and initial substrate amount is 2 moles of A and 4 moles of B. We will obtain:
 $K_c = [C] [D] [A]^{-1} [B]^{-1} = x \cdot x / ((2-x) \cdot (4-x)) = 1$
 $x^2 / (8-6x+x^2) = 1 \quad x^2 = x^2 - 6x + 8 \quad 6x = 8$
 $x = 1.33$ so we will obtain **1.33 mole of C and D** and after reaction there will be remaining **0.67 mole of A and 2.67 moles of B**.
- If we add one more A mole, (K_c is constant, so the ratio between reagents has to be maintained):
 $K_c = [C] [D] [A]^{-1} [B]^{-1} = x \cdot x / ((3-x) \cdot (4-x)) = 1$
 $x^2 / (12-7x+x^2) = 1 \quad x^2 = x^2 - 7x + 12 \quad 7x = 12$
 $x = 1.71$ so we will obtain **1.71 mole of C and D**, and after reaction there will be remaining **1.29 moles A and 2.29 moles of B**.
- Difference: 1 mole of A has been added, 0.38 moles of C and D were obtained additionally.

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Le Chatelier's principle

- Analogous to substrate addition, one can collect product. With collecting it, we get **higher yield** of product (in order to maintain K_c , more substrates will react).
- The above statement explains, why if gaseous product is escaping reaction mixture, reaction will run to the end (until depletion of substrate).

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By the way;)

- Degree of conversion** is a percent of substrate used in reaction until given moment.
- Reaction yield** is a product quantity which was achieved, in comparison with theoretical maximum amount (if all substrates would react ideally into product). Reaction yield lower than 100% (all reactions in reality) can be caused by side products formation and material losses, (remains in reactor, reagents' evaporation), etc.

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Le Chatelier's principle

- Temperature change is affecting equilibrium as well. K_c is a constant only at the given temperature.
- **Heating up** reagents of **endothermic** reaction shifts equilibrium **towards products**, in exothermic the opposite way round.
- **Cooling down** reagents in **exothermic** reaction shifts equilibrium **towards products**, in endothermic the opposite way round.

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Le Chatelier's principle

- Pressure change also affects equilibrium.
- Pressure influence (only when in gaseous state) depends on substrates to products volume ratio (more-less substrates to products molar ratio).
- If $V_{\text{substr}} > V_{\text{prod}}$, then **increasing pressure** shifts reaction equilibrium **towards products** (without externally imposed pressure changes, the pressure would naturally drop in constant volume as a result of such reaction. Thus, increasing pressure would activate Le Chatelier's principle and system would counteract external change by decreasing pressure – shifting the equilibrium towards products).
- If $V_{\text{prod}} > V_{\text{substr}}$, then **decreasing pressure** shifts reaction equilibrium **towards products**.

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Le Chatelier's principle

- Addition of one of substrates increases degree of conversion of second substrate. However, in gas phase reactions, addition of substrate excess would produce opposite effect by dilution (or pressure of second substrate would decrease so much, that equilibrium would start to shift toward substrates and that effect would start to predominate).
- Addition of gas that is not taking part in the reaction (e.g. argon in nitrogen and hydrogen reaction) causes smaller chance for reagents to collide and decreases reaction rate. Also, it shifts equilibrium towards substrates (causes reagents' pressure decrease).

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Catalysis again...

- Catalyst (apart from changing reaction mechanism) changes reaction rate in both directions in the same way. Catalyst is not affecting the final equilibrium, but influences the times needed to obtain the equilibrium.
- Quantity of catalyst do not affect equilibrium but do affect reaction rate acceleration (by increasing number of free active sites at the surface we increase number of individual reactions running at the moment, so we so accelerate the reaction).

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Le Chatelier's principle – applications

Industry uses Le Chatelier's principle in order to maximize reaction yield (and/or increase rate and/or economize process). Through product collecting process achieve better conversion of substrate. Through use of one substrate excess (cheaper one) process increase conversion rate of the second substrate (better use of more expensive one).

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Le Chatelier's principle – applications

- When process is designed, it is preferred (if other factors are comparable) to obtain products through endothermic reactions (high yield/reaction rate depends on heating). Why? Heating on industrial scale is cheaper than cooling (ca. 3 times less – that is a result of energy efficiency ratio of cooling and heating systems).
- Reactions in which gaseous reagents quantity is decreasing ($V_{\text{substr}} > V_{\text{prod}}$), are carried under high pressure (often 1000 atm or more).

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