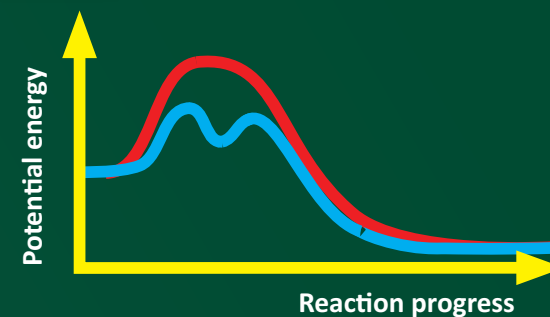
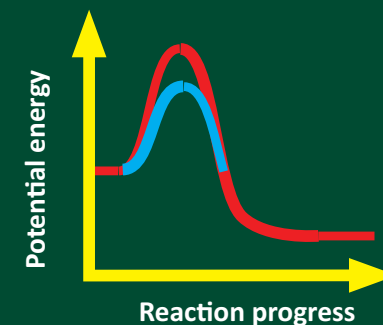
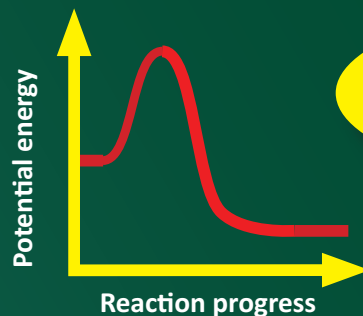
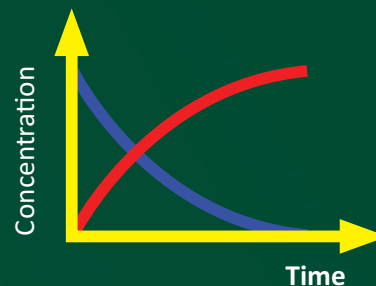
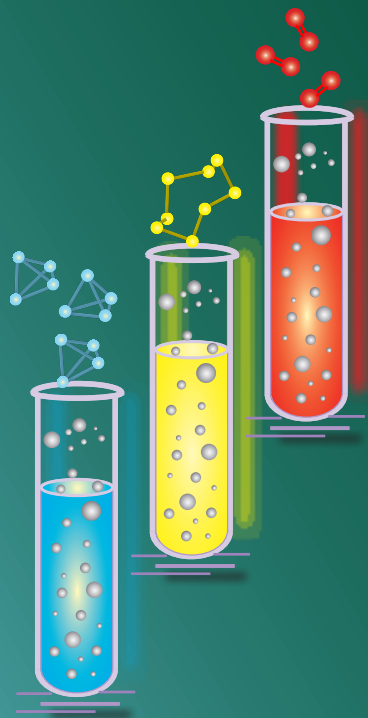


CHEMICAL PROCESSES



- Heat of reactions
- Exo- and endothermic reactions
- Rate of chemical reactions
- Chemical equilibrium

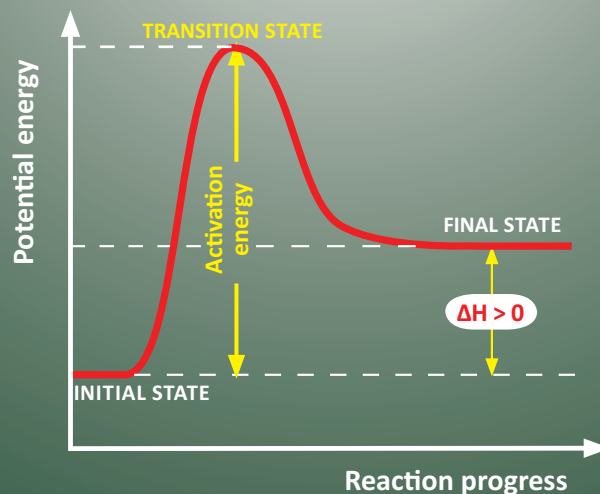
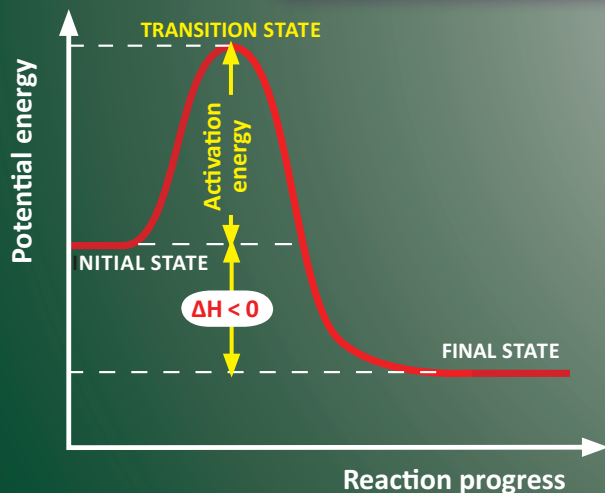
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1

Heat of chemical reactions. Exo- and endothermic reactions

KEY TOPICS

1. Does temperature change when a chemical reaction goes on?
2. What is heat of a chemical reaction?
3. What chemical reactions are exothermic and what – endothermic?
4. How to denote the amount of heat exchanged during a chemical transformation?



KEY WORDS

- Heat of reaction
- Exothermic reaction
- Endothermic reaction
- Thermochemical equation
- Activation energy

CAN A CHEMICAL REACTION BE A „GENERATOR“ OF ENERGY AS HEAT?

Usually, during chemical reactions energy (as heat and/or light) is liberated or absorbed. Temperature changes accompanying chemical reactions can be measured. This makes it possible to determine the amount of evolved or absorbed heat. **THERMOCHEMISTRY** is the science studying the heat effects of chemical reactions. The basic quantity is the **heat of reaction** (also named **enthalpy change** of a reaction if the pressure remains constant). It is denoted by ΔH . It strongly depends on the reaction conditions (temperature and either pressure or volume). The SI unit of the heat of reactions is joule **J**.

HEAT OF REACTION (ENTHALPY CHANGE) ΔH is the amount of heat released or absorbed during a chemical reaction undergoing at constant temperature and at either constant pressure or volume.

When **heat is released (lost)**, $\Delta H < 0$.

When **heat is absorbed (gained)**, $\Delta H > 0$.

The amount of heat evolved or absorbed during a chemical reaction depends on the quantity of reactants. (If only two logs burn in the fireplace the temperature in the room might be too low and to assure a pleasant comfort more logs must be burnt.) For this reason, heat of reactions usually refers to the same amount of reactants and products as in the balanced chemical equations of the reactions*. Most often heats of reactions refer to 25 °C and 10⁵ Pa. Heats of reactions at these conditions are denoted as ΔH^0 .

*It is often denoted as ΔH_{rxn}

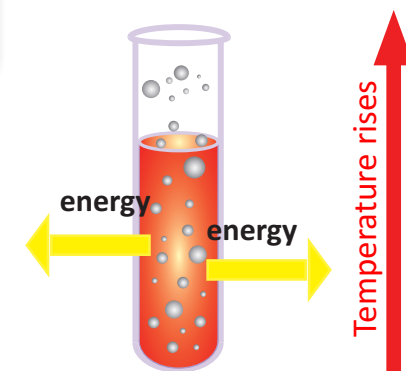
Depending on the heat effects (positive or negative) chemical reactions are classified as **exothermic** and **endothermic**.

EXOTHERMIC REACTIONS are chemical reactions that generate heat.
The temperature of the surrounding increases. $\Delta H < 0$

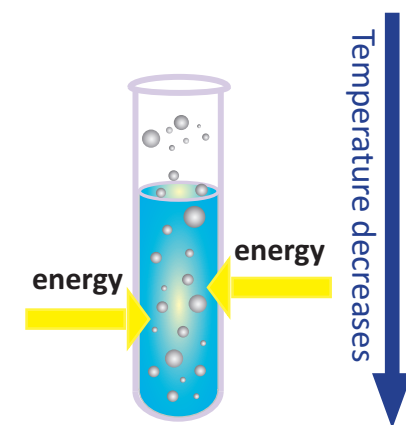
Well known exothermic reactions are respiration, combustion, neutralization, slaking of lime. Some exothermic reactions release a great amount of heat into the surrounding over a very short time and they can be explosive. For example, methane CH_4 mixed with pure oxygen O_2 or air is highly explosive. Spark or direct flame can initiate a vigorous reaction and the mixture can explode. At high pressure ethyne C_2H_2 decomposes into hydrogen and carbon releasing a great amount of heat and it can explode too.

ENDOTHERMIC REACTIONS are chemical reactions that absorb energy.
The temperature of the surrounding decreases. $\Delta H > 0$

Endothermic reactions are thermal decompositions, photosynthesis, cracking of alkanes, the reaction of ethanoic acid CH_3COOH with disodium carbonate Na_2CO_3 , the synthesis of nitrogen oxide NO from nitrogen N_2 and oxygen O_2 .

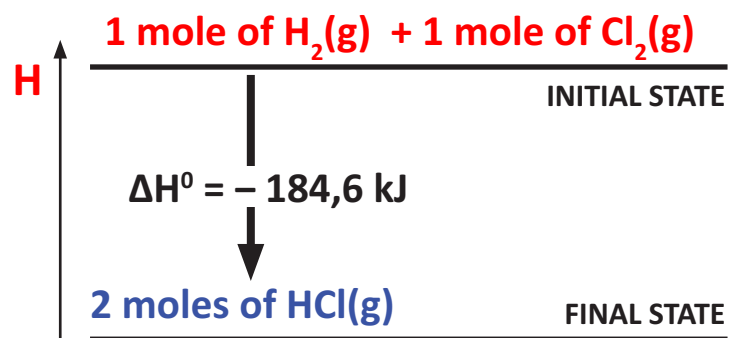


EXOTHERMIC REACTION
 $\Delta H < 0$



ENDOTHERMIC REACTION
 $\Delta H > 0$

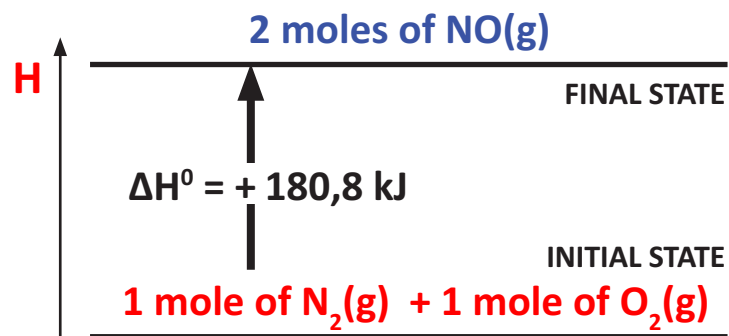
Thermochemistry uses **thermochemical equations** – the amount of energy lost or gained as heat is denoted after the chemical equation of the reaction. The physical states of reactants and products is always indicated. The abbreviations (s) is used for substances in solid state, (l) – for substances in liquid state, (g) – for substances in gaseous state, (aq) – for aqueous solutions of substances. It is important to indicate the state of reactants and products as additional energy is absorbed or released during phase transitions (solid-liquid, gas-liquid, etc.) as well as during physical processes as dissolution, dissociation, etc. For example:



EXOTHERMIC REACTION



The reaction of synthesis of hydrogen chloride HCl an **exothermic reaction** – heat is evolved. The graph to the left shows that energy is lost into the surrounding.



ENDOTHERMIC REACTION



The reaction of synthesis of nitrogen oxide NO is an **endothermic reaction** – heat is absorbed. The graph to the left shows that energy is gained from the surrounding.

The heat of a reaction is a very important quantity as it is used to calculate the total amount of heat transferred to the surrounding or absorbed from the surrounding when a chemical process goes on.

PROBLEM!

What is the amount of heat dissipated into the surrounding when 5 moles of sodium base dissolved in water neutralise 5 moles of nitric acid also dissolved in water?
The heat of this reaction is $\Delta H^0 = -57,3 \text{ kJ}$.

SOLUTION: 1. Express the balanced chemical equation of the reaction.



2. Calculate the total amount of heat dissipated into the surrounding.

The thermochemical equation shows that $-57,3 \text{ kJ}$ are dissipated into the surrounding when 1 mole of NaOH reacts with 1 mole of HNO_3 . It is obvious that when 5 moles of water are produced the amount of heat released is 5 times greater than the amount of energy released when 1 mole of water is produced, i.e. $5 \cdot (-57,3) = -286,5 \text{ kJ}$.

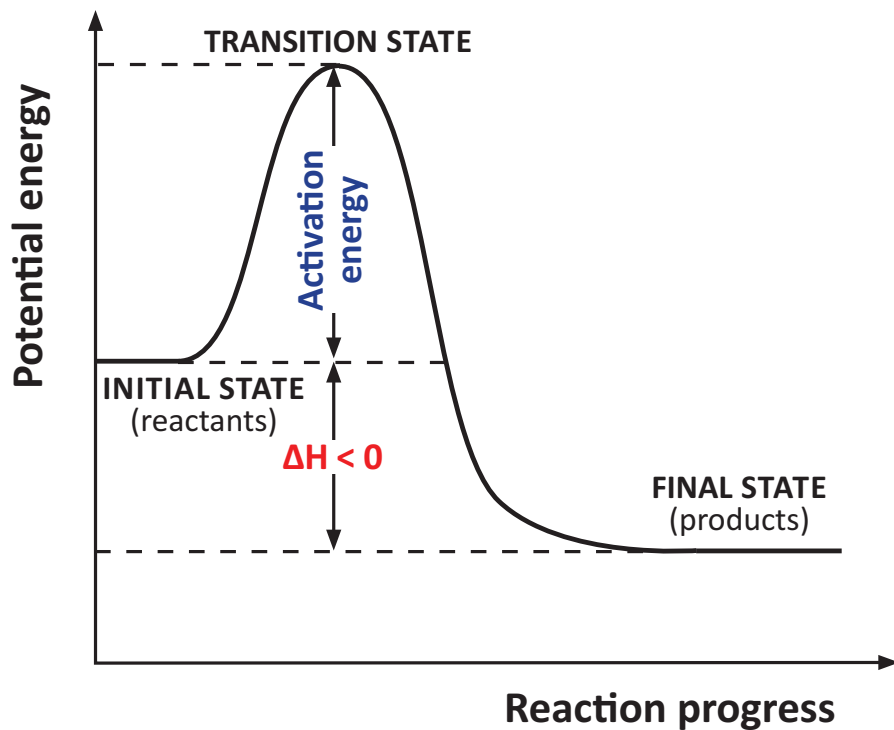
ANSWER: $-286,5 \text{ kJ}$ as heat are dissipated into the surrounding when 5 moles of NaOH neutralise 5 moles of HNO_3 .

WHY DO SOME REACTIONS GENERATE HEAT BUT OTHERS – ABSORB HEAT?

Generally, when a reaction is going on energy is transferred to the surrounding or energy from the surrounding is absorbed, i.e. some energy exchange accompanies chemical transformations. But what does really happen? In chemical transformations chemical bonds of the reacting species break down to „liberate“ atoms or ions that regroup forming the new chemical bonds of the products. Each chemical bond „stores“ potential energy and some amount of energy, called **activation energy**, must be supplied to the reacting species to overcome forces holding atoms (or ions) bonded to one another. A **transition state** of a higher potential energy is achieved – chemical bonds are unstable, they break down and the chemical reaction goes on.

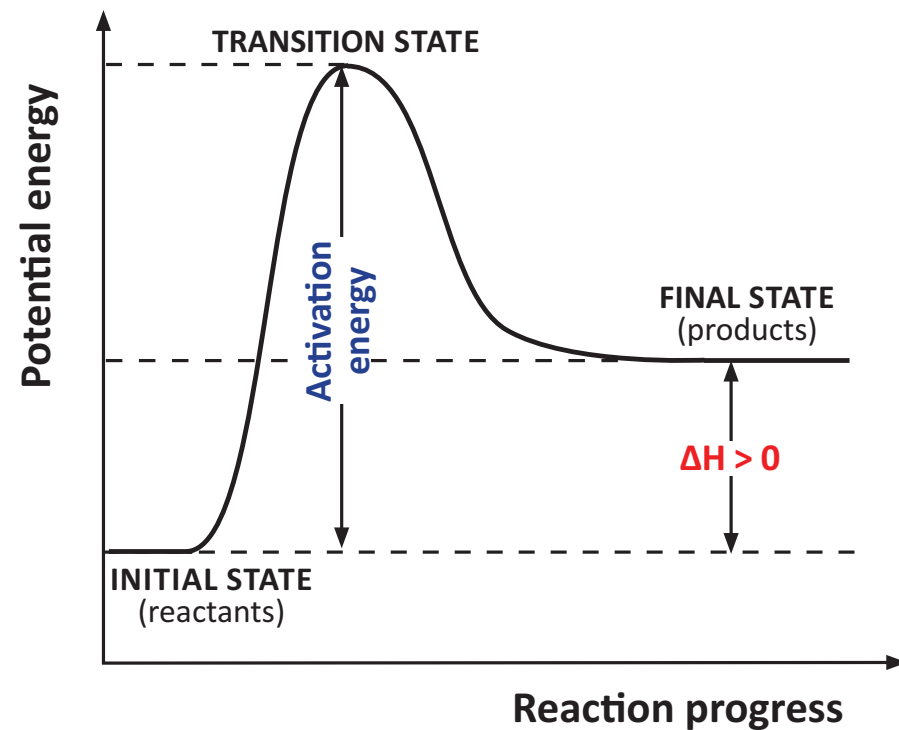
ACTIVATION ENERGY of a reaction is the minimum amount of energy that is required to initiate the chemical transformation.

Owing to the regrouping of atoms (or ions) the potential energy drops down because of the formation of the new stable chemical bonds of the products. If the potential energy of the initial state (the reactants) is high compared to the potential energy of the final state (the products), some amount of energy as heat (also light can be emitted) is transferred to the surrounding and its temperature rises – the reaction is **exothermic**. In contrary, if the potential energy of the initial state is low compared to the potential energy of the final state, some amount of heat from the surrounding is absorbed and its temperature decreases – the reaction is **endothermic**. These energy changes are presented in **energy diagrams**.



Energy is transferred to the surrounding.

Exothermic reaction

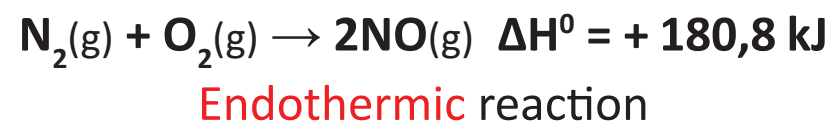
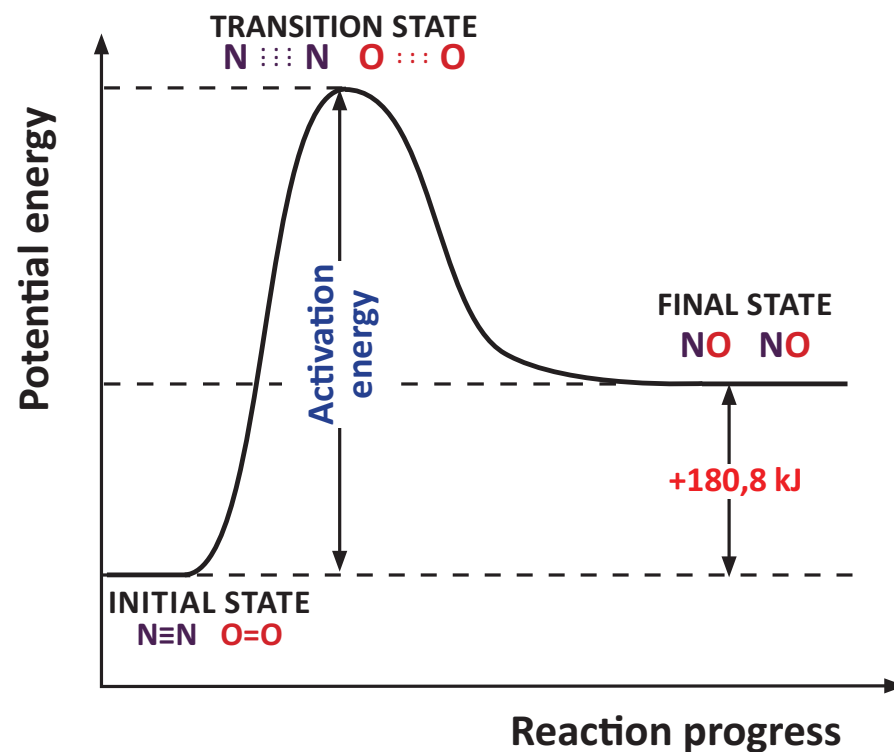
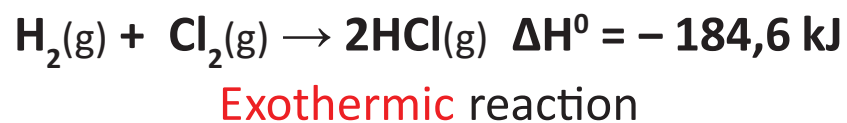
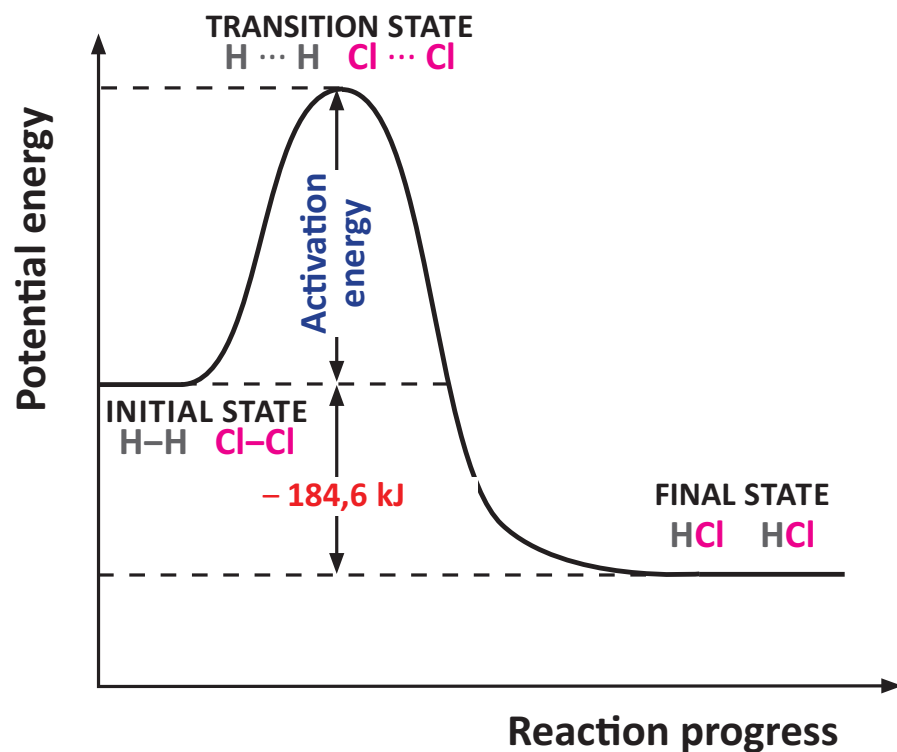


Energy is absorbed from the surrounding.

Endothermic reaction

ENERGY DIAGRAMS

As examples:



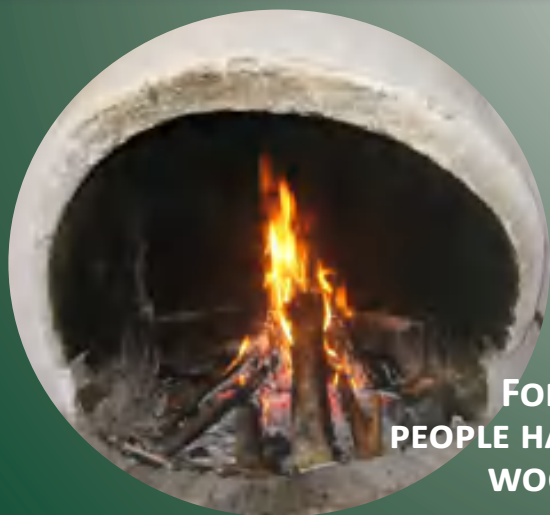
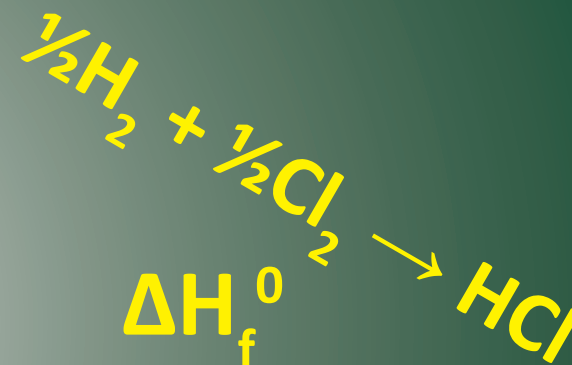
CAN YOU ANSWER THESE QUESTIONS ?

1. What is heat of reaction?
2. What reactions are exothermic and what – endothermic?
3. What is activation energy of a chemical reaction?
4. Why are some chemical reactions exothermic but others – endothermic?
5. How to prove that the reaction of slaking of lime is exothermic?
6. Why can some chemical reactions cause explosions?
7. What is thermochemical equation?
8. Why is it necessary to indicate the state of the reactants and the products in the thermochemical equations?
9. The heat of the neutralisation of $\text{NaOH}_{(\text{aq})}$ and $\text{HNO}_{3(\text{aq})}$ is $-57,3 \text{ kJ/mol}$. The same amount of heat is generated if 1 mole of $\text{NaOH}_{(\text{aq})}$ neutralises 1 mole of $\text{HCl}_{(\text{aq})}$. Why?
10. In a test tube 0,1 moles of $\text{KOH}_{(\text{aq})}$ react with 0,1 moles of $\text{H}_2\text{SO}_{4(\text{aq})}$. In another test tube 0,4 moles of $\text{KOH}_{(\text{aq})}$ react with 0,4 moles of $\text{H}_2\text{SO}_{4(\text{aq})}$? The temperature of which solution is higher?

2 Heat of formation. Heat of combustion Fuels calorific values

KEY TOPICS

1. What does the heat of formation stand for?
2. What does the heat of combustion stand for?
3. What substances are fuels?
4. Why is fuels calorific value their important characteristic?



FOR MILLENNIA
PEOPLE HAVE BEEN BURNING
WOOD TO HEAT.

KEY WORDS

- Formation reaction
- Heat of formation
- Combustion reaction
- Heat of combustion
- Calorific value

WHAT IS HEAT OF FORMATION OF A COMPOUND?

Chemical reactions forming 1 mole of a compound from its constituent elements each of the substances being in its standard state are called **FORMATION REACTIONS**.

The standard state is the most stable physical state of a simple substance or a compound at 10^5 Pa and a specified temperature, most often at 25°C . For example, hydrogen H_2 and chlorine Cl_2 are gases at 25°C and 10^5 Pa. Carbon (the most stable form is graphite) is solid. Carbon dioxide CO_2 is gaseous, sodium chloride NaCl is solid, water H_2O is liquid, etc.

Each compound can be considered as formed in a direct reaction of its constituent elements even such a reaction is not really undergoing. For example, the reaction of formation for glucose is:



Most of the reactions of formation of chemical compounds from their constituent elements are exothermic, some are endothermic. The heat of these reactions is called **standard heat of formation** and is denoted by ΔH_f° .

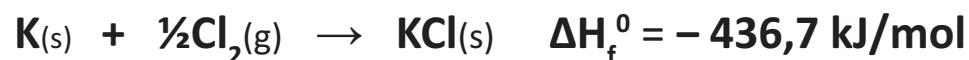
STANDARD HEAT OF FORMATION ΔH_f° of a compound is the amount of heat absorbed or evolved at 25°C and 10^5 Pa when 1 mole of the compound is formed from its constituent elements each of the substances being in its most stable physical state at these conditions.

The standard heat of formation always refers to 1 mole of the compound. Its basic unit is joules per mole, **J/mol**.

Compound	ΔH_f^0 kJ/mol	Compound	ΔH_f^0 kJ/mol	Compound	ΔH_f^0 kJ/mol
H ₂ O (l)	-285,8	NH ₃ (g)	-46,2	NaOH (s)	-425,6
H ₂ O (g)	-241,8	HCl (g)	-92,3	CH ₄ (g)	-74,9
H ₂ SO ₄ (l)	-814	HI (g)	+ 26,5	C ₂ H ₄ (g)	+ 52,5
HNO ₃ (l)	-174,1	NaCl (s)	-411,1	C ₆ H ₆ (l)	+ 48,7
SO ₂ (g)	-296,8	SO ₃ (s)	-395,7	C ₂ H ₅ OH	-277,7

STANDARD HEAT OF FORMATION FOR SOME COMPOUNDS

Standard heats of formation of various chemical compounds can be found in many handbooks. Keep in mind that the value of the heat of formation always refers to 1 mole of the compound. As an idea, the thermochemical equations for the formation reactions of HCl, C₆H₆ and KCl are expressed as:



If the reaction of synthesis of HCl is expressed as $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$, the amount of heat evolved during the interaction of 1 mole of H₂ with 1 mole of Cl₂ is twice as large, i.e. -184,6 kJ.

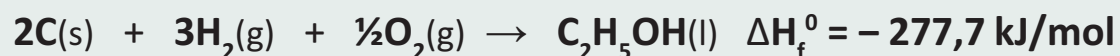
As a rule the standard heat of formation of simple substances is 0 J/mol. When a chemical element has two or more allotropes, one of the forms is considered energetically more stable than the others. Its heat of formation is considered to be 0 J/mol. For example, among the allotropes of carbon ΔH_f^0 of graphite is 0 J/mol. ΔH_f^0 (diamond) is 1,88 kJ/mol.

Heats of formation of chemical compounds are used to calculate heats of chemical reactions. You will become familiar with that matter in the next lesson.

PROBLEM!

At 25°C and 10⁵ Pa ethanol C₂H₅OH is liquid. Express its formation reaction. The heat of formation of ethanol is $\Delta H_f^0(\text{C}_2\text{H}_5\text{OH}) = -277,7 \text{ kJ/mol}$. What is the heat of the reaction if 5 moles of ethanol are formed?

SOLUTION: 1. Express the formation reaction of ethanol.



The heat of formation always refers to 1 mole of the product, i.e. the coefficient before the product is always 1. Some of the other coefficients in the balanced chemical equation are not always integers. In this example the coefficient before oxygen is 1/2.

2. Determine the heat of the reaction of formation of 5 moles of ethanol.

– 277,7 kJ/mol of heat are evolved if 1 mole of ethanol is formed at standard conditions.

The amount of heat evolved during the formation of 5 moles of ethanol is 5 times greater,

i.e.: $\Delta H^0 = n \cdot \Delta H_f^0(\text{C}_2\text{H}_5\text{OH}) = 5 \cdot (-277,7) = -1388,5 \text{ kJ}$.

ANSWER: The heat of the reaction of formation of 5 moles of ethanol C₂H₅OH is –1,4 MJ.

WHAT IS HEAT OF COMBUSTION OF A SUBSTANCE?

Combustion (commonly known also as burning) is one of the most important chemical reactions. Generally, combustion reaction is every chemical reaction generating heat and light (as flame). But more often the term „combustion“ refers to reactions with oxygen (pure or from the air) generating heat and light. Basic quantity is the **heat of combustion ΔH_c** . When the process undergoes upon 25 °C and 10⁵ Pa it is named **standard heat of combustion** and is denoted as **ΔH_c^0** .

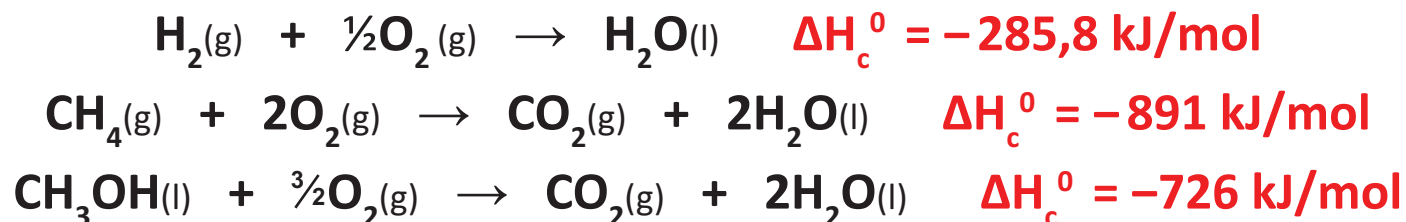
STANDARD HEAT OF COMBUSTION ΔH_c^0 of a substance is the amount of energy liberated when 1 mole of the substance undergoes complete combustion at 25 °C and 10⁵ Pa and with excess oxygen.

Heats of combustion are evaluated in joules per mole of burning compound. The SI unit is **J/mol**.

Typical combustion reactions are, for example, the flame tests of many metals – sodium and its salts burn producing an yellow flame, potassium and its salts turn the flame violet, etc. But the most important combustion reactions are the reactions of organic compounds with oxygen (pure or from the air). Especially, the combustion of fuels – compounds that generate great amounts of heat during their combustion. Fuels are fossil fuels as natural gas, petrol (gasoline), coal but also hydrogen H₂, methanol CH₃OH, ethanol C₂H₅OH and others. The overall equation of the combustion of fuels is:



The chemical products of a combustion reaction of fuels are most often CO_2 (or CO, even C, if the combustion is incomplete) and water vapours. At standard conditions 25°C and 10^5Pa the thermochemical equations of the combustion reactions for hydrogen, methane and methanol are expressed as:



The chemical products of fuels combustion are usually considered as waste (gases evolved into the atmosphere). The most important „product“ of the combustion of fuels is the generated significant amount of energy. It is used for heating, for cooking, in the internal-combustion engines, in explosives, to produce electricity, in rocket propulsion, etc. As a whole, the contemporary civilisation can not function without fuels.

FUEL	ΔH_c^0 kJ/mol	FUEL	ΔH_c^0 kJ/mol
H_2	-285,8	C_4H_{10}	-2874
CH_4	-891	C_8H_{18}	-5470
C_2H_6	-1560	CH_3OH	-726
C_3H_8	-2222	$\text{C}_2\text{H}_5\text{OH}$	-1370

HEAT OF COMBUSTION FOR SOME FUELS

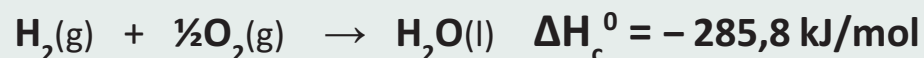
The amount of energy generated during the combustion of a fuel is its important characteristic. The **standard heats of combustion of fuels** are used to assess their quality as sources of energy. Here are values of the heats of combustion for some common fuels.

Pay attention that heats of formation are most often negative but can be positive too as some reactions of formation are endothermic. But heats of combustion are always negative because all reactions of combustion are exothermic reactions generating energy.

PROBLEM!

At 25°C and 10⁵ Pa hydrogen and oxygen are gases. Water is liquid. Express the combustion reaction of hydrogen. What is the amount of heat liberated during the combustion of 5 moles of hydrogen at 25°C and 10⁵ Pa? $\Delta H_c^0(\text{H}_2) = -285,8 \text{ kJ/mol}$

SOLUTION: 1. Express the combustion reaction of hydrogen.



Keep in mind that the heat of combustion always refers to 1 mole of the fuel (in this example this is hydrogen H₂), i.e. the coefficient before it must be always 1. Some of the other coefficients in the balanced chemical equation of combustion are not always integers. In this example the coefficient before oxygen is 1/2.

2. Determine the amount of energy liberated during the combustion of 5 moles of hydrogen.
– 285,8 kJ/mol of heat are evolved if 1 mole of hydrogen burns at 25°C and 10⁵ Pa.
The amount of heat evolved in the combustion of 5 moles of hydrogen is 5 times greater, i.e.:

$$\Delta H^0 = n \cdot \Delta H_c^0(\text{H}_2) = 5 \cdot (-285,8) = -1429 \text{ kJ.}$$

ANSWER: The heat generated during the combustion of 5 moles of H₂ at 25°C and 10⁵ Pa is 1,43 MJ.

In chemistry the heat of combustion always refers to 1 mole of burning compound upon standard conditions. But often it is convenient to compare different fuels using another quantity – their **calorific values**.

CALORIFIC VALUE of a fuel is the amount of heat liberated when 1 kg or 1 m³ of the substance undergoes complete combustion upon standard conditions and with excess oxygen.

For example:

COMMERCIAL FUEL	CALORIFIC VALUE MJ/kg	COMMERCIAL FUEL	CALORIFIC VALUE MJ/kg
Natural gas	54,0	Coal	15,0 - 34,0
Petrol	48,0	Ethanol	29,7
Diesel	44,8	Dry wood	14,4 - 17,4
Fuel oils	43,0 - 48,8	Hydrogen	141,8

The highest is the calorificity of hydrogen H₂ (141,8 MJ/kg). The lowest is the calorificity of wood. The calorific values of gaseous fuels are also estimated in J/m³. For example, the calorificity of hydrogen is 12,7 MJ/m³.

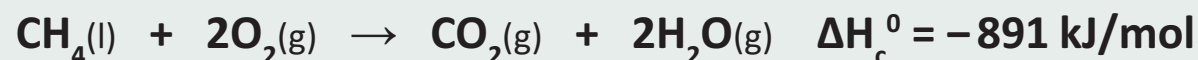
The heat of combustion similarly to the heat of formation of substances can be used to evaluate the heat of chemical reactions.

CAN YOU ANSWER THESE QUESTIONS ?

1. What chemical reactions are formation reactions?
2. Is neutralisation a formation reaction? Why?
3. Is the equation of the formation reaction of NaCl correctly written? Why?



4. What chemical reactions are combustion reactions?
5. What substances are fuels?
6. Is the equation of the combustion reaction of methane at standard conditions correctly written? Why?

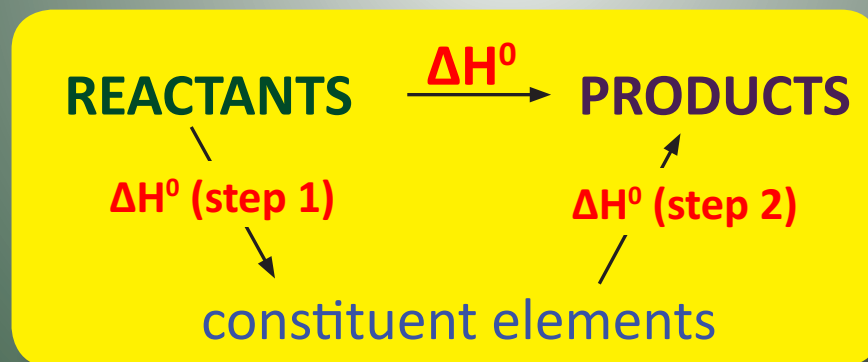


7. The heat of formation of liquid water $\text{H}_2\text{O}(\text{l})$ is identical with the heat of combustion of hydrogen H_2 ? Why?
8. What is the difference between the heat of combustion and the calorific value of a fuel?
9. Which fuel is more calorific – ethanol or petrol?
10. The heat of combustion of ethanol is greater than the heat of combustion of hydrogen. But hydrogen is more calorific than ethanol. Why?

3 Hess's law

KEY TOPICS

1. What does the Hess's law state?
2. How is Hess's law used to determine heats of reactions?
3. How to calculate the heat of a reaction using the heats of formation of the reaction components?
4. How to calculate the heat of a reaction using the heats of combustion of the reaction components?



KEY WORDS

- Hess's law

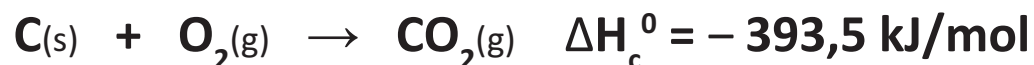
$$\Delta H^0 = \Delta H^0(\text{step 1}) + \Delta H^0(\text{step 2})$$

WHAT DOES THE LAW OF CONSERVATION OF ENERGY HAVE TO DO WITH CHEMICAL REACTIONS?

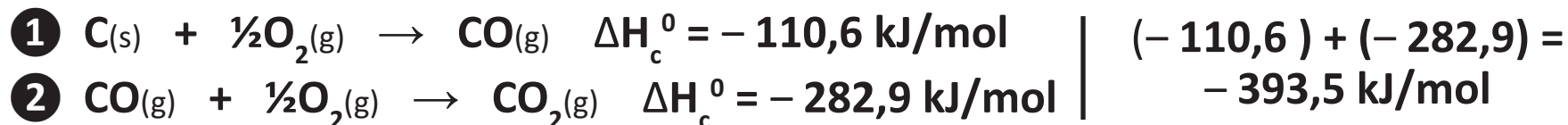
The law of conservation of energy applies to every process in the Universe. It applies to all chemical transformations too. When a chemical process is going on the energy, as a whole, can not be lost or gained. If some amount of energy is lost by the reacting system, the same amount of energy is gained by the surrounding. The energy change of the reacting system depends only on its initial and final states no matter how the chemical transformation undergoes. This empirical fact is the basis of the Hess's* law:

The heat absorbed or generated in a chemical reaction is independent of the route of the reaction but is determined only by the type and the state of the reactants and the products.

In other words the heat of a reaction is the same whether the transformation undergoes in one step or in many successive steps. That will become clearer with the help of a simple example. Carbon burns transforming into carbon dioxide:



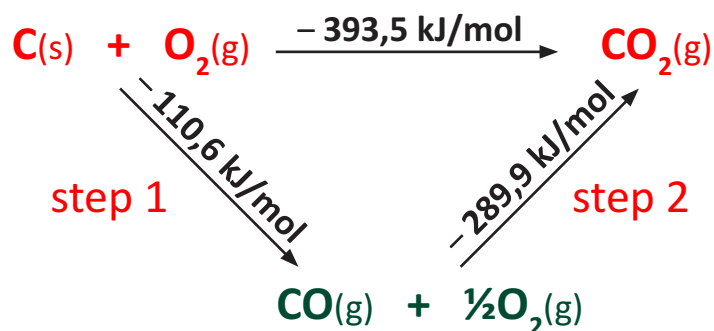
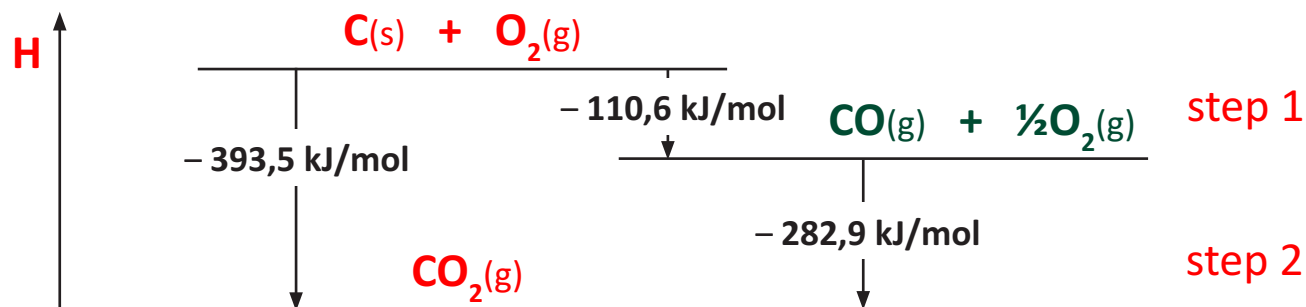
But this transformation can undergo in two steps. First CO is formed and it transforms into CO₂:



The heat of the overall reaction of transformation of C into CO₂ is equal to the sum of the heats of the two successive reactions of transformation of C into CO and after that – into CO₂.

*Germain Henri Hess has formulated the law in 1840.

The successive steps of a chemical transformation are presented with the help of simple graphs. For the example above Hess's law can be illustrated with each one of the diagrams shown below.

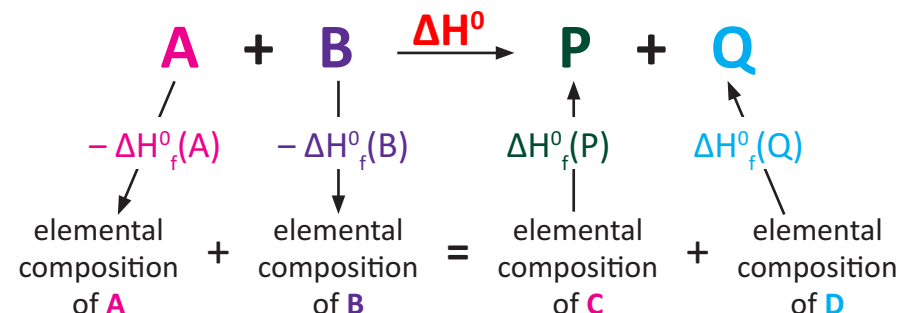


The heat of a reaction is equal to the sum of the heats of its successive steps.

$$\Delta H(\text{reaction}) = \Delta H(\text{step 1}) + \Delta H(\text{step 2}) + \Delta H(\text{step 3}) + \dots$$

HOW TO CALCULATE ΔH° USING ΔH_f° OF REACTION COMPONENTS?

The Hess's law makes it possible to calculate the standard heat of any reaction if the standard heats of formation of the reactants and the products are known. It is easy to understand that following the scheme to the right. Consider the chemical reaction $A + B \rightarrow P + Q$. Reactants **A** and **B** and the products **P** and **Q** can be formed from their constituent elements. The standard heats of formation are $\Delta H_f^\circ(A)$, $\Delta H_f^\circ(B)$, $\Delta H_f^\circ(P)$ and $\Delta H_f^\circ(Q)$. The Hess's law suggests that instead of the direct transformation of **A** and **B** into **P** and **Q** a 2-step transformation can be considered.



STEP 1 – decomposition of **A and **B** into their constituent elements**

$$\Delta H^\circ(\text{step 1}) = -(\Delta H_f^\circ(A) + \Delta H_f^\circ(B))$$

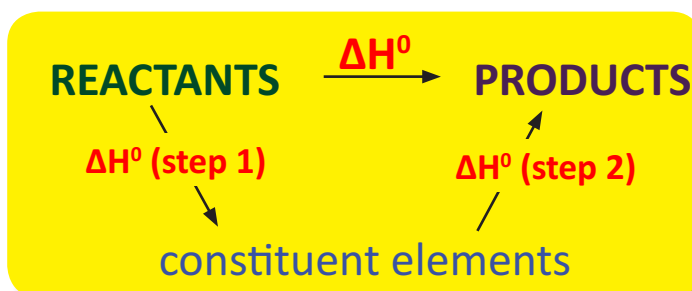
The sign „–“ is used as the reactions of decomposition are the opposite of the formation reactions.

STEP 2 – formation of **P and **Q** from their constituent elements**

$$\Delta H^\circ(\text{step 2}) = \Delta H_f^\circ(P) + \Delta H_f^\circ(Q)$$

The elemental composition of the reactants and the products is the same as the atoms or the ions of the reactants regroup to form the products. As a whole:

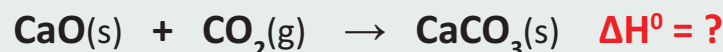
$$\Delta H^\circ = \Delta H^\circ(\text{step 1}) + \Delta H^\circ(\text{step 2}) = -\Delta H_f^\circ(A) - \Delta H_f^\circ(B) + \Delta H_f^\circ(P) + \Delta H_f^\circ(Q)$$



PROBLEM!

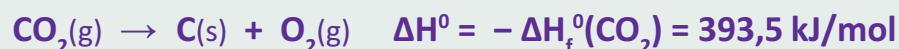
Determine the standard heat of the reaction of carbonation of calcium oxide CaO. The standard heats of formation of the reactants are: $\Delta H_f^\circ(\text{CaO}) = -635,1 \text{ kJ/mol}$; $\Delta H_f^\circ(\text{CO}_2) = -393,5 \text{ kJ/mol}$; $\Delta H_f^\circ(\text{CaCO}_3) = -1207,0 \text{ kJ/mol}$;

SOLUTION: 1. Express the thermochemical equation of the reaction of carbonation of CaO.



2. Suppose that the reaction is going on in two stages.

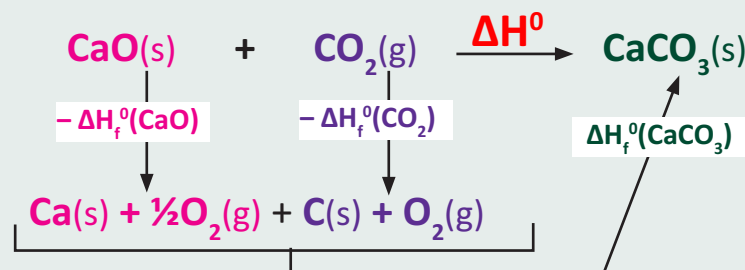
① Decomposition of reactants into their constituent elements.



② Formation of the reaction product.



3. Draw a graph of the two stage process.



4. Calculate the standard heat of the reaction ΔH° .

$$\Delta H^\circ = -\Delta H_f^\circ(\text{CaO}) - \Delta H_f^\circ(\text{CO}_2) + \Delta H_f^\circ(\text{CaCO}_3) = 635,1 + 393,5 - 1207,0 = -178,4 \text{ kJ}$$

ANSWER: The reaction of carbonation of CaO is exothermic $\Delta H^\circ = -178,4 \text{ kJ}$. During the formation of 1 mole of solid CaCO_3 178,4 kJ of energy as heat are liberated.

As a rule ΔH^0 of a reaction is equal to the sum of the standard heats of formation of the products minus the sum of the standard heats of formation of the reactants:

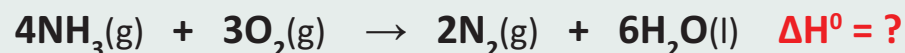
$$\Delta H^0 = \text{sum of } \Delta H_f^0(\text{products}) - \text{sum of } \Delta H_f^0(\text{reactants})$$

If in the balanced chemical equation the coefficient before a component of the reaction is not 1, the value of its standard heat of formation has to be multiplied by the value of the coefficient.

PROBLEM!

Ammonia NH_3 reacts with oxygen producing nitrogen N_2 and water. Determine the standard heat of the reaction. ($\Delta H_f^0(\text{NH}_3) = -46,1 \text{ kJ/mol}$ and $\Delta H_f^0(\text{H}_2\text{O(l)}) = -285,8 \text{ kJ/mol}$)

SOLUTION: 1. Express the thermochemical equation of the reaction.



2. Calculate the standard heat of the reaction.

$$\begin{aligned} \Delta H^0 &= [2 \cdot \Delta H_f^0(\text{N}_2) + 6 \cdot \Delta H_f^0(\text{H}_2\text{O})] - [4 \cdot \Delta H_f^0(\text{NH}_3) + 3 \cdot \Delta H_f^0(\text{O}_2)] = \\ &= [2 \cdot 0 + 6 \cdot (-285,8)] - [4 \cdot (-46,1) + 3 \cdot 0] = -1714,8 - (-184,4) = -1530,4 \text{ J} \end{aligned}$$

ANSWER: This is an exothermic reaction. The standard heat of the reaction is $\Delta H^0 = -1530,4 \text{ J}$. When 4 moles of NH_3 react with oxygen at 25°C and 10^5 Pa 1,53 MJ of heat go into the surrounding.

HOW TO CALCULATE ΔH° USING ΔH_c° OF REACTANTS?

Heat of chemical reactions can be calculated using the heats of combustion of the reactants and the products. Hess's law is applied. As a rule: $\Delta H^\circ = \text{sum of } \Delta H_c^\circ(\text{reactants}) - \text{sum of } \Delta H_c^\circ(\text{products})$

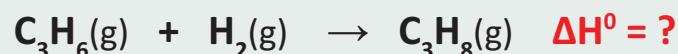
PROBLEM!

Determine the standard heat of the reaction of hydrogenation of propene C_3H_6 .

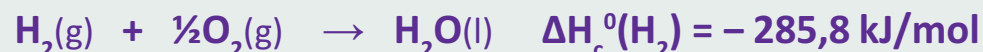
The standard heats of combustion of the reactants and the product are:

$$\Delta H_c^\circ(\text{C}_3\text{H}_6) = -2058 \text{ kJ/mol}; \quad \Delta H_c^\circ(\text{H}_2) = -285,8 \text{ kJ/mol}; \quad \Delta H_c^\circ(\text{C}_3\text{H}_8) = -2222 \text{ kJ/mol}$$

SOLUTION: 1. Express the thermochemical equation of the reaction.



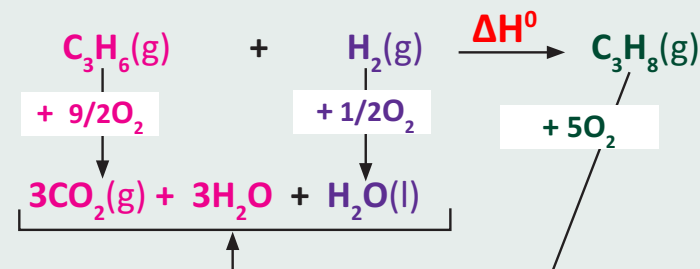
2. Express the thermochemical equations of the combustion reactions for C_3H_6 , H_2 and C_3H_8 .



3. Draw a graph of the process.

4. Calculate the standard heat of the reaction ΔH° .

$$\begin{aligned} \Delta H^\circ &= [\Delta H_c^\circ(\text{C}_3\text{H}_6) + \Delta H_c^\circ(\text{H}_2)] - \Delta H_c^\circ(\text{C}_3\text{H}_8) = \\ &= [-2058 - 285,8] - [-2222] = -121,8 \text{ kJ} \end{aligned}$$



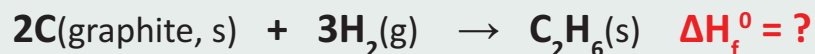
ANSWER: This is an exothermic reaction $\Delta H^\circ = -121,8 \text{ kJ}$. During the hydrogenation of 1 mole of propene 121,8 kJ of energy as heat is evolved into the surrounding.

Standard heats of combustion are used to determine the standard heats of formation of organic compounds as many of the reactions of formation of these compounds are very slow or practically do not undergo.

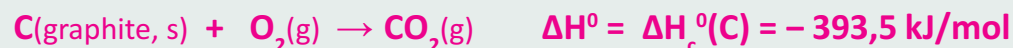
PROBLEM!

The standard heat of combustion of ethane is $\Delta H_c^\circ(\text{C}_2\text{H}_6) = -1560 \text{ kJ/mol}$. Determine its standard heat of formation. The standard heats of combustion of carbon and hydrogen are $\Delta H_c^\circ(\text{C}) = -393,5 \text{ kJ/mol}$; $\Delta H_c^\circ(\text{H}_2) = -285,8 \text{ kJ/mol}$;

SOLUTION: 1. Express the thermochemical equation of the reaction of formation of ethene C_2H_6 .



2. Express the thermochemical equations of the combustion reactions for C, H_2 and C_2H_6 .

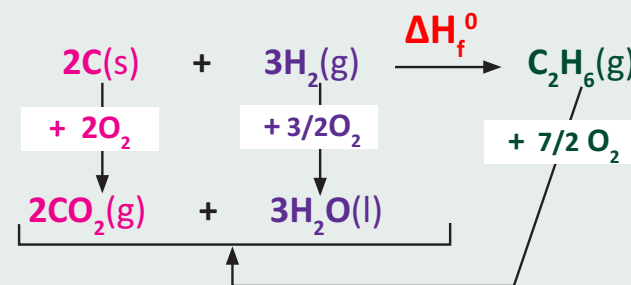


3. Draw a graph of the processes.

4. Calculate the standard heat of the reaction ΔH_f° .

$$\begin{aligned} \Delta H_f^\circ &= [2.\Delta H_c^\circ(\text{C}) + 3.\Delta H_c^\circ(\text{H}_2)] - \Delta H_c^\circ(\text{C}_2\text{H}_6) = \\ &= [2.(-393,5) + 3.(-285,8)] - (-1560) = -84,4 \text{ kJ/mol} \end{aligned}$$

ANSWER: When 1 mole of C_2H_6 is formed upon standard conditions, 84,4 kJ of energy as heat are evolved.



CAN YOU ANSWER THESE QUESTIONS ?

1. What does the Hess's law state?
2. A react with B, yielding C. The standard heat of the reaction is ΔH^0 . Suppose that the process undergoes in two steps. The standard heats of the successive reactions are $\Delta H^0(\text{step 1})$ and $\Delta H^0(\text{step 2})$. Which of the following equations is correct? Why?
 - a) $\Delta H^0 = \Delta H^0(\text{step 1}) - \Delta H^0(\text{step 2})$
 - b) $\Delta H^0 = \Delta H^0(\text{step 1}) + \Delta H^0(\text{step 2})$
 - c) $\Delta H^0 > [\Delta H^0(\text{step 1}) + \Delta H^0(\text{step 2})]$
 - d) $\Delta H^0 < [\Delta H^0(\text{step 1}) + \Delta H^0(\text{step 2})]$
3. Green plants transform carbon dioxide and water into glucose releasing oxygen. How to calculate the standard heat of this reaction?
4. The formation reaction for methane is $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$. This is a very, very slow interaction and it is impossible to measure experimentally the heat evolved or absorbed at 25 °C and 10⁵ Pa when carbon reacts with hydrogen to produce methane. How to determine the standard heat of formation of CH₄?

ENERGY CHANGES DURING CHEMICAL REACTIONS – KEY POINTS

- **HEAT OF REACTION ΔH** is the amount of heat evolved or absorbed during a chemical reaction undergoing at constant temperature and at either constant pressure or volume. It is evaluated in joules J.
- **EXOTHERMIC REACTIONS** generate heat. The temperature of the surrounding increases. The reacting system loses energy and $\Delta H < 0$.
- **ENDOTHERMIC REACTIONS** absorb energy. The temperature of the surrounding decreases. The reacting system gains energy and $\Delta H > 0$.
- **ACTIVATION ENERGY** of a reaction is the minimum amount of energy required to initiate the chemical transformation.
- **THERMOCHEMICAL EQUATIONS** are balanced chemical equations. The heat of reactions and the physical states of the reactants and the products are always indicated.
- **STANDARD HEAT OF A REACTION ΔH^0** is the heat of the reaction at standard temperature and standard pressure (25° C and 10⁵ Pa).

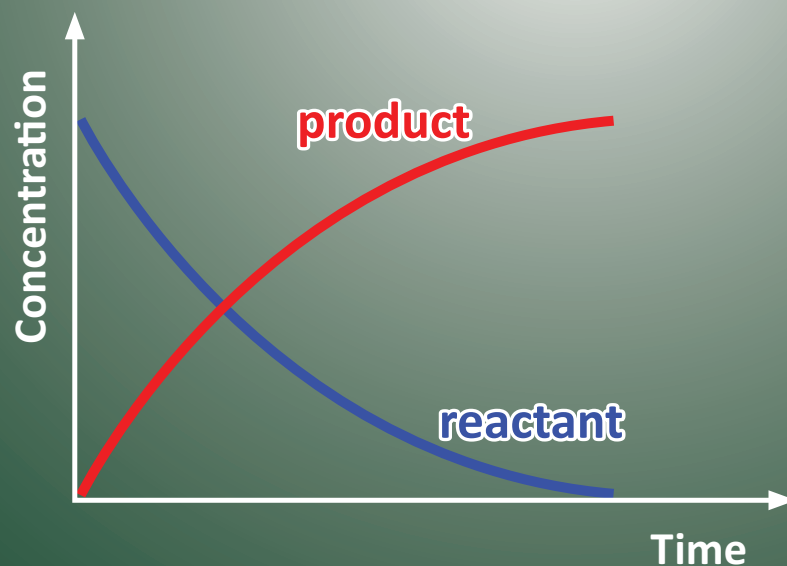
- **STANDARD HEAT OF FORMATION ΔH_f^0** is the amount of heat absorbed or evolved at 25 °C and 10⁵ Pa when 1 mole of the compound is formed from its constituent elements each of the substances being into its normal physical state.
- **STANDARD HEAT OF COMBUSTION ΔH_c^0** of a substance is the amount of energy liberated when 1 mole of the substance undergoes complete combustion at 25 °C and 10⁵ Pa and with excess oxygen.
- **CALORIFIC VALUE** of a fuel is the amount of heat liberated when 1 kg or 1 m³ of the substance undergoes complete combustion upon standard conditions (25 °C and 10⁵ Pa) and with excess oxygen.
- **HESS'S LAW** – the heat absorbed or generated in a chemical reaction is independent of the route of the reaction but is determined only by the type and the state of the reactants and the products.
- Standard heats of reactions ΔH^0 can be calculated using the standard heats of formation ΔH_f^0 or the standard heats of combustion ΔH_c^0 of reactants and products.

4

Rate of chemical reactions

KEY TOPICS

1. Are all chemical reactions instantaneous?
2. How to evaluate the „speed“ of chemical processes?
3. Are rates of disappearance of reactants and rates of appearance of products identical?
4. Do rates of chemical reactions change over time?



KEY WORDS

- Rate of reactions
- Instantaneous reactions
- Fast reactions
- Slow reactions

HOW TO EVALUATE THE „SPEED“ OF CHEMICAL REACTIONS?



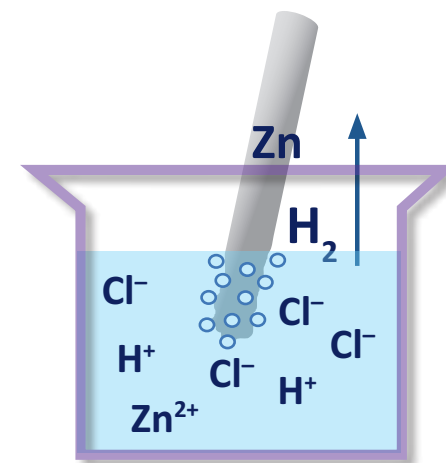
EXPLOSION IS AN INSTANTANEOUS PROCESS

Some chemical reactions are instantaneous. Such are explosions. The neutralisation of an acid with a base also undergoes instantaneously as H^+ ions combine immediately with OH^- forming water molecules H_2O . Other reactions are just fast – products are formed over a short period of time. For example, the reaction of solid zinc Zn with hydrochloric acid $\text{HCl}(\text{aq})$ is a fast reaction – bubbles of hydrogen H_2 rise up in the

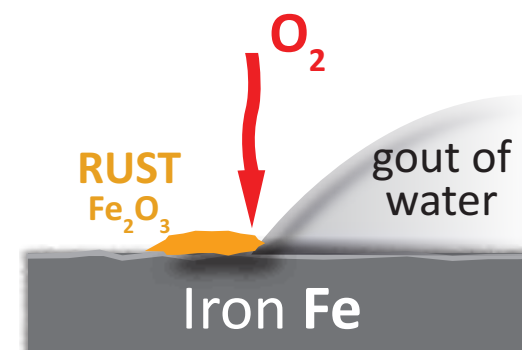
solution and the zinc piece quickly disappears. Corrosion of metals is a slow process – during years metals slowly transform into their oxides forming layers of rust. But some processes are so slow that they seem to not undergo. For example, fossil fuels have been formed over millions of years and they are nonrenewable energy resources.

In chemistry the quantity **rate of reaction** is used to assess the „speed“ of chemical transformations. It is denoted by „ v “.

RATE OF A CHEMICAL REACTION is the change in concentration of a reactant or a product over the change in time.

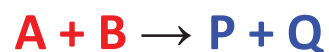


THE REACTION OF Zn WITH $\text{HCl}(\text{aq})$ IS A FAST REACTION.



CORROSION OF METALS IS A SLOW PROCESS.

For example, substances A and B react, yielding substances P and Q:



Data about the change in concentrations of A and B during the first 10 seconds of the reaction are shown in the table.

Time, s	0	10
$c(\text{A})$, mol/l	0,5	0,4
$c(\text{P})$, mol/l	0	0,1

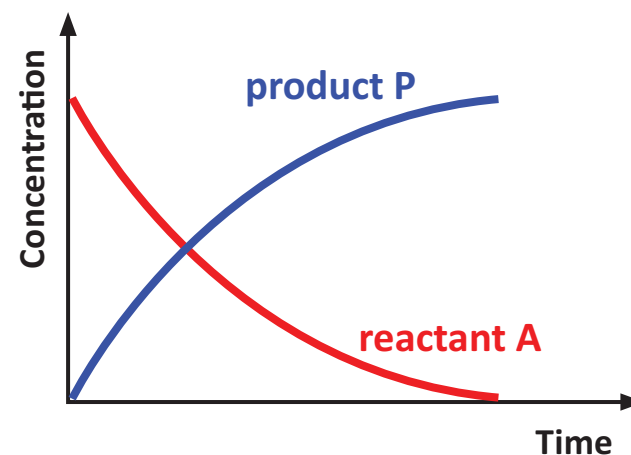
The average rate of disappearance of reactant **A** over the first 10 seconds of the reaction is:

$$\bar{v}(\text{A}) = -\frac{0,4 - 0,5}{10} = 0,01 \text{ mol.l}^{-1}.\text{s}^{-1}$$

The sign „–“ is used as the concentration of reactants always decreases as the reaction goes on.

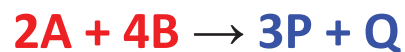
Similarly, the reaction rate can be evaluated from the increase of the concentration of a product. For example, the rate of appearance of **P** is:

$$\bar{v}(\text{P}) = \frac{0,1 - 0}{10} = 0,01 \text{ mol.l}^{-1}.\text{s}^{-1}$$



CHANGE IN CONCENTRATIONS
OF A REACTANT AND A PRODUCT
OF A CHEMICAL REACTION OVER TIME

Most often the coefficients in the balanced chemical equation of the reactions are not 1. For example:



The rates of consumption of reactants and formation of products are not identical. Look at the data in the table. At the beginning of the reaction the concentration of both A and B is 0,5 mol/l. The average rates of disappearance of **A** and **B** are:

Time, s	0	10
$c(\text{A}), \text{mol/l}$	0,5	0,4
$c(\text{B}), \text{mol/l}$	0,5	0,3
$c(\text{P}), \text{mol/l}$	0	0,15
$c(\text{Q}), \text{mol/l}$	0	0,05

$$\bar{v}(\text{A}) = - \frac{0,4 - 0,5}{10} = 0,01 \text{ mol.l}^{-1}.\text{s}^{-1}$$

$$\bar{v}(\text{B}) = - \frac{0,3 - 0,5}{10} = 0,02 \text{ mol.l}^{-1}.\text{s}^{-1}$$

The rates of appearance of **P** and **Q** are:

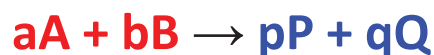
$$\bar{v}(\text{P}) = \frac{0,15 - 0}{10} = 0,015 \text{ mol.l}^{-1}.\text{s}^{-1}$$

$$\bar{v}(\text{Q}) = \frac{0,05 - 0}{10} = 0,005 \text{ mol.l}^{-1}.\text{s}^{-1}$$

These values would be identical if divided by the coefficients in the balanced chemical equation. The average reaction rate over the first 10 seconds is expressed as:

$$\begin{aligned} \bar{v} &= \frac{1}{2} \bar{v}(\text{A}) = \frac{1}{4} \bar{v}(\text{B}) = \frac{1}{3} \bar{v}(\text{P}) = \frac{1}{1} \bar{v}(\text{Q}) = \\ &= \frac{1}{2} \cdot 0,01 = \frac{1}{4} \cdot 0,02 = \frac{1}{3} \cdot 0,015 = \frac{1}{1} \cdot 0,005 = 0,005 \text{ mol.l}^{-1}.\text{s}^{-1} \end{aligned}$$

In general, the average rate of the reaction



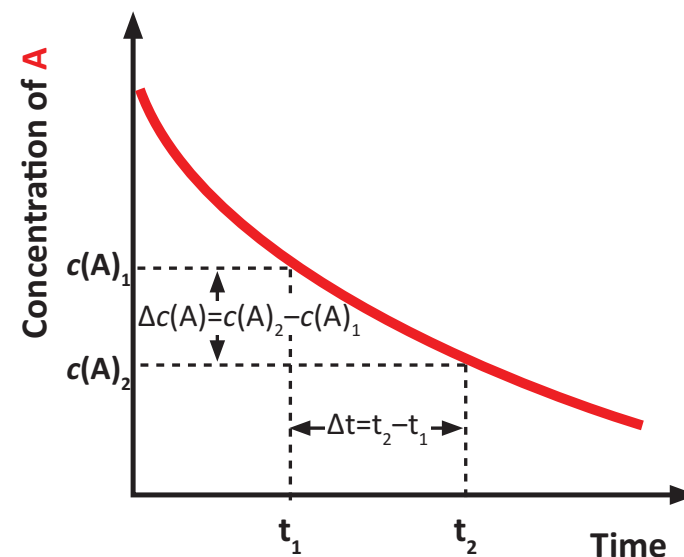
is expressed as:

$$\bar{v} = -\frac{1}{a} \cdot \frac{\Delta c(A)}{\Delta t} = -\frac{1}{b} \cdot \frac{\Delta c(B)}{\Delta t} = \frac{1}{p} \cdot \frac{\Delta c(P)}{\Delta t} = \frac{1}{q} \cdot \frac{\Delta c(Q)}{\Delta t}$$

The symbol „ Δ “ (delta) is used to express the difference between the final and initial values of a parameter:

$$\Delta t = t_2 - t_1$$

$$\Delta c(A) = c(A)_2 - c(A)_1 = \text{concentration of A at time } t_2 - \text{concentration of A at time } t_1$$



CHANGE IN CONCENTRATION
OF REACTANT **A** OVER TIME

For example, the average rate of the reaction of synthesis of ammonia $3H_2 + N_2 \rightleftharpoons 2NH_3$ at constant temperature and volume over the time interval Δt is expressed as:

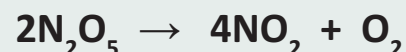
$$\bar{v} = -\frac{1}{3} \cdot \frac{\Delta c(H_2)}{\Delta t} = -\frac{1}{1} \cdot \frac{\Delta c(N_2)}{\Delta t} = \frac{1}{2} \cdot \frac{\Delta c(NH_3)}{\Delta t}$$

PROBLEM!

At standard conditions N_2O_5 is a white solid but at 47°C it sublimates. The products of its thermal decomposition are the highly toxic brown-reddish gas NO_2 (used to produce nitric acid HNO_3) and O_2 . A lab report presents data about the change in concentrations of N_2O_5 , NO_2 and O_2 over time at a given temperature and volume. How does the reaction rate change over time?

Time s	$c(\text{N}_2\text{O}_5)$ mol/l	$c(\text{NO}_2)$ mol/l	$c(\text{O}_2)$ mol/l
0	0,0400	0	0
100	0,0336	0,0128	0,00320
200	0,0283	0,0234	0,00585

SOLUTION: 1. Express the balanced chemical equation of the reaction of decomposition of N_2O_5 .



2. Calculate the average rate of the reaction during the first 100 seconds of decomposition.

$$\bar{v} = -\frac{1}{2} \cdot \frac{\Delta c(\text{N}_2\text{O}_5)}{\Delta t} = -\frac{1}{2} \cdot \frac{0,0336 - 0,0400}{100 - 0} = -\frac{1}{2} \cdot \frac{(-0,0064)}{100} = 3,2 \cdot 10^{-5} \text{ mol.l}^{-1}.\text{s}^{-1}$$

$$\bar{v} = \frac{1}{4} \cdot \frac{\Delta c(\text{NO}_2)}{\Delta t} = \frac{1}{4} \cdot \frac{0,0128 - 0}{100 - 0} = \frac{1}{4} \cdot \frac{0,0128}{100} = 3,2 \cdot 10^{-5} \text{ mol.l}^{-1}.\text{s}^{-1}$$

$$\bar{v} = \frac{1}{1} \cdot \frac{\Delta c(\text{O}_2)}{\Delta t} = \frac{1}{1} \cdot \frac{0,0032 - 0}{100 - 0} = \frac{1}{1} \cdot \frac{0,0032}{100} = 3,2 \cdot 10^{-5} \text{ mol.l}^{-1}.\text{s}^{-1}$$

3. Calculate the average rate of the reaction over the time interval from $t_1 = 100$ s to $t_2 = 200$ s.

$$\bar{v} = -\frac{1}{2} \cdot \frac{\Delta c(\text{N}_2\text{O}_5)}{\Delta t} = -\frac{1}{2} \cdot \frac{0,0283 - 0,0336}{200 - 100} = -\frac{1}{2} \cdot \frac{(-0,0053)}{100} = 2,65 \cdot 10^{-5} \text{ mol.l}^{-1}.\text{s}^{-1}$$

$$\bar{v} = \frac{1}{4} \cdot \frac{\Delta c(\text{NO}_2)}{\Delta t} = \frac{1}{4} \cdot \frac{0,0234 - 0,0128}{200 - 100} = \frac{1}{4} \cdot \frac{0,0106}{100} = 2,65 \cdot 10^{-5} \text{ mol.l}^{-1}.\text{s}^{-1}$$

$$\bar{v} = \frac{1}{1} \cdot \frac{\Delta c(\text{O}_2)}{\Delta t} = \frac{1}{1} \cdot \frac{0,00585 - 0,0032}{200 - 100} = \frac{1}{1} \cdot \frac{0,00265}{100} = 2,65 \cdot 10^{-5} \text{ mol.l}^{-1}.\text{s}^{-1}$$

ANSWER: The reaction slows down over time.

CAN YOU ANSWER THESE QUESTIONS ?

1. What is reaction rate?
2. Why is it necessary to determine reactions rates?
3. 3 moles of A react with 1 moles of B to produce 2 moles of C. How to express the rate of the reaction?
4. Consider the reaction of formation of hydrogen iodide $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$. Is it correct to express the average reaction rate as $\mathbf{v} = -\frac{\Delta c(\text{H}_2)}{\Delta t} = -\frac{\Delta c(\text{I}_2)}{\Delta t} = \frac{\Delta c(\text{HI})}{\Delta t}$? Why?
5. Hydrogen peroxide H_2O_2 decomposes into water and oxygen. Express the rate of disappearance of H_2O_2 and the rates of appearance of each of the products.
6. In general, reactions rate changes over time. Can you explain that?

5

Effect of reactants concentration on reaction rate. Rate law

KEY TOPICS

1. Why does reactants concentration affect reaction rate?
2. What does the rate law state?
3. Why to break to pieces solid blocks reacting with liquid or gaseous substances?



$$v = k.c(A)^{\alpha}.c(B)^{\beta}$$

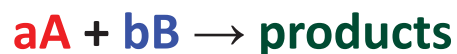
KEY WORDS

- Rate law
- Rate constant
- Surface area

DOES REACTION RATE DEPEND ON REACTANTS CONCENTRATION?

Consider the reaction $A + B \rightarrow \text{products}$. This chemical transformation goes on when **A** and **B** collide. The more reacting species in the reaction volume, the more likely the collisions between them and the greater the amount of products.

Generally, the rate of a chemical transformation is proportional to the concentration of reactants raised to some power. For the reaction:

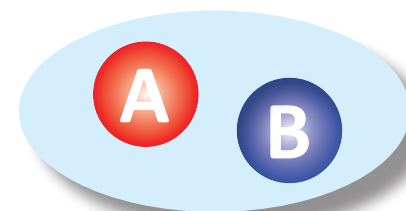


$$v = k \cdot c(A)^\alpha \cdot c(B)^\beta$$

This postulate is known as the **rate law**. It states that:

The rate of chemical reactions is directly proportional to the concentrations of reactants raised to some powers.

The constant of proportionality **k** is called **rate constant**. It does not depend on reactants concentration but it does depend on reaction conditions (temperature, pressure). For example, the rate constant for the reaction of thermal decomposition of N_2O_5 is equal to $4,82 \cdot 10^{-3} \text{ s}^{-1}$ at 64°C and to $1,68 \cdot 10^{-2} \text{ s}^{-1}$ at 83°C . The dimensions of the rate constant depends on the values of the coefficients **α** and **β** . Usually they are not identical with the coefficients **a** and **b** in the balanced chemical equation of the reaction. They are experimentally determined even for simple reactions.



NO REACTION



A COLLISION –
A CAN REACT WITH **B**.

For example, the rate law equation (known also as **rate equation**) for the reaction of synthesis of HBr from H_2 and Br_2 ($\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$) is:

$$v = k \cdot c(\text{H}_2) \cdot c(\text{Br}_2)^{1/2}$$

If the concentration of H_2 increases 4 times the reaction rate is also increased 4 times. But if the concentration of Br_2 increases 4 times the reaction rate is only doubled.

PROBLEM!

Consider the reaction of thermal decomposition of dinitrogen pentoxide $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$. The rate equation for the reaction is $v = k \cdot c(\text{N}_2\text{O}_5)$ and $k = 1,7 \cdot 10^{-3} \text{ s}^{-1}$. The initial concentration of N_2O_5 is 0,04 mol/l. It drops to 0,0336 mol/l after 100 s, to 0,0283 mol/l after 200 s and to 0,02 mol/l after 400 s. What is the initial reaction rate and the reaction rate after 100 s, after 200 s and after 400 s?

SOLUTION: 1. Write down the rate law for the reaction.

$$v = 1,7 \cdot 10^{-3} \cdot c(\text{N}_2\text{O}_5)$$

2. Calculate the reaction rates for the concentrations of N_2O_5 given above.

$$v_{(t=0)} = 1,7 \cdot 10^{-3} \cdot 0,04 = 6,8 \cdot 10^{-5} \text{ mol.l}^{-1} \cdot \text{s}^{-1}$$

$$v_{(t=100 \text{ s})} = 1,7 \cdot 10^{-3} \cdot 0,0336 = 5,7 \cdot 10^{-5} \text{ mol.l}^{-1} \cdot \text{s}^{-1}$$

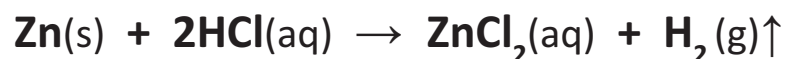
$$v_{(t=200 \text{ s})} = 1,7 \cdot 10^{-3} \cdot 0,0283 = 4,8 \cdot 10^{-5} \text{ mol.l}^{-1} \cdot \text{s}^{-1}$$

$$v_{(t=400 \text{ s})} = 1,7 \cdot 10^{-3} \cdot 0,02 = 3,4 \cdot 10^{-5} \text{ mol.l}^{-1} \cdot \text{s}^{-1}$$

ANSWER: The reaction slows down over time. Over a period of 400 s the concentration of N_2O_5 drops twice. Over this period the reaction rate also decreases twice as it is directly proportional to the concentration of N_2O_5 .

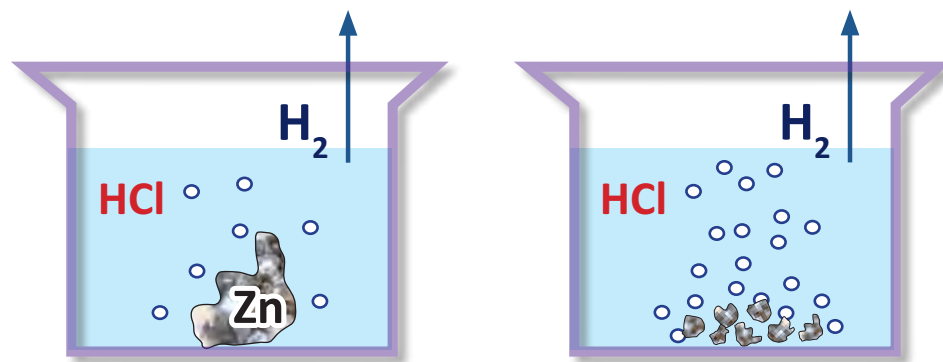
THE EFFECT OF THE SURFACE AREA OF A SOLID – IS IT BETTER TO USE POWDERED SOLID RATHER THAN SOLID LUMPS WHEN A SOLID REACTS WITH A LIQUID OR A GAS?

Zinc reacts with hydrochloric acid HCl, yielding the soluble salt ZnCl_2 and gaseous H_2 .



This is a fast reaction. But zinc Zn and hydrogen ions H^+ do not react instantaneously as the reaction undergoes when H^+ ions collide with the surface of the solid Zn. More H^+ ions are present in the liquid phase (the concentration of hydrochloric acid is higher), faster solid Zn disappears and more H_2 bubbles rise up. But the rate of the reaction can be increased also by breaking the Zn lump into small pieces. The surface area of the Zn particles accessible for H^+ ions is larger and the reaction speeds up.

In industrial processes granulated solids or powders of solids are used instead of big solid blocks when solid substances react with liquid or gaseous substances. The surface area of the solid contacting the liquid or gaseous reactants is larger and reactions speed up. If a gas bubbles in a liquid, special devices are used to sparge the gas thus increasing the gas-liquid interface area and consequently – the reaction rate.



THE REACTION OF Zn(s) WITH HCl(aq) SPEEDS UP WHEN THE SURFACE AREA OF SOLID Zn INCREASES.

CAN YOU ANSWER THESE QUESTIONS ?

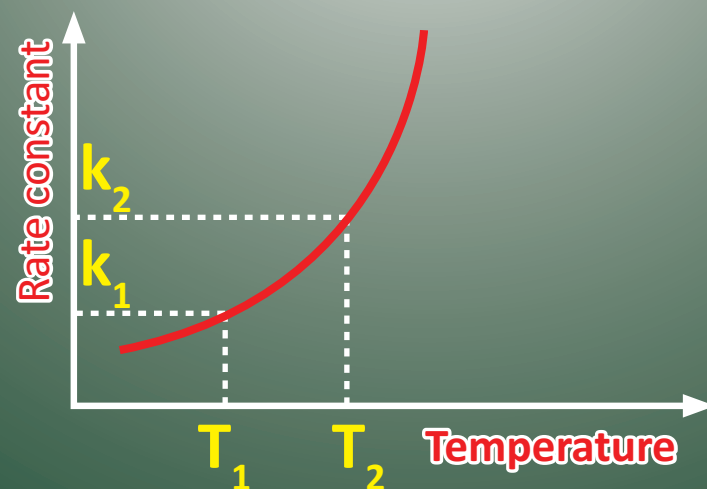
1. Why does reactants concentration affect reactions rate?
2. What is rate equation of a reaction?
3. Are the coefficients in the balanced chemical equation of a reaction identical with the coefficients in the rate equation of the reaction?
4. The rate equation of the reaction of decomposition of hydrogen peroxide into water and hydrogen is expressed as $v = k.c(\text{H}_2\text{O}_2)$. If the concentration of H_2O_2 is doubled what is the rate of the reaction?
 - a) The reaction rate does not change.
 - b) The reaction rate is doubled too.
 - c) The reaction rate is twice as slow.
 - d) The reaction is four times faster.
5. Look at the values of the reaction rates for the N_2O_5 thermal decomposition calculated on p. 37 and p. 41. Why aren't they identical?
6. In two test tubes there are 200 ml of 1 M HCl. A piece of 1 g of magnesium is put in the first test tube. To the solution in the second test tube is added 1 g of powdered magnesium. In which test tube magnesium will disappear first?

6

Effect of temperature on reaction rate

KEY TOPICS

1. Why does temperature affect reaction rate?
2. Why do many reactions undergo only at high temperature?
3. Why do both exo- and endothermic reactions speed up with increasing temperature?
4. What does the van't Hoff's empirical rule state?



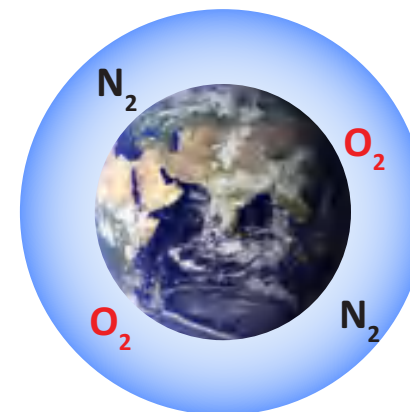
KEY WORDS

- van't Hoff's rule

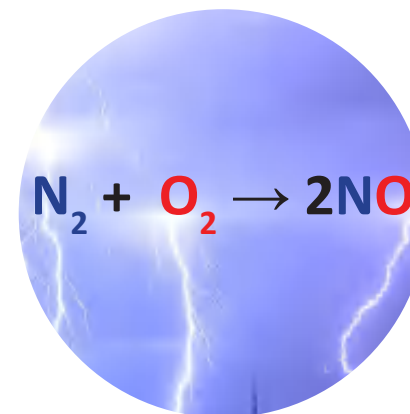
DOES TEMPERATURE AFFECT CHEMICAL REACTIONS RATE?

The Earth atmosphere (the air) is composed mainly of gaseous nitrogen N_2 and oxygen O_2 . These two gases can react to produce nitrogen oxide NO . In the atmosphere at normal temperature this reaction does not really undergo. But during lightning discharge, when temperature dramatically rises, nitrogen and oxygen combine and form NO molecules. Oxygen and hydrogen do not react at $25\text{ }^{\circ}\text{C}$ too. But if the mixture is heated up to $400\text{ }^{\circ}\text{C}$ oxygen combines with hydrogen forming water but the reaction is very slow. It speeds up with increasing temperature and at $800\text{ }^{\circ}\text{C}$ the mixture explodes.

Many chemical reactions undergo only at high temperature whether they are exothermic or endothermic. For example, the formation of nitrogen oxide NO is an endothermic reaction that undergoes only at very high temperature. The synthesis of ammonia NH_3 from nitrogen N_2 and hydrogen H_2 is an exothermic process carried out at high temperature as at standard conditions the interaction is too slow.



AT NORMAL CONDITIONS
NITROGEN N_2 AND OXYGEN O_2 IN
THE ATMOSPHERE DO NOT REACT.



AT VERY HIGH TEMPERATURE
(AS DURING LIGHTNING DISCHARGE)
NITROGEN N_2 AND OXYGEN O_2
COMBINE TO FORM
NITROGEN OXIDE NO .

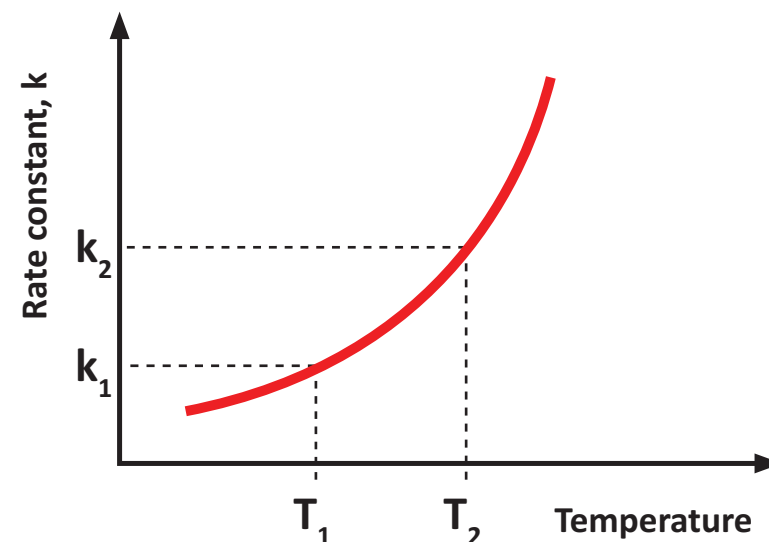
In general, chemical reactions speed up when temperature increases. But why? What does really change in a reacting system when temperature rises? The rate law gives a very simple explanation of that phenomena.

The rate equation for the reaction $aA + bB \rightarrow \text{products}$ is $v = k \cdot c(A)^\alpha \cdot (B)^\beta$. Reactants concentrations are not affected by changes in temperature. As the coefficients α and β remain constant, the rate constant k is the only parameter that changes with increasing temperature. The higher the temperature, the higher the value of the rate constant as the energy of the reacting species increases with temperature. On one hand, the higher the energy of reactants, the more likely the collision between A and B . On the other hand, not all collisions result in the formation of a new substance. Some minimum of energy (the activation energy of the reaction) is needed to initiate the reaction. The higher the temperature, the greater the amount of reacting species capable to overcome this „barrier“. Both factors cause chemical transformations to speed up.

Jacobus van't Hoff* formulated an empirical rule generalising the effect of temperature on reactions rate:

The rate constant of a chemical reaction gets doubled to quadrupled for each rise of 10 °C in temperature.

For example, when the temperature rises from 25 °C to 35 °C the rate constant of the hydrolysis of methyl ethanoate $\text{CH}_3\text{OOC}_2\text{H}_5$ almost doubles, while the rate constant of the hydrolysis of saccharose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ increases a little bit more than four times.

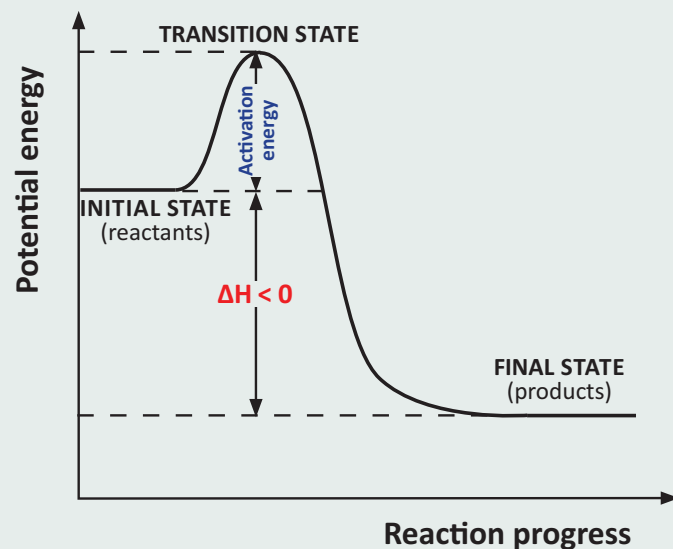


THE RATE CONSTANT OF A REACTION INCREASES WITH INCREASING TEMPERATURE

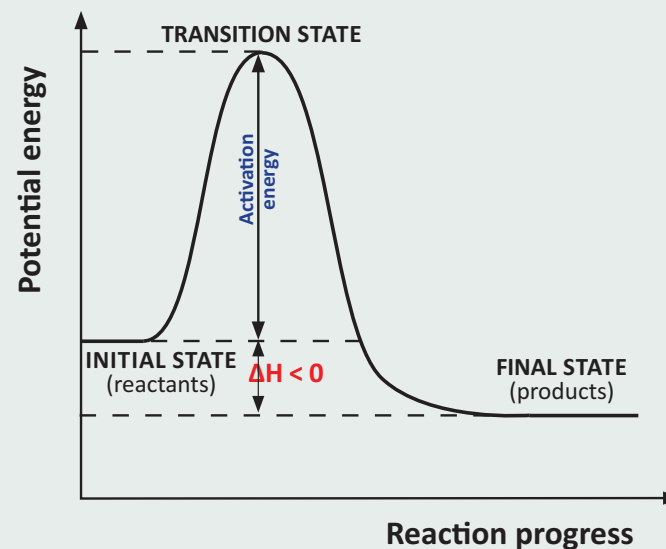
*Jacobus Henricus van't Hoff was the first winner of the Nobel Prize for chemistry in 1901.

PROBLEM!

Consider the two energy diagrams shown below. The rate of which reaction rises more rapidly with increasing temperature?



Reaction ①



Reaction ②

ANSWER: Both reactions need some additional energy (supplied, for example, as heat) to start. But the energy barrier that reactants in reaction ② have to overcome is high compared to the energy barrier for reactants in reaction ① – the activation energy of reaction ② is greater than the activation energy of reaction ①. The number of reacting species with an energy equal to or greater than the activation energy rises more quickly when the energy barrier is high. It may be concluded that the rate of reaction ② rises more rapidly with increasing temperature.

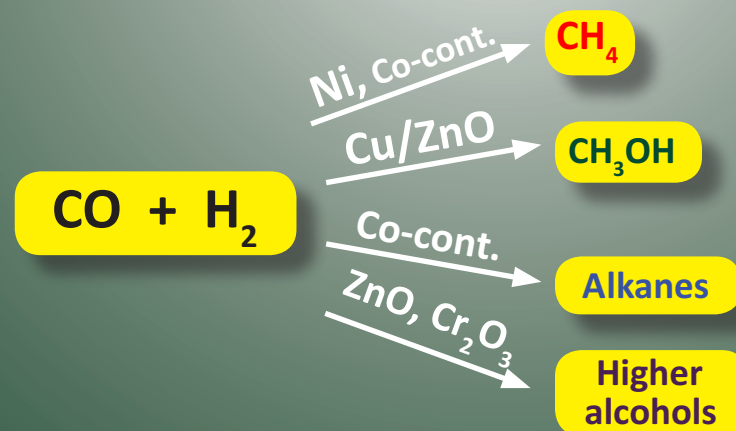
CAN YOU ANSWER THESE QUESTIONS ?

1. Does temperature affect reaction rate?
2. Why do both exo- and endothermic reactions speed up with increasing temperature?
3. Hydrogen and oxygen do not react at 25 °C but the gaseous mixture explode at 800 °C. Why?
4. Why does combustion need some external energy to start (for example, a lit match or a spark) but further the reaction undergoes without supplying external energy?
5. The activation energy of the reaction of nitrogen oxide NO with ozone O₃ is low compared to the activation energy of the reaction of synthesis of nitrogen oxide from nitrogen N₂ and oxygen O₂. At a given temperature which of the reactions is faster? Why?
6. Why are foods stored in refrigerators?

7 Catalysis. Catalysts

KEY TOPICS

1. What is catalysis?
2. What are catalysts?
3. What substances are catalysts?
4. How do catalysts accelerate chemical reactions?

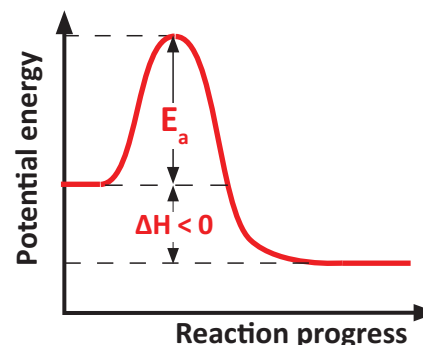


KEY WORDS

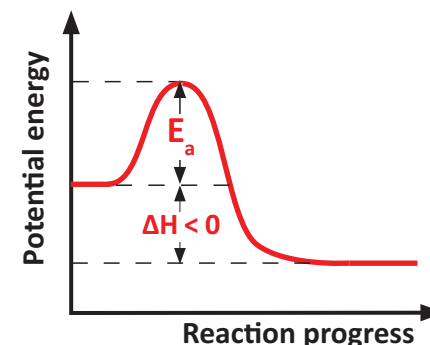
- Catalysis
- Catalyst
- Intermediate
- Inhibitor

WHAT IS CATALYSIS?

Chemical industry needs huge investments and chemical products must „pay“ these investments. Accelerating chemical transformations is a key point for many industrial processes to make them paying. Generally, both increasing temperature and reactants concentration speed up chemical interactions as more molecules overcome the energy barrier of the reaction and more intermolecular collisions result in the formation of reaction products. But both factors do not alter the activation energy E_a of the chemical reaction. The lower the activation energy, the faster the reaction for both exo- and endothermic transformations. At a given temperature and reactant concentrations reaction ② is faster than reaction ① and reaction ④ is faster than reaction ③. Lowering the energy barrier of a reaction, i.e. its activation energy, is a promising way to accelerate chemical reactions. To make it possible chemists have launched the idea of adding to the reacting system some special substances changing the route of the chemical reaction without themselves being consumed, i.e. they remain unchanged after the completion of the reaction. These substances are called **catalysts** and the process itself is known as **catalysis** (in greek language it means „destruction“).

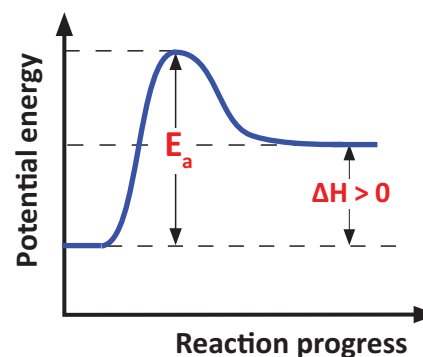


①

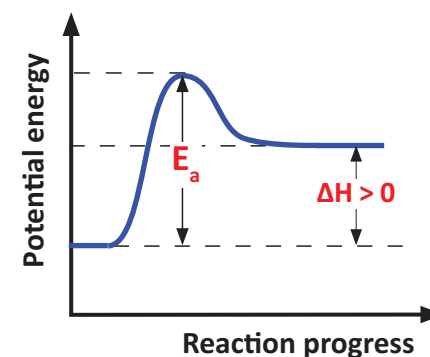


②

Exothermic reactions



③



④

Endothermic reactions

A REACTION SPEEDS UP
IF ITS ENERGY OF ACTIVATION E_A LOWERS.

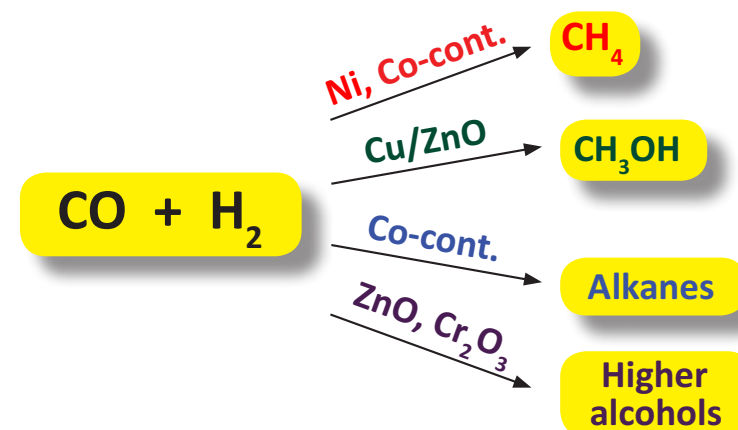
CATALYSIS is the acceleration of the rate of a chemical reaction by adding substances not consumed during the reaction.

CATALYST is a substance that increases the rate of a reaction without itself being consumed.

Catalysts are solid, liquid and gaseous substances. Solid catalysts are most often metals or their oxides, sulfides and halides. Also oxides, sulfides and halides of silicon, boron and aluminum. For example, iron Fe catalyses the synthesis of ammonia NH_3 . Divanadium pentaoxide V_2O_5 catalyses the transformation of SO_2 into SO_3 – a key intermediate for the production of sulfuric acid H_2SO_4 . The hydrogenation of unsaturated hydrocarbons is a process catalysed by nickel Ni, platinum Pt and palladium Pd. The slow process of esterification is catalysed by H^+ ions.

Some processes, as for example corrosion of metals, must be slowed down. Substances that lower the reaction rate are called **inhibitors**.

Catalysts are very useful when it is necessary to accelerate one of several simultaneously undergoing chemical reactions. It is often the case in organic synthesis. For example, when carbon monoxide CO is mixed with hydrogen H_2 different products form depending on the type of catalyst. Nickel Ni, cobalt-containing catalysts accelerate the synthesis of methane CH_4 . Methanol CH_3OH is the main product if the catalyst is CuO/ZnO. Higher alcohols form if a mixture of ZnO and Cr_2O_3 is used to catalyse the reaction. If the catalyst is a cobalt-containing substance alkanes are produced.



Enzymes are proteins that accelerate many biochemical reactions. They are naturally occurring catalysts. The transformation of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ into ethanol $\text{C}_2\text{H}_5\text{OH}$ and carbon dioxide CO_2 is catalysed by the enzyme zymase. The burning of glucose in the human body is catalysed by the hormone insulin. More than 800 enzymes are known up to day.

HOW DO CATALYSTS ACT?

Catalysts accelerate chemical reactions by changing the their mechanism. They create another route for the transformation of reactants into products thus **lowering the activation energy** of the reaction. Catalysts chemically react with some of the reactants (or with all reactants) and form intermediate substances which easily react to form the products. During the reaction catalysts regenerate.

For example, consider the slow transformation of a substance A into the substance B. The reaction is undergoing in one step $A \rightarrow B$. A catalyst X is added to accelerate this transformation. The rout of the reaction is changed. It is carried out in 2 steps:

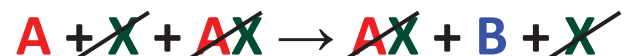
Step 1. Reaction of A with the catalyst X resulting in the formation of an **intermediate AX**.



Step 2. Transformation of the intermediate AX into the product B.



The overall transformation is not affected as the intermediate is chemically transformed into the product and the catalyst is regenerated. The sum of the two steps gives:



The intermediate AX and the catalyst X in both sides cancell out and the overall equation of the catalysed process is identical with the equation of the uncatalysed reaction, i.e. $A \rightarrow B$ but the process is accelerated as the activation energy of the two stages process is lower.

CAN YOU ANSWER THESE QUESTIONS ?

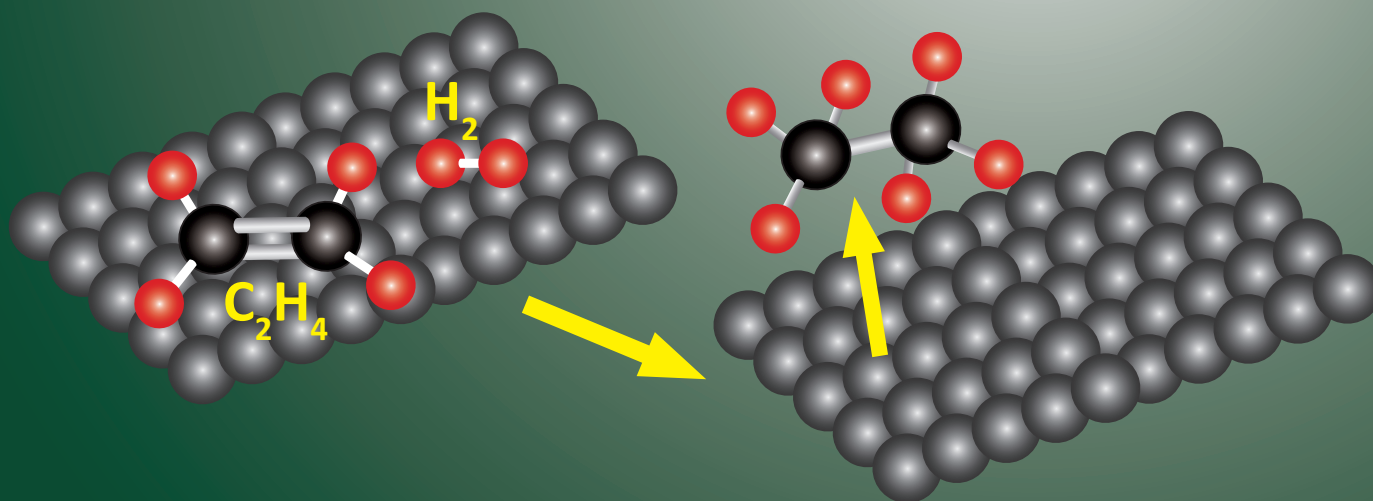
1. What is catalysis?
2. Why is catalysis so important for industry?
3. Why are enzymes catalysts?
4. How do catalysts accelerate chemical reactions?
5. The activation energy of an uncatalysed reaction is E_a . The reaction is speeded up by adding a catalyst. What is the activation energy of the catalysed reaction?
 - a) It is identical with E_a .
 - b) It is greater than E_a .
 - c) It is lower than E_a .
 - d) It is greater or lower than E_a .
6. Can you give examples of reactions that must be slowed down but not speeded up?

8

Homogeneous catalysis. Heterogeneous catalysis

KEY TOPICS

1. What is homogeneous catalysis and homogeneous catalyst?
2. What is heterogeneous catalysis and heterogeneous catalyst?
3. Why does the catalysed pathway differ from the uncatalysed pathway of a reaction?
4. Why is catalyse of huge importance for life and industry?



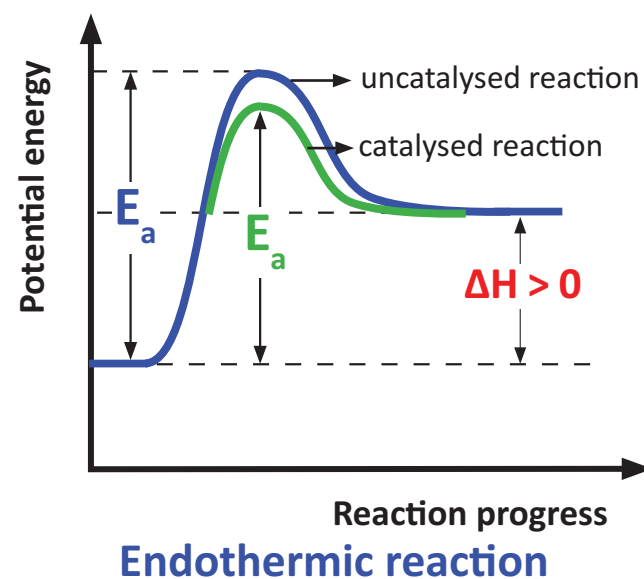
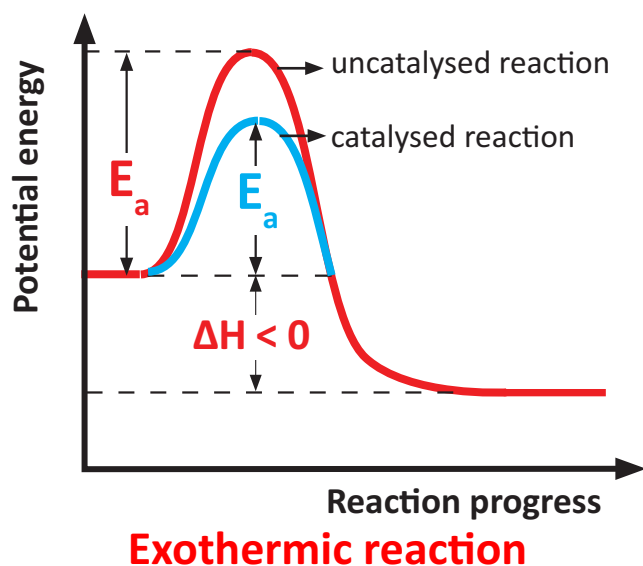
KEY WORDS

- Homogeneous catalysis
- Homogeneous catalyst
- Phase
- Heterogeneous catalysis
- Heterogeneous catalyst

The mechanism of acting of catalysts is very complex. But, in general, the mechanism of catalysis when catalysts and reacting species are in the same phase is completely different compared to the mechanism of acting of catalysts that are not in the same phase* with reactants. The first type of catalysts are called **homogeneous catalysts** and the process itself – **homogeneous catalysis**. The second type of catalysts are called **heterogeneous catalysts** and the process is known as **heterogeneous catalysis**.

HOW DO HOMOGENEOUS CATALYSTS ACT?

Like all catalysts homogeneous catalysts reduce the activation energy of chemical reactions. The catalyst and the reactants are in the same phase and the catalyst forms intermediates with some of the reactants (or with all reactants). As reactants and catalysts are present in the same phase **the rate of the homogeneous catalytic reactions increases with the increase of the catalysts concentration**. The intermediates easily react with one another or with other reactants. The average rate of the reaction is high compared to the uncatalysed reaction because the reactants overcome a lower energetic barrier – the activation energy of the catalysed reaction is lower than the activation energy of the uncatalysed reaction. The potential energy of reactants and products remain unchanged.

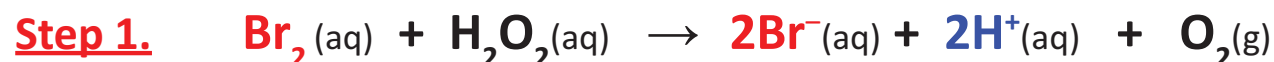


*A phase is matter that is uniform throughout its chemical composition and physical state.

A simple example of homogeneous catalysis is the decomposition of hydrogen peroxide H_2O_2 :



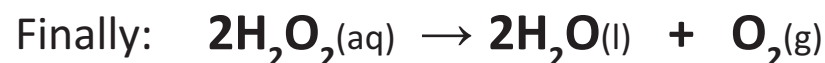
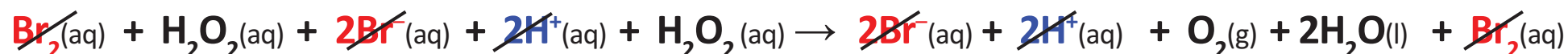
This reaction is very slow but different catalysts speed it up. For example, bromine Br_2 is a homogeneous catalyst that accelerate this transformation. First Br_2 reacts with H_2O_2 .



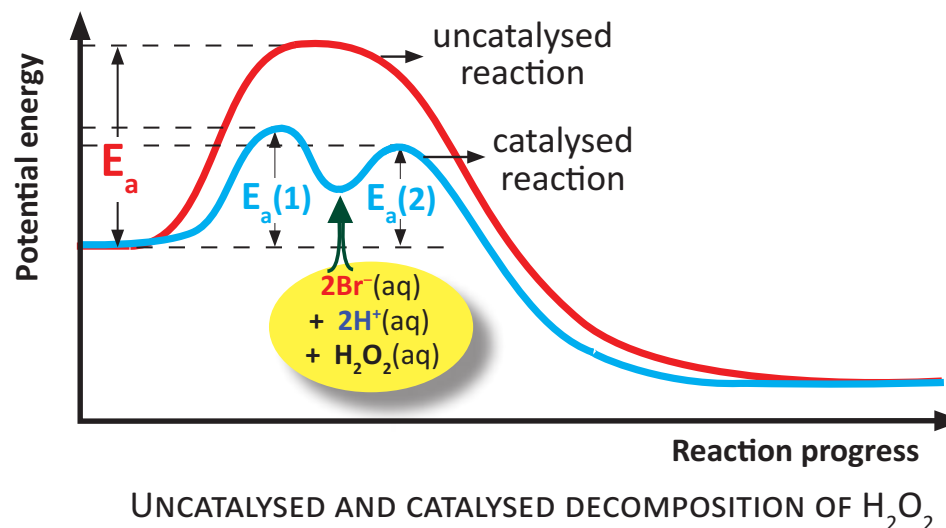
The next step is the reaction of bromide ions Br^- with other molecules of H_2O_2 and H^+ ions.



The overall equation of the catalysed reaction (step 1 + step 2) is:



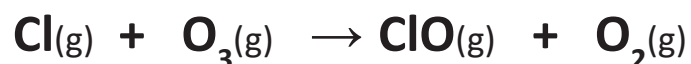
The two steps catalytic decomposition of H_2O_2 is much faster than the one step uncatalysed reaction. Bromine molecules Br_2 , acting as a catalyst, are regenerated during the reaction. The energy diagram for the catalysed process clearly shows that the activation energy of the two steps reaction is low compared to the activation energy of the uncatalysed reaction.



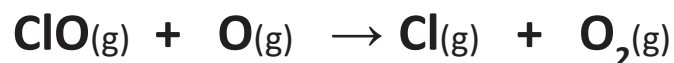
Iodide ions $\text{I}^-(\text{aq})$ also catalyse the decomposition of H_2O_2 . The rate constant of the reaction increases 2 000 times as the activation energy drops from 76 kJ/mol to 57 kJ/mol. The enzyme catalase is much more effective – the activation energy drops to 8 kJ/mol and at 25 °C the reaction of decomposition is 10^{15} times faster.

Hydrogen ions H^+ and hydroxide ions OH^- can act as homogeneous catalysts. For example, the hydrolysis of saccharose $\text{C}_{22}\text{H}_{11}\text{O}_{11}$ is catalysed by H^+ ions. This is an example of **acid catalysis**. If OH^- ions act as a catalyst, the process is called **base catalysis**.

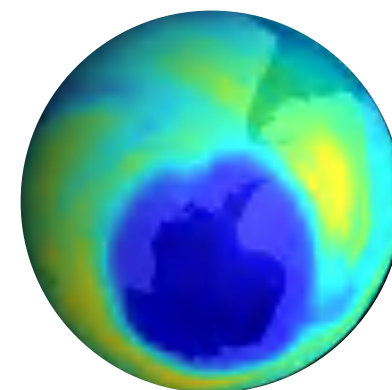
An example of homogeneous catalysis undergoing in gaseous phase is the destruction of the ozone layer in the stratosphere. Ozone O_3 spontaneously transforms into oxygen O_2 under the action of sunlight. This reaction is very slow but chlorine atoms $\text{Cl}^\cdot$ (products of the decomposition of freons like CF_2Cl_2 , CFCl_3 , CHFC_2 , $\text{C}_2\text{Cl}_2\text{F}_4$, $\text{C}_2\text{Cl}_3\text{F}_3$, etc., upon the action of the cosmic uv-radiation) accelerate this process dramatically. Chlorine atoms are very reactive and „attack“ ozone molecules:



ClO is an intermediate. It reacts with nascent oxygen O present in the stratosphere (under the action of uv-radiation oxygen molecules are broken down: $\text{O}_2 \xrightarrow{\text{uv}} 2\text{O}$).



Chlorine atoms are regenerated like all catalysts. The overall reaction is $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$. Ozone molecules are destroyed and transform into molecules of oxygen O_2 . One chlorine atom Cl destroys one ozone molecule O_3 . As it is regenerated, it reacts with another molecule of O_3 and so on. One chlorine atom can repeat this cycle 100 000 times.



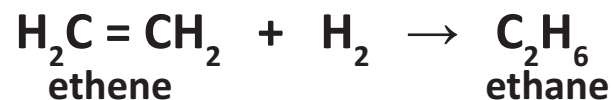
THE FORMATION OF OZONE HOLES OVER THE EARTH'S POLES IS AN EXAMPLE OF UNDESIRABLE HOMOGENEOUS CATALYTIC REACTIONS.

HOW DO HETEROGENEOUS CATALYSTS ACT?

Homogeneous catalysts and reactants are always in the same phase. Oppositely, heterogeneous catalysts and reactants are in different phases. For example, solid catalysts accelerate reactions in solutions or in gaseous phase. As the catalyst and the reactants are in different phases, they are separated from one another by some boundary. If the catalyst is solid this boundary is its surface. All successive steps of a heterogeneous catalysis undergo onto this surface. The pathway of this process is very complex but the following steps are common for all processes catalysed by solid catalysts:

- 1 Attachment of molecules of reactants to the solid surface. The process is known as **adsorption**.
- 2 Activation of the adsorbed species.
- 3 Chemical reaction of the adsorbed species.
- 4 Detachment of the products from the catalyst surface. The process is known as **desorption**.

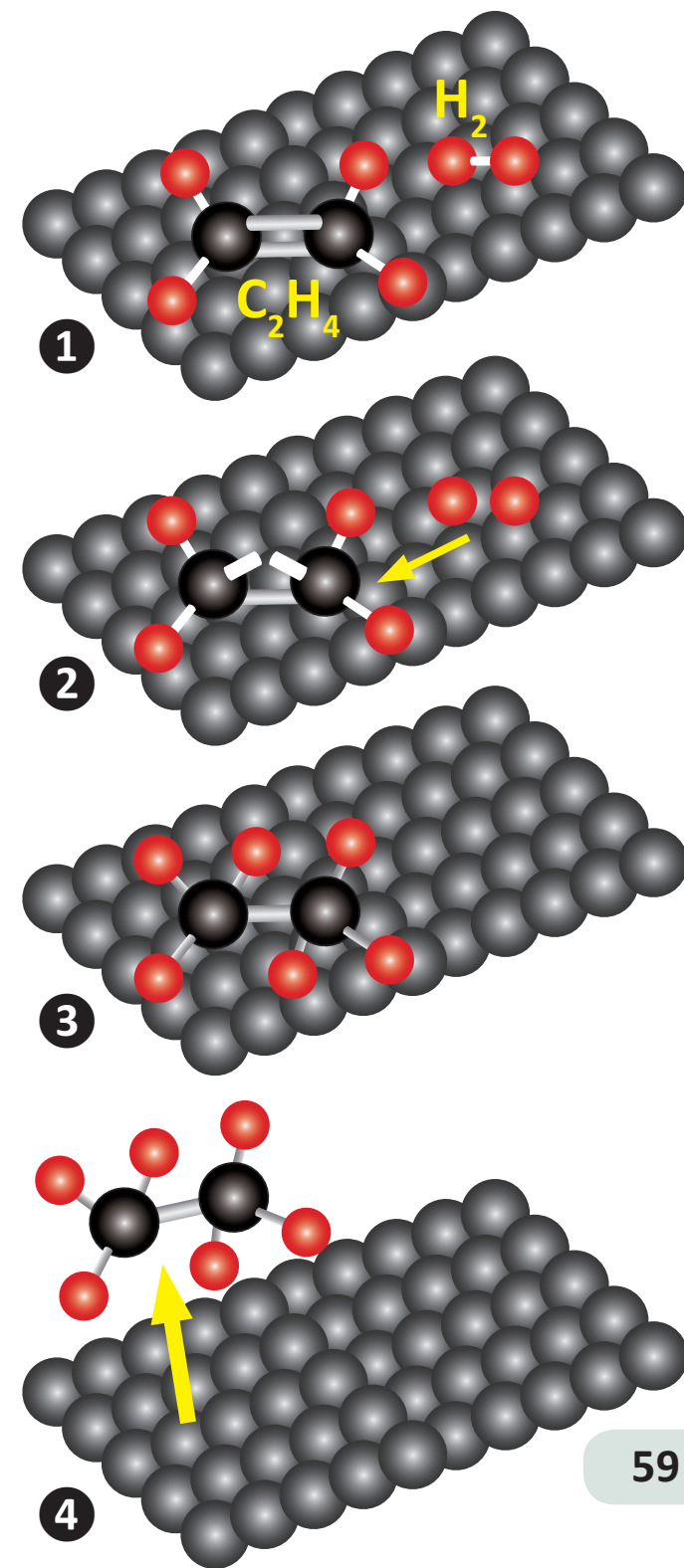
The hydrogenation of alkenes is a heterogeneous catalytic process. The hydrogenation of ethene, i.e. the adding of one molecule of hydrogen H_2 to one molecule of ethene C_2H_4 , is expressed with the simple equation:



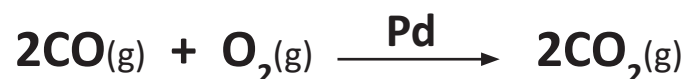
The gases practically do not react unless a catalyst (for example, nickel Ni) is added to the mixture.

The catalysed pathway of this reaction is illustrated to the right.

- 1 Molecules of both reactants are absorbed onto the catalyst surface.
- 2 One of the sheared electron pair of the double carbon-carbon bond of ethene $\text{H}_2\text{C}=\text{CH}_2$ disrupts. The hydrogen-hydrogen bond in the H_2 molecule also breaks down thus liberating lone hydrogen atoms H.
- 3 Hydrogen atoms are mobile and easily move across the metallic surface. When a hydrogen atom collides with an absorbed activated ethene molecule a new carbon-hydrogen bond forms. Molecules of ethane C_2H_6 are produced.
- 4 Molecules of ethane C_2H_6 are desorbed from the catalyst surface – they are not strongly attached to metal atoms of the catalyst surface and easily quit the catalyst. The catalyst surface is free and can adsorb other C_2H_4 molecules.



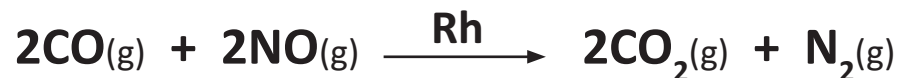
A key factor for the catalyst efficiency is the surface area available for the adsorption of reactants. **The rate of the heterogeneous catalytic reactions increases with the increase of the surface area of catalysts.** But not all atoms on the surface of a catalyst are capable to trap the reactants molecules. The catalytic efficiency of an ideal metallic surface (as shown in the figure on the previous page) is not very high. Surfaces with defects like ridges, „terraces“, kinks and others are much more efficient. To increase their surface area, solid catalysts are often produced in the form of small granules (some of them are porous solid substances), even as fine powders dispersed on a suitable support. For example, the catalytic convertors for motors vehicles contain palladium Pd and rhodium Rh dispersed on a ceramic support that resembles a honeycomb. Palladium catalyses the oxidation of the exhaust carbon monoxide to carbon dioxide:



Rhodium catalyses the reaction of the unburned hydrocarbons with excess oxygen. They are transformed into CO_2 and water. For example, for octane:



Rhodium catalyses also the removal of exhaust NO. It reacts with the exhaust CO and transforms into CO_2 and N_2 .



This is an example of how catalysis can help to safeguard the environment. Catalytic processes are also of huge importance for maintaining life as enzymes are biological catalysts regulating many biochemical processes in nature and in the human body. A lot of industrial process are realised thanks to the development of efficient catalysts. The production of new or improved catalysts itself is a very important and rapidly growing branch of the chemical industry.

CAN YOU ANSWER THESE QUESTIONS ?

1. Why are homogeneous and heterogeneous catalysis considered as the two main types of catalytic processes?
2. Do homogeneous and heterogeneous catalysts affect the heats of reaction?
3. Are both homogeneous and heterogeneous catalysts regenerated during the reaction?
4. How does a homogeneous catalyst act?
5. How does a heterogeneous catalyst act?
6. Why does the rate of a heterogeneous reaction rise with the increase of the surface area?
7. Why is citric acid added when preparing at home a fruit jam or a jelly?
8. Why is the production of new catalysts a rapidly growing industry?
9. There is not an universal catalyst, i.e. a substance that can accelerate all known chemical reactions. Why?
10. Is it possible to initialise a reaction that is not undergoing at all by adding a catalyst?

9

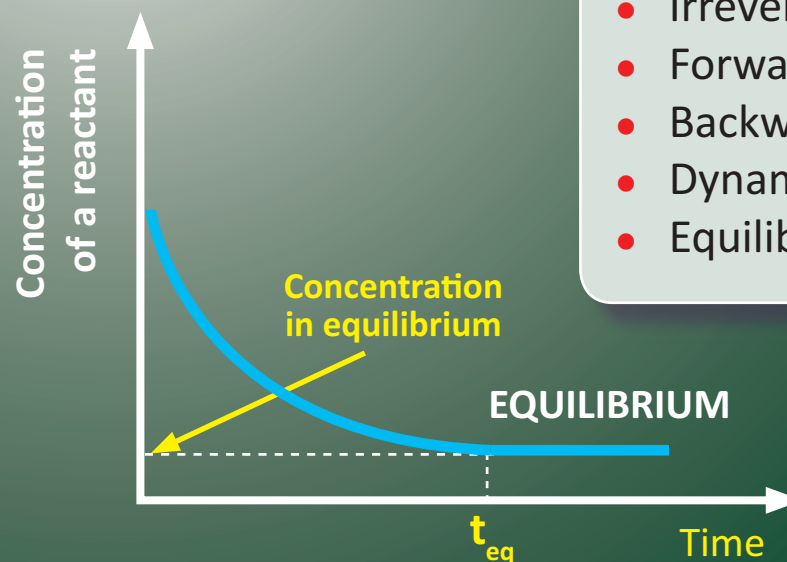
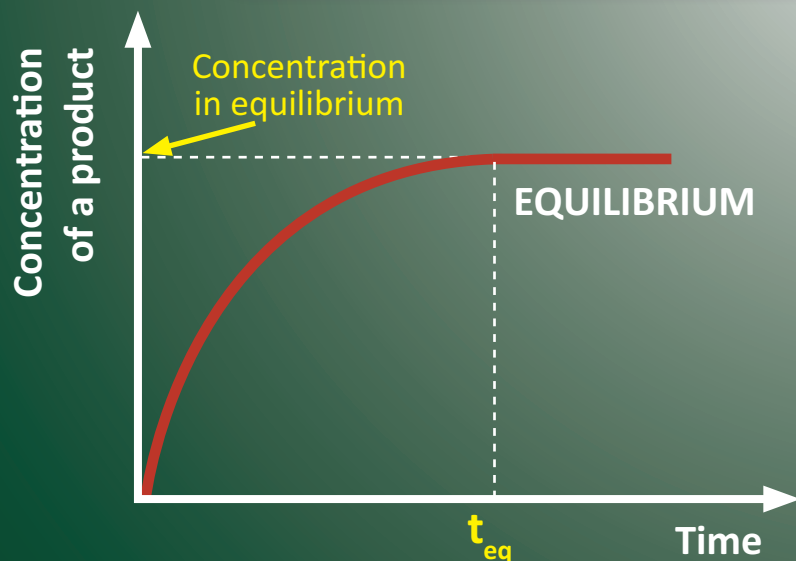
Reversible and irreversible chemical reactions. Chemical equilibrium

KEY TOPICS

1. What reactions are reversible and what – irreversible?
2. What is equilibrium?
3. Why is equilibrium a dynamic state?
4. What is equilibrium constant?

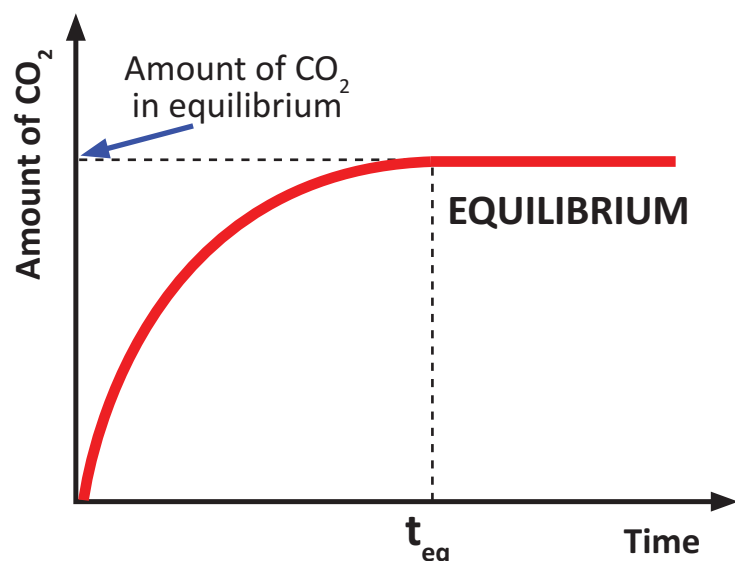
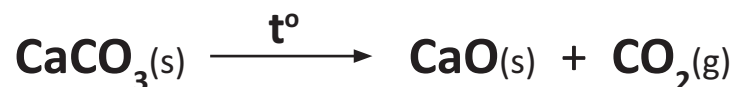
KEY WORDS

- Reversible reaction
- Irreversible reaction
- Forward reaction
- Backward reaction
- Dynamic state
- Equilibrium constant



WHAT IS CHEMICAL EQUILIBRIUM?

In the everyday life the word „equilibrium“ is used to indicate that something does not change over time (for instance, an object that does not move). Chemical reactions always deal with visible changes as reactants transform into products. So what has to do an equilibrium state with chemical transformations? Consider the thermal decomposition of limestone CaCO_3 , yielding calcium oxide CaO and carbon dioxide CO_2 (the oldest technological process invented by man):



CHANGE IN THE AMOUNT OF CO_2
PRODUCED DURING THE THERMAL
DECOMPOSITION OF CaCO_3 OVER TIME
(CLOSED SYSTEM)

If the gaseous product CO_2 is swept away, the thermal decomposition continues until the heated solid limestone is completely consumed. But if the reacting **system is closed** (no reactants are added and none of the products quit the system), after a period of time the reaction seems to stop. The heated solid limestone is not completely consumed but for time $t > t_{\text{eq}}$ the amount of CO_2 does not increase any more over time if the temperature and the pressure (or the volume) remain unchanged. This is the **equilibrium state** of the system.

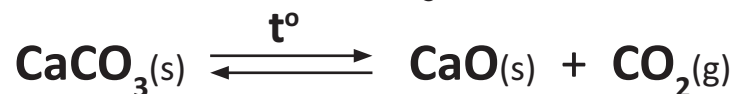
In general:

CHEMICAL EQUILIBRIUM is a state of a reacting system in which both reactants and products are present but their concentrations do not change over time.

The equilibrium state is a **dynamic state** – the forward reaction continues to go on but the backward reaction (transformation of the products into the reactants) also undergoes. The concentration of the components of the reaction do not change over time because the rate of the forward reaction is equal to the rate of the backward reaction.

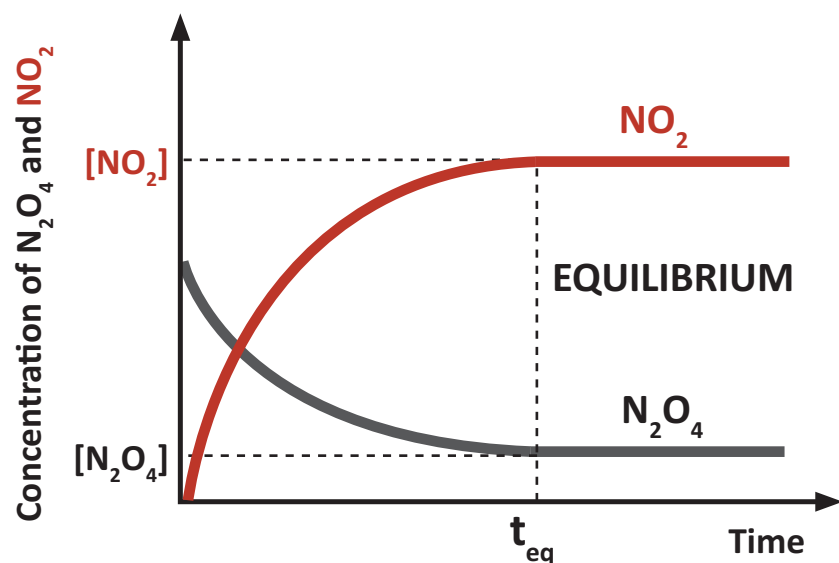
! In equilibrium: **Rate of the forward reaction** = **Rate of the backward reaction**

For example, in equilibrium the rate of the thermal decomposition of CaCO_3 ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) is equal to the rate of the backward reaction of synthesis of CaCO_3 ($\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$). If 10 molecules of CaCO_3 decompose in the same time 10 molecules of CaCO_3 are synthesised from CaO and CO_2 . The reaction is **reversible**. It undergoes in both directions – forward and backward. For all reversible reactions the one way arrow $\rightarrow$ in the chemical equation has to be replaced with an **equilibrium arrow** $\rightleftharpoons$. For the reversible decomposition of CaCO_3 in a closed system:



If the produced CO_2 goes away in the air (the system is open) the equilibrium state can not be reached and the chemical transformation is **irreversible**. In **closed systems most of the reactions are reversible**. But if in equilibrium the concentrations of the reactants are very small compared to the concentrations of the products, the reactions are considered as irreversible. For example, the neutralisation reaction $\text{NaOH}(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$ is practically irreversible.

In the example above (the thermal decomposition of CaCO_3), in equilibrium reactants and products are in different phases – CaCO_3 and CaO are solid, CO_2 is a gas. Equilibrium can be established also in one phase. For example, at room temperature dinitrogen tetraoxide N_2O_4 (a colourless gas), placed in a flask with a stopper,



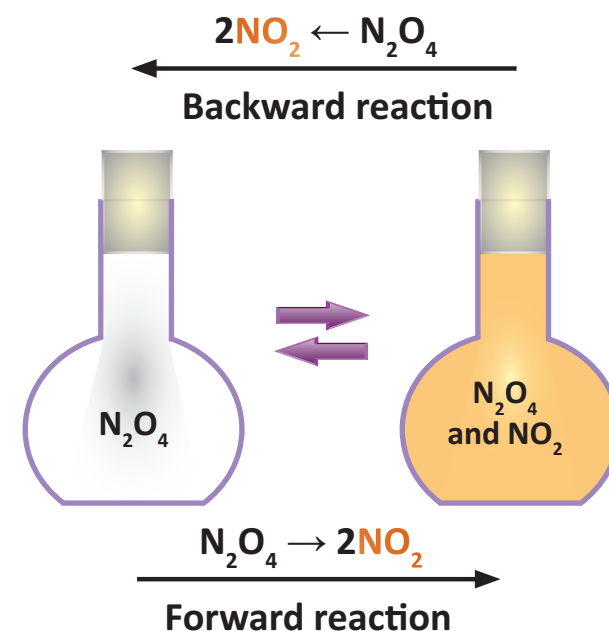
CHANGE IN THE CONCENTRATIONS OF N_2O_4 AND NO_2 IN A CLOSED SYSTEM



gradually darkens as it transforms into nitrogen dioxide NO_2 (a brown gas). The reaction is reversible.



The colourless N_2O_4 is not completely consumed. An equilibrium is established and the colour of the gaseous mixture does not change over time – the gaseous phase is a mixture of N_2O_4 and NO_2 that concentrations $[\text{N}_2\text{O}_4]$ and $[\text{NO}_2]$ remain unchanged over time.



HOW TO QUANTIFY CHEMICAL EQUILIBRIUM?

Equilibrium mixtures composition changes with temperature, pressure and concentrations of reactants. But at a given temperature **the reaction quotient of products concentrations over reactants concentrations, raised to powers equal to their coefficients in the balanced chemical equation, is constant***. It is denoted by K_c and is called **equilibrium constant**. For the reaction $aA + bB \rightleftharpoons cC + dD$ it is expressed as:

$$K_c = \frac{[C]^c \cdot [D]^d}{[A]^a [B]^b}$$

Equilibrium constants are dimensionless, i. e. they are expressed without units. The equilibrium concentrations of the components of a reversible reaction are most often expressed in mol/l.

The equilibrium constant value changes with temperature but is unaffected by changes in pressure or in concentrations of products or reactants. For example, the equilibrium constant of the reversible reaction

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is expressed as $K_c = \frac{[NO_2]^2}{[N_2O_4]}$. Its value does not change if an additional amount of

N_2O_4 is pumped into the gaseous mixture provided that the temperature remains unchanged.

If both products and reactants are gases the amount of the reaction components in equilibrium can be expressed by their partial pressures** instead of their concentrations. This equilibrium constant is

denoted by K_p . For the above reaction $K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}}$.

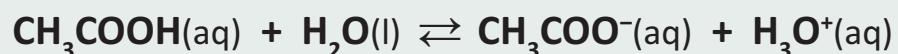
*This relationship has been established experimentally by C. Guldberg and P. Vaage over the period 1864 – 1879. It is based on the empirical **law of mass action** that is only of historical significance today. The modern science has proved that this expression is correct, for example, for dilute aqueous solutions of weak acids or bases and slightly soluble salts.

**The pressure that a gas would exert if it was alone in the reacting space.

PROBLEM!

Ethanoic acid CH_3COOH is a weak acid. In water it partially dissociates liberating CH_3COO^- ions and H^+ ions. In equilibrium in the liquid phase are present CH_3COO^- ions, H_3O^+ ions and molecules CH_3COOH . What is the expression for the equilibrium constant K_c ?

SOLUTION: The chemical equation of the reversible dissociation of ethanoic acid is expressed as:



The equilibrium constant K_c has to be expressed as $\frac{[\text{CH}_3\text{COO}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}] \cdot [\text{H}_2\text{O}]}$. But the concentration of the pure water does not change during the reaction. For this reason it is omitted in the expression for the equilibrium constant and the expression for K_c is:

$$K_c = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

COMMENTS: At 25 °C the equilibrium constant of the dissociation of ethanoic acid in water is $1,74 \cdot 10^{-5}$.

PROBLEM!

Given the reversible reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$. What are the expression for the equilibrium constants of the reaction K_c and K_p ?

SOLUTION: The equilibrium constant K_c has to be expressed as $\frac{[\text{CO}_2] \cdot [\text{CaO}]}{[\text{CaCO}_3]}$. But the concentrations of

the pure solid CaO and CaCO_3 do not change during the reaction. For this reason they are not included in the expression for K_c and the value of the equilibrium constant is determined only by the concentration of CO_2 in equilibrium:

$$K_c = [\text{CO}_2]$$

By analogy, $K_p = p_{\text{CO}_2}$.

As a rule:

Concentrations or partial pressures of pure liquids and pure solids are not included in the expressions for the equilibrium constants.

CAN YOU ANSWER THESE QUESTIONS ?

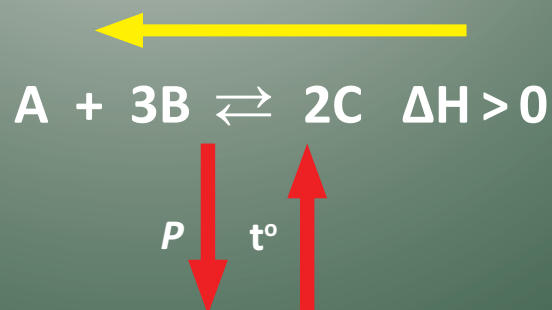
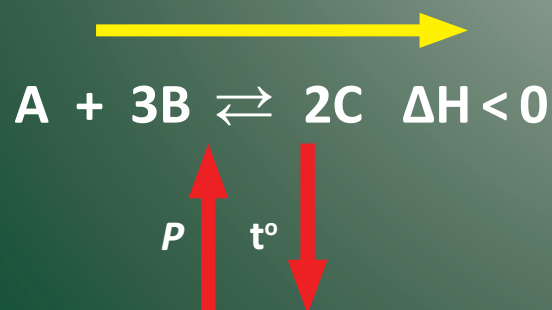
1. What reactions are reversible?
2. Why is esterification a reversible reaction but neutralisation of a strong base with a strong acid is an irreversible reaction?
3. How does the rate of the forward reaction change over time till equilibrium is achieved?
4. What is true?
 - a) In equilibrium the rate of the forward reaction is greater than the rate of the backward reaction.
 - b) In equilibrium the rate of the forward reaction is lower than the rate of the backward reaction.
 - c) In equilibrium the rate of the forward reaction is equal to the rate of the backward reaction.
 - d) In equilibrium both the forward and the backward reactions stops.
5. Nitrogen N_2 and hydrogen H_2 react to form NH_3 : $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$. The reaction is reversible. What is the composition of the equilibrium gaseous mixture?
 - a) It is composed of N_2 and H_2 .
 - b) It is composed of N_2 , H_2 and NH_3 .
 - c) It is composed of N_2 and NH_3 .
 - d) It is composed of pure NH_3 .
6. What is the equilibrium constant K_c of the reaction of synthesis of ammonia?
7. Powdered CaCO_3 is put into a closed container. The air is swept away and the container is heated to a high temperature (for example, 800°C). CaCO_3 decomposes into CaO and CO_2 . Does the pressure of CO_2 in equilibrium depend on the initial amount of CaCO_3 in the container?

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Effect of concentration, pressure and temperature on chemical equilibrium

KEY TOPICS

1. What does the Le Chatelier-Braun principle stand for?
2. How is equilibrium affected by changes in reactants and products concentration?
3. How is equilibrium affected by changes in temperature?
4. How is equilibrium affected by changes in pressure?
5. What are optimal conditions of a reversible reaction?



KEY WORDS

- Le Chatelier-Braun principle

WHAT DOES THE LE CHATELIER-BRAUN PRINCIPLE STAND FOR?

In equilibrium the concentration of reactants and products do not change over time as the forward and the backward reactions undergo with equal rates. Changes in concentrations of reactants or products (by adding or removing them), in pressure (by compressing or decompressing the system) and in temperature disturb the equilibrium state. The equilibrium shifts to the reactants or to the products thus overcoming these disturbances. As a rule:

A system in equilibrium, when subjected to a disturbance, responds in a way that tends to minimise the effect of the disturbance.

This empirical rule is known as the **Le Chatelier-Braun principle***.

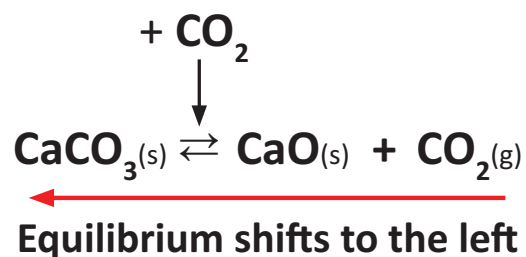
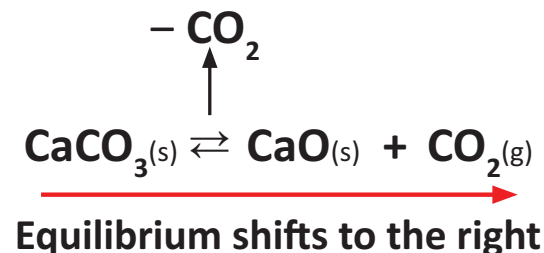
HOW DO CHANGES IN REACTANTS AND PRODUCTS CONCENTRATION AFFECT CHEMICAL EQUILIBRIUM?

When some amount of a reactant or a product is added to the equilibrium mixture, or removed from it, the value of the equilibrium constant does not change provided that the temperature is constant. But the concentrations of reaction components change and a new equilibrium is established.

A good example to explain how the Le Chatelier-Braun principle works when concentration of reactants or products changes is the already well known reversible reaction of thermal decomposition of CaCO_3 in a closed container.

*The principle has been formulated by Henri Louis Le Chavalier and Karl Ferdinand Broun over the period 1884-1914.

If heated in a closed container, calcium carbonate CaCO_3 decomposes and the amount of the liberated CO_2 increases over time until the equilibrium state is achieved. The equilibrium constant is expressed as $K_c = [\text{CO}_2]$. **If some amount of CO_2 is removed** from the container the system reacts by producing an additional amount of CO_2 until the equilibrium concentration of CO_2 is achieved. The value of K_c does not change if the temperature is maintained constant. The only change in the system is the decomposition of some additional amount of CaCO_3 . **The forward reaction of thermal decomposition $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$ is favored.** The equilibrium shifts in the direction of production of CO_2 .



If some amount of CO_2 is pumped into the container, the system reacts by consuming CO_2 – an additional amount of CaCO_3 is produced until the equilibrium concentration of CO_2 is achieved. The value of K_c does not change if the temperature is maintained constant. The only change in the system is the formation of some additional amount of CaCO_3 . **The backward reaction of synthesis of calcium carbonate $\text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s)$ is favoured.** The equilibrium shifts in the direction of consumption of CO_2 .

AS A RULE:

Changes in concentrations of reactants or products affect equilibrium. If a component of the reaction is added to the equilibrium mixture, the equilibrium shifts towards the reaction decreasing its concentration. If some amount of a component of the reaction is removed from the equilibrium mixture, the equilibrium shifts towards the reaction increasing its concentration.

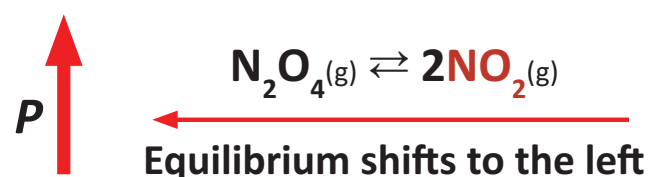
At a given temperature the value of the equilibrium constant does not change.

HOW DO CHANGES IN PRESSURE AFFECT CHEMICAL EQUILIBRIUM?

When gases are involved in a reversible reaction the composition of the equilibrium mixture can change with increasing or decreasing pressure if the system is compressed or decompressed.

According to the Le Chatelier's principle the system reacts in a way to minimise the disturbance. The already well known reaction of transformation of N_2O_4 into NO_2 ($\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$) is a good example

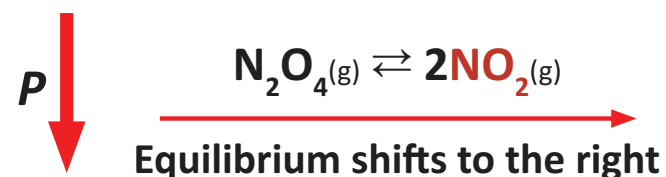
to show how this principle works. The equilibrium constant is expressed as $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$.



If the gas mixture is **compressed** the equilibrium state is disturbed. The **pressure is increased** and the system react by **decreasing the number of molecules** thus **reducing the pressure**. The backward reaction is favoured as 2 molecules of

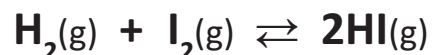
NO_2 form 1 molecule of N_2O_4 . The equilibrium shifts to the left.

Oppositely, if the gas mixture is **decompressed** (the pressure is **decreased**) the system reacts by **increasing the number of molecules** thus **increasing the pressure**. The forward reaction is favoured as from 1 molecule of N_2O_4 are produced 2 molecules of NO_2 . The equilibrium shifts to the right.



In both cases the value of K_c does not change provided that the temperature is constant. The ratio $[\text{NO}_2]^2 / [\text{N}_2\text{O}_4]$ does not change. But the values of $[\text{NO}_2]$ and $[\text{N}_2\text{O}_4]$ change, i.e. **the composition of the equilibrium mixture changes**.

If the balanced chemical equation shows that **the number of moles of the gaseous reactants is equal to the number of moles of the gaseous product**, the equilibrium is not affected by any changes in the **pressure**. For example, at a given temperature, the equilibrium state of the reaction of synthesis of hydrogen iodide **HI** is not affected by any changes in the pressure.



AS A RULE:

Changes in pressure affect equilibrium in gaseous phase if as a result of the chemical transformation the overall number of moles in the system changes. At a given temperature the value of the equilibrium constant does not change.

If the system is compressed (the pressure rises) the equilibrium shifts towards the reaction reducing the number of moles.

If the system is decompressed (the pressure lowers) the equilibrium shifts towards the reaction increasing the number of moles.

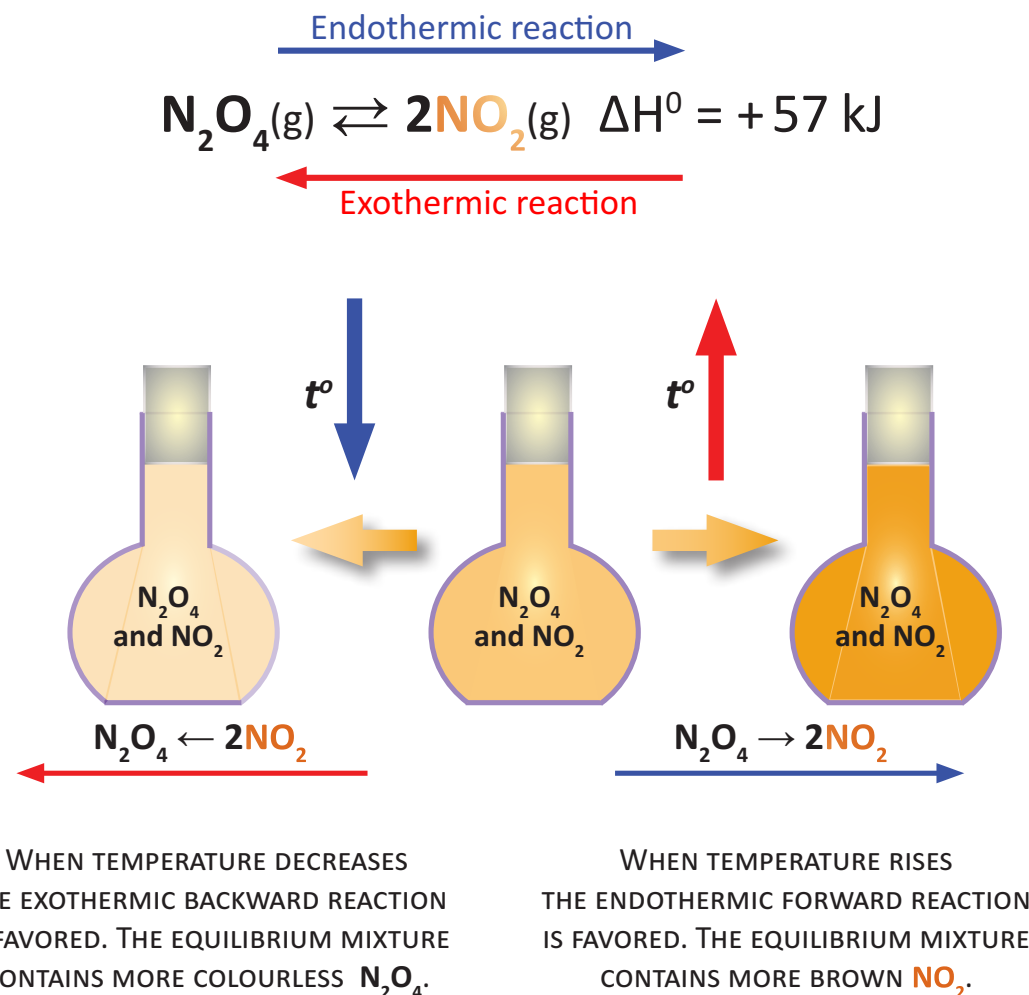
HOW DO CHANGES IN TEMPERATURE AFFECT CHEMICAL EQUILIBRIUM?

When the temperature changes, the equilibrium, generally, moves towards the products or towards the reactants depending on the heat of the reaction.

if the forward reaction is exothermic, the backward reaction is endothermic and the heats of both reactions are equal in value but differ in their sign. For example, the reaction of transformation of N_2O_4 into NO_2 is endothermic and $\Delta H^\circ = +57 \text{ kJ}$. The reverse reaction of synthesis of N_2O_4 from NO_2 is exothermic and $\Delta H^\circ = -57 \text{ kJ}$.

If the temperature rises, according to the Le Chatelier's principle, the system reacts in a way to decrease the temperature. As the forward reaction $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$ is endothermic, i.e. during the reaction heat is absorbed, the equilibrium shifts towards the product – the brown NO_2 , and the mixture darkens.

If the temperature decreases, the system tends to produce heat to overcome the disturbance. Now the exothermic backward reaction of formation of the colourless N_2O_4 ($\text{N}_2\text{O}_4 \leftarrow 2\text{NO}_2$) is favoured and the gaseous mixture lightens.



In both cases the value of the equilibrium constant K_c changes when the temperature of the gaseous mixture is increased or lowered. The forward reaction is **endothermic ($\Delta H > 0$)** and K_c **increases with increasing temperature**. The backward reaction is **exothermic ($\Delta H < 0$)** and K_c **decreases with increasing temperature**.

AS A RULE:

The effect of temperature on equilibrium depends on the heats of reactions. When temperature rises equilibrium shifts in favour of the endothermic reaction. When temperature lowers equilibrium shifts in favour of the exothermic reaction.

REMEMBER THAT:

Catalysts do not affect chemical equilibrium!

They can not cause the equilibrium to shift towards the desired products. **Catalysts only accelerate reactions** and equilibrium is achieved over a shorter period of time but **the yield does not change**.

HOW TO CHOOSE THE OPTIMUM CONDITIONS TO CARRY OUT A REVERSIBLE REACTION?

In many industrial processes equilibrium is shifted in favour of the desired product taking into consideration the effects of concentration, pressure and temperature on equilibrium compositions. But the impact of these parameters on the reactions rate is also considered. Most often, some optimal conditions are fixed to make the industrial process profitable.

The synthesis of ammonia NH_3 is an example of how the Le Catelier-Braun principle is considered simultaneously with factors affecting the rate of the reaction in a way to obtain a sufficient amount of NH_3 over an acceptable period of time, i.e. to choose the **optimum conditions** for this synthesis.

The reaction undergoes in gaseous phase as the reactants and the product are gases. In a closed system the reaction is reversible:



The reaction is exothermic and the amount of molecules in the system decreases during the reaction (from 1 molecule N_2 and 3 molecules of H_2 only two molecules of NH_3 are formed). Lowering the temperature and compressing the gas mixture (increasing the pressure) shift the equilibrium in favour of the reaction of formation of ammonia NH_3 (the forward reaction). But at low temperature the rate of the reaction is too slow. At normal conditions nitrogen and hydrogen practically does not react. The reaction rate can be increased by increasing temperature but this lowers the yield of NH_3 as the equilibrium shifts towards the backward endothermic reaction of ammonia decomposition (at temperature equal to or greater than 1000°C the yield of ammonia is practically 0). This negative effect is partially overcome with the help of a catalyst (iron Fe and small amounts of Al_2O_3 and K_2O). In industry the synthesis of ammonia is realised at 30 MPa and 450°C . The yield is only about 22 %. The gaseous mixture leaving the reactor is cooled to the temperature of liquefying of NH_3 . It is collected and the unused hydrogen and nitrogen are returned back into the reactor.

CAN YOU ANSWER THESE QUESTIONS ?

1. How do systems in equilibrium react when subjected to a disturbance?
2. Hydrogen iodide HI is synthesised from hydrogen H_2 and iodine I_2 . The reaction is exothermic and reversible. How to increase the yield of HI?
3. Ethanoic acid is a weak acid dissociating in water. In an aqueous solution an equilibrium between CH_3COO^- ions, H_3O^+ ions and CH_3COOH molecules is established. What will happen if water is added to the solution?
4. The reaction of synthesis of nitrogen oxide NO from nitrogen N_2 and oxygen O_2 is reversible. Is it possible to generate more NO by compressing the reacting gases? Why?
5. The thermal decomposition of $CaCO_3$ in a closed container is reversible. Is it possible to increase the amount of decomposed $CaCO_3$ by pumping an inert gas into the container or by decreasing the volume of the container? Why?
6. If temperature rises, the yield of a reversible endothermic reaction is increased. Why?
7. The thermal decomposition of Ag_2CO_3 is an exothermic reaction. In a closed system the process is reversible. The value of the equilibrium constant is $1,4 \cdot 10^{-2}$ at $127^\circ C$. What is the value of the equilibrium constant at $77^\circ C$?
a) $4 \cdot 10^{-4}$ b) $1,9 \cdot 10^{-1}$
8. The reaction of synthesis of ammonia NH_3 from nitrogen N_2 and hydrogen H_2 is reversible and exothermic. Why is the industrial process of production of NH_3 from N_2 and H_2 realised at high temperature? Is it possible to increase the yield of NH_3 by adding catalyst to the reacting mixture?

RATE OF REACTIONS AND CHEMICAL EQUILIBRIUM – KEY POINTS

- **RATE OF A CHEMICAL REACTION** is the change in concentration of a reactant or a product over the change in time.
- The **RATE LAW** states that the rate of a chemical reaction is directly proportional to the concentrations of reactants raised to some powers: $v = k.[A]^{\alpha}[B]^{\beta}....$. The constant **k** is called **rate constant** of the reaction.
- If reactants are not present in the same phase, reaction rate increases with the increase of the **surface area** (solid-liquid, solid-gas or liquid-gas).
- According to the **VAN'T HOFF'S RULE**, the rate constant of a chemical reaction gets doubled to quadrupled for each rise of 10 °C in temperature.
- **CATALYSIS** is the acceleration of the rate of a chemical reaction by adding substances not consumed during the reaction.
- **CATALYST** is a substance that increases the rate of a reaction without itself being consumed. They create another route for the transformation of reactants into products thus lowering the activation energy of reactions. **INHIBITOR** is a substance that lowers the rate of a reaction.

- **HOMOGENEOUS CATALYTIC REACTIONS** speed up if the concentration of the homogeneous catalyst is increased.
- **HETEROGENEOUS CATALYTIC REACTIONS** speed up if the surface area of the catalyst available for the adsorption of reactants is increased.
- **CATALYSTS** can not initialise a reaction that is not undergoing.
- Reactions undergoing in both forward and backward direction are **REVERSIBLE** reactions. In their chemical equations an equilibrium arrows $\rightleftharpoons$ is used instead of an one way arrow $\rightarrow$. Reaction that undergo only in one direction (i.e. products can not react to produce the reactants) are **IRREVERSIBLE**. In closed systems most of the chemical reactions are reversible.
- **CHEMICAL EQUILIBRIUM** is a state of a reacting system in which both reactants and products are present but their concentrations do not change over time. **IN EQUILIBRIUM** the rate of the forward reaction is equal to the rate of the backward reaction.

- The **EQUILIBRIUM CONSTANT** of the reaction $aA + bB \rightleftharpoons cC + dD$ is expressed as $K_c = \frac{[C]^c \cdot [D]^d}{[A]^a [B]^b}$

Concentrations of pure liquids and pure solids are not included in the expressions for the equilibrium constants. If the reaction undergoes in gaseous phase the equilibrium constant can be expressed in terms of the partial pressure of gases and is denoted by K_p .

- Chemical equilibrium is dynamic. According to the **Le CHATELIER-BRAUN PRINCIPAL** a system in equilibrium, when subjected to a disturbance, responds in a way that tends to minimise the effect of the disturbance.
- Equilibrium constant does not depend on reactants and products concentration. But adding reactants or removing products shifts the equilibrium towards products. Removing reactants or adding products shifts the equilibrium towards reactants.
- Equilibrium constant does not depend on pressure. But the equilibrium mixture composition changes if the overall number of moles in the system changes. A rise in pressure favours the reaction reducing the number of moles. A decrease in pressure favours the reaction increasing the number of moles.
- Equilibrium constant value changes with temperature. The composition of the equilibrium mixture also changes. If temperature increases equilibrium shifts towards the endothermic reaction. If temperature decreases equilibrium shifts towards the exothermic reaction.
- Catalysts do not affect equilibrium. They only accelerate reactions and reduce the period of time over which the equilibrium is achieved.
- In industry all factors that affect the efficiency of chemical process are considered in terms of profit from investments, energy consumption and environmental protection. Chemical processes undergo at **optimal conditions**.

PROJECTS

1. CALORIFIC VALUES OF FUELS AND GLOBAL ENVIRONMENTAL ISSUES

Compare the calorificity of different fuels. Discuss the impact of fuels combustion on the environment. Are low molecular weight fuels less harmful for man and nature?

2. CALORICITY OF FOODS

What is foods calorificity? Why is it important to balance the everyday menu by choosing foods assuring the indispensable for the body functioning energy? What foods are the most calorific?

3. RATE OF REACTIONS IN THE EVERYDAY LIFE

Give examples of chemical reactions in the everyday life (in cooking, cleaning, painting, etc.) What does their rate depend on? Give examples of processes that should be slowed down.

4. PRODUCTION OF AMMONIA. THE HABER-BOSCH PROCESS

Learn more about the industrial production of ammonia. Pay attention to the reaction conditions. Why is this process so important for industry?