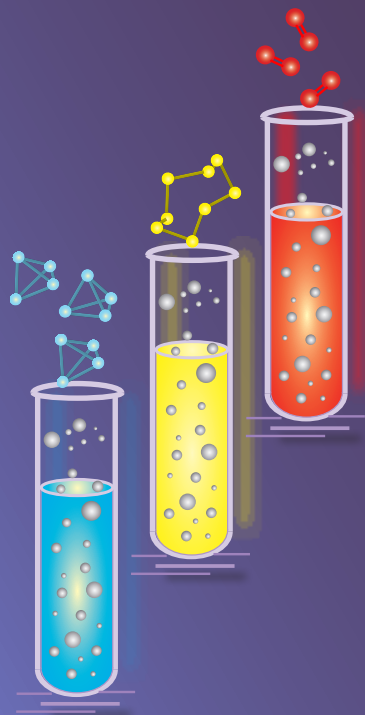


SOLUTIONS. CHEMICAL REACTIONS IN SOLUTIONS



- *Osmosis*
- *Diffusion*
- *Solubility*
- *Oxidation state*
- *Boiling and melting point*
- *pH of aqueous solution*
- *Electrolytes and nonelectrolytes*
- *Oxidation-reduction reactions*

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11 Aqueous solutions

KEY TOPICS

1. What are solutions?
2. Why is water a good solvent?
3. How do substances dissolve in water?
4. Do all substances dissolve in water?

Lakes and rivers are natural solutions

KEY WORDS

- Solutions
- Solute
- Aqueous solutions
- Hydrogen bonds
- Hydration shell

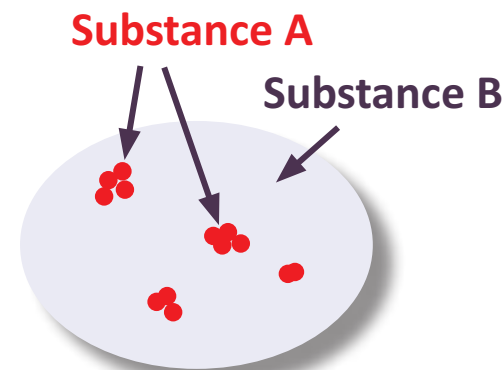
WHAT ARE SOLUTIONS?

Solutions are mixtures of two or more substances (simple substances or chemical compounds). But not all mixtures are solutions. For example, water and sunflower oil can be mixed but as oils, generally, do not dissolve in water, the mixture is not uniform and it is not a solution of sunflower oil in water. In contrary, if sugar is mixed with water, an uniform in composition liquid mixture is formed as sugar dissolves in water. All solutions are homogeneous mixtures. Generally, the quantity of one of the substances is much more than the quantities of the other components of the solution. It is called **solvent**. The other substances composing a solution are called **solutes**.

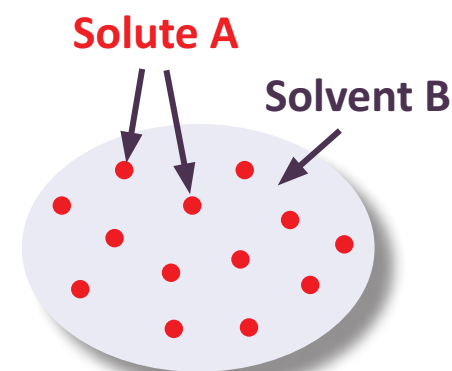
SOLUTIONS are homogeneous mixtures of two or more substances. The minor component (the solute) is uniformly distributed within the major component (the solvent).

If the solvent is water, solutions are called **aqueous solutions**. Only substances that dissolve in water can form aqueous solutions.

For example, sugar and table salt both dissolve in water forming aqueous solutions, if well mixed. The aqueous solution of sugar is a mixture of H_2O molecules and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ molecules. Sugar molecules are uniformly distributed within water molecules. Table salt not only dissolves in water but also dissociates forming positive Na^+ ions and negative Cl^- ions. The aqueous solution of table salt is composed of Na^+ and Cl^- ions uniformly distributed within water molecules.



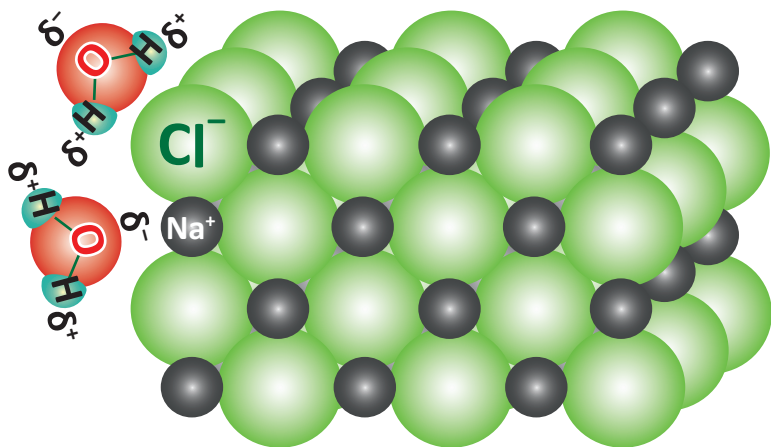
MIXTURE OF **A** AND **B**



SOLUTION OF **A** IN **B**

WHY IS THERE NOT A UNIVERSAL SOLVENT?

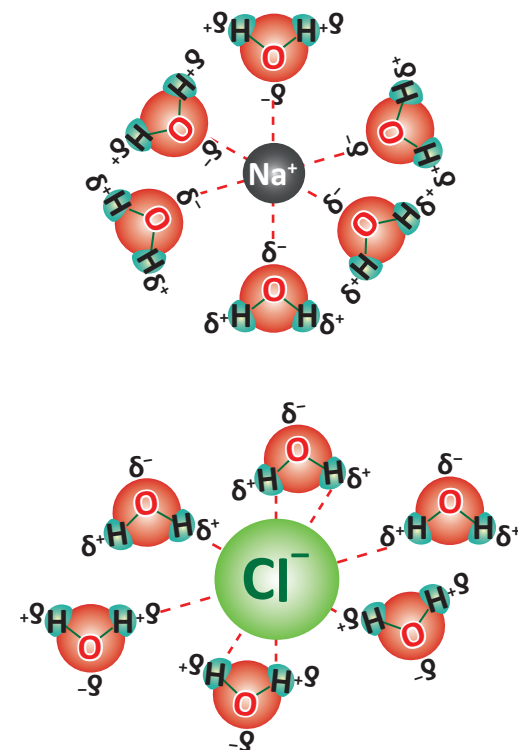
Many substances dissolve in water but not all substances. Oceans, rivers, lakes are natural solutions of many substances. But if oil leaks from a tanker and spreads over the sea, it is a disaster. Oil does not dissolve in water and oil spills are a serious pollutant. Many hydrocarbons that do not dissolve in water dissolve, for example, in tetrachloromethane CCl_4 . But salts do not dissolve in this organic solvent. Why? To answer this question it is necessary to understand the mechanism of dissolution.



POLAR WATER MOLECULES ARE ATTRACTED BY IONS BUILDING UP THE NaCl IONIC LATTICE.

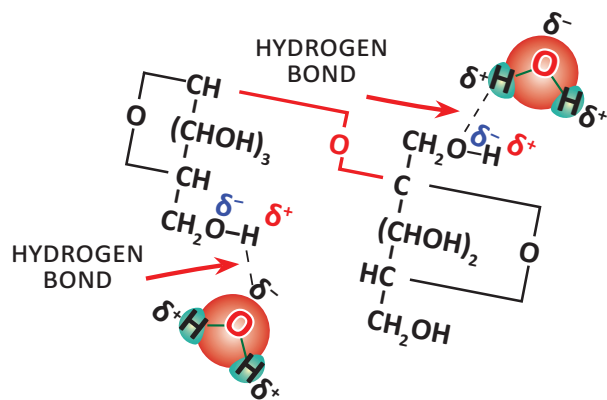
negative part of water molecules is attracted by the positive Na^+ ions. The electrostatic attraction between water molecules and salt ions is strong enough to pull out the ions of the crystal surface. They detach from the crystal lattice and the salt dissociates into Na^+ and Cl^- ions freely moving throughout the liquid. In the solution each ion is surrounded by water molecules forming a three dimensional **hydration shell**.

A very simple example is the dissolution of sodium chloride NaCl in water. This is an ionic salt made up of Na^+ ions and Cl^- ions forming an ionic lattice. Ions are held together thanks to strong electrostatic forces of attraction between the oppositely charged ions. In water the surface of the ionic crystal is in contacts with polar water molecules. The positive part of water molecules is attracted by the negative Cl^- ions. The



HYDRATION SHELLS OF Na^+ AND Cl^- IONS IN AQUEOUS SOLUTIONS OF NaCl

Another simple example is the dissolution of saccharose in water. Saccharose molecule $C_{12}H_{22}O_{11}$ is polar as it has 8 hydroxy groups ($-OH$). Oxygen atoms are more electronegative than hydrogen atoms and oxygen atoms have partial negative charges (δ^-) while hydrogen atoms have partial positive charges (δ^+). During dissolution saccharose molecules at the surface of the sugar crystal are in contact with water molecules. Their partially negatively charged O atoms attract the partially positively charged H atoms of water molecules and the partially positively charged H atoms of saccharose molecules attract the partially negatively charged O atoms of water molecules. These electrostatic forces are stronger than the intermolecular forces of attraction holding the saccharose molecules in the crystal. Saccharose dissolves liberating saccharose molecules that freely move throughout the solution.



HYDROGEN BONDS BETWEEN A SACCHAROSE MOLECULE AND WATER MOLECULES

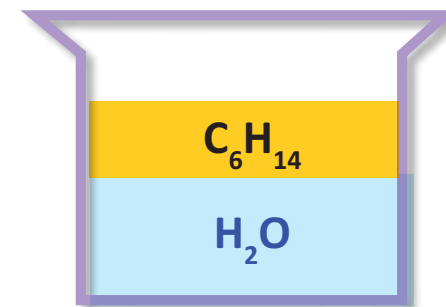
In the aqueous solution polar saccharose molecules interact with polar water molecules – again the partially negatively charged O atoms of saccharose molecules attract the partially positively charged H atoms of water molecules and the partially positively charged H atoms of saccharose molecules attract the partially negatively charged O atoms of water molecules. These intermolecular interactions are considered as intermolecular bonds called **hydrogen bonds***. All 8 hydroxy groups of the saccharose molecule can form hydrogen bonds. These bonds are weaker than the polar covalent O–H bonds of saccharose molecules. Hydrogen

bonds exist also between water molecules. Around each saccharose molecule (as around Na^+ and Cl^- ions) forms a three dimensional hydration shell of water molecules thanks to the hydrogen bonding of water and saccharose molecules.

*Generally, hydrogen bonding occurs between polar molecules with H-atoms covalently bonded to electronegative atoms with lone (unshared) electron pairs (F, N, O).

Oil does not dissolve in water as hydrocarbons are nonpolar compounds. The polar water molecules are not attracted by the nonpolar hydrocarbon molecules. For example, hexane C_6H_{14} forms a layer over the water if poured in a beaker with water.

Nonpolar compounds dissolve in nonpolar solvents. The nonpolar molecules of a compound are held together thanks to intermolecular forces that are weaker than hydrogen bonds. But the intermolecular forces between solute and solvent molecules are stronger than the intermolecular forces between the solute molecules themselves. Hexane C_6H_{14} , for example, mixes with tetrachloromethane CCl_4 in all proportions forming homogeneous solutions because the intermolecular forces between its molecules and CCl_4 molecules are strong compared to the intermolecular forces between hexane molecules themselves.



HEXANE C_6H_{14} IS NONPOLAR.
IT DOES NOT DISSOLVE IN WATER
AND OTHER POLAR SOLVENTS.

As a rule of the thumb „LIKE DISSOLVES LIKE“.
Polar solvents (water, ethanol, etc.) dissolve ionic and polar substances.
Nonpolar solvents (CCl_4 , C_6H_{14} , C_6H_6 , etc.) dissolve nonpolar substances.

Water is the most abundant chemical compound on the Earth and is a very good but not a universal solvent. As its molecules are highly polar it can not dissolve nonpolar substances.

CAN YOU ANSWER THESE QUESTIONS ?

1. What are solutions?
2. Is a mixture of sugar and powdered cacao a solution? Why?
3. Why is water a good solvent of many ionic and polar substances?
4. Some processes of dissolution are endothermic but others are exothermic. Why?
5. Ethanol mixes with water in all proportions? Why?
6. CO_2 is a nonpolar gas but natural waters are containers of CO_2 . Why?
7. Do you remember what molarity of a solution stands for?
8. AgCl is an ionic compound but it is insoluble in water. Can you guess why?
9. Why are aqueous solutions so important for life?

12

Properties of liquids Solubility

KEY TOPICS

1. What is solubility?
2. What is saturated solution?
3. What are miscible substances?
4. What is the effect of temperature on solubility?
5. What is the effect of pressure on solubility?

KEY WORDS

- Solubility
- Unsaturated solution
- Saturated solution
- Supersaturated solution
- Miscible substances
- Soluble substance
- Slightly soluble substance
- Insoluble substance

O_2 (0,27 mmol/ℓ)

N_2 (0,51 mmol/ℓ)

A SUBSTANCE IS SOLUBLE IN A SOLVENT. WHAT DOES THIS MEAN?

A substance (simple substance or chemical compound) is soluble in a solvent if some amount of it dissolves if mixed with the solvent. The more the amount of the dissolved substance (the solute), the higher the concentration of the solution. But the amount of the solute in the solution can be increased to some extent. If the maximum amount of a solute in a given amount of a solvent is reached, the dissolution stops. This is an equilibrium state. If a new amount of the solute is added to the solution, it does not dissolve. For example, the maximum amount of NaCl that can be dissolved in 100 g of water at 20 °C and 101,3 kPa is 36 g. It means that if you dump 100 g of NaCl into 100 g of water, only 36 g of the salt dissolve and 64 g precipitate on the bottom of the vessel.

The ability of a substance to dissolve in a solvent is called **solubility**. It is expressed as the maximum amount of the solute that dissolves in a given amount of the solvent.

SOLUBILITY of a substance in a solvent is its maximum amount that can dissolve in a given amount of the solvent at a specific temperature and pressure.

Different substances dissolve to different extent in different solvents. Most often their solubility is expressed as the maximum amount of the solute (in g) that dissolves in 100 g of solvent.

A solution containing the maximum amount of a solute that can be dissolved at a given temperature and pressure is called **saturated solution**. If the concentration of the solute is lower, the solution is **unsaturated**. If by some reason the concentration exceeds the solubility of the solute, the solution is **supersaturated**. These solutions are very instable.

Solubilities range from infinitely soluble to insoluble substances. If two substances are soluble in all proportions (like water and ethanol) they are **miscible**. Substances as AgNO_3 , NaCl , K_2SO_4 , NaOH , CuSO_4 , CH_3COONa are considered as **soluble** in water. Their solubilities are greater than 1,0 g per 100 g of water. Other substances as CaSO_4 , Ag_2SO_4 , PbCl_2 are considered as **slightly soluble** in water. Their solubilities are low (0,1 - 1,0 g/100 g of water). Substances as AgCl , BaSO_4 , CaS , MgS are considered as **insoluble** in water. In fact all substances are soluble to some extent but the concentration of the saturated solutions of the substances considered as insoluble is very, very low.

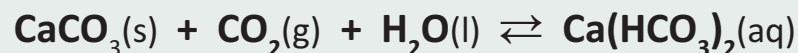
Data about substances solubilities are presented in tables that can be found in many handbooks. But some general rules could be very useful:

- **All nitrates are soluble** (NaNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, etc.)
- **All ethanoates are soluble** (CH_3COONa , $(\text{CH}_3\text{COO})_2\text{Ca}$, etc.)
- **Chlorides, bromides, iodides are soluble** (NaCl , CuCl_2 , BaBr_2 , KI , etc.). Except salts of Ag, Pb.
- **Sulfates are soluble** (Na_2SO_4 , MgSO_4 , CuSO_4 , $\text{Al}_2(\text{SO}_4)_3$, etc.). Except Ag_2SO_4 , BaSO_4 , CaSO_4 , PbSO_4 .
- **Salts of sodium Na, potassium K and salts containing NH_4^+ ions are soluble.**
- **Most of hydroxides are insoluble. Hydroxide of alkali metals and $\text{Ba}(\text{OH})_2$ are soluble.** $\text{Sr}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ are slightly soluble.
- **Most of carbonates are insoluble.** Carbonates of alkali metals are soluble.
- **Most of sulfides are insoluble.** Sulfides of alkali metals are soluble.
- **Most of metal oxides are insoluble.** Except oxides of alkali and alkaline earth metals.

PROBLEM!

Stalactites and stalagmites in caves are mainly made up of the insoluble in water CaCO_3 . How do they form?

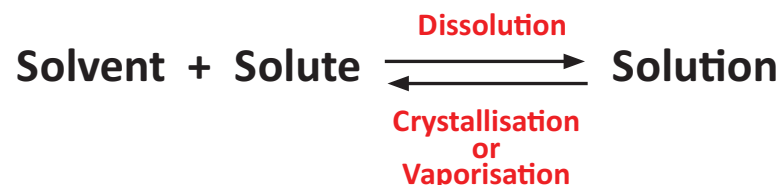
ANSWER: Ca forms two salts of carbonic acid H_2CO_3 – CaCO_3 (calcium carbonate) and $\text{Ca}(\text{HCO}_3)_2$ (calcium dihydrogencarbonate). CaCO_3 is insoluble in water but $\text{Ca}(\text{HCO}_3)_2$ is slightly soluble in water (0,16 g/100 g of water). The insoluble CaCO_3 transforms into the slightly insoluble $\text{Ca}(\text{HCO}_3)_2$ in a reversible reaction with carbon dioxide CO_2 and water:



If the amount of CO_2 in underground waters increases, according to the Le Chatelier's principle, the equilibrium shifts towards the formation of the slightly soluble $\text{Ca}(\text{HCO}_3)_2$. Some amount of limestone (CaCO_3) dissolves. For this reason underground waters in karst regions contain Ca^{2+} ions. But if the amount of CO_2 dissolved in water decreases (for example, underground water comes into contact with air in a cave) the equilibrium shifts to the left. Water drips slowly depositing CaCO_3 and forming stalactites and stalagmites. These reversible transformation creates the astonishing beauty of caves.

DO TEMPERATURE AND PRESSURE AFFECT SOLUBILITY?

When a solution is saturated the system composed of the solute and the solvent is in equilibrium – the rate of dissolution of the solute is equal to the rate of its crystallisation (if a solid dissolves in a liquid) or to the rate of its vaporisation (if a gas dissolves in a liquid). As a whole, for saturated solutions:

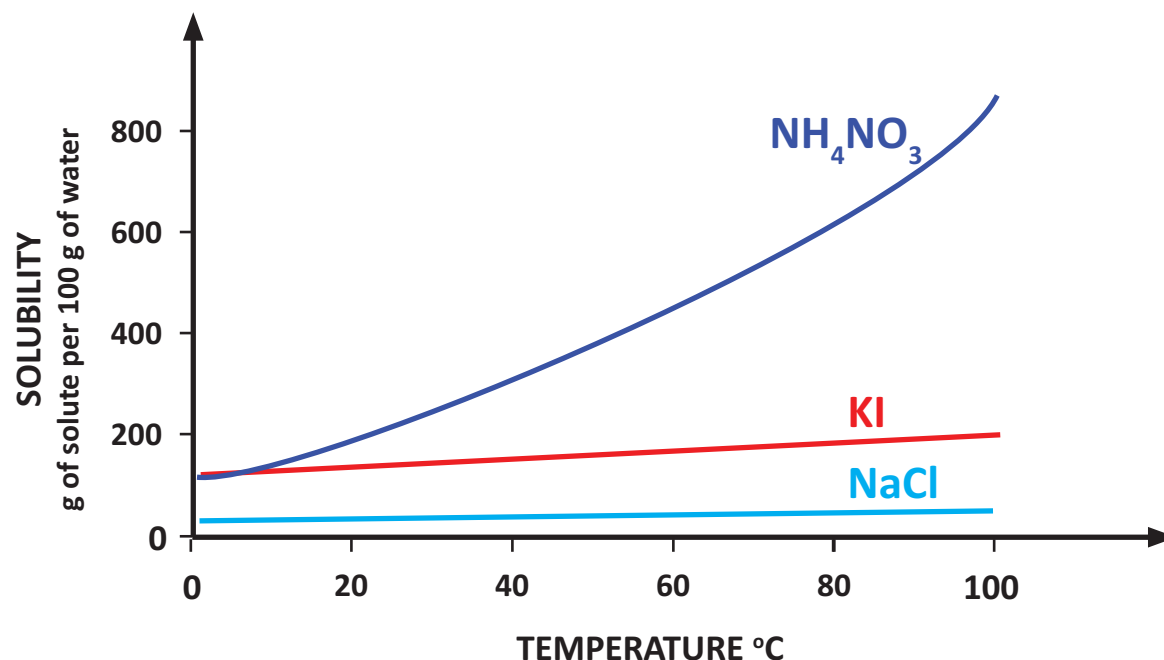


Solubility of substances depends mainly on the identity of the solvent and the solute. But changes in temperature or pressure can lower or increase the solubility of a substance in a given solvent as the above equilibrium can shift towards the increase or towards the decrease of the concentration of the solution.

EFFECT OF TEMPERATURE

Dissolution is a process accompanied by a gain or a loss of energy of the system, i.e. dissolution processes are endo- or exothermic and changes in temperature affect substances solubility.

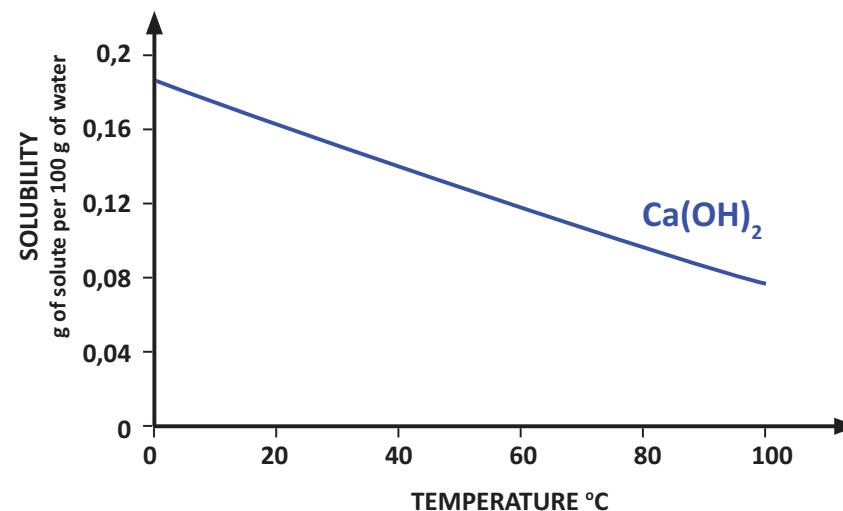
Dissolution of solids can be both exo- and endothermic. If the process is endothermic, solubility rises with increasing temperature.



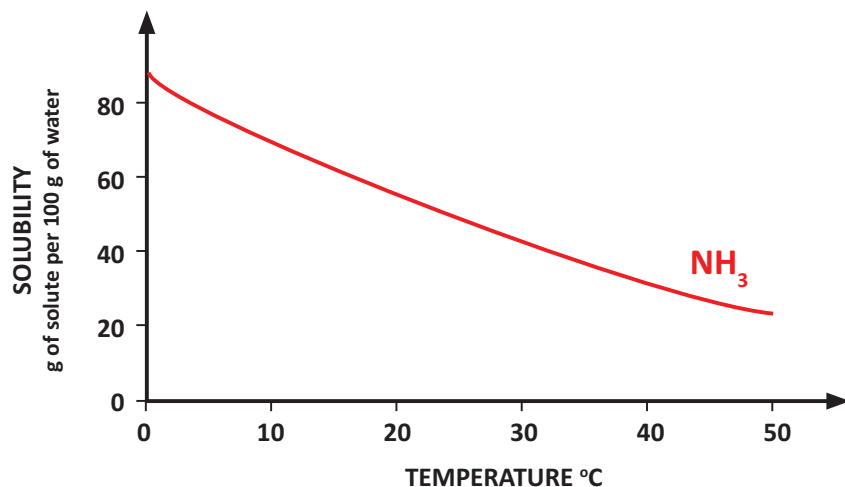
EFFECT OF TEMPERATURE ON THE SOLUBILITY OF SOME SALTS

The solubility of some solid substances is strongly affected by changes in temperature. For example, the solubility of ammonium nitrate NH_4NO_3 increases dramatically with the increase in temperature. The solubility of other substances, like NaCl , is only slightly dependant on temperature. (look at the graphic on the previous page).

During the dissolution of some compounds heat is lost and an increase in temperature results in a decrease of the solubility. For example, the solubility of Ca(OH)_2 drops more than twice when temperature rises from 0°C to 100°C .



EFFECT OF TEMPERATURE ON THE SOLUBILITY OF Ca(OH)_2



EFFECT OF TEMPERATURE ON THE SOLUBILITY OF NH_3

Dissolution of gases is an exothermic process and their solubility decreases with increasing temperature. The solubility of ammonia NH_3 decreases about four times when temperature rises from 0°C to 50°C . Carbon dioxide CO_2 is much less soluble in water than ammonia but its solubility decreases about 6 times when temperature increases from 0°C to 60°C .

EFFECT OF PRESSURE

Solids and liquids are practically incompressible and changes in pressure do not affect their solubility. Gases are compressible and changes in pressure result in changes of gases solubility.

A solution of a gas in a liquid solvent is in equilibrium state when the number of gaseous molecules living the liquid phase is equal to the number of gaseous molecules dissolving in the liquid. If the system is compressed, the pressure over the liquid surface increases. According to the Le Chatelier's principle, the system reacts to overcome this change. The only way to lower the pressure is to decrease the number of gas molecules in the gaseous phase, i.e. to dissolve some amount of the gas in the solvent. As a result the concentration of the gas in the solvent rises – the solubility of the gas increases. In contrary, if the system is decompressed, the decrease in pressure is overcome by an increase in the rate of vaporisation of the gas – the solubility of the gas decreases.

A simple empirical equation, known as the Henry's law*, states that for dilute solutions the amount of a dissolved gas is proportional to its partial pressure** p_B in the gas phase above the solution:

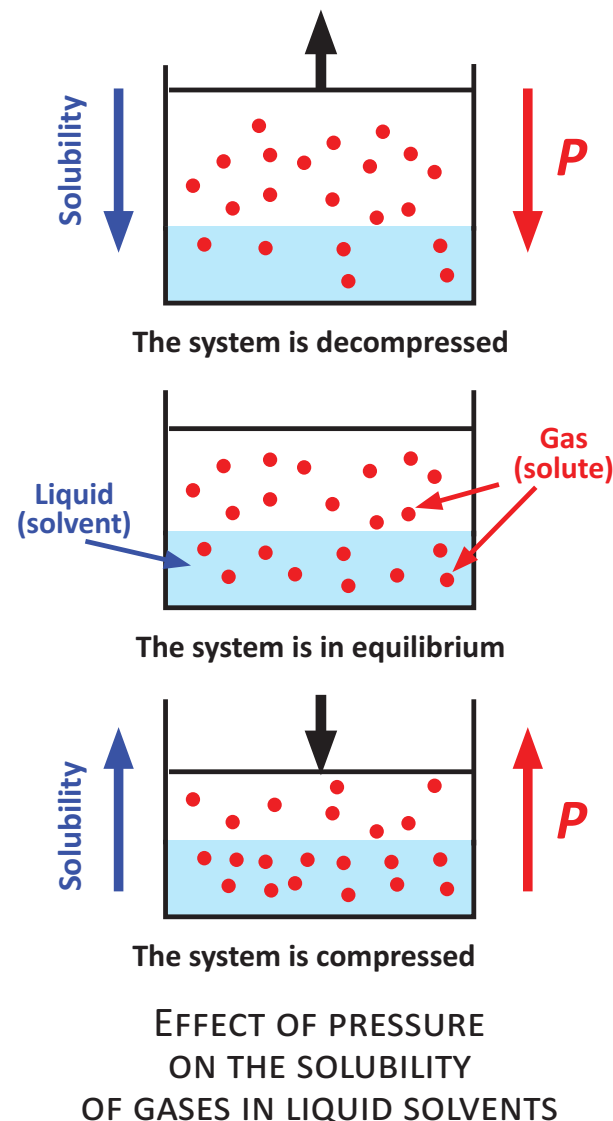
$$p_B = H_B \cdot x_B$$

H_B is an empirical constant depending on the nature of the solvent and the solute and on the temperature. It is called Henry's law constant. x_B is the mole fraction*** of the dissolved gas in the solution.

*This relationship has been established experimentally by William Henry in 1803.

**The pressure that a gas would exert if it was alone in the volume occupied by a gas mixture.

***The mole fraction of a substance in a mixture x_B is equal to the number of moles of this substance n_B divided by the total number of moles in the mixture: $x_B = n_B / (n_A + n_B + n_C + \dots)$



PROBLEM!

What is the solubility (as molarity) of oxygen O_2 in natural waters exposed to air at 25 °C at sea level? $H_{O_2} = 4,3 \cdot 10^9$ Pa

SOLUTION: 1. Determine the partial pressure of O_2 .

The mole fraction of O_2 in dry air is $x_{O_2} = 0,21$.

The atmospheric pressure at sea level is 101 325 Pa.

The partial pressure of oxygen is:

$$p_{O_2} = 0,21 \cdot 101\,325 = \mathbf{21\,278,25\,Pa}$$

2. Calculate the solubility of oxygen in water using the Henry's law.

$$x_{O_2} = \frac{p_{O_2}}{H_{O_2}} = \frac{21\,278,25}{4,3 \cdot 10^9} = 4,95 \cdot 10^{-6}$$

3. Convert the mole fraction into mol/ℓ.

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} \approx \frac{n_{O_2}}{n_{H_2O}} \quad (\text{for a dilute solution } n_{O_2} \ll n_{H_2O})$$

For 1 ℓ of a dilute solution at 25 °C $n_{H_2O} \approx 997:18 = \mathbf{55,4\,moles}$

(The mass of 1 ℓ of water at 25 °C is 997 g; $M(H_2O) = 18$ g/mol)

It follows that the amount of dissolved oxygen O_2 in 1 ℓ of solution is:

$$n_{O_2} = x_{O_2} \cdot n_{H_2O} = 4,95 \cdot 10^{-6} \cdot 55,4 = \mathbf{0,000274\,moles}$$

ANSWER: The solubility of O_2 in natural waters exposed to air at 25 °C and at sea level is 0,27 mmol/ℓ.

CAN YOU ANSWER THESE QUESTIONS ?

1. What is solubility?
2. What substances are soluble, slightly soluble and insoluble in water?
3. What is the difference between a miscible with a solvent and a soluble in a solvent substance?
4. Why does water in karst regions cause the formation of scale in boilers, kettles and washing machines?
5. At standard conditions methanol CH_3OH , ethanol $\text{C}_2\text{H}_5\text{OH}$ and propanol $\text{C}_3\text{H}_7\text{OH}$ are miscible with water. Butanol $\text{C}_4\text{H}_9\text{OH}$ and pentanol $\text{C}_5\text{H}_{11}\text{OH}$ are soluble in water. Hexanol $\text{C}_6\text{H}_{13}\text{OH}$ and heptanol $\text{C}_7\text{H}_{15}\text{OH}$ are slightly soluble in water. Higher alcohols practically do not dissolve in water at normal conditions? Why?
6. To prepare a syrup the water solution of sugar is heated. But to dissolve more slaked lime in water the temperature of the solution is lowered. Why?
7. Why does the solubility of gases decrease with increasing temperature?
8. Why is it important to know the solubility of gases composing air in natural waters?

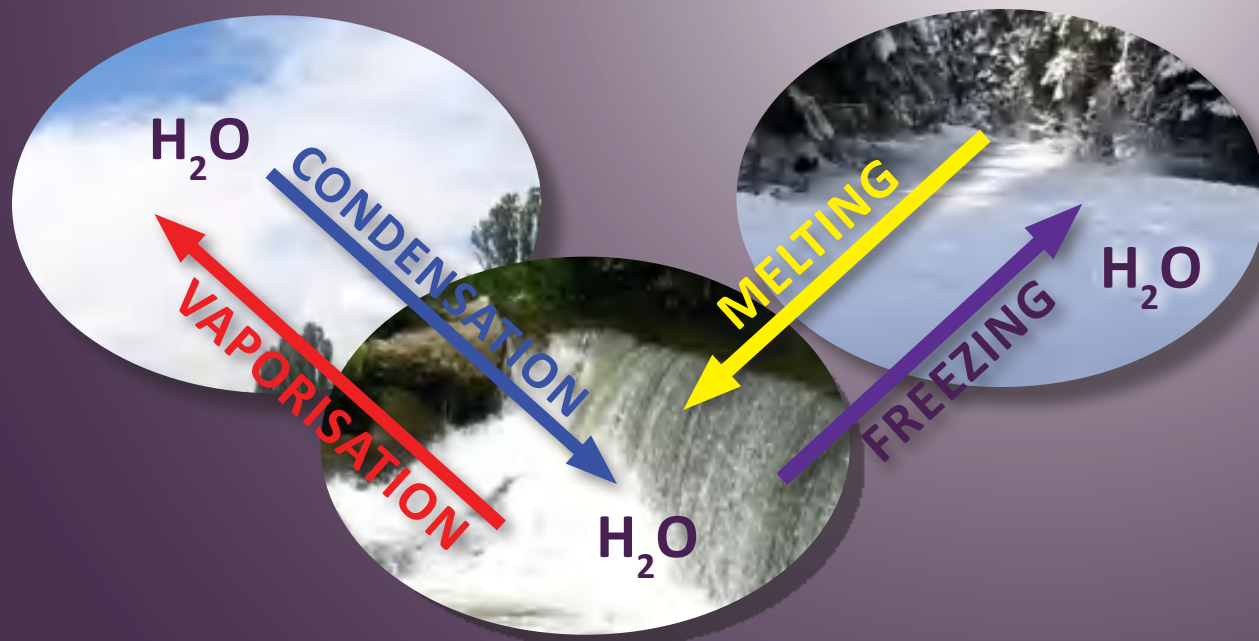
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Vapour pressure

Boiling and melting temperature

KEY TOPICS

1. Why do liquids boil and melt?
2. Why do different liquids boil and melt at different temperatures?
3. Does a liquid solution boil and melt at the same temperature as the solvent?
4. What properties of liquid solutions are called colligative properties?



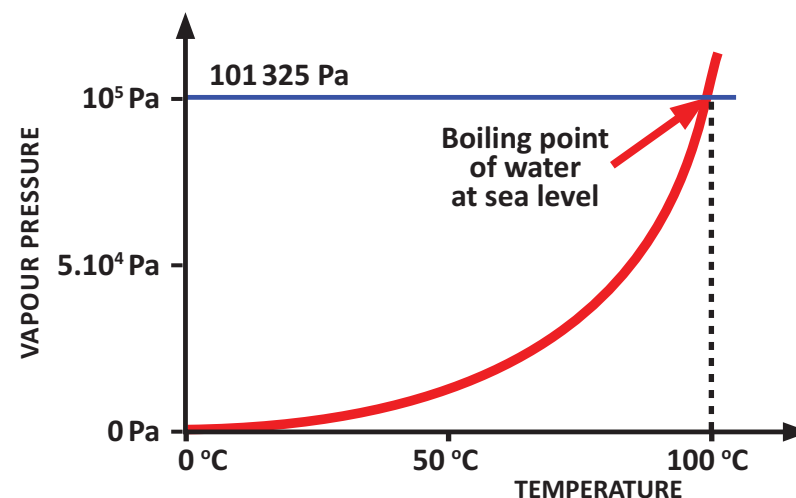
KEY WORDS

- Vapour pressure
- Boiling temperature (point)
- Melting temperature (point)
- Colligative properties
- Elevation of the boiling temperature of a solution
- Depression of the freezing temperature of a solution

WHY DO DIFFERENT SUBSTANCES BOIL AND MELT AT DIFFERENT TEMPERATURES?

When a pure liquid in a closed vessel is in equilibrium state the quantity of molecules vaporising from its surface is equal to the quantity of condensing molecules, i.e. the rate of vaporisation of the liquid is equal to the rate of its condensation. The pressure of the vapour in equilibrium with the liquid is called **vapour pressure**.

When the liquid is heated, its temperature rises and the number of molecules on the liquid surface, whose kinetic energy is high enough to overcome intermolecular forces holding them together in the liquid phase, increases. These molecules vaporise from the liquid surface and the vapour pressure increases. If the liquid is heated in an open vessel, when the vapour pressure is equal to the external pressure, the liquid boils – it vaporises not only from its surface but also throughout its volume and freely expands into the surrounding. This temperature is called **boiling temperature** or simply **boiling point**. A liquid boils until it completely vaporises and during this period the temperature remains constant.



INCREASING OF VAPOUR PRESSURE
OF WATER AT SEA LEVEL
WITH TEMPERATURE

The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the **BOILING TEMPERATURE** at that pressure.

The boiling temperature of a pure liquid at a pressure of 101325 Pa is called **normal boiling point**. The normal boiling point of water is 100 °C.

Boiling temperature depends on the nature of the liquid and on the external pressure. At a given pressure substances boil over a wide temperature range as intermolecular forces holding molecules together in the liquid phase depend strongly on the identity of the pure liquid substance. If intermolecular forces are strong, the vapour pressure is low and the boiling point is high. In contrary, if intermolecular forces are weak, the vapour pressure is high and the boiling point is low. At 101,3 kPa Helium boils at $-268,9\text{ }^{\circ}\text{C}$, hydrogen H_2 at $-253\text{ }^{\circ}\text{C}$, ammonia NH_3 – at $-33,3\text{ }^{\circ}\text{C}$, ethanol $\text{C}_2\text{H}_5\text{OH}$ – at $78,3\text{ }^{\circ}\text{C}$, water H_2O – at $100\text{ }^{\circ}\text{C}$, sulfuric acid H_2SO_4 – at $337\text{ }^{\circ}\text{C}$, mercury Hg – at $356,9\text{ }^{\circ}\text{C}$, sulfur S_8 – at $444,6\text{ }^{\circ}\text{C}$, tungsten W – at $5930\text{ }^{\circ}\text{C}$, etc.

Substances that have high vapour pressure are called substances with high **volatility**. For example, the vapour pressure of ethanol $\text{C}_2\text{H}_5\text{OH}$ is high compared to the vapour pressure of water as intermolecular forces between ethanol molecules are weaker than the intermolecular forces holding together water molecules. Ethanol is more volatile than water.

Boiling temperatures of pure liquids are their characteristic parameter and are used to identify them.

Another phase transition occurs when a solid is heated to its **melting temperature** – the solid structure breaks down and the substance melts, i.e. the substance changes from a solid to a liquid state. The temperature of the solid-liquid system remains constant until the solid completely melts. Pure crystalline substances (simple substances and compounds) melts at a fixed temperature at a given pressure. By definition:

The temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium is called the **MELTING TEMPERATURE at that pressure.**

The melting temperature of a pure crystalline substance is the same as its freezing temperature (or temperature of crystallisation). The freezing temperature of a pure liquid at a pressure of 101,3 kPa is called **normal freezing point**. The normal freezing point of water is 0 °C.

Crystalline substances melt over a wide temperature range. For example, at 101,3 kPa helium He melts at -272 °C, hydrogen H₂ – at -259 °C, chlorine Cl₂ – at -101 °C, water – at 0 °C, gallium Ga – at 30 °C, CH₃COOH – at 16,7 °C, sodium Na – at 97,8 °C, sodium base NaOH at 318 °C, sodium chloride NaCl at 800,7 °C, CaO – at 2613 °C, Tungsten W – at 3422 °C, etc.

Melting temperatures of pure crystalline solids are their characteristic parameter and are used to identify them.

Amorphous pure substances melt over a temperature range.

DO SOLUTIONS BOIL AND FREEZE AT THE SAME TEMPERATURE AS THE SOLVENT?

In general, solutions do not boil and freeze at the same temperature as the pure solvent. The effect of the solute on the boiling and freezing temperature depends on the nature of the solvent and the solute and on the concentration of the solution. But if the solute is not a volatile substance, the effect on the vapour pressure and consequently on the boiling and the melting temperature of the solution, does not depend on the identity of the solute – this is a colligative (depending on the collection) property of the solution. By definition:

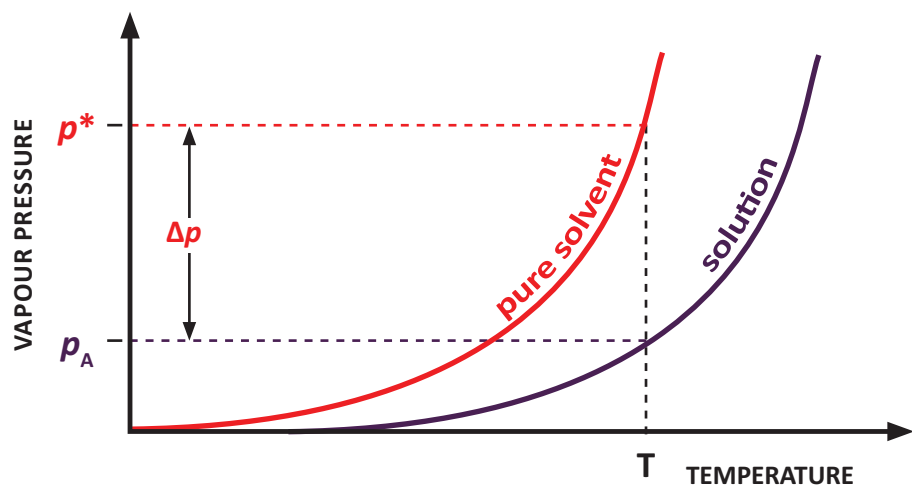
The properties of solutions that depend only on the number of solute particles present are called **COLLIGATIVE PROPERTIES.**

Colligative properties of solutions of not volatile substances are:

- Lowering of the vapour pressure of the solution
- Elevation of the boiling temperature of the solution
- Depression of the freezing temperature of the solution
- Osmosis

LOWERING OF THE VAPOUR PRESSURE OF THE SOLUTION

Solutes that are not volatile lower the vapour pressure over the liquid phase at a given temperature. As solutions are homogeneous systems, some particles of the solute are present on the liquid-gas interface. The quantity of molecules of the solvent on the liquid-gas interface is decreased. Consequently,



LOWERING OF THE VAPOUR PRESSURE OF THE SOLUTION

the number of molecules whose kinetic energy is enough to overcome the intermolecular forces keeping them together in the liquid phase is lowered. Solute molecules do not contribute to the vapour pressure of the solution as they are not volatile. As a consequence, at a given temperature, the vapour pressure of the solution is low compared to the vapour pressure of the pure solvent.

A simple equation, known as the Raoult's

law*, states that for ideal solutions**, at a given temperature, the partial pressure of the solvent p_A is proportional to its mole fraction in the solution x_A :

$$p_A = p^* \cdot x_A \quad (p^* \text{ is the vapour pressure of the pure solvent})$$

When the solute is a not volatile substance the lowering of the vapour pressure of the solution is:

$$\Delta p = p^* - p_A = p^* - p^* \cdot x_A = p^* (1 - x_A)$$

For a solution containing only one solute **B** the mole fraction of the solute is $x_B = 1 - x_A$ and finally:

$$\Delta p = p^* \cdot x_B$$

*Fransois-Marie Raoult has formulated the law in 1887.

**In ideal solutions intermolecular forces between solvent and solute molecules are the same as between solvent molecules.



VAPOUR PRESSURE OF A PURE SOLVENT



VAPOUR PRESSURE OF A SOLUTION
● particles of a not volatile solute

This equation is used to calculate the lowering of the vapour pressure of dilute solutions.

PROBLEM!

The vapour pressure of water at 25 °C is 3 160 Pa. What is the vapour pressure of a solution of 12 g of saccharose in 1 ℓ of water? The density of water at 25 °C is 997 kg/m³.

SOLUTION: 1. Calculate the mole fraction of saccharose x_B .

The molar mass of saccharose is $M(C_{12}H_{22}O_{11}) = 342 \text{ g/mol}$

The amount of saccharose is: $n_B = \frac{\text{mass of } C_{12}H_{22}O_{11}}{M(C_{12}H_{22}O_{11})} = 12:342 = \underline{\underline{0,035 \text{ moles}}}$

The mole fraction of saccharose is: $x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$ (as $n_A \gg n_B$)

The amount of water is $n_A = (\text{mass of 1 ℓ of water}):M(H_2O) = 997:18 = \underline{\underline{55,4 \text{ moles}}}$

The mole fraction of saccharose is: $x_B = 0,035:55,4 = 6,3 \cdot 10^{-4}$

2. Calculate the lowering of the vapour pressure of the solution.

$$\Delta p = p^* \cdot x_B = 3160 \cdot 6,3 \cdot 10^{-4} = 2 \text{ Pa}$$

3. Calculate the vapour pressure of the solution.

$$p_A = p^* - \Delta p = 3160 - 2 = 3158 \text{ Pa}$$

ANSWER: At 25 °C the vapour pressure of a solution of 12 g of saccharose in 1 ℓ of water is 3,158 kPa.

ELEVATION OF THE BOILING TEMPERATURE OF THE SOLUTION

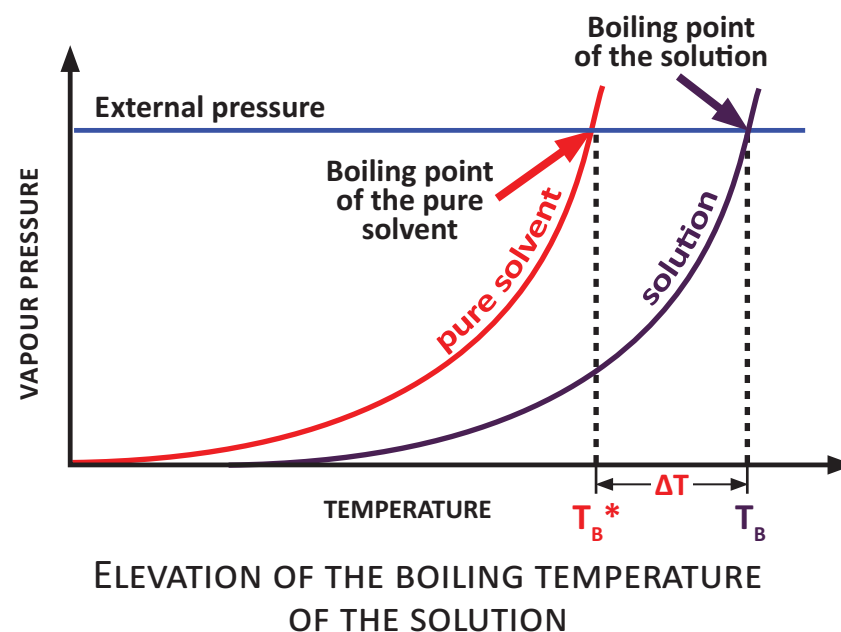
A solution boils when its vapour pressure is equal to the external pressure. A not volatile solute lowers the vapour pressure of the solution. As consequence more heat is needed to rise the vapour pressure of the solution up to the external pressure and the solution boils at a high temperature as compared to the pure solvent (see the graph).

The boiling point elevation ΔT is equal to the difference between the boiling point of the solution T_B and the boiling point of the pure solvent T_B^* at the same pressure, i.e. $\Delta T = T_B - T_B^*$. Usually, it refers to an external pressure of 101,325 kPa and T_B^* is the normal boiling point of the pure solvent. The boiling point elevation for a dilute solution of a not volatile substances is proportional to the amount of solute in 1000 g of solvent (m_b):

$$\Delta T = K_b m_b$$

K_b is an empirical constant known as **boiling-point constant** of the solvent. For example, K_b of water is $0,51 \text{ K.kg.mol}^{-1}$. m_b is called **molality** of the solution. The boiling point elevation does not depend on the identity of the not volatile solute.

The boiling-point elevation of a dilute solution of a not volatile substance can be used to determine experimentally the molar mass of the solute.



PROBLEM!

What is the boiling temperature of a solution of 50 g of sugar in 2 kg of water at 101 325 Pa? The boiling-point constant of water is $0,51 \text{ K.kg.mol}^{-1}$

SOLUTION: 1. Determine m_b .

The molar mass of saccharose is $M(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 342 \text{ g/mol}$

The amount of saccharose is: $n_b = \frac{\text{mass of } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{M(\text{C}_{12}\text{H}_{22}\text{O}_{11})} = 50:342 = \underline{\underline{0,146 \text{ moles}}}$

The molality m_b of a solution of 50 g of saccharose in 2 ℓ of water is:

$$m_b = \frac{n_b(\text{saccharose})}{\text{mass of water}} = 0,146:2 = \underline{\underline{0,073 \text{ mol/kg}}}$$

2. Calculate the boiling-point elevation of the solution.

$$\Delta T = K_b \cdot m_b = 0,51 \cdot 0,073 = \underline{\underline{0,037 \text{ } ^\circ\text{C}}}$$

3. Calculate the boiling temperature of the solution.

The boiling temperature of water at 101 325 Pa is $100 \text{ } ^\circ\text{C}$. So $\Delta T = T_b - 100$. Or:

$$T_b = \Delta T + 100 = 0,037 + 100 = \underline{\underline{100,037 \text{ } ^\circ\text{C}}}$$

ANSWER: At 101 325 Pa a solution of 50 g of saccharose in 2 kg of water boils at $100,037 \text{ } ^\circ\text{C}$.

DEPRESSION OF THE FREEZING TEMPERATURE OF THE SOLUTION

When a liquid substance freezes its liquid and solid phases coexist in equilibrium. If the solute does not dissolve in the solid solvent, the solvent separates when the solution is frozen (for example, when a solution of NaCl in water freezes, the solid phase is a mixture of ice (frozen water) and NaCl). The solute is present in the liquid phase but is not present in both the vapours and the solid solvent. Under these conditions, the solution freezes at a lower temperature than the pure solvent.

The freezing point depression is defined as $\Delta T = T_f^* - T_f$ where T_f^* is the freezing point of the solvent at a given pressure and T_f is the freezing point of the solution at the same pressure. Usually, the external pressure is 101,3 kPa and T_f^* is the normal freezing point of the pure solvent.

Similarly to the boiling point elevation, the freezing point depression for a dilute solution of a not volatile substances is proportional to the amount of solute in 1000 g of solvent (m_b):

$$\Delta T = K_f m_b$$

K_f is an empirical constant known as **freezing-point constant** of the solvent. For example, K_f of water is 1,86 K.kg.mol⁻¹. m_b is the molality of the solution (the amount of solute in 1000 g of solvent). The freezing point depression does not depend on the solute identity.

The freezing-point depression of a dilute solution of a not volatile substance that does not dissolve in the pure solid solvent can be used to determine experimentally the molar mass of the solute.

PROBLEM!

What is the freezing temperature of a solution of 10 g of NaCl in 1000 g of water?
The freezing-point constant of water is $1,86 \text{ K.kg.mol}^{-1}$

SOLUTION: 1. Determine m_b .

The molar mass of sodium chloride is $M(\text{NaCl}) = 58,5 \text{ g/mol}$

The amount of NaCl is: $n_b(\text{NaCl}) = 10:58,5 = \underline{\underline{0,17 \text{ moles}}}$

NaCl dissociates in water into Na^+ and Cl^- ions. So the amount of solute particles in the solution is twice as large as the amount of NaCl, i.e. $0,17 \cdot 2 = \underline{\underline{0,34 \text{ moles}}}$

The amount of solute particles in 1000 g (1 kg) of water is:

$$m_b = 0,34:1 = \underline{\underline{0,34 \text{ mol/kg}}}$$

2. Calculate the freezing-point depression of the solution.

$$\Delta T = K_f \cdot m_b = 1,86 \cdot 0,34 = \underline{\underline{0,63 \text{ } ^\circ\text{C}}}$$

3. Calculate the freezing temperature of the solution.

The freezing temperature of water at 101 325 Pa is $0 \text{ } ^\circ\text{C}$. So $\Delta T = 0 - T_f$. Or:

$$T_f = 0 - \Delta T = 0 - 0,63 = \underline{\underline{-0,63 \text{ } ^\circ\text{C}}}$$

ANSWER: At 101 325 Pa a solution of 10 g of NaCl in 1000 g of water freezes at $-0,63 \text{ } ^\circ\text{C}$.

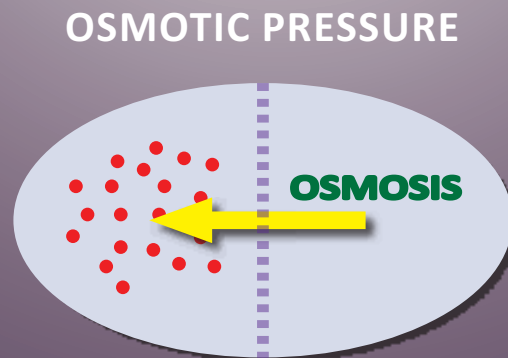
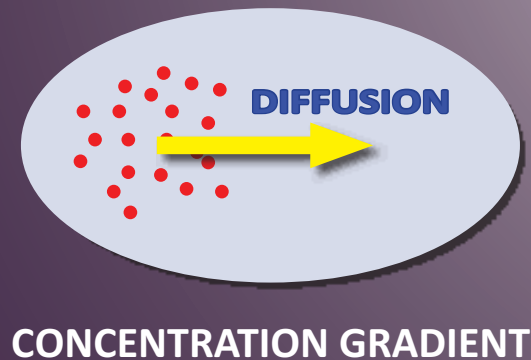
CAN YOU ANSWER THESE QUESTIONS ?

1. What is boiling temperature of a liquid?
2. What is melting temperature of a solid?
3. Why is the boiling temperature of ethanol lower than the boiling temperature of water?
4. Why does the boiling temperature of water vary with altitude?
5. Where will water come to a boil soon – in Sofia, in Varna or at Mousala? Where the time needed to cook an egg is the longest?
6. Which solution boils at the highest temperature at 101 325 Pa?
1 M NaCl; 1 M CaCl₂; 1 M AlCl₃
8. Which of the solutions above freezes at the lowest temperature at 101 325 Pa?
9. How to determine the molecular weight of a not volatile substance dissolved in a liquid solvent from the elevation of the boiling point of the solution or from the depression of the freezing point of the solution?
10. Why does sea water freeze at a lower temperature than fresh water?

14 Diffusion. Osmosis

KEY TOPICS

1. What are diffusion and osmosis?
2. Why are species diffusing from regions of high concentration to regions of low concentration of the solute?
3. Why are solvent molecules moving across a semipermeable membrane from regions of low concentration to regions of high concentration of the solute?
4. Why is osmosis so important for all living organisms?



KEY WORDS

- Diffusion
- Concentration gradient
- Osmosis
- Osmotic pressure

WHAT IS DIFFUSION?

Dissolution of soluble substances in water or other solvents is a spontaneous process. But it is not an instantaneous process. Solutions become homogeneous mixtures after a period of time. The particles of the dissolving substance „penetrate“ in the solvent. They move from a region with high concentration (next to the point of injection of a gas in a solvent, just near to the surface of dissolving solid particles, near to the surface of a liquid droplet, etc.) to a region with low concentration. This spontaneous flow continues till molecules, atoms or ions of the dissolving substance distribute evenly throughout the entire volume of the solution (the concentration of the solution is the same in the entire solution). This physical process is called **DIFFUSION**.

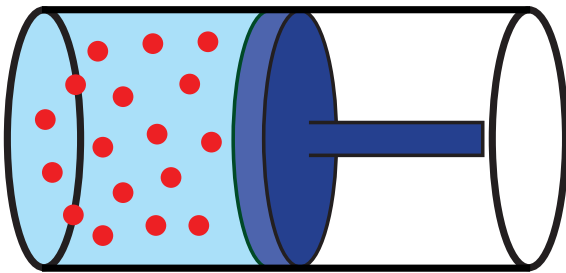
The spontaneous movement of molecules, atoms or ions from a region with high concentration to a region with low concentration is called **DIFFUSION.**

A substance diffuses throughout another substance when the two substances are miscible or can form a solution. For example, CO_2 , O_2 can diffuse in air. Sugar and table salt can diffuse in water. Oil does not dissolve in water. It forms spills on the water surface as its molecules diffuse only in a thin layer of water near the oil-water interface.

Some simple examples of diffusion are the expansion of a gas, the mixing of two gases that initially occupy different volumes and the colouring of a liquid.

- Expansion of a gas

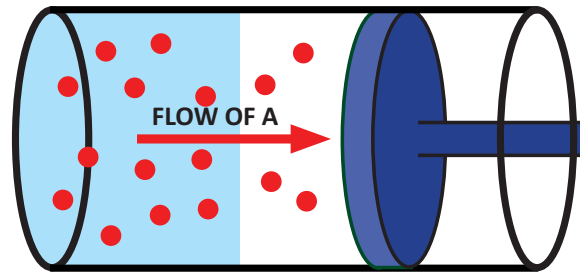
At a given temperature the gas **A** in a closed cylinder is in equilibrium state **1**. The pressure, exerted by the randomly moving gaseous molecules on the walls of the container, is constant. But if the piston moves the volume of the closed cylinder is increased and the concentration of gaseous molecules is not any more the same throughout this volume. Gaseous molecules spontaneously move from the volume initially occupied by the gas to the new „added“ volume **2**. They move from a region with high concentration to a region with low concentration – this is a process of diffusion. It stops when the concentration of gaseous molecules is the same in the entire new volume. This is a new equilibrium state **3**. The pressure exerted by the gaseous molecules is again constant but lower than the initial pressure.



The gas **A** occupy the volume of the cylinder.

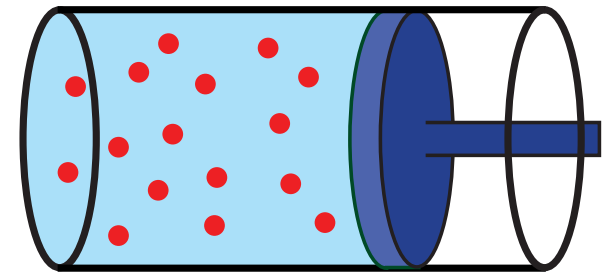
The pressure p_1 is constant.
The system is in equilibrium.

1



Diffusion of **A**
The system is not in equilibrium.

2



The pressure p_2 is constant.

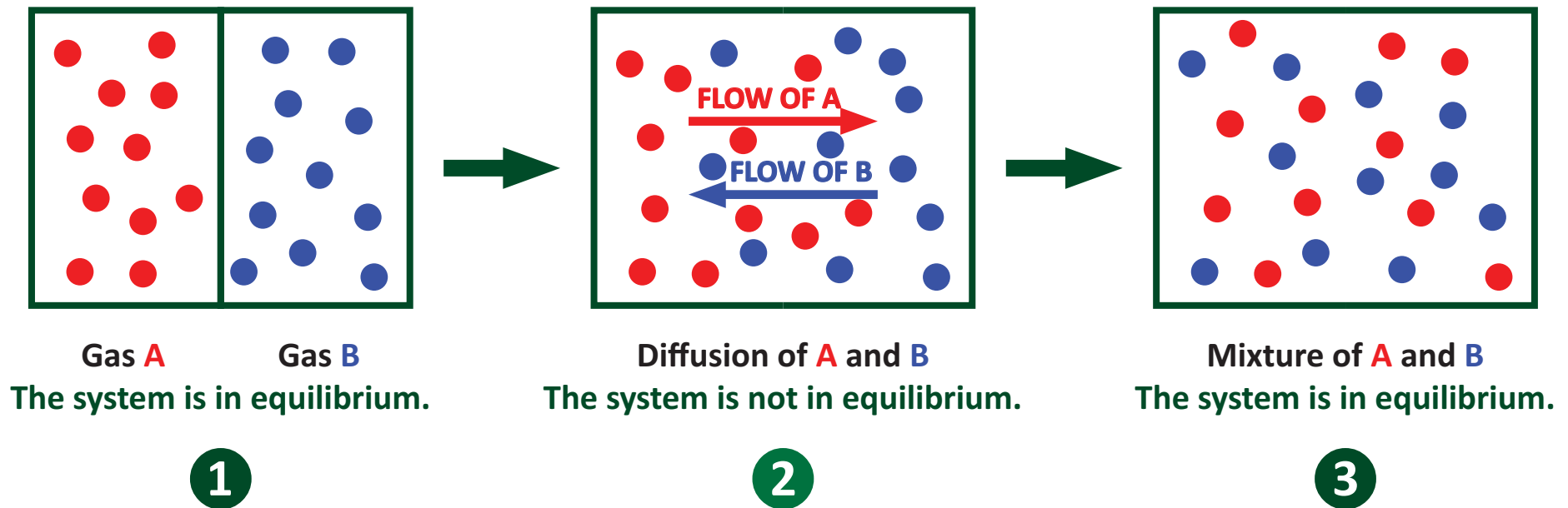
$$p_2 < p_1$$

The system is in equilibrium.

3

- **Mixing of two gases that initially occupy different volumes**

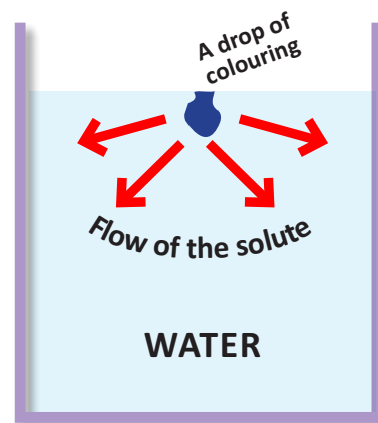
Two gases (**A** and **B**) are separated by a barrier in a container **1**. When the barrier is removed **2**, molecules of **A** move spontaneously towards the volume occupied initially only by the molecules of **B**. In the same time molecules of **B** move spontaneously towards the volume occupied initially only by the molecules of **A**. There is a net flow of **A** from a region of high concentration (the left half of the container) to a region with low concentration of **A** (the right half of the container). **B** moves in the opposite direction. Both gases diffuse. The process stops when the gases are evenly distributed in the entire volume. A mixture of **A** and **B** is formed **3**. The system is in a new equilibrium state.



● Colouring of a liquid

The process of diffusion can be observed during the colouring of a liquid. For example, when a food colouring is mixed with water. If a drop of a liquid dye is placed in a glass of water initially exist two regions – a region of high concentration (just near the drop of colouring) and a region of zero concentration of the liquid colouring (the entire volume of water) **1**. The difference in solute concentration over a distance (two different regions of the solvent volume) is called **concentration gradient**. Diffusion occurs only if a concentration gradient exists in the solvent volume. The concentration gradient is the driving force of the diffusion process. In the beginning the difference in solute concentration between the region where the drop of colouring is placed and the rest of the solvent volume is high and the colouring diffuses quickly in all directions. Mixing and heating of the solution speed up the process.

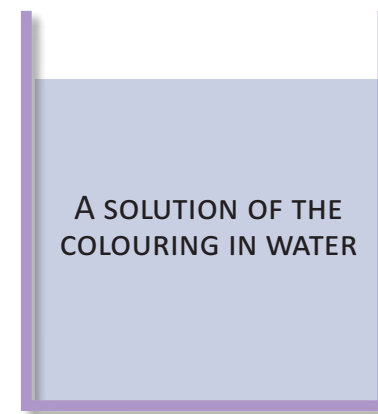
The solute diffuses throughout the volume of the liquid and the differences in solute concentrations in the bulk of the liquid lowers. The concentration gradient lowers and the rate of diffusion decreases. The process stops when the colouring is uniformly spread throughout the entire volume. The solute concentration (the colour of the liquid) is the same in the entire volume **2**. There is not a concentration gradient in the liquid any more and a solution of the colouring in water is formed.



The soluble solute (the colouring) diffuses in all directions.

THE SYSTEM IS NOT IN EQUILIBRIUM STATE.

1



A solution of the colouring in water is formed.

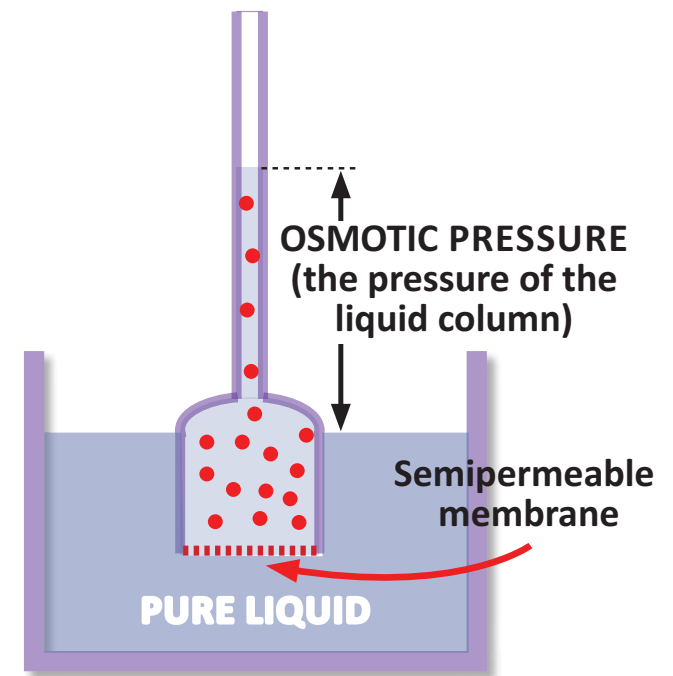
THE SYSTEM IS IN EQUILIBRIUM STATE.

2

WHAT IS OSMOSIS?

OSMOSIS* (in Greek language means „push“), like diffusion, is a spontaneous physical process. It occurs when a solution is separated by a semipermeable membrane (like membranes of cells) from the pure solvent. Semipermeable membranes allow solvents molecules to pass but are not permeable for the solute molecules. For example, water molecules pass across a membrane made of cellulose but saccharose molecules are not capable to cross the membrane. Generally, small molecules, like CO_2 , H_2O , O_2 , pass across semipermeable membrane, but large molecules, like proteins, can not pass across it. There is a net flow of solvent molecules from the region of the pure solvent to the solution.

The spontaneous passage of a pure solvent into a solution, separated from it by a semipermeable membranes, is called **OSMOSIS.**



● SOLUTE MOLECULES

OSMOSIS

ONLY MOLECULES OF THE PURE LIQUID PASSE ACROSS THE SEMIPERRMEABLE MEMBRANE.

*The term was introduced by Thomas Graham in 1854.

Wilhelm Pfeffer was the first to study thoroughly this phenomenon in 1877.

The passage of solvent molecules into the solution results in a rise of the pressure on this side of the membrane. It acts in a direction opposite to the direction of net flow of solvent molecules. When this pressure is high enough osmosis stops. This pressure is called **osmotic pressure**. If additional pressure equal to the osmotic pressure is applied to the solution before the osmosis starts, the process will not undergo at all.

**The additional pressure that must be applied to the solution to stop the influx of solvent, is called
OSMOTIC PRESSURE.**

When osmosis stops the system is in equilibrium. The amount of solvent molecules moving from the region of the pure solvent to the solution and vice versa is the same (as it is always in equilibrium). If the membrane is removed the solute molecules diffuse throughout the volume of the pure solvent. Finally a uniform solution forms in the entire volume of the system.

According to the van't Hoff equation*, the osmotic pressure Π of a dilute solution at a given temperature is proportional to the molar concentration of the dissolved species c_b :

$$\Pi = 1000 \cdot c_b RT$$

where **R** is the gas constant. Its value is $8,314 \text{ J.K}^{-1}.\text{mol}^{-1}$. **T** is the absolute temperature.

For substances that do not dissociate into ions when dissolved in water (e.g. glucose) c_b is identical with the solute concentration **c**. For substances that dissociate into ions when dissolved in water $c_b = i c$. „i“ is the van't Hoff factor. Its value depends on the number of ions that the solute forms. As an idea for dilute aqueous solution of NaCl $i=2$, for CaCl_2 $i=3$, etc.

As the gas constant is universal (its value is independent of the chemical nature of the gas), the osmotic pressure is a colligative property of dilute solutions.

*Jacobus Henricus van't Hoff has established this relationship experimentally in 1886.

PROBLEM!

What is the osmotic pressure of 0,155 M solution of NaCl in water at 25 °C?
What is the osmotic pressure of a 0,31 M solution of glucose at 25 °C?

SOLUTION: 1. Calculate the absolute temperature T.

$$T = \text{temperature expressed in } ^\circ\text{C} + 273,15 = \underline{298,15 \text{ K}}$$

2. Calculate the molar concentration c_b of the species in 0,155 M solution of NaCl.

NaCl dissociates in water into Na^+ and Cl^- ions. For this reason the amount of species in the solution is twice as big as the molar concentration of NaCl. The ions does not passe across a semipermeable membrane because water molecules form 3D hydration shells around each ion (see p. 5). The molar concentration of the dissolved species is:

$$c_b = 2 \cdot 0,155 = \underline{0,31 \text{ mol/l}}$$

3. Calculate the osmotic pressure of the solution.

$$\Pi = 1000 \cdot 0,31 \cdot 8,314 \cdot 298,15 = \underline{768434 \text{ Pa}}$$

4. Determine the osmotic pressure of 0,31 M $\text{C}_6\text{H}_{12}\text{O}_6$.

Glucose dissolves in water and the amount of species in the solution is 0,31 moles per litre, the same as in 0,155 M NaCl. Consequently, the osmotic pressure of the solution is equal also to 768434 Pa.

ANSWER: The osmotic pressure of 0,155 M NaCl and 0,31 M $\text{C}_6\text{H}_{12}\text{O}_6$ at 25 °C is 768,4 kPa.

When two solutions with different concentrations are separated by a semipermeable membrane the solvent also moves from the solution with low solute concentration to the solution with high concentration of the solute and tend to equalize the concentration of the solutions. If the osmotic pressure of the solutions is the same, there is not a net flow of solvent across the membrane. The system is in equilibrium. Such solutions are called **isotonic solutions**. 0,155 M NaCl and 0,31 M $C_6H_{12}O_6$ are isotonic solutions (see the example above). The osmotic pressure of blood at the same temperature is also $7,7 \cdot 10^5$ Pa. Solutions that have a higher osmotic pressure compared to another solution are called **hypertonic solutions** and those that have a lower osmotic pressure are called **hypotonic solutions**.

The experimental determination of the osmotic pressure of dilute solutions of macromolecules (proteins, polymers) is used to determine their molecular masses. For example, the molecular mass of haemoglobin was first determined in 1925 by measuring the osmotic pressure of its solutions.

Osmosis is a process of huge importance for living organisms as it controls the transport of water across cell membranes.

CAN YOU ANSWER THESE QUESTIONS ?

1. Why are diffusion and osmosis spontaneous processes?
2. Is the capability of substances to diffuse in pure solvents or solutions a colligative property?
3. Does temperature affect diffusion and osmosis?
4. Which of the substances – hydrogen gas H_2 or glucose $C_5H_{12}O_6$, will diffuse more rapidly in water under the same external condition? Why?
5. When erythrocytes are placed in pure water they swell up and burst. Why?
6. Dehydrated fruits or vegetables are placed in bowls of water. Why?
7. What process is going on when a lump of sugar is placed in a cup of tea?
8. The ions of NaCl are small species but they can not pass across a semipermeable membrane. Why?
9. The osmotic pressure of which solution is the highest?
a) 0,1 M NaCl b) 0,1 M $C_{12}H_{22}O_{11}$ c) 0,1 M $CaCl_2$
10. Which solutions are isotonic?
a) 0,2 M NaCl and 0,1 M $C_{12}H_{22}O_{11}$
b) 0,1 M NaCl and 0,1 M $C_{12}H_{22}O_{11}$
c) 0,1 M NaCl and 0,2 M $C_{12}H_{22}O_{11}$

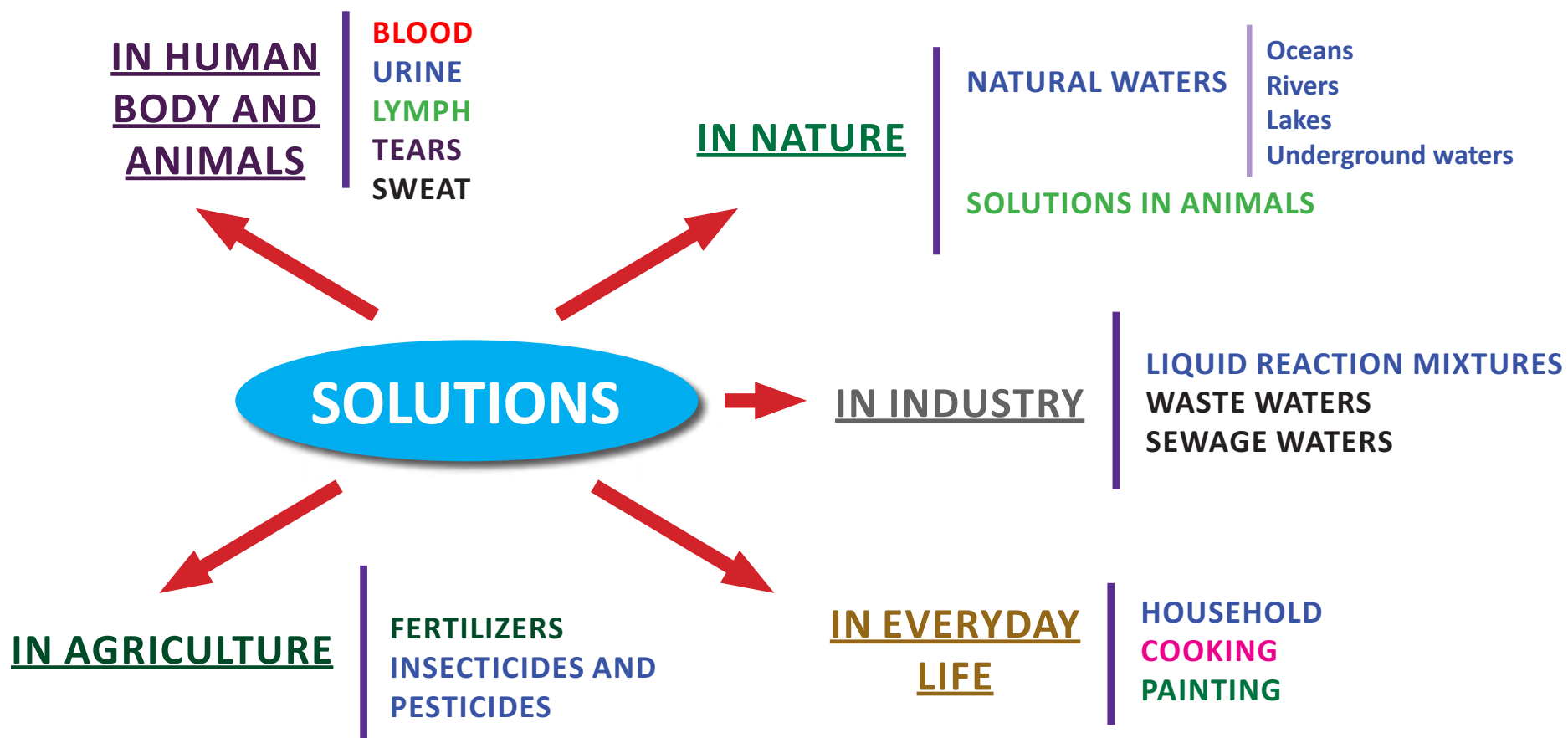
15

**Solutions in nature,
living organisms, industry
and everyday life**



SOLUTIONS are encountered everywhere – in nature, in human body and animals. Industry and agriculture require the use of different solutions, waste and sewage waters are solutions too. In the everyday life we use also many different solutions. The scheme below give an idea about the great diversity of solutions (natural and man-made) in our life.

It is up to you to prepare a report concerning the properties and the uses of a solution on your choice.



PROPERTIES OF SOLUTIONS – KEY POINTS

- **SOLUTIONS** are homogeneous mixtures of two or more substances. The minor component (the solute) is uniformly distributed within the major component (the solvent).
- If the solvent is water, solutions are called **AQUEOUS SOLUTIONS**. Only substances that dissolve in water can form aqueous solutions.
- In aqueous solutions ions and polar molecules are surrounded by water molecules forming a 3D **HYDRATION SHELL**.
- AS A RULE OF THE THUMB „**LIKE DISSOLVES LIKE**“. Polar solvents dissolve ionic and polar substances. Nonpolar solvents dissolve nonpolar substances.
- **SOLUBILITY** of a substance in a solvent is its maximum amount that can dissolve in a given amount of the solvent at a specific temperature and pressure.
- If a solution contains the maximum quantity of the solute that can be dissolved at a given temperature and pressure, it is called **SATURATED SOLUTION**. If the concentration of the solute is lower, the solution is **UNSATURATED**.

- **MISCIBLE** substances are soluble in all proportions. Substances whose solubility is greater than 1,0 g/100 g of water are considered as **SOLUBLE** in water. Substances whose solubility is low (0,1 - 1,0 g/100 g of water) are considered as **SLIGHTLY SOLUBLE** in water. Substances whose solubility is lower than 0,1 g/100 g of water are considered as **INSOLUBLE** in water.
- Temperature affects solubility of substances. Dissolution can be both an exo- or an endothermic process and solubility decreases or increases with temperature. Dissolution of gases is always an exothermic process and their solubility decreases with temperature.
- Pressure does not affect solubility of liquids and solids. Solubility of gases increases with pressure. In accordance with Henry's law, for dilute solutions $p_B = H_B \cdot x_B$.
- The pressure of the vapour in equilibrium with a pure liquid is called **VAPOUR PRESSURE**. Substances that have high vapour pressure are called substances with high **VOLATILITY**.
- The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the **BOILING TEMPERATURE** at that pressure. Boiling temperatures of pure liquids are their characteristic parameter and are used to identify them. The boiling temperature of a pure liquid at a standard pressure of 101 325 Pa is called **NORMAL BOILING POINT**.

- The temperature at which, under a specified pressure, the liquid and solid phases of a substance coexist in equilibrium is called the **MELTING (FREEZING) TEMPERATURE** at that pressure. The freezing temperature of a pure liquid at a standard pressure of 101 325 Pa is called **NORMAL FREEZING POINT**. Melting temperatures of pure crystalline solids are their characteristic parameter and are used to identify them. Amorphous pure substances melt over a temperature range.
- The properties of solutions that depend only on the number of solute particles present are called **COLLIGATIVE PROPERTIES** (lowering of the vapour pressure of the solution; elevation of the boiling temperature of the solution; depression of the freezing temperature of the solution; osmosis).
- The **VAPOUR PRESSURE LOWERING** for an ideal solution of a nonvolatile substance is proportional to the mole fraction of the solute $\Delta p = p^* \cdot x_B$ (p^* is the vapour pressure of the pure solvent) at a given temperature.
- The **BOILING POINT ELEVATION** for a dilute solution of a not volatile substance is proportional to the amount of solute in 1000 g of solvent (m_B): $\Delta T = K_b m_B$ (K_b is the **boiling-point constant** of the solvent.)
- The **FREEZING POINT DEPRESSION** for a dilute solution of a not volatile substance is proportional to the amount of solute in 1000 g of solvent (m_B): $\Delta T = K_f m_B$ (K_f is the **freezing-point constant** of the solvent.)

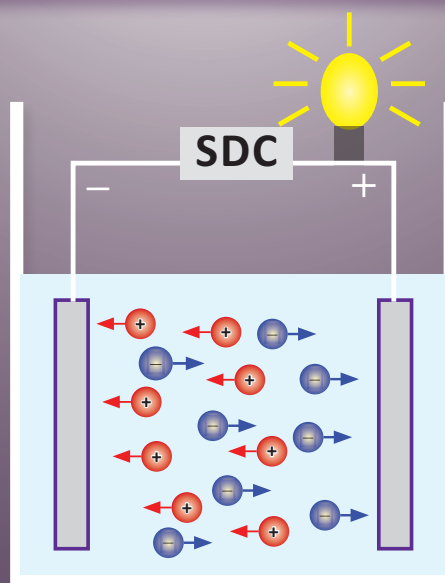
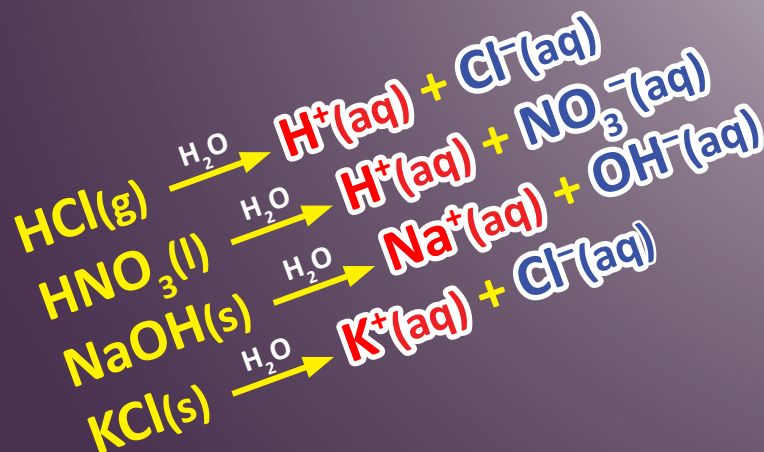
- The spontaneous movement of molecules, atoms or ions from a region with high concentration to a region with low concentration is called **DIFFUSION**. Gases, liquids and solids can diffuse in gaseous, liquid or solid media. A substance diffuses throughout another substance when the two substances are miscible or can form a solution.
- The difference in solute concentration over a distance (two different regions of the solvent volume) is called **CONCENTRATION GRADIENT**. Diffusion occurs only if a concentration gradient exists in the solvent volume. The concentration gradient is the driving force of the diffusion process.
- The spontaneous passage of a pure solvent into a solution, separated from it by a semipermeable membranes, is called **OSMOSIS**. The additional pressure that must be applied to the solution to stop the influx of solvent, is called **OSMOTIC PRESSURE**.
- In accordance with the equation of van't Hoff, the osmotic pressure Π of a dilute solution at a given temperature is proportional to the molar concentration of the solute c_B .
 $\Pi = 1000 \cdot c_B \cdot R \cdot T$ (R is the gas constant $8,314 \text{ J K}^{-1} \text{ mol}^{-1}$ and T is the absolute temperature).
Solutions with the same osmotic pressure are called **ISOTONIC SOLUTIONS**.
- **SOLUTIONS** are encountered everywhere – in nature, in human body and animals, in plants, in Industry and agriculture, in everyday life.

16

Electrolytes and nonelectrolytes Strong and weak electrolytes

KEY TOPICS

1. What are electrolytes?
2. Why are some compounds electrolytes?
3. What are nonelectrolytes?
4. Why are some electrolytes considered as strong electrolytes but others – as weak electrolytes?



KEY WORDS

- Electrolyte
- Nonelectrolyte
- Degree of dissociation
- Cation
- Anion
- Strong electrolyte
- Weak electrolyte

WHAT ARE ELECTROLYTES?

Some compounds, like NaCl, H₂SO₄, NaOH, etc., not only dissolve in water but also dissociate into ions. Their solutions conduct electricity. Therefore, these substances are called **ELECTROLYTES**. Many of them are soluble ionic compounds:

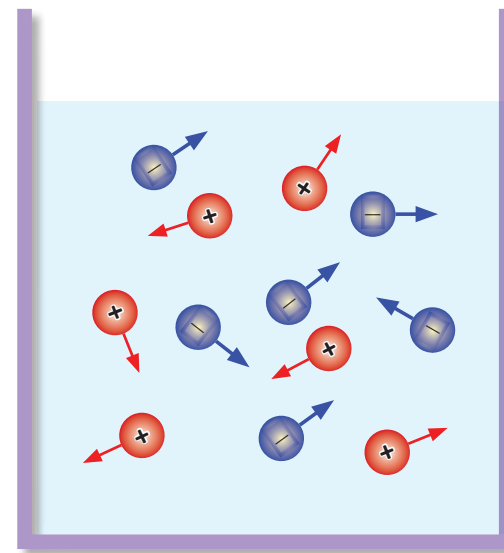


Others are liquid or gaseous covalent substances with polar bonds. They do not contain ions in their molecules. The ions form only in solutions:



These solutions conduct electricity and the solutes are electrolytes. Electrolytes are **ionic conductors**. The electrical conductivity depends on the concentration of the electrolyte and on the temperature.

Molten ionic compounds also conduct electricity. At a temperature equal to or greater than their melting temperature they decompose into ions that are mobile. For example, at a temperature of 801 °C NaCl melts decomposing into Na⁺ and Cl⁻ ions and the melt is a conductor of electrical current.



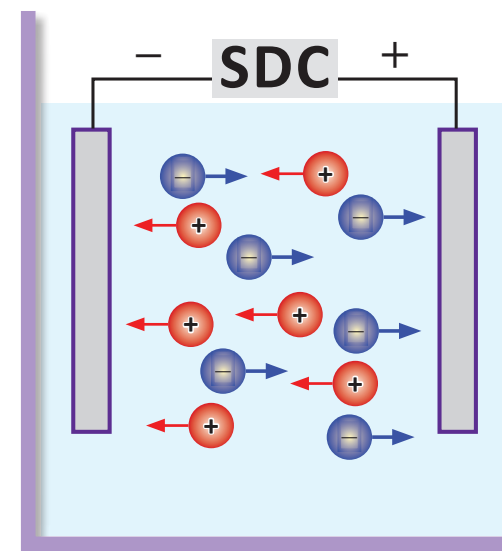
Electrolytes dissociate into ions when dissolved in water. Positively and negatively charged ions move randomly throughout the liquid.

ELECTROLYTES are compounds that conduct electricity when dissolved in water or in the molten state.

The ions in the solutions move spontaneously in all directions. When two electrodes, connected to a source of direct current (SDC), are immersed into the solution of an electrolyte, the movement of ions is no longer random. The positively charged ions move towards the negative electrode (the cathode). That is why, positively charged ions are called **cations**. The negatively charged ions move towards the positive electrode (the anode). Therefore, negatively charged ions are called **anions***.

Solids, called fast ionic conductors, have highly mobile ions. They are also known as solid electrolytes or superionic conductors. Their structure is intermediate between crystalline and liquid. They are used, for example, in fuel cells (they produce electricity by oxidizing a fuel). Typical examples of solid electrolytes are the solid silver iodide AgI (Ag^+ ions become mobile upon heating the solid to 146°C), solid polymeric ionic conductors.

Many soluble substances do not decompose into ions in water medium. For example, glucose $\text{C}_6\text{H}_{12}\text{O}_6$, saccharose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, alcohols. These substances are **NONELECTROLYTES**. If dissolved in water or molten, they do not conduct the electrical current.



Solutions of electrolytes conduct electricity.
Positively charged ions move towards the negative electrode (the cathode)
Negatively charged ions move towards the positive electrode (the anode)

*These terms have been introduced by Michael Faraday in 1834 to interpret the electrical conductivity of aqueous solutions of salts.

WHAT IS THE DIFFERENCE BETWEEN A STRONG AND A WEAK ELECTROLYTE?

Electrolytes that can ionise completely are **strong electrolytes**. NaCl, CaCl₂, KI, AgNO₃, HCl, HNO₃, KOH, etc., are strong electrolytes.

Some electrolytes partially decompose in water into ions. In their aqueous solutions are present not only ions but also electrically neutral molecules. For example, ethanoic acid CH₃COOH dissolves in water partially decomposing into ethanoate anions CH₃COO⁻ and H⁺ cations. Some molecules dissolve in water without dissociating into ions. At 25 °C 0,4 % of the molecules in a 1 M aqueous solution ionise (decompose into ions). The dissociation of ethanoic acid is a reversible process:

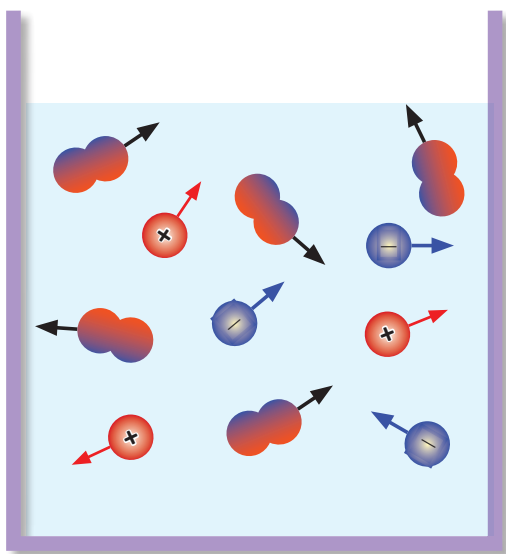


If water is added to the solution the equilibrium shifts towards the formation of CH₃COO⁻ and H⁺ ions but most of the CH₃COOH molecules still do not dissociate – in a 0,1 M solution only 1,3 % of the molecules of ethanoic acid decompose into ions.

The **degree of dissociation α** is defined as the fraction of the compound that has decomposed. It is also expressed in %. For example, if n moles of a compound are initially put in a beaker of water and 10 % of them decompose into ions, the degree of dissociation is 0,1 or 10 %. Electrolytes that ionise in water to a small degree are **weak electrolytes**.

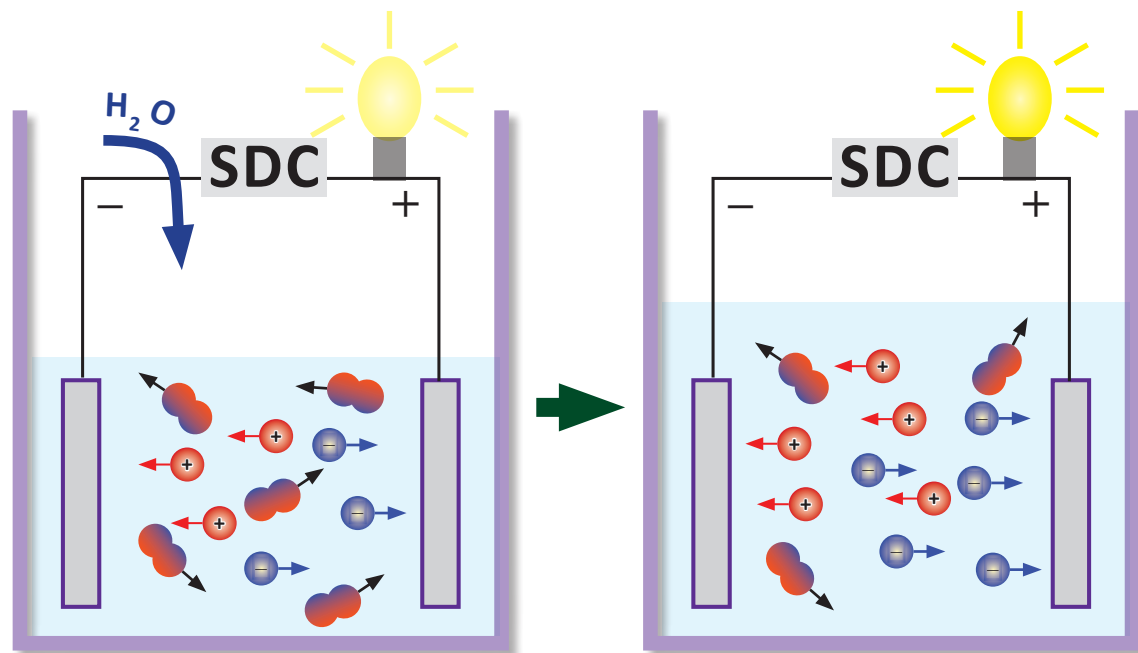
In dilute solutions the degree of dissociation of strong electrolytes is almost 100 %.

Nonelectrolytes do not ionise in water. Their degree of dissociation is 0 %.



Weak electrolytes do not dissociate totally into ions when dissolved in water. Cations, anions and neutral molecules move randomly throughout the liquid.

HF, H_2CO_3 , NH_4OH , CH_3COOH are weak electrolytes. Their degree of dissociation in 0,1 M aqueous solutions at 25 °C ranges from 0,0017 (H_2CO_3) to 0,15 (HF). It rises if water is added to the solution. The illustration bellow shows a simple experimental setup. It is used to prove that dilution of a solution of a weak electrolyte results in an increase of the degree of dissociation of the electrolyte and consequently – of the conductivity of the solution.



In aqueous solutions only a small part of molecules of weak electrolytes ionise.

When an electric field is applied, anions move towards the anode and cations move towards the cathode.

The undissociated molecules move randomly throughout the volume of the liquid.

If water is added to the solution, the degree of dissociation increases.

The conductivity of the solution increases and the bulb glows brighter.

Today, digital devices are used to measure solutions conductivity and such experimentations are only of historical interest. But this simple experiment is very helpful for understanding the nature of ionic conductivity.

CAN YOU ANSWER THESE QUESTIONS ?

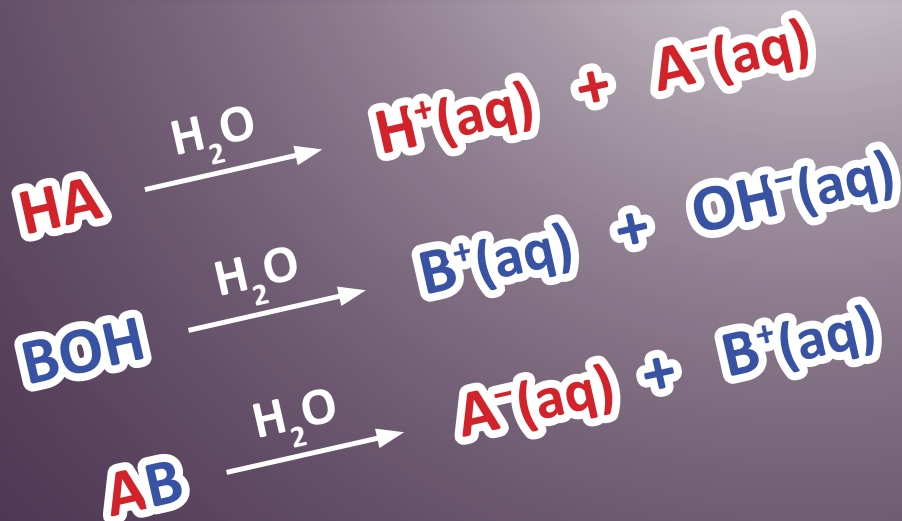
1. What are electrolytes?
2. Is water an electrolyte?
3. Are solutions of electrolytes electrically neutral systems? Why?
4. Is methane CH_4 an electrolyte? Why?
5. What ions are present in an aqueous solution containing NaCl and NaOH ?
6. What species are present in an aqueous solution of CH_3COOH ?
7. What does degree of dissociation stand for?
8. The degree of dissociation of AgNO_3 in a 0,01 M solution at 25 °C is 99 %. Is AgNO_3 a strong or a weak electrolyte?
9. The degree of dissociation of H_2S in a 0,1 M solution at 25 °C is 0,0007. Is H_2S a strong or a weak electrolyte?
10. If the concentration of CH_3COOH doubles the number of ions in the solution does not double. Why?

17

Acids, bases and salts as electrolytes

KEY TOPICS

1. Why are some acids strong electrolytes but others are weak electrolytes?
2. Why are some bases strong electrolytes but others are weak electrolytes?
3. Why are soluble salts electrolytes?



KEY WORDS

- Acid
- Base
- Salt
- Electrolyte

WHY ARE ACIDS ELECTROLYTES?

Swante Arrhenius, in the attempt to explain the electrical conductivity of some aqueous solutions, has been the first to suppose that some soluble compounds dissociate in water into ions. About 140 years ago he has formulated the basis of the theory of electrolytic dissociation. According to this concept:

ACIDS are compounds that, upon dissolution in water, dissociate into positive hydrogen ions H^+ and negative acidic ions.

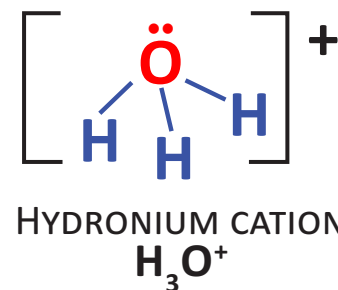
Acids are polar covalent compounds (HCl , HNO_3 , H_2SO_4 , CH_3COOH , etc). One ore more hydrogen atoms are covalently bonded to a more electronegative atom (O in the molecules of oxygen-containing acid or F, Cl, Br, S, etc. in binary acids). When acids dissolve in water theses bonds break down and H^+ ions are liberated. If we denote an acid as HA , this spontaneous process is expressed as:



Acidic anions A^- are, for example, Cl^- , NO_3^- , SO_4^{2-} , CH_3COO^- , etc. Hydrogen cations H^+ do not move alone throughout the solution. They bond to water molecules forming H_3O^+ ions (called hydronium ions). The dissociation of acids is also expressed as:



Acids that can completely dissociate into ions in water medium, are strong electrolytes. They are **HCl**, **HBr**, **HI**, **HNO₃**, **H₂SO₄**, **HClO₃**, **HClO₄**, **HMnO₄**.



PROBLEM!

What is the concentration of hydrogen cations H^+ in a 0,01 M HCl? (Assume $\alpha = 100\%$)

SOLUTION: 1. Express the equation of the dissociation of HCl in water.

Hydrochloric acid is a strong electrolyte. The equation of its dissociation in water is:



2. Determine the concentration of H^+ ions.

1 molecule of HCl dissociates into 1 H^+ ion and 1 Cl^- ion. All molecules can dissociate and the concentration of H^+ ions is equal to the concentration of Cl^- ions and to the concentration of HCl.

$$[\text{H}^+] = [\text{Cl}^-] = [\text{HCl}] = \underline{0,01 \text{ mole/l}}$$

ANSWER: A 0,01 M solution of HCl contains 0,01 mol/l H^+ ions and 0,01 mol/l Cl^- ions.

Weak acids are **weak electrolytes**. They partially dissociate upon dissolution in water. In the solution are present H^+ (H_3O^+) and A^- ions and undissociated molecules. An equilibrium is established:



For example: $\text{CH}_3\text{COOH}_{(l)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(\text{aq})} + \text{CH}_3\text{COO}^-_{(\text{aq})}$

In the solution are present H_3O^+ cations, CH_3COO^- anions and undissociated molecules CH_3COOH .

WHY ARE BASES ELECTROLYTES?

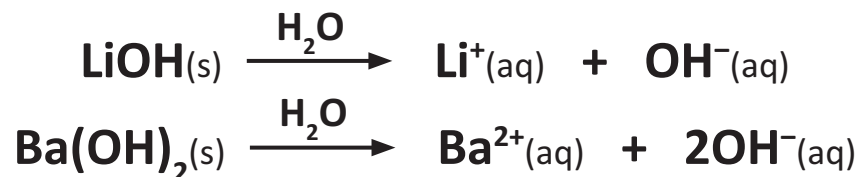
Soluble bases are electrolytes. According to the classical concepts:

BASES are compounds that, upon dissolution in water, dissociate into positive ions (most often metal ions) and negative hydroxide ions OH^- .

Bases are crystalline ionic compounds. When dissolved in water, the metal-oxygen bond of soluble bases breaks down and bases dissociate liberating one or more hydroxide anions OH^- . If we denote a base as BOH this spontaneous process is expressed as:



Bases that can completely dissociate into ions when dissolved in water, are strong electrolytes. Those are the **hydroxides of 1 (IA) and 2 (IIA) groups elements** (except Be). The B^+ cations are Li^+ , Na^+ , K^+ , Ca^{2+} , Ba^{2+} , etc. Hydroxides of 1 (IA) group elements are highly soluble substances, while hydroxides of 2 (IIA) group elements are much less soluble in water (especially $\text{Mg}(\text{OH})_2$) but all are strong electrolytes. For example:



PROBLEM!

What is the concentration of hydroxide anions OH^- in a 0,01 M $\text{Ca}(\text{OH})_2$?

SOLUTION: 1. Express the equation of the dissociation of $\text{Ca}(\text{OH})_2$ in water:

$\text{Ca}(\text{OH})_2$ is a slightly soluble hydroxide but it is a strong electrolyte. The equation of its dissociation in water, assuming $\alpha = 100\%$, is:



2. Determine the concentration of OH^- ions.

$\text{Ca}(\text{OH})_2$ dissociates into 1 Ca^{2+} ion and 2 OH^- ions. It is a strong electrolyte and in an aqueous solution the concentration of OH^- ions is twice as large as the overall concentration of $\text{Ca}(\text{OH})_2$.

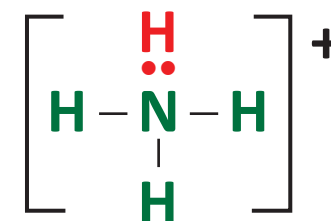
$$[\text{OH}^-] = 2[\text{Ca}(\text{OH})_2] = \underline{0,02 \text{ mole/l}}$$

ANSWER: A 0,01 M solution of $\text{Ca}(\text{OH})_2$ contains 0,02 mol/l OH^- ions.

Some molecular compounds, like NH_3 , react with water forming solutions that have the properties of solutions of bases. Hydrogen ions H^+ bond to NH_3 molecules using the lone electron pair of the N atom. In the solution are present cations (NH_4^+), anions (OH^-) and dissolved molecules NH_3 . An equilibrium is established:



Such compounds are **weak bases**.



AMMONIUM CATION

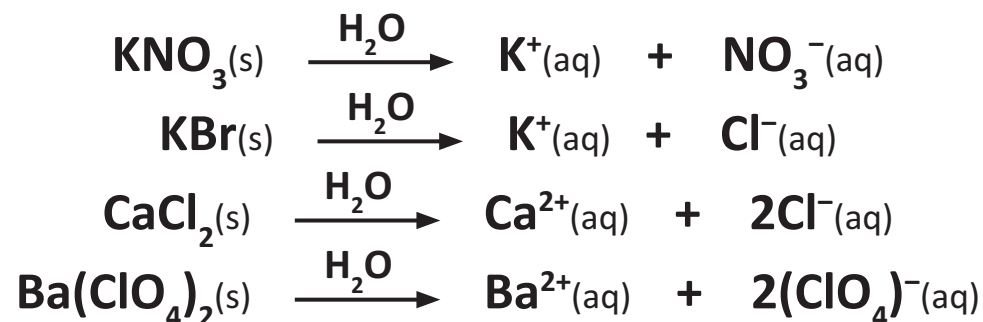


WHY ARE SOME SALTS ELECTROLYTES?

Soluble salts are electrolytes. According to the classical concepts of the theory of electrolytic dissociation:

SALTS are compounds that, upon dissolution in water, dissociate into positive ions (more often metal cations) and acidic anions.

For example, NaCl, Na₂SO₄, KNO₃, KBr, CaCl₂, CaSO₄, CaBr₂, Ba(ClO₄)₂, etc. These salts can completely dissociate into ions when dissolved in water. They are **strong electrolytes**.



The ions concentration depends on the salt composition. A 0,01 M KCl contains 0,01 mol/ℓ K⁺ ions and 0,01 mol/ℓ Cl⁻. A 0,01 M CaCl₂ contains 0,01 mol/ℓ Ca²⁺ ions and 0,02 mol/ℓ Cl⁻ ions. In the solutions are present only the ions of the ionic lattices of salts.

CAN YOU ANSWER THESE QUESTIONS ?

1. HNO_3 is a strong electrolyte but CH_3COOH is a weak electrolyte. Why?
2. $\text{Ca}(\text{OH})_2$ is not a highly soluble substance but it is a strong electrolyte. Why?
3. What is the concentration of H^+ ions in a 0,02 M HBr?
4. What is the concentration of OH^- ions in a 0,05 M NaOH?
5. The concentration of Ca^{2+} ions is twice as large as the concentration of Cl^- in the aqueous solutions of CaCl_2 . Are these solutions electrically neutral? Why?
6. Are all salts electrolytes?
7. What ions are present in an aqueous solution of $\text{Ca}(\text{NO}_3)_2$?
8. Ammonia NH_3 is a binary compound containing H atoms bonded to a more electronegative atom N. But when dissolved in water it does not dissociate liberating H^+ ions. Just oppositely, it „accept“ one H atom and form NH_4^+ ions. Why?

18

Acidity and alkalinity of aqueous solutions. pH

KEY TOPICS

1. Why is water a weak electrolyte?
2. What is ionic product of water?
3. What is pH of a solution?
4. Why is pure water neither acidic nor alkaline?
5. What are indicators?



$$K_w = [\text{H}^+].[\text{OH}^-]$$

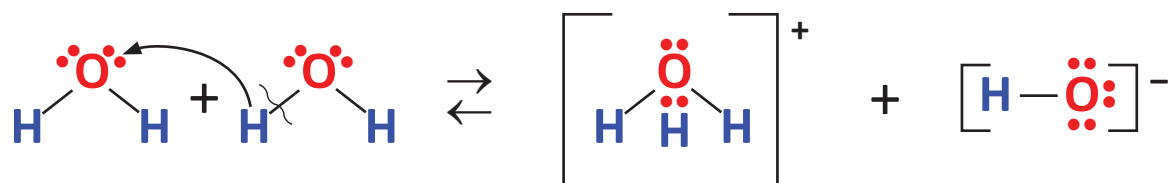
$$\text{pH} = -\log[\text{H}^+]$$

KEY WORDS

- Self-dissociation of water (Self-ionisation of water)
- Ionic product of water
- pH
- Acidity of a solution
- Alkalinity (basicity) of a solution
- Indicator
- Universal indicator

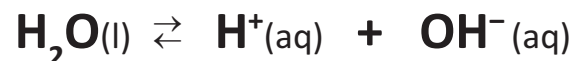
WHY IS WATER A WEAK ELECTROLYTE?

All solutions of electrolytes conduct electricity (that is the reason to name them electrolytes). Pure water also conducts electricity and consequently it is an electrolyte. This means that pure water contains some amount of ions. As pure water does not contain any dissolved electrolyte it is obvious that water molecules dissociate to a some extent. This process is called **self-dissociation** or **self-ionisation of water**. In liquid state some water molecules dissociate forming H^+ ions and OH^- ions. The liberated H^+ ions bond to a lone electron pair of the oxygen atom of another water molecule forming hydronium cations H_3O^+ .



The hydrogen cation H^+ is a hydrogen atom without its single electron and in fact this is just a proton. It is very mobile and bonds to a water molecules forming a hydronium cation H_3O^+ but not for a long time. It detaches from the water molecule and immediately bonds to another water molecule and so on. A proton H^+ jumps from one H_2O molecule to another H_2O molecule about 1000 times per second.

For simplicity, the self-ionisation of water is expressed as:



The amount of dissociated molecules is small – about 1 of 100 000 000 molecules and water is a weak electrolyte.

The equilibrium constant of the process of self-dissociation of water is expressed as:

$$K = \frac{[\text{H}^+].[\text{OH}^-]}{[\text{H}_2\text{O}]}$$

The concentration of undissociated molecules $[\text{H}_2\text{O}]$ is constant and much greater than $[\text{H}^+]$ and $[\text{OH}^-]$ at a given temperature. Therefore, it is omitted in the expression for the equilibrium constant of the self-ionisation of water. The product of the molar concentrations of H^+ and OH^- ions:

$$K_w = [\text{H}^+].[\text{OH}^-]$$

is called **ionic product of water**. Its value depends on the temperature as all equilibrium constants.

At 25 °C* $K_w = 10^{-14}$. Remember that the concentrations are always expressed as moles per one litre of solution, i.e. as molarities. **In pure water, at 25 °C, $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol/l}$** . This value is really small and pure water is a weak electrolyte.

From the point of view of the theory of electrolytic dissociation water is both an acid (it liberates H^+ ions) and a base (it liberates OH^- ions). You can imagine that water is something like a chameleon – its behaviour depends on the nature of the dissolved electrolyte. If, for example, NaOH is added to pure water, the concentration of OH^- increases. As the value of K_w does not change, the concentration of H^+ decreases. In contrary, If HCl is dissolved in pure water, the concentration of H^+ ions is increased and the concentration of OH^- ions lowers.

*The value of K_w is exactly 10^{-14} at 22 °C but its change when temperature rises to 25 °C can be neglected.

WHAT IS pH OF AN AQUEOUS SOLUTION?

At constant temperature the value of K_w does not change when a substance dissolves in pure water. But the equilibrium concentrations $[H^+]$ and $[OH^-]$ can change. For many process in nature and industry the concentration of H^+ ions in the solutions is a parameter of crucial importance. Working with concentrations, for example, of the type $10^{-1,3}$ might be confusing. In the early 20th century Sören Sörencen proposed to quantify the molar concentration of H^+ ions in water solutions only by the exponent taken with a sign „–“ (for example 1,3 for a concentration of $10^{-1,3}$ mol/l). This parameter is denoted as **pH**. From mathematical point of view:

$$\text{pH} = -\log[H^+]$$

This is the definition of pH. It states that **pH of a solution is equal to minus the power to which 10 must be risen to yield the value of the molar concentration of the hydrogen ions H^+ in the solution.** More often pH is in the range from **0** (corresponds to 1 M $[H^+]$) to **14** (corresponds to 10^{-14} M $[H^+]$ or 1 M $[OH^-]$). That seems a little bit confusing but it demands only some practice.

For pure water at 25 °C $[H^+] = [OH^-] = 10^{-7}$. **pH = 7 for pure water.**

Solutions with **pH = 7** are **neutral solutions**. For example, solutions of salts (KCl , $MgCl_2$, $Ba(NO_3)_2$).

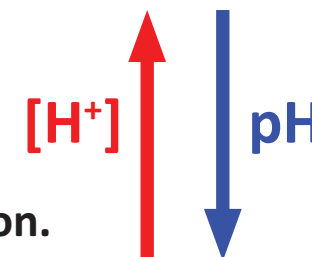
Solutions with **pH < 7** are **acidic solutions**. For example, solutions of acids (HCl , HNO_3 , H_2SO_4).

Solutions with **pH > 7** are **basic (alkaline) solutions**. For example, solutions of bases ($NaOH$,

*The decimal logarithm **log** of a number is equal to the power to which 10 must be risen to yield that number. For example, $\log 100 = \log 10^2 = 2$

Using pH is just a more convenient way to work with $[H^+]$ concentrations in solutions. Some rules can be helpful:

- When pH decreases, $[H^+]$ increases and $[OH^-]$ decreases.
- The lower the pH value, the higher $[H^+]$ and the more acidic the solution.
- When pH increases, $[H^+]$ decreases and $[OH^-]$ increases.
- The higher the pH value, the higher $[OH^-]$ and the more alkaline the solution.
- For every factor of 10 increase in $[H^+]$, pH value decreases by 1.



PROBLEM!

What is the pH of 0,1 M HCl and 0,1 M NaOH at 25 °C?

SOLUTION: By definition: $pH = -\log[H^+]$

1. Calculate the pH of 0,1 M HCl ($0,1 = 10^{-1}$).

$$pH = -\log[H^+] = -\log 10^{-1} = \underline{1}$$

(if you are not familiar with logarithms you can use a scientific calculator.)

2. Determine the concentration of $[H^+]$ ions in a 0,1 M NaOH.

$$K_w = [H^+].[OH^-] = [H^+].10^{-1} = 10^{-14}$$

$$[H^+] = 10^{-14} / 10^{-1} = 10^{-13} \text{ mol/l}$$

3. Calculate the pH of 0,1 M NaOH.

$$pH = -\log[H^+] = -\log 10^{-13} = \underline{13}$$

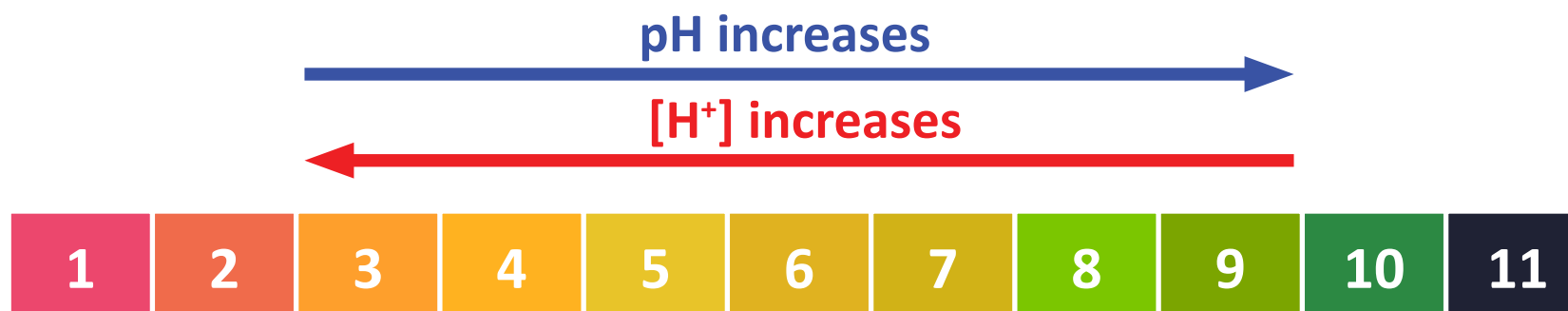
ANSWER: The pH of a 0,1 M HCl is 1. The solution is acidic.

The pH of a 0,1 M NaOH is 13. The solution is alkaline (basic).

WHAT ARE INDICATORS?

Values of pH are measured experimentally using pH-metres. But indicators also give a good idea about the acidity or the alkalinity of solutions. Indicators are substances (more often water solutions of weak acids) that when added to a solution change their colour depending on the acidity (or the alkalinity) of the solution. Often strips of paper impregnated with a solution of the indicator are used. You already know litmus and phenolphthalein. The violet solution of litmus turns red in acidic solutions and blue – in alkaline solutions. Red litmus paper does not change its colour in acidic solutions but turns blue in alkaline solutions. Blue litmus paper turns red in acidic solutions. Phenolphthalein is colourless in acidic solutions and pink-red in alkaline solutions. For a more precise determination of pH are used indicators that change their colour over a narrow range of pH.

The most widely used indicator is the so called **universal indicator**. This is a roll of a narrow strip of paper soaked with a liquid mixture of different indicators. When a piece of this paper is dipped in an aqueous solution its colour changes depending on the acidity (or the alkalinity) of the solution. The paper colour is visually compared to a colour scale. This indicator is easily used even at home.

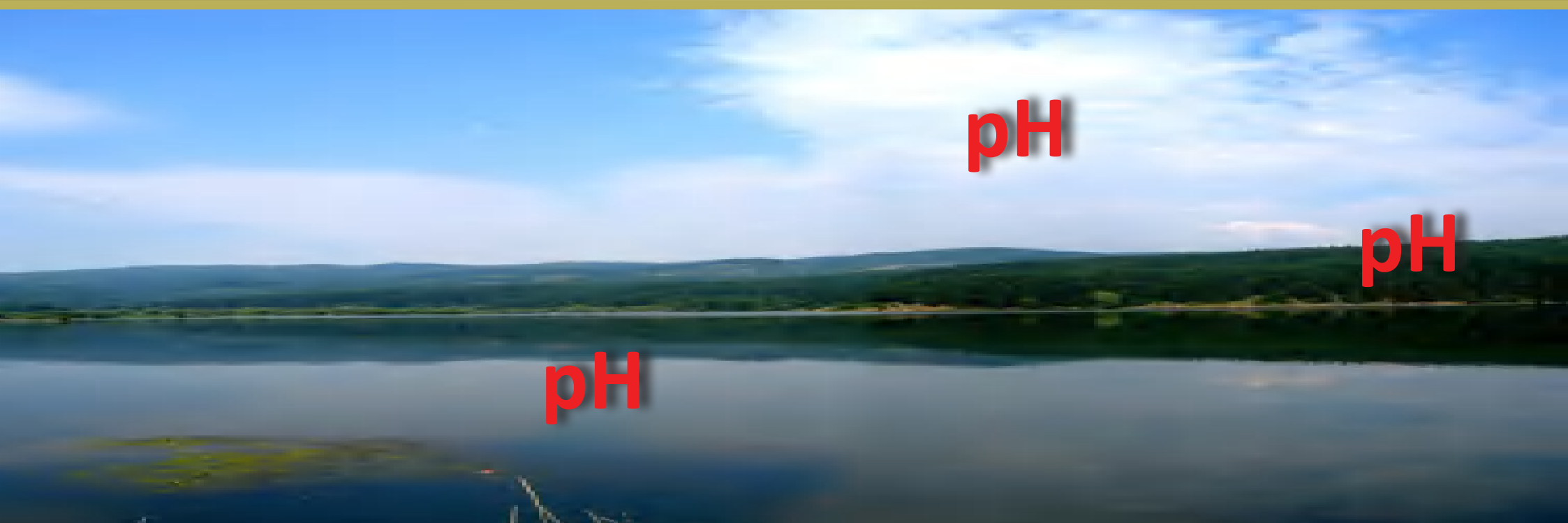


COLOUR SCALE OF AN UNIVERSAL INDICATOR.
PH RANGES FROM 1 TO 11

CAN YOU ANSWER THESE QUESTIONS ?

1. Is pure water an electrolyte? Why?
2. Does all water molecules dissociate into ions?
3. Why is the ionic product of water constant at a given temperature?
4. What is pH of a solution?
5. Does the pH of solution decrease if an acid is added?
6. Which solution is more acidic – with pH = 2 or with pH = 3?
7. Which solution is more alkaline – with pH = 8 or with pH = 9?
8. Solutions of NaCl are neutral (pH = 7). Why?

19 Importance of pH of solutions for living organisms, industry and everyday life



Most of the solutions in nature, in the human body, in industry, in everyday life, etc. are acidic or basic. The value of pH is often of great importance for their properties and consequently for their biological activity or uses. Here are some typical examples of solutions with different values of pH.

	Carbonated beverages		Aspirin Wine	Banana Pure rain	Saliva Urine	Pure water	Sea water	Soaps Window cleaner		Ammonia solution
1	2	3	4	5	6	7	8	9	10	11
Gastric fluid	Lemon juice Vinaigre	Orange juice	Beer Coffe	Egg yolks	Milk	Human blood	Baking soda		Milk of magnesia	

The pH of battery acids is even negative (for example, $-0,8$).

Soapy water (pH ≈ 12), cleaning products (pH ≈ 12), caustic oven cleaner (pH ≈ 13), household bleach (pH ≈ 13), liquid drain cleaner (pH ≈ 14) are highly alkaline solutions.

Now, it is again up to you. Prepare a report on the importance of the pH value of a solution on your choice concerning its biological activity or uses.

20

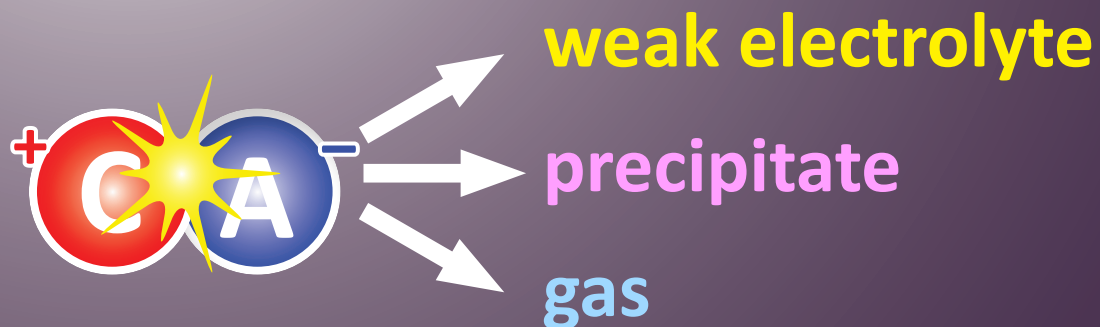
Reactions between ions in aqueous solutions

KEY TOPICS

1. How do ions in solutions combine to form chemical compounds?
2. Is the identity of ions important?
3. What compounds form during the reactions between ions in solutions?
4. What is net ionic equation of a chemical reaction?

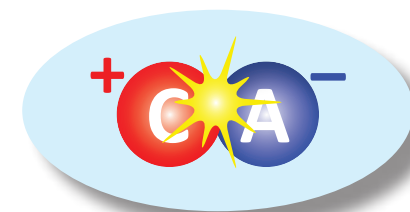
KEY WORDS

- Complete ionic equation
- Net ionic equation
- Spectator ions
- Precipitation reaction



HOW DO IONS IN SOLUTIONS COMBINE TO FORM CHEMICAL COMPOUNDS?

Electrolytes dissociate in water into positively charged cations and negatively charged anions. They move randomly throughout the entire volume of the liquid. As a whole the solution is electrically neutral. But what happens if the solution is mixed with a solution of another electrolyte or another electrolyte is dissolved in the liquid? Now in the solution are present two different cations and two different anions. Again all ions move randomly throughout the liquid but when the anion of one of the electrolytes and the cation of the other electrolyte collide a new compound can be formed. Depending on the identity of the dissolved electrolytes and consequently – on the identity of the reaction products, a chemical transformation can occur or not. Consider the cases:

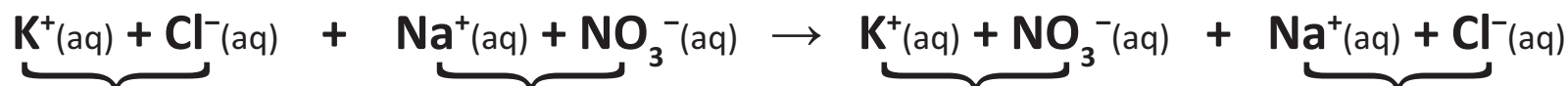


**WHEN A CATION C^+
COLLIDES WITH AN
ANION A^-
A NEW COMPOUND AC
CAN FORM.**

- **All reaction components are strong electrolytes.**

For example, a solution of KCl is mixed with a solution of NaNO_3 . In the mixture are present Na^+ , K^+ , Cl^- and NO_3^- ions*. The compounds that could form are KNO_3 and NaCl . The equation of the reaction would be: $\text{KCl}_{(\text{aq})} + \text{NaNO}_{3(\text{aq})} \rightarrow \text{KNO}_{3(\text{aq})} + \text{NaCl}_{(\text{aq})}$

But both products are soluble salts that are strong electrolytes. They dissociate into K^+ and Cl^- ions and NO_3^- and Na^+ ions. A chemical reaction is not realised. This becomes clear if the so called **complete ionic equation** of the reaction is expressed instead of the molecular equation of the reaction:

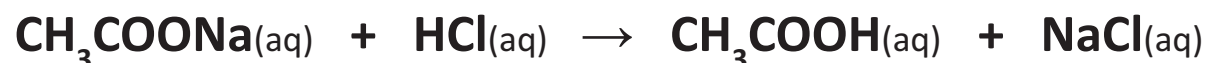


Neither new molecules nor new ions or insoluble substances are formed. **No reaction occurs.**

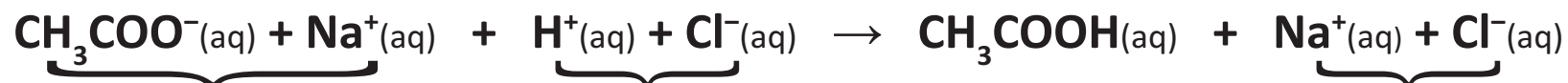
*The amount of H^+ and OH^- ions resulting from the self-dissociation of water is very small (10^{-7} mol/l) and it is neglected.

- **At least one of the products is a weak electrolyte.**

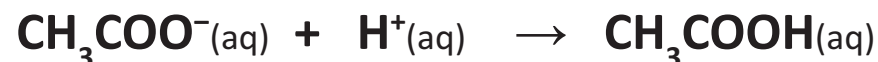
For example, a solution of CH_3COONa is mixed with a solution of HCl . The molecular equation of the reaction that occurs is:



Both reactants and NaCl are strong electrolytes. They dissociate completely into ions. But ethanoic acid CH_3COOH is a weak electrolyte. CH_3COO^- ions combine with H^+ ions and form CH_3COOH molecules. The complete ionic equation of the reaction is:



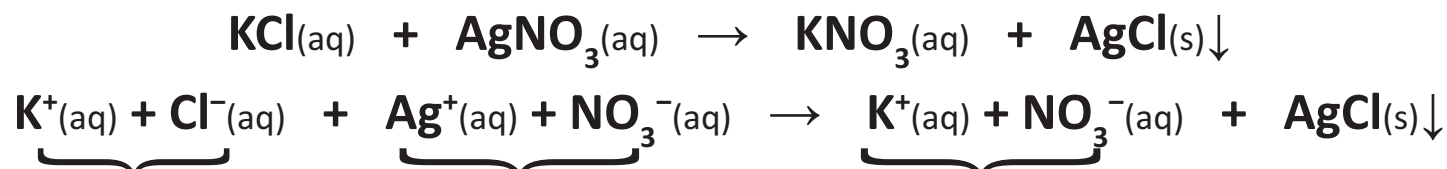
Sodium cations Na^+ and chloride anions Cl^- do not react with other ions, i.e. they do not participate in the chemical reaction. Such ions are called **spectator ions**. For convenience, the spectator ions can be omitted in the ionic equation of the reaction. A **net ionic equation** can be expressed as:



A chemical reaction occurs – a new compound (the weak electrolyte CH_3COOH) is formed.

- **At least one of the products is an insoluble compound.**

For example, a solution of KCl is mixed with a solution of AgNO₃. The molecular and the complete ionic equations of the reaction are:



Silver chloride AgCl is practically insoluble in water and it precipitates on the bottom of the vessel. K⁺ cations and NO₃⁻ anions are spectator ions. The net ionic equation is:



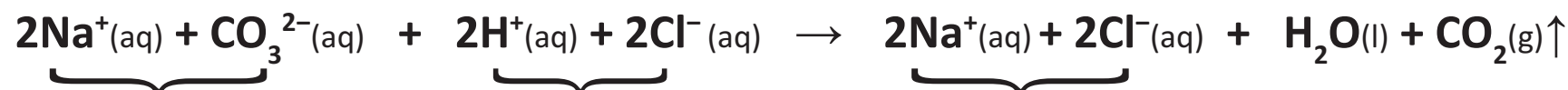
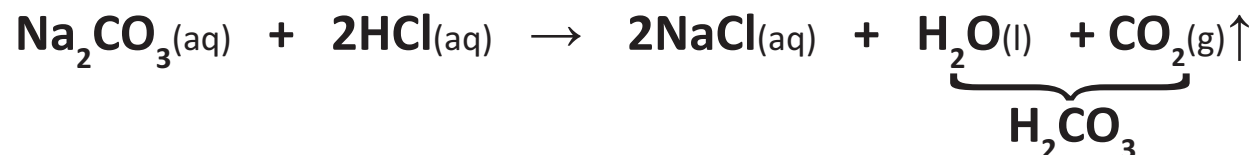
A chemical reaction occurs – a new insoluble compound AgCl is formed.

Such reactions are called **precipitation reactions**. They are often used to identify the ions present in a solution. In the table below are summarised some common test reactions.

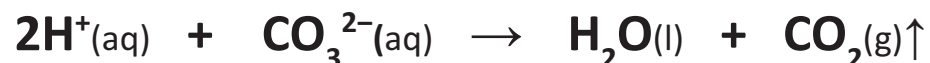
IONS	REAGENT CONTAINING IONS OF:	TEST REACTION	OBSERVATIONS
Ca ²⁺	CO ₃ ²⁻	Ca ²⁺ (aq) + CO ₃ ²⁻ (aq) → CaCO ₃ (s)↓	A white precipitate 
Cu ²⁺	OH ⁻	Cu ²⁺ (aq) + 2OH ⁻ (aq) → Cu(OH) ₂ (s)↓	A blue precipitate 
Al ³⁺	OH ⁻	Al ³⁺ (aq) + 3OH ⁻ (aq) → Al(OH) ₃ (s)↓	A white gelatinous precipitate
Pb ²⁺	SO ₄ ²⁻	Pb ²⁺ (aq) + SO ₄ ²⁻ (aq) → PbSO ₄ (s)↓	A white precipitate 
Cl ⁻	Ag ⁺	Ag ⁺ (aq) + Cl ⁻ (aq) → AgCl(s)↓	A white precipitate 
I ⁻	Ag ⁺	Ag ⁺ (aq) + I ⁻ (aq) → AgI(s)↓	A yellow precipitate 
S ²⁻	Cu ²⁺	Cu ²⁺ (aq) + S ²⁻ (aq) → CuS(s)↓	A black precipitate 
SO ₄ ²⁻	Ba ²⁺	Ba ²⁺ (aq) + SO ₄ ²⁻ (aq) → BaSO ₄ (s)↓	A white precipitate 
CO ₃ ²⁻	Ca ²⁺	Ca ²⁺ (aq) + CO ₃ ²⁻ (aq) → CaCO ₃ (s)↓	A white precipitate 

- **At least one of the products is a gas.**

For example, a solution of Na_2CO_3 is mixed with a solution of HCl . The molecular and the complete ionic equations of the reaction are:



Carbonic acid H_2CO_3 is unstable. It decomposes into water and gaseous CO_2 which is evolved in the atmosphere. Na^+ cations and Cl^- anions are spectator ions. The net ionic equation is:



A chemical reaction occurs – liquid water H_2O and the gas CO_2 are formed.

In general, in aqueous solutions of electrolytes reactions take place when:

1. **A weak electrolyte is produced.**
2. **A precipitate is formed.**
3. **A gas is evolved.**

CAN YOU ANSWER THESE QUESTIONS ?

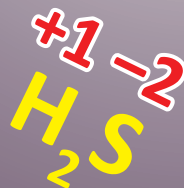
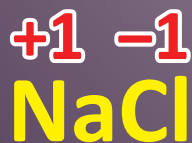
1. Can ions in solutions combine to form new compounds?
2. A solution of NaCl is mixed with a solution of HNO_3 ? Does a reaction go on? Why?
3. Do the following reactions occur? Why?
 - a) $\text{NaOH(aq)} + \text{Na}_2\text{CO}_3\text{(aq)}$
 - b) $\text{HCl(aq)} + \text{Na}_2\text{CO}_3\text{(aq)}$
 - c) $\text{NaOH(aq)} + \text{HCl(aq)}$
4. What happens when $\text{Na}_2\text{CO}_3\text{(aq)}$ reacts with HCl(aq) in a closed vessel?
5. Which of the following reactions can be used as a test for the presence of Cl^- ions? Why?
 - a) $\text{Cl}^-\text{(aq)} + \text{Na}^+\text{(aq)}$
 - b) $\text{Cl}^-\text{(aq)} + \text{Ag}^+\text{(aq)}$
 - c) $\text{Cl}^-\text{(aq)} + \text{NH}_4^+\text{(aq)}$
6. A test tube contains 100 ml of 0,1 M NaOH. Another test tube contains 100 ml of 0,1 M HCl. The solutions are mixed in a beaker. What ions are present in this solution? Is the solution acidic, basic or neutral?

21 Oxidation state



KEY TOPICS

1. What is oxidation number?
2. What is oxidation state?
3. Why is the oxidation number of fluorine F always -1 ?
4. Why isn't the oxidation number of hydrogen H always $+1$?
5. How to determine the oxidation numbers of elements in a chemical compound?

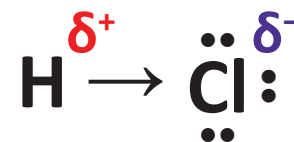


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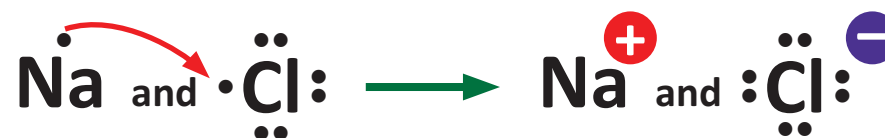
- Oxidation number
- Oxidation state

WHAT DOES OXIDATION STATE STAND FOR?

Atoms bond to one another by sharing valence electrons or by gaining and losing valence electrons. If the bond is covalent, the bonding pair is shared between the bonding atoms and the more electronegative atom acquires a partial positive charge, while the less electronegative atom acquires a partial positive charge. If the difference in the electronegativity of the bonding atoms is high, the more electronegative atom traps valence electrons initially belonging to the less electronegative atom and transforms into a negatively charged ion. The other atom loses valence electrons and transforms into a positively charged ion. The charges of ions in chemical compounds are quantified by assigning to each ion a number that is equal to the number of electrons that atoms lose or gain when they bond to other atoms. it is called **oxidation number**.



PARTIAL ELECTRICAL CHARGES OF THE ATOMS IN THE HYDROGEN CHLORIDE MOLECULE HCl



ELECTRICAL CHARGES OF IONS IN THE SODIUM CHLORIDE NaCl IONIC CRYSTAL

The charge number of an ion is called **OXIDATION NUMBER**.

For example, the oxidation numbers of sodium and chlorine in NaCl are +1 for Na and −1 for Cl.

When two different atoms are covalently bonded, they acquire partial positive or negative charges. The oxidation number of an element in a covalent compound is equal to the charge that the atom of the element would acquire if the bond was ionic. For example, hydrogen H is less electronegative than chlorine and in HCl its oxidation number is +1 as it shares 1 electron with a chlorine Cl atom. The bonding electron pair is attracted by the chlorine Cl atom and its oxidation number is -1.

The physical state of an atom with a given oxidation number is called **OXIDATION STATE**. When a sodium Na atom loses 1 electron, it is present in the oxidation state Na^+ . When a chlorine Cl atom gains 1 electron, it is present in the oxidation state Cl^- . In MgS magnesium is present in the oxidation state Mg^{2+} and the oxidation number of magnesium is +2. Sulfur is present in the oxidation state S^{2-} . The oxidation number of sulfur is -2. Often, both terms „oxidation state“ and „oxidation number“ are considered as equivalent and it is said that, for example, the oxidation state of sodium in NaCl is +1.

The oxidation numbers are written above the symbols of the elements in the chemical compounds. For example:



Here are some common rules that are helpful when determining the oxidation numbers of elements in chemical compounds:

- **The oxidation number of simple substances** (uncombined elements) **is „0“**. For example, the oxidation number of chlorine in Cl_2 is „0“. It is the same, for example, for Na, He, S, O_2 , etc. as simple substances.
- **The oxidation number of metallic elements is always positive**. For 1 (IA) and 2 (IIA) groups it corresponds to the number of the group. For example, $\overset{+1}{\text{Na}}\overset{-1}{\text{Cl}}$, $\overset{+1}{\text{K}}\overset{-1}{\text{Br}}$, $\overset{+2}{\text{Mg}}\overset{-1}{\text{Cl}}_2$, $\overset{+2}{\text{Ca}}\overset{-2}{\text{O}}$.
- **The oxidation number of HYDROGEN H is +1**, except in compounds with metals (hydrides), where it is -1 as metallic elements are less electronegative than hydrogen. For example, $\overset{+1}{\text{Na}}\overset{-1}{\text{H}}$, $\overset{+2}{\text{Mg}}\overset{-1}{\text{H}}_2$.
- **The oxidation number of FLUORINE F is always -1** , as fluorine is the most electronegative element.
- **The oxidation number of OXYGEN O is -2** , except in OF_2 , where it is $+2$ and H_2O_2 , where it is -1 .
- **The sum of the oxidation numbers of the elements in a neutral compound is „0“**. For example, the oxidation numbers of magnesium Mg and chlorine Cl in MgCl_2 are $+2$ and -1 . The sum of all oxidation numbers is $(+2) + 2 \cdot (-1) = 2 - 2 = 0$.
- **In a polyatomic ion the sum of the oxidation numbers of the elements is equal to the charge of the ion**. For example, the oxidation numbers of sulfur and oxygen in SO_4^{2-} are $+6$ and -2 . The sum of all oxidation numbers is $(+6) + 4 \cdot (-2) = 6 - 8 = -2$.

- **The highest oxidation number of the elements of the main groups with variable valences (IVA – VIIA group) is equal to the number of the group.** For example, the highest oxidation number of nitrogen is +5 and it is located in VA group. Carbon is located in IVA group and its maximum oxidation number is +4.
- **The oxidation number of the more electronegative element in a compound is negative. The oxidation number of the less electronegative element in a compound is positive.** For example, nitrogen is more electronegative than hydrogen. In NH_3 the oxidation number of nitrogen is -3 and the oxidation number of hydrogen is $+1$. In Cl_2O_7 the oxidation number of chlorine is $+7$ as chlorine is less electronegative than oxygen (its oxidation number is -2).

PROBLEM!

What are the oxidation numbers of nitrogen in nitrous acid HNO_2 and nitric acid HNO_3 ?

SOLUTION: In HNO_2 and HNO_3 the most electronegative element is oxygen. Its oxidation number is -2 . Hydrogen is the least electronegative element and its oxidation number is $+1$.

1. Determine the oxidation number of nitrogen in HNO_2 .

The sum of the oxidation numbers of the elements in the compound is „0“.

If the oxidation number of nitrogen is denoted by „x“, that gives:

$$(+1) + x + 2 \cdot (-2) = 0 \quad \text{or} \quad x = -(-4 + 1) = +3$$

2. Determine the oxidation number of nitrogen in HNO_3 .

$$(+1) + x + 3 \cdot (-2) = 0 \quad \text{or} \quad x = -(-6 + 1) = +5$$

ANSWER: The oxidation number of nitrogen in HNO_2 is $+3$.

The oxidation number of nitrogen in HNO_3 is $+5$.

CAN YOU ANSWER THESE QUESTIONS ?

1. What do oxidation number and oxidation state stand for?
2. What is the oxidation number of fluorine in all known chemical compounds? Why?
3. Why is the oxidation number of hydrogen in HF +1 but in MgH_2 -1?
4. What is the oxidation number of aluminum in AlCl_3 ?
5. What is the highest oxidation number of phosphorus?
6. What are the oxidation numbers of carbon in CO, CO_2 and methane CH_4 ?
7. What is the oxidation number of chlorine in chloric acid HClO_3 ?
8. What is the oxidation number of manganese in permanganic acid HMnO_4 ?
9. What is the oxidation number of carbon in $(\text{HCO}_3)^-$?
10. What is the oxidation number of phosphorus in $(\text{PO}_4)^{3-}$?

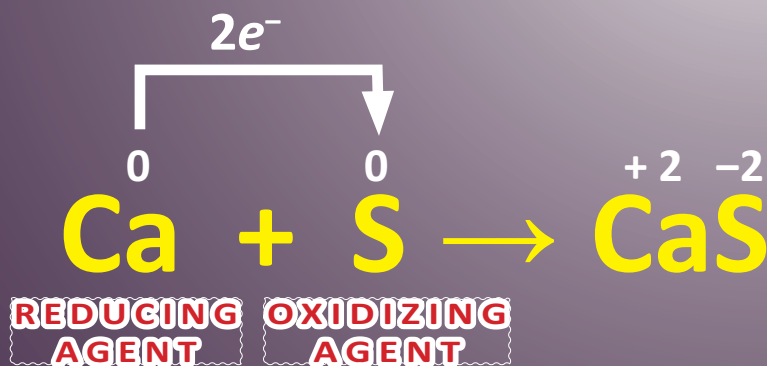
22

Oxidation-reduction reactions

Oxidizing and reducing agents

KEY TOPICS

1. What reactions are oxidation-reduction reactions?
2. What is electron-half-reaction?
3. What is oxidizing agent?
4. What is reducing agent?

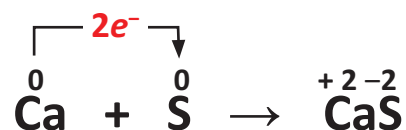


KEY WORDS

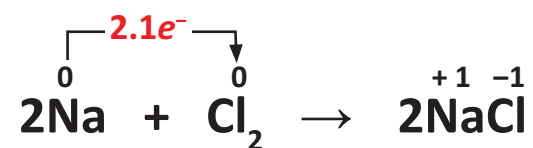
- Oxidation-reduction reaction
- Electron-half-reaction
- Oxidation
- Reduction
- Oxidizing agent (oxidant)
- Reducing agent (reductant)

WHAT IS OXIDATION-REDUCTION REACTION?

In chemical reactions oxidation numbers of reacting species can change or remain unchanged. For example, in a reaction of neutralisation ($\text{Na}^+ + \overset{-2}{\text{O}}\overset{+1}{\text{H}}^- + \text{H}^+ + \text{Cl}^- \rightarrow \text{Na}^+ + \text{Cl}^- + \overset{+1}{\text{H}}_2\overset{-2}{\text{O}}$) hydrogen cations H^+ combine with hydroxide anions OH^- and form water molecules H_2O . The oxidation numbers of both hydrogen and oxygen atoms remain constant (+1 for hydrogen and -2 for oxygen). But when calcium Ca reacts with sulfur S the oxidation numbers of both calcium and sulfur change. The oxidation number of calcium changes from „0“ (Ca is a simple substance) to +2 in CaS. The oxidation number of sulfur also changes – from „0“ (in the simple substance S) to -2 in CaS. There is a transfer of electrons from calcium atoms to sulfur atoms.



Similarly, when sodium Na reacts with chlorine Cl_2 the oxidation numbers of both sodium and chlorine change. Each sodium atom loses 1 electron and transforms into a sodium cation Na^+ . Each chlorine atom gains 1 electron and transforms into a chloride anion Cl^- . There is a transfer of electrons from sodium atoms to chlorine atoms.



Such reactions are **oxidation-reduction reactions**. By definition:

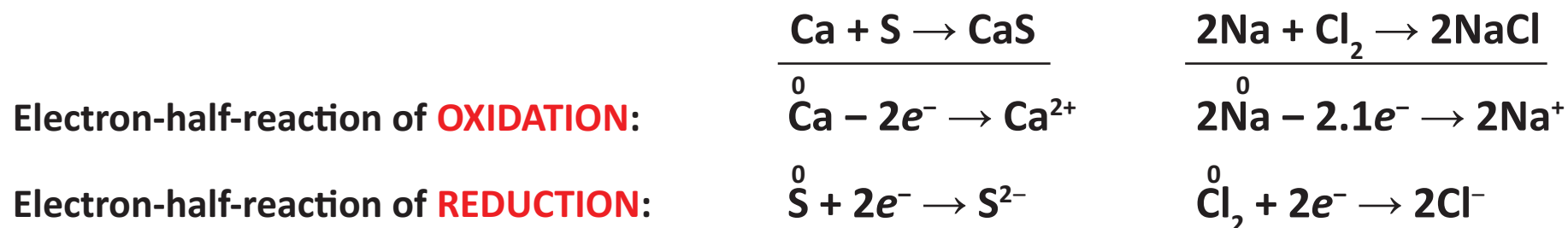
Chemical reactions in which the oxidation numbers of participating species change are called **OXIDATION-REDUCTION REACTIONS**.

Oxidation-reduction reactions, as suggests their name, involve two processes – atoms of an element lose electrons and atoms of another element gain electrons. These are two electron-half-reactions of an oxidation-reduction reaction. They are called oxidation and reduction reactions. By definition:

The electron-half-reaction of electron loss is called **OXIDATION.**
The electron-half-reaction of electron gain is called **REDUCTION.**

A mnemonic rule can help to remember: **OIL RIG** (**O**xidation **I**s **L**oss **R**eduction **I**s **G**ain).

The electron-half-reactions of the oxidation-reduction reactions of the synthesis of CaS and NaCl are expressed as follows:



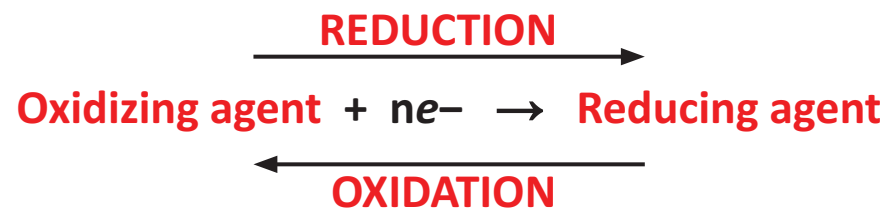
In an oxidation half-reaction the oxidation number increases – the oxidation number of calcium Ca increases from 0 to +2 and the oxidation number of sodium Na increases from 0 to +1.

In a reduction half-reaction the oxidation number decreases – the oxidation number of sulfur S decreases from 0 to –2 and the oxidation number of chlorine Cl decreases from 0 to –1.

- | Oxidation and reduction half-reactions always occur simultaneously. The number of the electrons**
- lost in the oxidation half-reaction is equal to the number of electrons gained in the reduction half-reaction.**

WHAT ARE OXIDIZING AND REDUCING AGENTS?

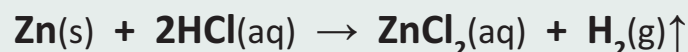
In an oxidation-reduction reaction the species that is the **donor** of electrons is called **reducing agent** (or **reductant**). It is oxidized and its oxidation number increases. The species that is the **acceptor** of electrons is called **oxidizing agent** (or **oxidant**). It is reduced and its oxidation number decreases. In the example above reducing agents are calcium Ca and sodium Na. They are oxidized by sulfur S and chlorine Cl₂ respectively.



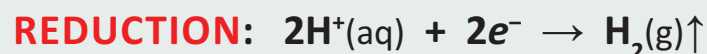
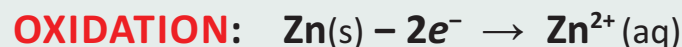
PROBLEM!

Zn powder is put in a beaker containing hydrochloric acid HCl. An oxidation-reduction reaction occurs. What are the oxidizing and the reducing agents?

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



2. Express the electron-half-reactions:



3. Determine the oxidizing and the reducing agents.

Zn atoms lose electrons – they are the reducing agent.

H⁺ cations gains electrons – they are the oxidizing agent.

ANSWER: In the reaction of Zn with HCl the reducing agent is Zn. It is oxidized and its oxidation number increases from 0 to +2 (it is the electrons donor).

H⁺ cations are the oxidizing agent. They are reduced and their oxidation number decreases from +1 to 0 (they are electrons acceptors).

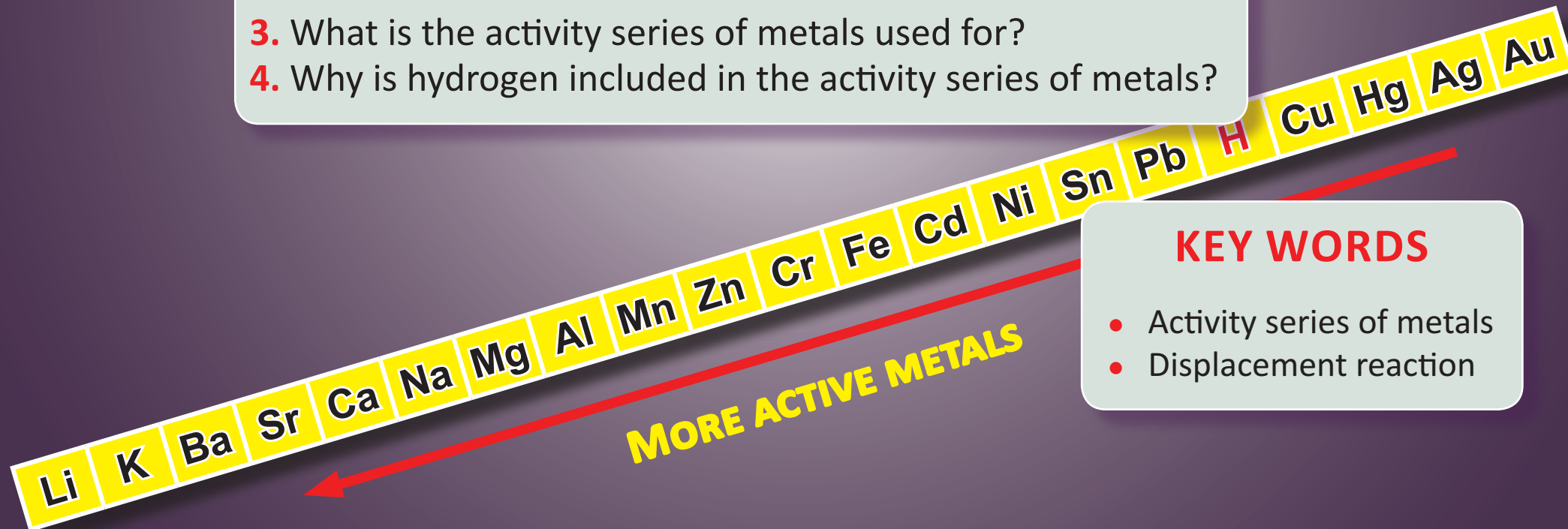
CAN YOU ANSWER THESE QUESTIONS ?

1. What reactions are called oxidation-reduction reactions?
2. What name is given to the process of losing electrons?
3. What name is given to the process of gaining electrons?
4. Is the number of gained electrons always equal to the number of lost electrons in an oxidation-reduction process?
5. Is the slaking of lime ($\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$) an oxidation-reduction reaction? Why?
6. In oxidation-reduction reactions alkali metals are always reducing agents? Why?
7. What are the oxidizing and the reducing agents in the reaction of potassium K with water?
8. Combustion of hydrocarbons is a well known reaction. What is the oxidizing agent?
9. Are photosynthesis and respiration oxidation-reduction reactions? Why?
10. Why are oxidation-reduction processes used in batteries?

23 Activity series of metals

KEY TOPICS

1. What is activity series of metals?
2. What metals are very reactive and what metals are poorly reactive?
3. What is the activity series of metals used for?
4. Why is hydrogen included in the activity series of metals?



KEY WORDS

- Activity series of metals
- Displacement reaction

WHAT IS ACTIVITY SERIES OF METALS?

Alkali metals (1 (IA) group) and alkaline earth metals (2 (IIA) group) are active metals. They take part in oxidation-reduction reactions with simple substances and chemical compounds. They are strong reducing agents. Other metals, like copper Cu, silver Ag, gold Au, platinum Pt are much less active. They are not strong reducing agents. The **activity series of metals** is an empirical (experimental) series of metals listed in order of declining reactivity.

Li	K	Ba	Sr	Ca	Na	Mg	Al	Mn	Zn	Cr	Fe	Cd	Ni	Sn	Pb	H	Cu	Hg	Ag	Au
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THE REACTIVITY OF METALS DECLINES

The series is used to predict at a rough guess metals activity. The series starts with lithium Li. Metals from lithium Li to sodium Na are very reactive. They easily react with oxygen in the air, also react with water and dilute acids. Metals from magnesium Mg to lead Pb are less reactive. Their reactions with oxygen and water are slow and usually undergo at elevated temperature. They also react with dilute acids. Metals to the right of hydrogen do not react with dilute acids. They are found free in nature (as simple substances) as they are not reactive elements.

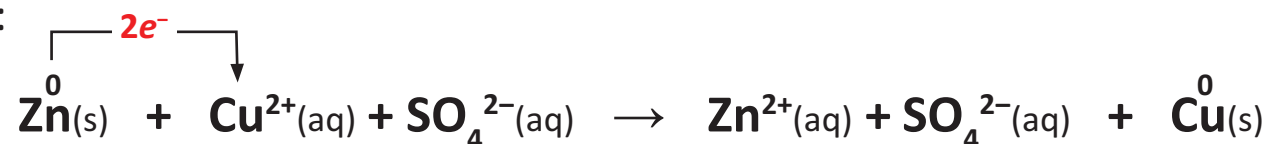
The activity series of metals is used to predict, for example, the products in reactions of metals with soluble salts of other metals or with dilute acids.

● REACTIONS OF METALS WITH SOLUBLE SALTS OF OTHER METALS

Active metals can displace less active metals from their compounds. For example, zinc Zn can displace copper Cu from its compounds as copper Cu is after zinc Zn in the activity series of metals. If a zinc plate is dipped in an aqueous solution of copper sulfate CuSO_4 , the following changes are observed:

- Zn, the more active metal, slowly dissolves in the aqueous solution.
- The blue colour of the CuSO_4 solution fades and finally the solution discolours.
- The less reactive metal coats the zinc surface – a thin reddish layer of elemental copper Cu is formed.

The oxidation-reduction reaction that goes on is expressed as:

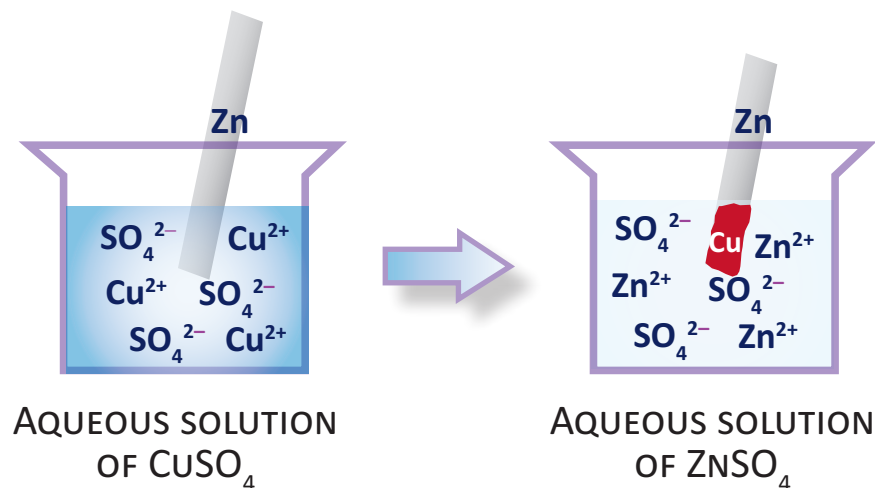


Zn is the reducing agent. It is oxidized. Its oxidation number rises from 0 to +2. The half-reaction of **oxidation** is: $\text{Zn}^0_{(\text{s})} - 2e^- \rightarrow \text{Zn}^{2+}_{(\text{aq})}$

Cu^{2+} is the oxidizing agent. It is reduced to elemental Cu. Its oxidation number decreases from +2 to 0. The half-reaction of **reduction** is: $\text{Cu}^{2+}_{(\text{aq})} + 2e^- \rightarrow \text{Cu}^0_{(\text{s})}$

As a whole, Zn dissolves and displaces the Cu^{2+} cations of CuSO_4 . A colourless solution of ZnSO_4 is formed and copper is pushed out of the solution – it coats the Zn surface.

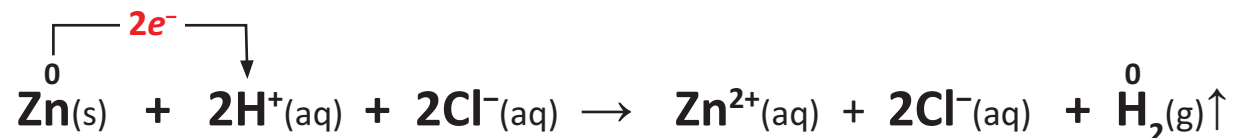
Copper Cu displaces metals that are after it in the activity series of metals (they are less reactive). For example, silver from aqueous solutions of AgNO_3 .



● REACTIONS OF METALS WITH DILUTE ACIDS

Aqueous solutions of dilute acids contain hydrogen cations H^+ and acidic anions (Cl^- , SO_4^{2-} , NO_3^- , etc.). Metals that are before hydrogen H in the activity series of metals can reduce the H^+ cations to H_2 . The metal dissolves. Metal cations are present in the solution and H_2 is evolved in the air. A solution of a salt is formed.

For example, if a zinc Zn plate is dipped in a solution of dilute hydrochloric acid HCl, Zn slowly dissolves and bubbles of H_2 are evolved. The oxidation-reduction reaction that takes place is expressed as:

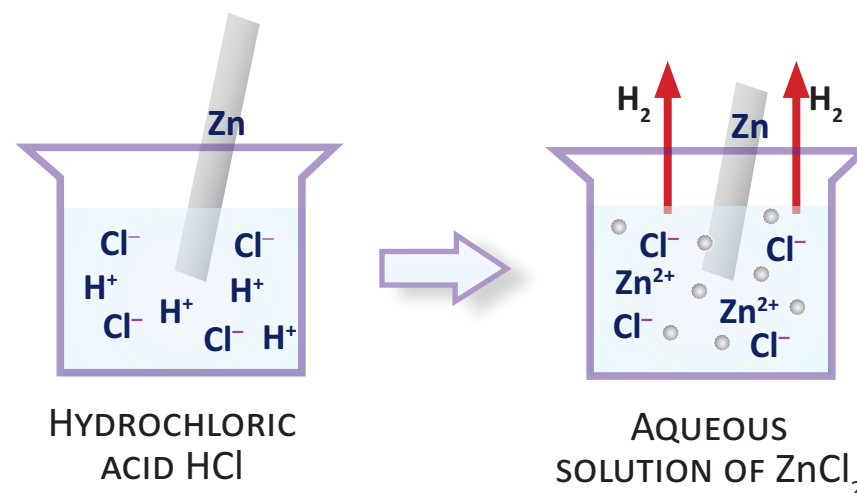


Zn is the reducing agent. It is oxidized. Its oxidation number rises from 0 to +2. The half-reaction of **oxidation** is: $\text{Zn}^0(\text{s}) - 2e^- \rightarrow \text{Zn}^{2+}(\text{aq})$

H^+ is the oxidizing agent. It is reduced. Its oxidation number changes from +1 to 0. The half-reaction of **reduction** is: $2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2^0(\text{g})\uparrow$

As a whole, Zn dissolves and displaces the H^+ cations of the hydrochloric acid HCl. A solution of ZnCl_2 is formed and hydrogen is pushed out of the solution – it is evolved in the air as a gas (H_2).

Copper Cu, mercury Hg, silver Ag, gold Au are after hydrogen H in the activity series of metals. They cannot react with dilute acids.



CAN YOU ANSWER THESE QUESTIONS ?

1. What is activity series of metals?
2. What metal is much reactive – magnesium Mg or iron Fe?
3. Zn powder is put in an aqueous solution of MgCl_2 ? Does a reaction occur?
4. What metals can displace iron Fe from aqueous solutions of its soluble salts?
5. Is it a good idea to handle hydrochloric acid HCl in a container made of iron? Why?
6. Which of the metals dissolves when dipped in dilute sulfuric acid – zinc Zn, copper Cu or silver Ag?
7. In the reaction between an active metal and a dilute acid the ions H^+ of the acid are a reducing or an oxidizing agent?
8. There are three beakers, one with a solution of sodium chloride NaCl, one with dilute hydrochloric acid HCl and another one with a solution of copper dichloride CuCl_2 . A zinc Zn strip is dipped in each beaker. Does a reaction occur in all three beakers?

24

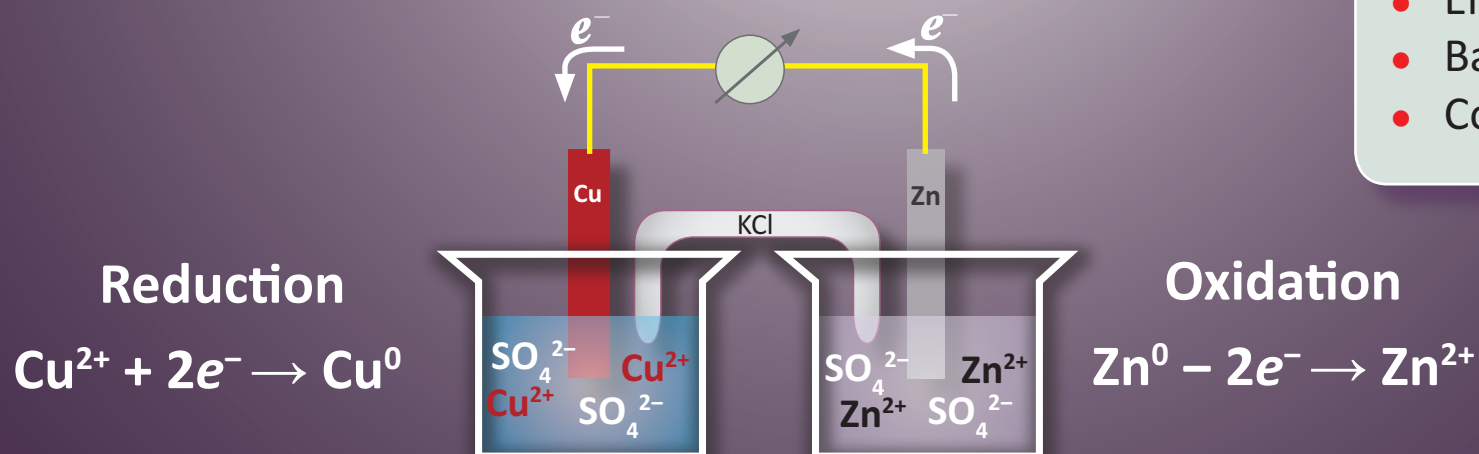
Oxidation-reduction reactions – real-life applications

KEY TOPICS

1. Why are oxidation-reduction reactions so important for industry?
2. What is electrolysis?
3. What are batteries?
4. Why is corrosion of metals a huge problem for the contemporary world?

KEY WORDS

- Extraction of metals
- Electrolysis
- Batteries
- Corrosion

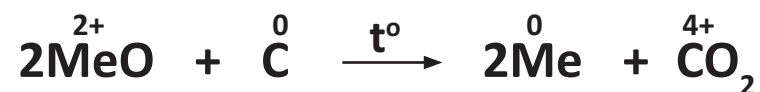


OXIDATION-REDUCTION REACTIONS IN INDUSTRY

Oxidation-reduction reactions are widely used in industry. Some very important applications of these type of chemical reactions are the **extraction of metals from their ores**, the **electrolysis** of salts (melt or dissolved in water) and the production of **batteries**.

● EXTRACTION OF METALS FROM THEIR ORES

The least reactive metals (platinum Pt and gold Au) are found in nature only as simple substances (elemental platinum and gold). Most of the metals are more reactive and form oxides and salts that compose their ores. They can be extracted with the help of more active elements that can displace them in their compounds. For example, Zn, Fe, Sn, Pb and Cu in their oxides can be reduced to elemental form with carbon. The oxidation-reduction reaction that occur is expressed as:



Carbon C is the reducing agent. It is oxidized to CO_2 .

For example, copper CuO is reduced to elemental copper Cu in a reaction with carbon C.
(Solve the problem in the Study book.)

On an industrial scale iron Fe is extracted from its ores (Fe_2O_3) in blast furnaces. The reducing agent is carbon monoxide CO. It is oxidized to CO_2 . (Solve the problem in the Study book.)

● ELECTROLYSIS OF SALTS

Electrolytes in molten state and dissolved in water conduct electricity. When two electrodes connected to a source of direct current (SDC) are put in the melt or the solution, a non spontaneous chemical transformations can occur. This process is called **electrolysis**.

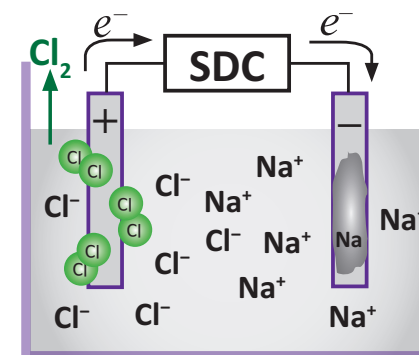
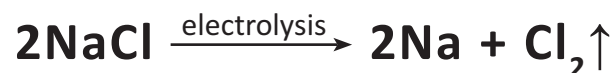
For example, NaCl melts at 801 °C. The sodium Na^+ cations and the chloride Cl^- anions building up the ionic lattice become mobile as the salt decomposes: $\text{NaCl} \xrightarrow{801\text{ }^\circ\text{C}} \text{Na}^+ + \text{Cl}^-$

When two electrodes connected to a SDC are dipped in the melt, the positive Na^+ ions moves towards the negative electrode (the cathode). The negative chloride ions Cl^- moves towards the positive electrode (the anode). An oxidation-reduction reaction undergoes and the half-reactions take place at the electrodes:

oxidation (at the anode): $2\text{Cl}^- - 2.1e^- \rightarrow \text{Cl}_2\uparrow$

reduction (at the cathode): $2\text{Na}^+ + 2.1e^- \rightarrow 2\text{Na}^0$ (or $\text{Na}^+ + e^- \rightarrow \text{Na}^0$)

As a whole, a non spontaneous reaction of decomposition of sodium chloride NaCl is realised.



ELECTROLYSIS OF
MOLTEN NaCl

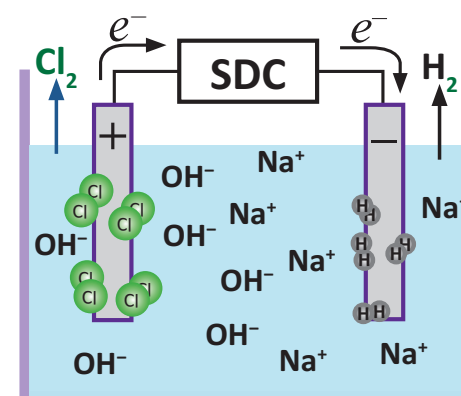
In the aqueous solution of NaCl apart from the ions of the salt, Na^+ and Cl^- , the ions of H^+ and OH^- are present too. Sodium Na is before hydrogen in the activity series of metals. It is a stronger reducing agent than hydrogen. But the Na^+ ions are a weaker oxidizing agent than H^+ ions. During electrolysis the H^+ cations are reduced to gaseous H_2 . At the anode are oxidized the Cl^- anions as they are a stronger reducing agent than hydroxide anions OH^- . Sodium cations Na^+ and hydroxide anions OH^- do not take part in a chemical transformation.

Oxidation (at the anode): $2\text{Cl}^-_{(\text{aq})} - 2.1e^- \rightarrow \text{Cl}_2^0_{(\text{g})}\uparrow$

Reduction (at the cathode): $2\text{H}^+_{(\text{aq})} + 2.1e^- \rightarrow \text{H}_2^0_{(\text{g})}\uparrow$

As a whole, gaseous Cl_2 and gaseous H_2 are evolved in the atmospheres and a solution of sodium base NaOH is formed. This is a non spontaneous process named chlorine-alkali electrolysis. It is applied for the production of chlorine Cl_2 , hydrogen H_2 and sodium base NaOH.

The process of electrolysis is used in the production of various substances – hydrogen, oxygen, chlorine, bases, organic substances and so on. Aluminum is obtained by electrolysis of molten dialuminum trioxide Al_2O_3 . Electrolytic processes are also applied for metal coating.



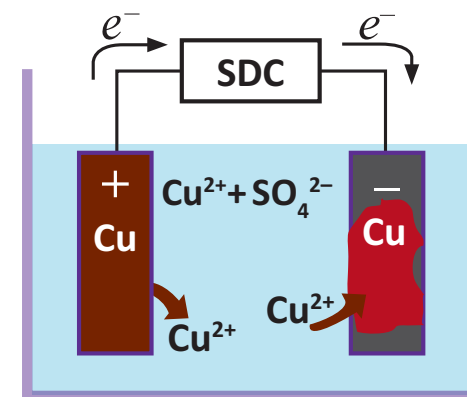
ELECTROLYSIS OF AN
AQUEOUS SOLUTION OF
NaCl

Electrolysis is also used to produce pure metals. For example, copper, extracted from ores contains also iron Fe, silver Ag, gold Au, platinum Pt, palladium Pd and others. It is called black copper. During the *refining of copper* these impurities are separated from the pure copper with the help of a process of electrolysis. Sheets of black copper, a few centimeters thick, are used as anodes. The cathode is made of plates of black copper coated with graphite. Both electrodes are dipped in a solution of copper sulfate CuSO_4 . During electrolysis at the anode only copper is oxidized (dissolved). Pure copper coats the surface of the cathode.

oxidation (at the anode): $2\text{Cu}^0(\text{s}) - 2\text{e}^- \rightarrow \text{Cu}^{2+}(\text{aq})$

reduction (at the cathode): $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}^0(\text{s})$

The impurities fall on the bottom of the vessel and are later processed to extract the other metals.

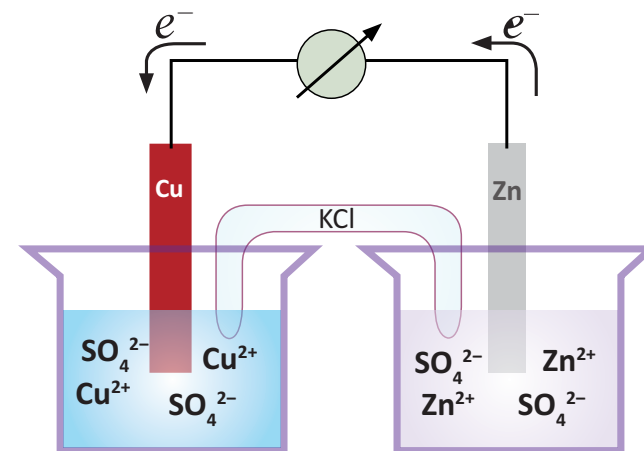
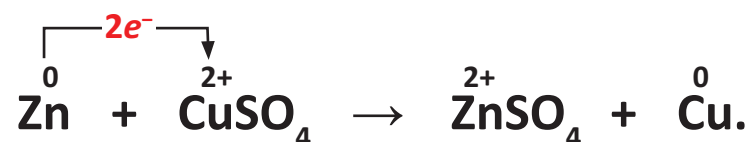


REFINING OF COPPER Cu

● BATTERIES

Oxidation-reduction reactions are also used in batteries. They are **chemical current sources**. The simplest (and the first) chemical current source is the Daniell-Jacobi galvanic cell. It consists of two glass vessels. One of the vessels contains a solution of zinc sulfate ZnSO_4 . The other contains a solution of copper sulfate CuSO_4 . A zinc Zn plate is dipped in the ZnSO_4 solution and a copper Cu plate is dipped in the CuSO_4 solution. The porous ends of a glass tube, filled with a solution of an electrolyte (potassium chloride KCl), are dipped in the solutions in both vessels.

When the metal plates are connected to an ammeter, it detects the electric current in the circuit. The oxidation-reduction process generating the electrical current is expressed with the chemical equation:



DANIELL - JACOBI GALVANIC CELL

The half-reactions of oxidation and reduction occur in two different vessels. The half-reaction of oxidation takes place in the right vessel. The zinc plate dissolves ($\text{Zn}^0 - 2e^- \rightarrow \text{Zn}^{2+}$). The half-reaction of reduction takes place in the left vessel – copper is deposited on the copper plate ($\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0$). These chemical transformations do not occur when the electrical circuit is open.

Batteries are widely used in many electronic devices (smartphones, tablets, laptops, etc.). The storage cells are used in cars, buses, aeroplanes, trains. Fuel cells (they produce electricity by oxidizing a fuel) are used in many power plants, vehicles, in space shuttles.

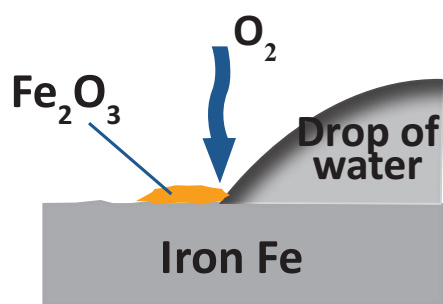
OXIDATION-REDUCTION REACTIONS IN NATURE AND EVERYDAY LIFE

Many vital for man, animal or plants processes involve oxidation-reduction reactions. Such are photosynthesis and respiration. For example, during photosynthesis ($6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$) in green plants under the action of sunlight carbon dioxide CO_2 is reduced to carbohydrates (glucose). Water is oxidized to oxygen O_2 . Alcohols are oxidized to aldehydes ($\text{CH}_3\text{OH} \xrightarrow{[\text{O}]} \text{HCHO}$). They are oxidized to carboxylic acids ($\text{HCHO} \xrightarrow{[\text{O}]} \text{HCOOH}$). In hydrogenation reactions, for example, aldehydes are reduced to alcohols ($\text{CH}_3\text{CHO} \xrightarrow{\text{H}_2} \text{CH}_3\text{CH}_2\text{OH}$).

The widely used process of combustion is also an oxidation-reduction reaction. For example, hydrocarbons are oxidized to CO_2 and oxygen is reduced to water ($\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$).

Oxidation-reduction processes are not always „good“ processes. For example, aging of humans, aging of plastics, spoiling of foods are processes involving oxidation-reduction reactions. Another

undesired oxidation-reduction process is corrosion (the spontaneous destruction of metals in contact with harmful environmental agents). It causes annually the loss of trillions of tonnes of metals. A well known type of corrosion is rusting (iron Fe in contact with oxygen and water is oxidized and transforms into rust Fe_2O_3). The corrosion protection of metals is a problem of huge importance for the contemporary world.



RUSTING IS AN UNDESIRE
D OXIDATION-REDUCTION
PROCESS



COMBUSTION IS A
WIDELY USED OXIDATION-
REDUCTION PROCESS

CAN YOU ANSWER THESE QUESTIONS ?

1. What is the role of oxidation-reduction reactions in metal production and processing?
2. What are the products of the electrolysis of molten KCl?
3. Why are hydrogen cations but not sodium cations reduced on the cathode during chlorine-alkali electrolysis?
4. Which devices used at home need batteries for their functioning?
5. Why is respiration an oxidation-reduction process?
6. Why is combustion an oxidation-reduction process?
7. Why is corrosion of metals an undesired oxidation-reduction process?

OXIDATION-REDUCTION REACTIONS – KEY POINTS

- The charge number of an ion is called **OXIDATION NUMBER**. The physical state of an atom with a given oxidation number is called **OXIDATION STATE**. Often, both terms „oxidation state“ and „oxidation number“ are considered as equivalent.
- Chemical reactions in which the oxidation numbers of participating species change are called **OXIDATION-REDUCTION REACTIONS**.
- The electron-half-reaction of losing of electrons is called **OXIDATION**.
- The electron-half-reaction of gaining of electrons is called **REDUCTION**.
- Oxidation and reduction reactions always occurs simultaneously. The number of the electrons lost in the oxidation reaction is equal to the number of the electrons gained in the reduction reaction.

- The species that is the **donor** of electrons in an oxidation-reduction reaction, is called **REDUCING AGENT** (or **REDUCTANT**). It is oxidized and its oxidation number increases.
- The species that is the **acceptor** of electrons in an oxidation-reduction reaction, is called **OXIDIZING AGENT** (or **OXIDANT**). It is reduced and its oxidation number decreases.
- The **ACTIVITY SERIES OF METALS** is an empirical (experimental) series of metals listed in order of declining reactivity. More active metals can displace less active metals from their compounds. Metals that are before hydrogen in the activity series react with dilute acids.

PROJECTS

1. OCEANS, RIVERS AND LAKES – NATURAL SOLUTIONS

Learn more about the composition of oceans, rivers and lakes waters. Is their pH almost constant? What salts and dissolved gas do they contain? How is the flora and fauna of these enormous water reservoirs affected by some disastrous changes in their composition?

2. ACIDITY AND BASICITY OF MINERAL WATERS

Learn more about the mineral waters on the market. Which of them are acidic and which – alkaline? How do the mineral water composition vary with pH?

3. ELECTROLYTES IN THE HUMAN BODY

What electrolytes are important for the maintenance of life in the human body? Why is it important to maintain a normal level of these electrolytes?

4. CORROSION OF METALS

Explain why corrosion is an undesired process. Learn how metals are protected from the harmful environmental agents causing their destruction.