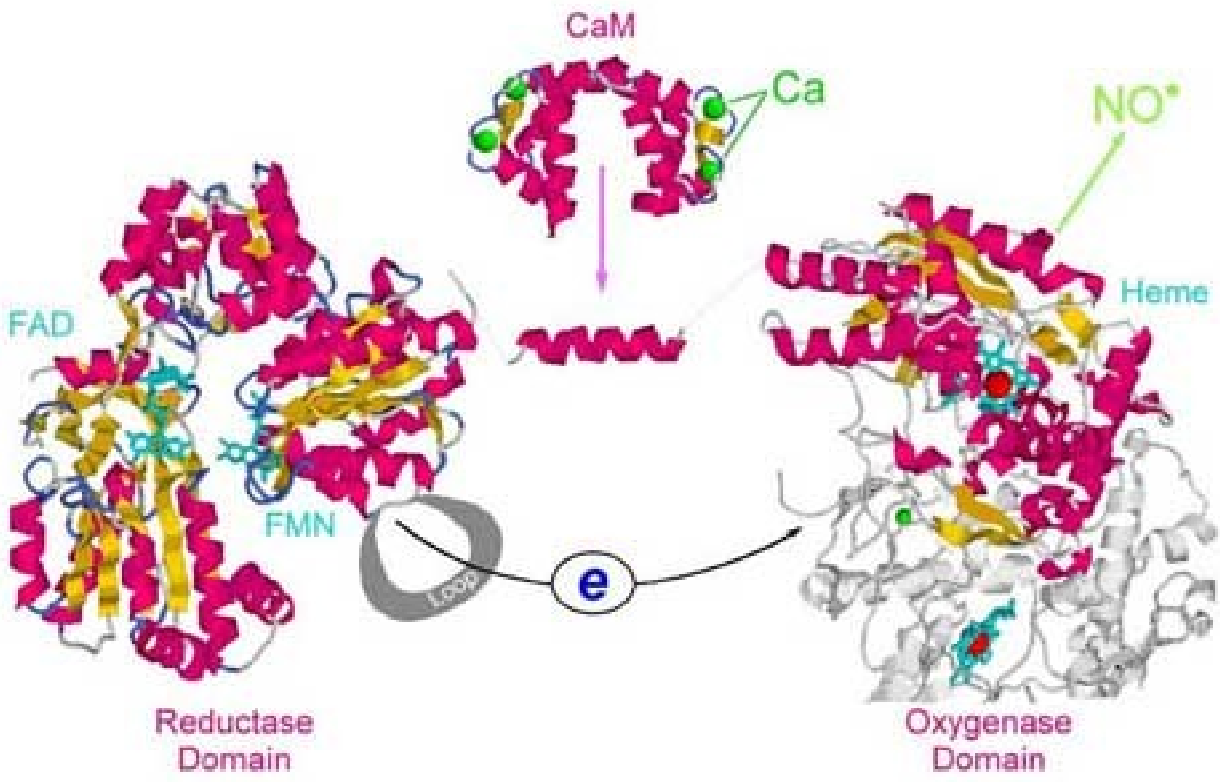
# Basic concepts, variables, and classifications



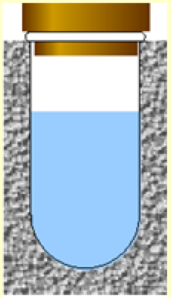
# Dynamics, Thermodynamics, Chemical Kinetics

**Dynamics** is a scientific discipline that studies the forces and consequences of their action, ie cause and quality changes (move, events): ( i) **Newtonian dynamics** studies gravitation events induced by forces, ie the gradient of the gravitational potential. ( ii ) **Electrodynamics** studying events induced by Coulomb forces, ie the gradient of electric potential. ( iii ) **Magnetodynamics** studying events induced magnetic forces, ie the gradient of the magnetic potential .

**Thermodynamics** studies events induced by thermodynamic forces. ie the gradients of thermodynamic potentials: Gibbs energy G or Helmholtz energy F. **Gradient G or F** induced by local **differences in composition** within the system (maintaining its overall composition) is the driving force of **diffusion**. Gradient G or F caused by **temperature differences** within the system is the driving force of **termodiffusion**. Gradient G or F associated with a **change in the overall composition** of the system is the driving force of chemical transformations in the system - **chemical reactions**.

# Thermodynamic system

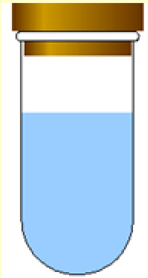
$\Delta X = X_{after} - X_{before}$



Isolated

$(\Delta m = 0; Q = 0)$

The changes are spontaneous if $\Delta S_t > 0$



Closed

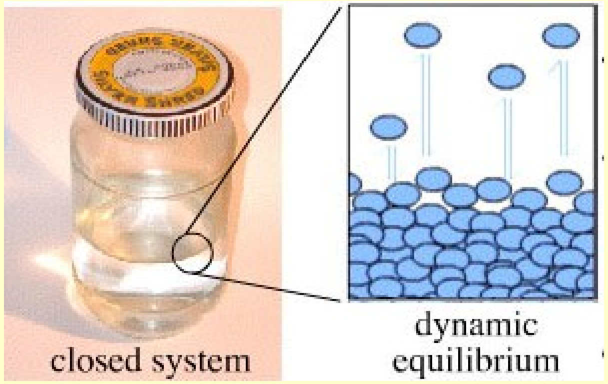
$(\Delta m = 0; Q \neq 0)$

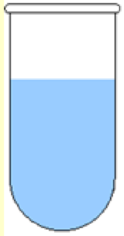
The changes are spontaneous at constant **p,t** if

$\Delta G = \Delta H - T\,\Delta S < 0$

The changes are spontaneous at constant **V,t** if

$\Delta F = \Delta U - T\,\Delta S < 0$

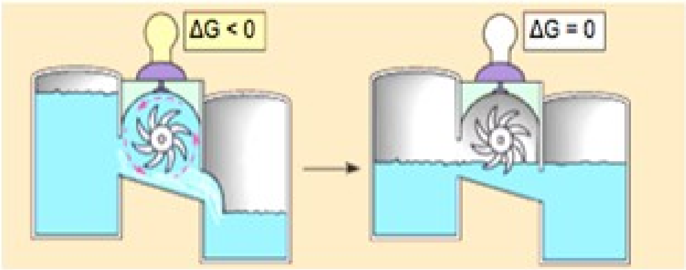


Open

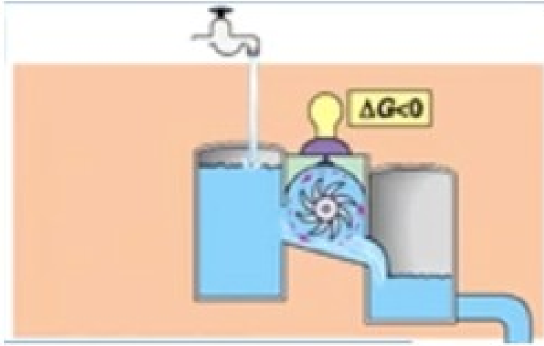
$(\Delta m \neq 0; Q \neq 0)$

$\Delta G$ can be any sign, ie. also positive if one product is removing




Isolated systems reach equilibrium
Maximum stability

Open systems do not reach equilibrium
Minimum stability




**Thermodynamics** can provide both qualitative and quantitative answer to the question of what changes may occur in the reaction system under certain conditions. Provides notice of the potential feasibility of changes in the system. It does not provide information about the speed of these changes.

**Kinetics** of the scientific disciplines studying velocity changes induced by force .

**Chemical kinetics** is a scientific disciplines studying the rate of chemical reactions and the factors that influence them.

**What question deals with the chemical kinetics ?**

1**. Speed** and **rate equations** of chemical reactions
2. Derivation of rate equations of the **mechanisms of chemical reactions**.
3. **Experimental methods** of studying the rate of chemical reactions.
4. Analysis and **interpretation** of chemical - kinetic data .
5. **Theory of elementary chemical reactions**.

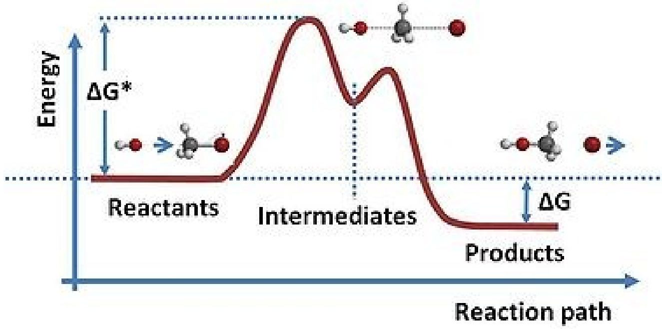
- models of elementary reactions ,
- calculations of the rate constants of the structural parameters of the reactants ,
- selection rules (prohibitions) relating to elementary reactions.

6. **Effects of physical and chemical environmental parameters** on the reaction rate (temperature, pressure, solvent, pH , ionic strength, latent state system, the presence of phase interface).
7. **The effects of substance and energy flows** inside the reaction system and the reaction system and its surroundings on the reaction rate.
8. **Relationships between chemical structure and reactivity** of substances .
9. **Catalysis and inhibition** of chemical reactions.

# Chemical reactions and equations

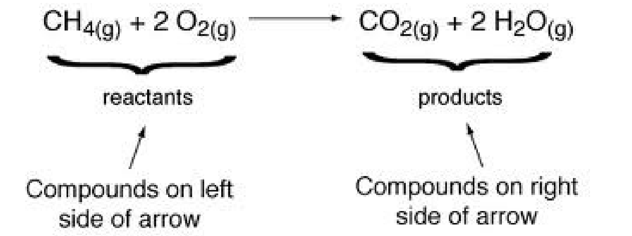
**Chemical reaction** is a process taking place on the electron structure of chemical species (atoms, molecules, ions, radicals, coordinating particles, clusters, etc. ), The original particle structural changes in the new particles with different chemical structure.

- The **reactant** is a substance or its particles, which enters in chemical reaction.
- The **product** is a substance or its particle, which creates during chemical reaction.
- **Intermediate** means a substance or a its particle, which occurs and subsequently disappears during chemical reaction. When continuing the reaction is slow, the intermediate can be obtained even in isolatable form.




**Chemical reactions are carried out** following elementary processes:
- **splitting** the original chemical bonds;
- **creation** of new chemical bonds;
- **the transfer** of electrons between reactants (different redox reaction)

**Stoichiometric (chemical ) equation** is a brief, formal description of a chemical reaction in which the left side of the figure symbols (or acronyms ) and number of particles of reactants and right of the symbols and the number of particles of products are equivalent to **<u>one basic reaction turnover</u>**.




$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

1 basic reaction turnover was realized if 1 mol $CH_4$ and $2O_2$ were converted to 1mol$CO_2$ and 2mol $H_2O$.

# Stoichiometric chemical equation

**Chemical equations can be supplemented by other data** related to the conditions and the manner of its execution. These are mainly:

- **heat of reaction, reaction enthalpy, reaction Gibbs energy, etc**., which are shown in the chemical equation
- **the catalyst, solvent, reaction temperature, reaction pressure**, etc., which are usually printed above or below the arrow pointing from reactants to products.

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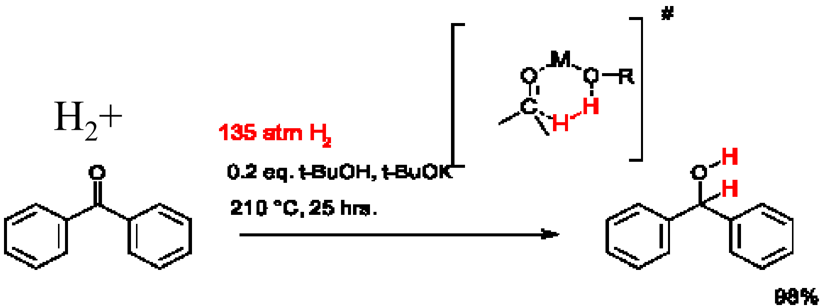
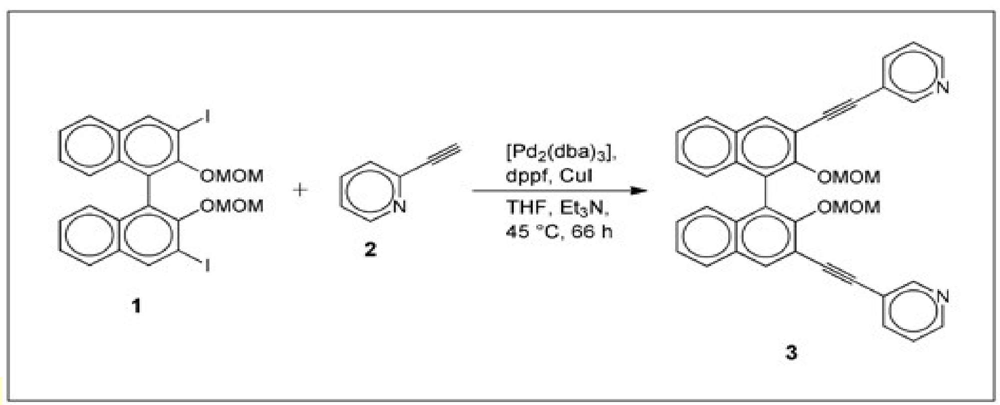
For example the synthesis of ammonia from the elements describing the stoichiometric equation:

$$N_2 + 3\,H_2 \xrightarrow[600\ °C]{(Fe)} 2\,NH_3 \qquad \Delta H = -\,92\ kJ/mol \qquad (1\text{-}1)$$



# Proper writing of chemical equations for the kinetics

**Stoichiometric coefficient.** The figures indicating the number of particles of reactants and products participating in one basic reaction turnover are called stoichiometric coefficients of the reaction.

**The correct chemical equation has all stoichiometric coefficients equal smallest possible natural numbers (none of them is a fraction)!**

| Wrong | Correct |
|---|---|
| $^{1}/_{2}\, N_2 + {}^{2}/_{3}\, H_2 \longrightarrow NH_3$ | $N_2 + 3\, H_2 \longrightarrow 2\, NH_3$ |
| $2\, N_2 + 6\, H_2 \longrightarrow 4\, NH_3,$ | |

# Mathematic notation of chemical equation

$$-N_2 - 3\,H_2 + 2\,NH_3 = 0$$

$$-5\,PbO_2 - 2\,Mn^{2+} - 4\,H_3O^+ + 2\,MnO_4^- + 5\,Pb^{2+} + 6\,H_2O = 0$$

**Extent of reaction** is defined as the number of moles of basic reaction turnover realized from the start chemical reactions in the reaction time t. The extent of reaction calculated from the equation:

$$\xi = \frac{n_B^t - n_B^0}{\nu_B} = \frac{\Delta n_B^t}{\nu_B} \tag{1-3}$$

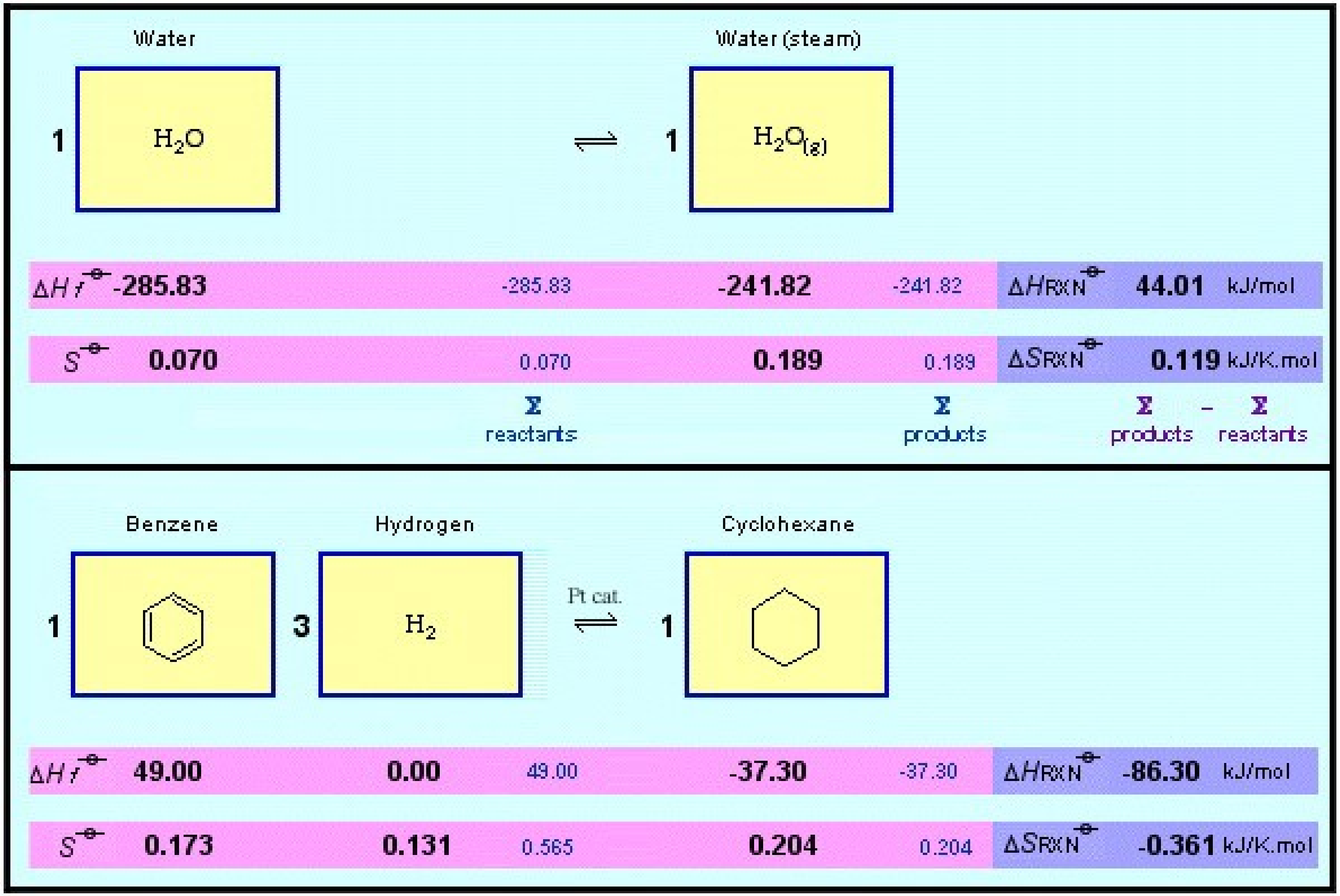
where $n_0$ $n_B{}^t$ resp. $n_B{}^0$ are the amount of component B in the reaction system after the reaction time t, respectively at the beginning of the reaction (t = O). $\nu_B$ is stoichiometric coefficient of the B component.

Example:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

$$\xi = \frac{n_{N_2}^t - n_{N_2}^0}{-1} = \frac{n_{H_2}^t - n_{H_2}^0}{-3} = \frac{n_{NH_3}^t - n_{NH_3}^0}{2} \tag{1-4}$$

# Discussion


Water
Water (steam)
1
H2O
1
H2O(g)
ΔHf -285.83
-285.83
-241.82
-241.82
ΔHRXN 44.01 kJ/mol
S 0.070
0.070
0.189
0.189
ΔSRXN 0.119 kJ/K.mol
Σ reactants
Σ products
Σ products - Σ reactants
Benzene
Hydrogen
Cyclohexane
1
3
H2
Pt cat.
1
ΔHf 49.00
0.00
49.00
-37.30
-37.30
ΔHRXN -86.30 kJ/mol
S 0.173
0.131
0.565
0.204
0.204
ΔSRXN -0.361 kJ/K.mol