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# 1. SAFETY MEASURES IN THE CHEMICAL LABORATORY. LABORATORY EQUIPMENT. BALANCE AND WEIGHING

**Characteristic of the subject.** When accomplishing practical work the students must be able to use the laboratory equipment and know the rules of behavior in the chemical laboratory. The acquired skills can be used further on when carrying out experiments in biochemistry and pharmacology.

## **Goals:**

1. To learn the instruction on safety measures in the chemical laboratory.
2. To get to know the laboratory equipment.
3. To acquire a habit in work with the electric balance.
4. To define what measuring utensils are the most precise.

## **Instructions for safety measures in the chemical laboratory**

1. One may enter the laboratory and do any work only with the teacher's permission.
2. Work in the laboratories with chemical agents without white overall is forbidden.
3. Before beginning the work you must read the theoretical material on the subject.
4. The students are forbidden to perform the work, which is not related to the subject of the lesson.
5. When heating the solution in the test-tubes it is restricted to direct the opening of the test-tube at yourself or at your colleagues, take the test-tube by hands, because if the possible emission occurs, there may be an accident.
6. It is forbidden to close the test-tube with your finger when shaking the solution. In cases when it is necessary to smell the solution or the fragrant, you should direct the air stream towards yourself with a slight hand movement and smell carefully.
7. It is forbidden to taste chemicals.

8. When taking the concentrated acids and alkalis with pipettes it is forbidden to suck in the substance with the mouth. In order to avoid such things the pipettes are provided with rubber bulbs.
9. All the works with substances that produce smoke, fog, miasma with a specific smell, and gases must be carried out under the draft.
10. After use all instruments, utensils and chemicals must be put back on their places. The utensils must be washed up after the experiment.

### **Safety requirements in emergency cases**

1. In case of an accident the victim must be given the first help and the doctor must be called for if necessary. Before the arrival of the medical worker the victim must be provided with rest and fresh air.
2. In case of thermal burns the burnt place must be sprinkled with sodium bicarbonate (soda), starch, talc or fresh-made lotion of 2% soda, or manganese permanganate solutions, or neat ethyl alcohol must be applied.
3. In case of burns caused by chemicals, especially by acids (except sulphuric acid) or by alkalis the hurt skin spot must be carefully irrigated with lots of water, then the lotion must be done: when burnt by an acid – 2% soda solution; when burnt by alkalis – 1–2% acetic acid solution.
4. If acid hurts the eyes, they must be washed thoroughly with lots of water and a 3% soda solution.
5. If the hands or other body parts are cut with glass, the small glass pieces must be extracted from the body, then the wound must be irrigated by the 2% potassium permanganate solution or ethyl alcohol, smeared with tincture of iodine, and bandaged.

## Theoretical material

### Laboratory equipment and its use.

Chemical utensils are manufactured from the glass of special types that can bear significant temperature fluctuations. Two kinds of utensils are distinguished: thin-walled (Fig.1) and the thick-walled (Fig.2).

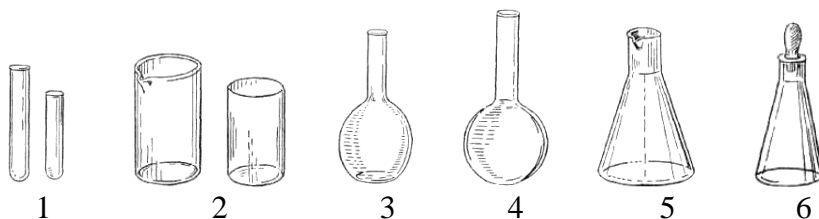


Figure 1 - The thin-walled utensils:

1 – test-tube; 2 – beaker; 3, 4, 5 – flasks: flat-bottom, round-bottom, conical; 6 – weighing bottle

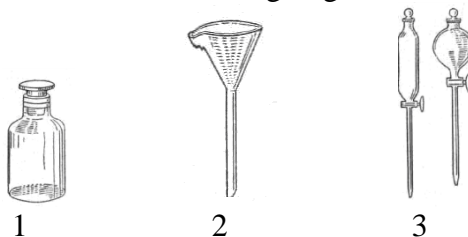


Figure 2 - The thick-walled utensils:

1 – bottle for substances storage; 2 – conical funnel; 3 – separating funnel

The thin-walled utensils comprise test-tubes, beakers, flasks.

*Test-tubes* are used when carrying out the experiments with small quantities of substances.

*Beakers* are used for preparing and temporary storing solutions.

*Flat-bottom flasks* are used for storing distilled water, dissolvents, solutions. They cannot be used for carrying out the experiments that require strong heating.

*Round flasks* are used for carrying out the reactions that require strong heating.

*Conical flasks* are used for titration of solutions.

*Weighing bottles* are used for precise firing the substances in the furnaces.

The thick-walled utensils are used for carrying out the experiments that do not require heating.

*Measuring glass* is used for measuring volume of a substance. The measuring glass (Fig.3) comprises measuring cylinders, thistle tubes, pipettes, burettes, graduated flasks.

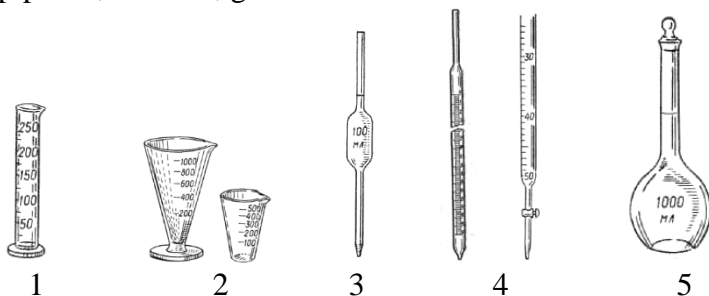


Figure 3 – Measuring glass:

1 – measuring cylinder; 2 – graduated beakers; 3 – pipette; 4 – burettes; 5 – graduated flask

*Measuring cylinders and graduated beakers* are used for measuring definite volumes of liquids. In measuring cylinders the density of the solutions can also be defined. There are 10, 25, 50, 100, 250, 300, 1000 ml cylinders.

*Pipettes* are used for measuring small volumes of liquids up to 0.005 ml. There are graduated and ungraduated pipettes. Ungraduated pipettes can be used to measure only the volumes of liquids that they are designed for. Graduated pipettes can be used to measure any volumes. The pipettes are graduated taking into account

an outflow of a liquid, so one mustn't blow the rest of the liquid out of them.

*Burettes* are used for measuring exact volumes of liquids in the quantitative analysis (for titration). With the help of burettes one can measure volumes of liquids up to 0.3-0.5 ml (for common burettes) and 0.005 ml (for microburettes).

*Graduated flasks* are flasks with the elongated neck with a mark on it in the shape of a thin ring that defines the volume of a flask. Graduated flasks are used for preparing solutions of exact concentration. There exist 25, 50, 100, 200, 250, 500, 1000 ml flasks. The level of a liquid in the cylinders, pipettes, burettes can be defined by the mark (Fig.4).

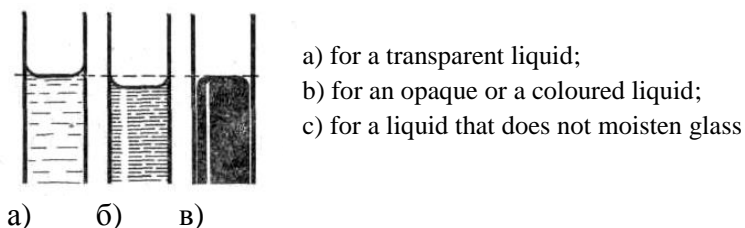


Figure 4 – Position of the meniscus

When filling the utensils with liquids the eyes of the observer must be on a level with the mark on the flask.

Besides the glass utensils, porcelain utensils can also be used in the laboratory: basins, mortars, crucibles (Fig.5).

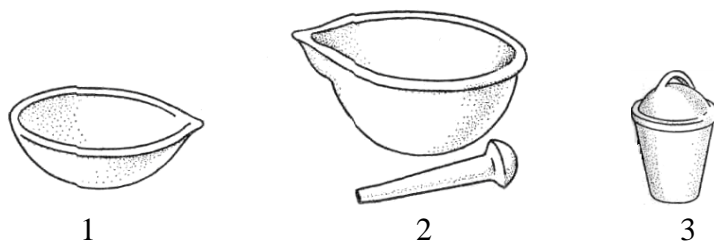


Figure 5 – Porcelain utensils

1 – evaporating basin; 2 – mortar with pestle; 3 – crucible

*Evaporating basin* is used for evaporating liquids and calcination of substances.

*Mortar with pestle* are used for grinding solid substances.

*Crucible* is used for firing substances in the furnaces.

When accomplishing the laboratory works, of great importance is an optional equipment (Fig.6).

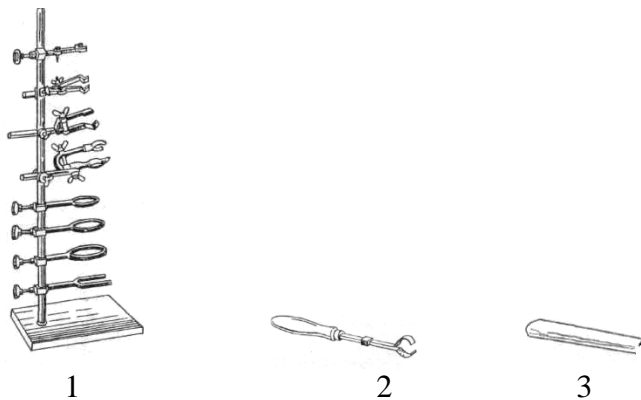


Figure 6 – Optional laboratory equipment and instruments:  
1 – laboratory support stand; 2 – test-tube holder; 3 – spatula

*Laboratory support stand with a set of clamps and tongs, which* are used for fixing various equipment: flasks, test-tubes, refrigerators.

*Test-tube holder* is used for fixing test-tubes when they are heated. First of all, the whole test-tube is heated, and then – its bottom with a substance.

*Spatula* is used for laying or removing small quantities of friable solid substances.

*Heating instruments* consist of electric ovens and spirit-lamps. One can use dry fuel, firing it on special supports.

*Thermometer* is an instrument for temperature measurement.

*Aerometer* is an instrument for liquids density measurement.

In order to weigh substances they use *balance* – pharmaceutical, apothecary, electric and analytical ones.

Pharmaceutical balance is designed to weigh substances up to 100 g.

Apothecary balance is more precise than the pharmaceutical one. The preciseness of weighing is up to within 0.01 g.

The preciseness of weighing with the help of analytical balance is 0.0001 g.

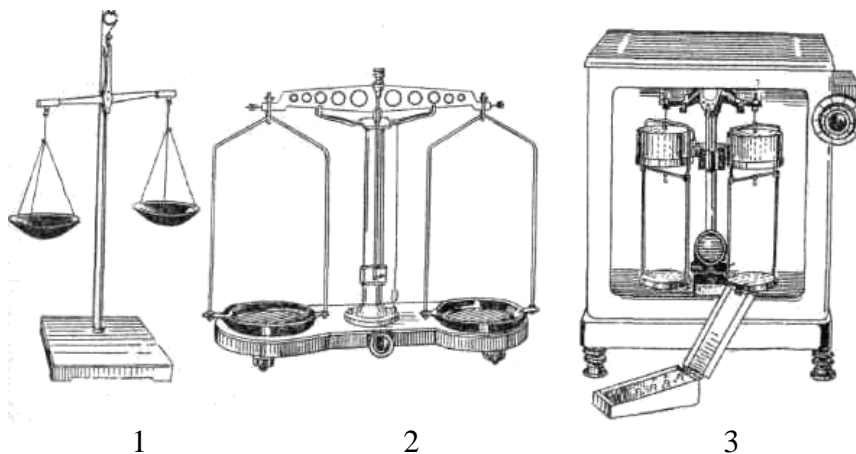


Figure 7 – The balance

## LABORATORY WORK

### Balance and weighing

**Materials and equipment:** weighing bottle, measuring cylinder, burette, pipette, filter paper, water.

### The operation process

The laboratory work is carried out by a group of 4 students.

1. Weigh the weighing bottle and write down the findings into the table.



2. With the help of the measuring cylinder measure 10 ml of water, pour it into the weighing bottle and weigh it. Put down the results into the table and calculate the mass of the measured water.
3. Pour out the water from the weighing bottle, dry the weighing bottle with the filter paper.
4. Once again measure 10 ml of water with the help of the measuring cylinder and weigh it. Calculate the average value of the measured water.
5. Pour 10 ml of H<sub>2</sub>O from the burette into the dry weighing bottle, weigh it. Repeat the experiment twice.
6. Pour 10 ml of H<sub>2</sub>O from the pipette into the dry weighing bottle, weigh it. Repeat the experiment twice.
7. After finishing the work put your work place in order.

## Recording of the experiment

Table 1

Mass of empty weighing bottle: $m_{\text{weighing bottle}} =$						
No.	Cylinder		Burette		Pipette	
	$m_{\text{weighing bottle with water}}$	$m_{\text{water}}$	$m_{\text{weighing bottle with water}}$	$m_{\text{water}}$	$m_{\text{weighing bottle with water}}$	$m_{\text{water}}$
1						
2						
$m_{\text{average}}$	—		—		—	
Absolute error	—		—		—	
Relative error	—		—		—	

Calculate the values of the absolute error and the relative error, if the theoretical water mass  $m_{\text{theoretical}} = 10.00$  g.

$$\text{Absolute error} = |m_{\text{theoretical}} - m_{\text{practical}}|.$$

$$\text{Relative error} = \frac{\text{absolute error}}{m_{\text{theoretical}}} \cdot 100 \%$$

## Conclusions

On the basis of the received results, draw a conclusion about what measuring glass is the most precise.

## Questions for class work and independent work

1. When are you allowed to enter the chemical laboratory and do any work?
2. What must we do in case of thermal burn?
3. What must we do in case of acid burn?
4. What must we do in case of alkali burn?

## 2. COORDINATION COMPOUNDS

### Characteristic of the subject

Coordination compounds are present in minerals and living organisms. Many biologically important compounds are coordination compounds in which complicated organic species are bound to metal ions. The red color of blood is caused by the presence of hemoglobin – a coordination compound containing Fe(II). Chlorophyll, which is found in plants, is a coordination compound similar in structure to hemoglobin, containing Mg(II) instead of Fe(II). Iron enters the composition of myoglobin, oxidases, peroxidases and cytochromes. More than 60 biologically active substances contain zinc. Cobalt is a part of vitamin B<sub>12</sub> (cyanocobalamin).

- Goals:**
1. To learn different types of coordination compounds (complex).
  2. To learn chemical properties and preparation of complex compound.

## Objectives

1. Structure of coordination compounds. The A. Werner's coordination theory.
2. Classification of coordination compounds.
3. Nomenclature of coordination compounds.
4. Coordinate bonds. Geometry (shape) of the complex ion. Isomers.
5. Coordination compounds in medicine.

## Practical skills

After studying the subject you should be able:

1. To determine the type of the complex compound.
2. To name the complex compound.
3. To determine the oxidation state of the central ion (atom), the charge of the complex ion, coordination number.
4. To know the application of coordination compounds in medicine.

## Theoretical material

### 2.1 Structure of the Coordination Compounds.

#### The A. Werner's Coordination Theory

**Coordination compounds** (complex compounds, complexes) are the compounds that contain complex ions that retain their stability when dissolved.

The theory of the complex compound structure was worked out by the Swiss chemist A. Werner (1893).

According to the coordination theory, in the centre of a molecule of a coordination compound the central atom (ion) is situated.

Around the central atom (ion), there are oppositely charged ions or neutral molecules, called **ligands**, or **addends**.

The central atom (ion) together with its ligands is called a **complex ion**.

**Coordination number** reflects the number of bonds formed between the metal ion and the ligands in the complex ion.

The complex ion makes the **inner sphere** of a coordination compound, denoted by square brackets.

The ions, that do not enter the inner sphere, form the **outer sphere** (Fig. 2.1).

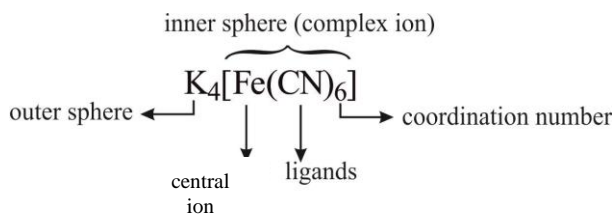


Figure 2.1 – Structure of the coordination compounds

The **charge of the complex ion** is equal to the algebraic sum of the charges of the central atom (ion) and ligands. If the ligands are electrically neutral molecules, the charge of the complex ion is equal to the charge of the central ion. **A molecule of a complex compound is electrically neutral.**

For example, the charge of the  $[\text{Fe}^{2+}(\text{CN})_6]^-$  is equal to  $2 + 6 \cdot (-1) = -4$ , the charge of  $[\text{Cu}^{+2}(\text{H}_2\text{O})_6]^0$  is equal to  $2 + 6 \cdot (0) = +2$ , the charge  $\text{K}_4^+[\text{Fe}^{+2}(\text{CN})_6]^-$  is equal to  $4 \cdot (1) + 2 + 6 \cdot (-1) = 4 + 2 - 6 = 0$ .

Let's consider the structure of complex compound in detail.

**Central atom (ion).** d-block elements (transition elements) or ions (Pt, Pd, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg) show the highest complex formation tendency. Most of the transition element complexes have coordination number 2, 4 or 6.

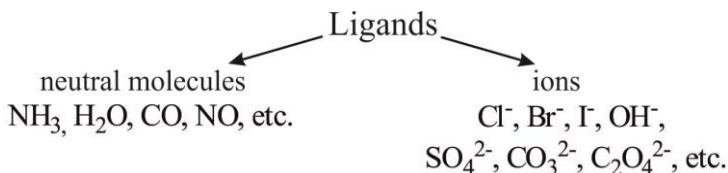
Table 2.1. – Relationship between the oxidation state of the central ion and its coordination number

Oxidation state of the central ion	Coordination number (CN)	Example	
		ion	complex compound
+1	<b>2, 3</b>	$\text{Cu}^+$ , $\text{Ag}^+$ , $\text{Au}^+$	$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
+2	<b>3, 4, 6</b>	$\text{Cu}^{2+}$ , $\text{Co}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Pd}^{2+}$ , $\text{Pt}^{2+}$ , $\text{Fe}^{2+}$	$[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$ , $\text{K}_4[\text{Fe}(\text{CN})_6]$
+3	<b>4, 5, 6</b>	$\text{Fe}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Co}^{3+}$	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$
+4	<b>6, 8</b>	$\text{Sn}^{4+}$ , $\text{Pt}^{4+}$	$\text{K}_2[\text{PtCl}_6]$ , $\text{H}_2[\text{SnCl}_6]$

The central atom (ion) may be presented by nonmetals, for example by boron ( $\text{K}[\text{BF}_4]$ ), silicon ( $\text{K}_2[\text{SiF}_6]$ ), phosphorus ( $\text{K}[\text{PF}_6]$ ).

The oxidation state of the central atom (ion) may be positive –  $\text{K}_3[\text{Fe}^{+3}(\text{CN})_6]$ ,  $\text{K}[\text{BF}_4]$ ; negative –  $[\text{NH}_4]\text{Cl}$ ; and zero –  $[\text{Cl}_2(\text{H}_2\text{O})_4]$ ,  $[\text{Ni}(\text{CO})_4]$ . Oxidation state of the central atom is the main factor affecting the coordination number (tab. 2.1).

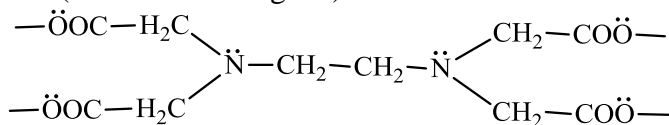
**Ligands.** The ligands are divided into neutral molecules and ions.



Ligands are the species that donate electron pairs to the central atom (ion). The atom in the ligands which can donate the electron pairs, is called **donor atom**. For example, in  $\text{NH}_3$  nitrogen is the donor atom.

The ligands may contain one or more donor atoms for coordination with the central atom. Accordingly, the ligands are classified as follows:

1. **Monodentate** (or unidentate) ligands are ligands that donate just one electron pair. For example,  $\text{NH}_3, \text{H}_2\text{O}, \text{Cl}^-, \text{CN}^-, \text{OH}^-$ , etc.
2. **Bidentate** ligands are ligands that donate two electron pairs to an atom. For example,  $\text{SO}_4^{2-}, \text{CO}_3^{2-}, \text{C}_2\text{O}_4^{2-}, \text{H}_2\ddot{\text{N}}\text{-CH}_2\text{-CH}_2\text{-}\ddot{\text{N}}\text{H}_2$  (a classic bidentate ligand is ethylenediamine which is abbreviated to en).
3. **Polydentate** (or multidentate) ligands donate more than two electron pairs. For example, ethylenediaminetetraacetate EDTA (a hexadentate ligand).



The porphyrin ligands in heme group in haemoglobin are also polydentate.

**The polydentate ligands generally form a complex which is called the chelate effect.**

**Complex ion.** The complex ion may be defined as an electrically charged species which consists of a central atom (ion) surrounded by

a group of ions or neutral molecules. For example,  $[\text{Fe}(\text{CN})_6]^{4+}$  is a complex ion in which the central ferrum ion,  $\text{Fe}^{2+}$ , is surrounded by six cyanide ions (ligands).

All complex ions are divided into 3 groups: **complex ion – cation** –  $[\text{Cu}^{2+}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Co}^{+3}\text{Br}(\text{NH}_3)_5]^{2+}$ ; **complex ion – anion** –  $[\text{Fe}^{2+}(\text{CN})_6]^{4-}$ ; **complex neutral molecule** –  $[\text{Co}^{3+}(\text{NH}_3)_3\text{Cl}_3]^{-0}$ ,  $[\text{Pt}^{+2}(\text{NH}_3)_4\text{Br}_2]^0$ .

If the complex ion is a cation, there are anions in the outer sphere complexes:  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ,  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ .

If the complex ion is an anion, there are cations in the outer sphere complexes. Cations are usually the cations of the alkali and alkaline-earth metals, and the ammonium cation:



## 2.2 Classification of coordination compounds

According to the charge of the complex ions, coordination compounds are divided into neutral coordination compounds, anionic coordination compounds and cationic coordination compounds.

For example, a **neutral complex** is a complex ion which is neutral in charge:  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]^0$ ,  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]^0$ .

**An anionic complex** is a complex ion which is negative in charge:  $\text{K}_4[\text{Fe}(\text{CN})_6]^{4-}$ ,  $\text{Na}[\text{Ag}(\text{CN})_2]^-$ .

**A cationic complex** is a complex ion which is positive in charge:  $[\text{Cu}(\text{NH}_3)_4]^{2+}\text{Cl}_2$ ,  $[\text{Ag}(\text{NH}_3)_2]^+\text{Cl}$ .

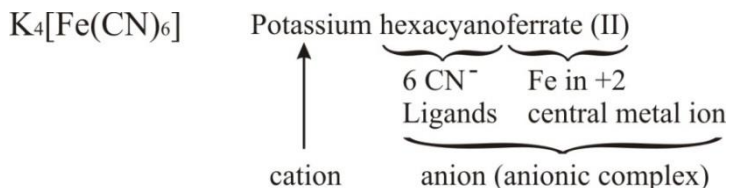
According to **ligands** coordination compounds are divided into **hydroxo complexes**, **acido complexes**, **ammines**, **aqua complexes**.

Ligand	Name of the coordination compound type	Example
hydroxo ions $\text{OH}^-$	hydroxo complexes	$\text{Na}_2[\text{Zn}(\text{OH})_4]$
anions of acid residues: $\text{CN}^-$ , $\text{NO}_2^-$ , $\text{Cl}^-$ , $\text{I}^-$ , $\text{Br}^-$ and others	acido complexes	$\text{K}_4[\text{Fe}(\text{CN})_6]$ , $\text{K}_2[\text{HgI}_4]$ , $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
neutral molecules: $\text{NH}_3$ , $\text{H}_2\text{O}$	ammines aqua complexes	$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ , $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$

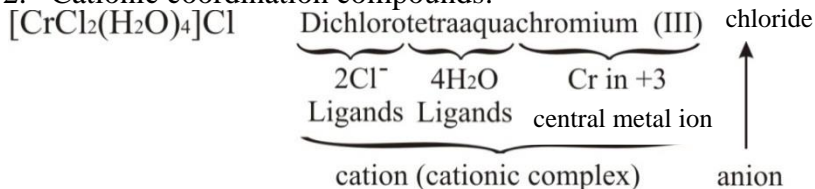
### 2.3 Nomenclature of Coordination Compounds

Coordination compounds are named according to the nomenclature, recommended by the International Union of Pure and Applied Chemistry (IUPAC). The following examples illustrate how the rules are applied.

#### 1. Anionic coordination compounds:

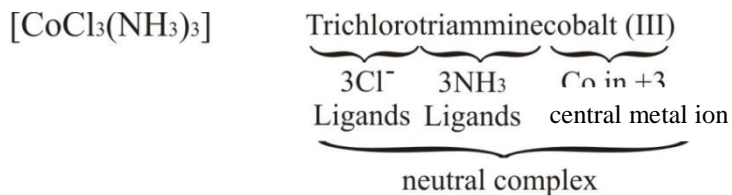


#### 2. Cationic coordination compounds:





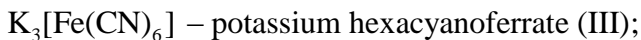
### 3. Neutral coordination compounds:



The nomenclature can be summarized as follows:

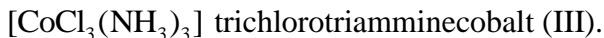
#### 1. Naming of a coordination compound:

a) if the coordination compound is ionic, then the cation is named before the anion:



$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$  – dichlorotetraaquachromium (III) chloride.

b) if the coordination compound is neutral, then the name of the complex ion is the name of the compound:



#### 2. Naming of a complex ion in a coordination compound

All present ligands and the central atom (ion) are named together as one word. The ligands are named before the central atom (ion):



#### 3. Naming of the ligands in a complex ion:

a) the order of the ligands is anionic, neutral, or cationic:



- the names of anionic ligands end in – o:

$\text{CN}^-$  – cyano;

$\text{Cl}^-$  – chloro.

- the names of neutral ligands are the names of the molecules, except  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{NO}$  :

$\text{NH}_3$  – ammine;

H<sub>2</sub>O – aqua.

Table 2.2 shows the names of some common ligands.

Table 2.2 – Names of some common ligands

Anionic Ligand	Ligand Name	Neutral Ligands	Ligand Name
bromide (Br <sup>-</sup> ),	bromo,	ammonia (NH <sub>3</sub> ),	ammine,
chloride (Cl <sup>-</sup> ),	chloro,	water (H <sub>2</sub> O),	aqua (aquo),
cyanide (CN <sup>-</sup> ),	cyano,	carbon monoxide (CO),	carbonyl,
fluoride (F <sup>-</sup> ),	fluoro,	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	ethylenediam ine
hydroxide (OH <sup>-</sup> ),	hydroxo,		
sulphate (SO <sub>4</sub> <sup>2-</sup> ),	sulphato,		
amide (NH <sub>2</sub> ),	amido,		
nitrite (NO <sub>2</sub> <sup>-</sup> ),	nitro,		
nitrate (NO <sub>3</sub> <sup>-</sup> )	nitrato		

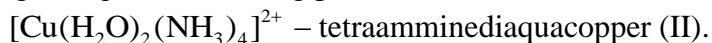
b) within each type of ligand (cationic, anionic or neutral):

- if the number of a particular ligand is more than one, then the number is indicated with the appropriate Greek prefix as shown in table 2.3;

Table 2.3 – Greek prefix of a number

Number	Greek prefix	Number	Greek prefix
2	Di-	5	Penta-
3	Tri-	6	Hexa-
4	Tetra-		

- the ligands are arranged in alphabetical order, ignoring the numbering prefixes:



#### 4. Naming of the central atom (ion) in a complex:

- a) if the complex is anionic, then the name of the metal ends in -ate:

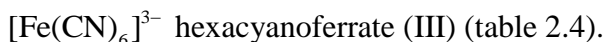


Table 2.4 – Names of some common metals in anionic complexes

Metal	Name in Anionic Complex	Metal	Name in Anionic Complex
Titanium (Ti)	Titanate	Nickel (Ni)	Nickelate
Chromium (Cr)	Chromate	Zinc (Zn)	Zincate
Manganese (Mn)	Manganate	Platinum (Pt)	Platinate
Cobalt (Co)	Cobaltate		

For the following metals the English name is replaced by the Latine name, to which the “ate” ending is added:

(Sn) Tin – Stannate;

(Pb) Lead – Plumbate;

(Fe) Iron – Ferrate;

(Ag) Silver – Argentate;

(Cu) Copper – Cuprate;

(Au) Gold – Aurate.

If the complex is cationic or neutral, then the name of the metal remains unchanged:



Note that the oxidation number of the central metal ion is named immediately after it in Roman numerals, enclosed in brackets.

## 2.4 Coordinate Bonds. Shape of the Complex Ion. Isomers

**Ionic bonds** are the electrostatic forces of attraction between oppositely charged ions; the ions are the result of electron transfer between atoms. (Fig. 2.1)

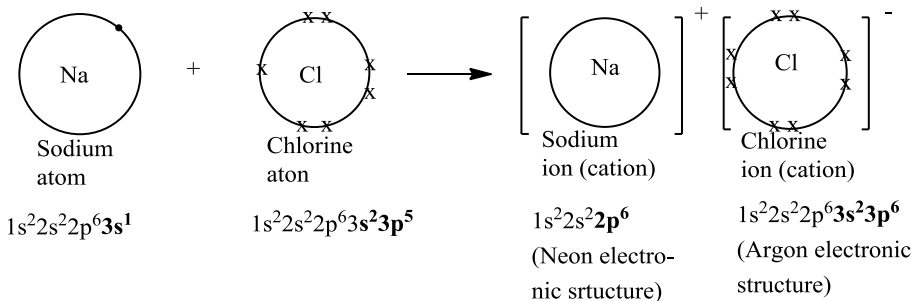


Fig. 2.1 – Electron transfer during the reaction between sodium and chlorine

A **covalent bond** is a chemical bond that involves the sharing of electron pairs between two non-metal atoms.

The octet rule states that an atom tries to attain the octet configuration through bond formation. (Fig. 1.2)

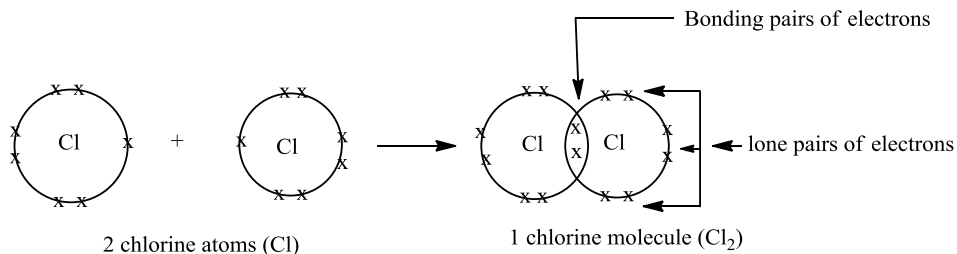


Fig. 2.2 – A single covalent bond in a chlorine molecule

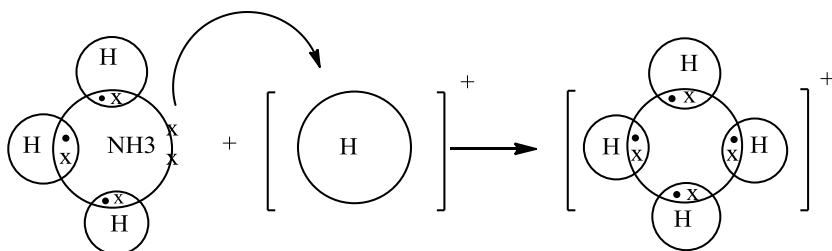
In the chlorine molecule, each chlorine atom achieves a stable [Ar] electronic configuration by sharing a pair of electrons. There are electron pairs in the outermost shell of an atom that are not shared or bonded to another atom, and are known as the **lone pairs of electrons**.

**A dative covalent bond** (also known as a **coordinate bond**) is the type of covalent bonding in which the shared pair of electrons is supplied by only one of the bonded atoms.

The atom that supplies the shared pair of electrons is known as the electron donor, while another atom, involved in the dative covalent bond, is known as the electron acceptor. The donor must have an unshared electron pair (i.e. lone pair) in its outer shell, while the acceptor must have at least one empty orbital in its outer shell.

An ammonia molecule will combine with a hydrogen ion by forming a dative covalent bond as shown below (Fig. 2.3):

a)



b)

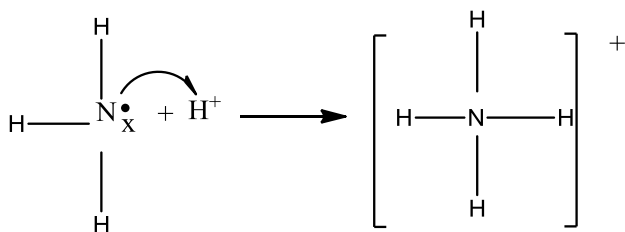


Fig. 2.3 – Formation of the dative covalent bond in an  $\text{NH}_4^+$  ion: a) dot and cross diagram; b) single line representation.

The central metal ion in the complex makes a number of empty orbitals available for the formation of coordinate bonds with suitable ligands. The number of empty orbitals, that are made

available for this purpose, is equal to coordination number of the central metal ion. For example, if coordination number is 4, four empty orbitals are made available in the central metal ion:

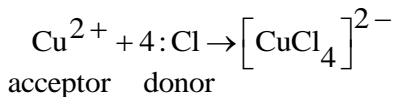


Figure 2.4 – Shows the schematic view of coordination compound molecule  $\text{K}_2[\text{CuCl}_4]$

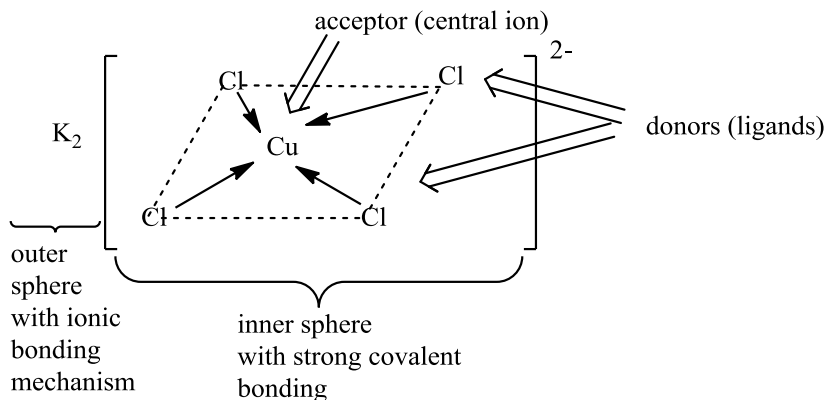



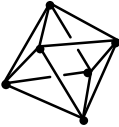


Fig. 2.4 – A schematic view of coordination compound molecule  $\text{K}_2[\text{CuCl}_4]$ .

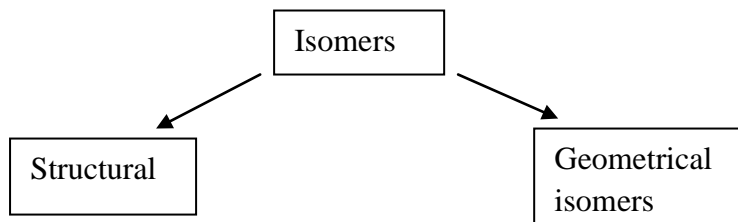
Central ions or atoms with different coordination numbers undergo different hybridizations, giving rise to a number of different empty hybrid orbitals with different shapes. (Table 2.5)

Table 2.5 – Relationship between coordination numbers, hybridisations and shapes of complexes

Coordination number	Hybrid orbitals involved	Shape of resulting complex	Example
2	sp	linear 	
4	sp <sup>3</sup>	tetrahedral 	$[\text{Zn}(\text{NH}_3)_4]^{2+}$ $[\text{CoCl}_4]^{2-}$
4	dsp <sup>2</sup>	square planar 	$[\text{Cu}(\text{NH}_3)_4]^{2+}$ $[\text{CuCl}_4]^{2-}$
6	d <sup>2</sup> sp <sup>3</sup> or sp <sup>3</sup> d <sup>2</sup>	octahedral 	$[\text{Cr}(\text{NH}_3)_6]^{3+}$ $[\text{Fe}(\text{CN})_6]^{3-}$

**Isomers** are compounds having the same molecular formula but different structural formula.

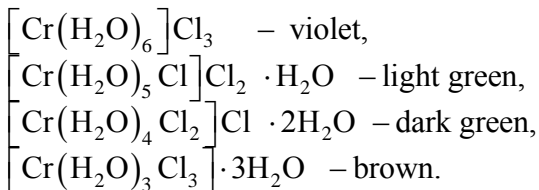
There are two kinds of isomers – structural isomers and geometric isomers.



**Structural isomers** are isomers that have different ligands coordinated with the central metal ion.

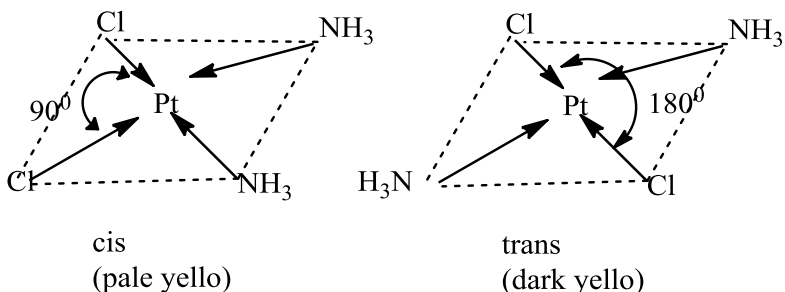
For example,  $[\text{Co}(\text{NH}_3)_5 \text{Br}]^{2+} \text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5 \text{SO}_4]^+ \text{Br}^-$  are two structural isomers.

The compound  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$  have four structural isomers:



**Geometric isomers** are isomers in which the composition of the first coordination sphere is the same but the geometric arrangement of the ligands varies.

Geometric isomers are possible for both square planar (4-coordinated) and octahedral (6-coordinated) complexes only. For example, the complex  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  have two isomers differing in colour, solubility, reactivity, and the way of preparation. In one of the isomers, the chlorine atoms are diagonally opposite (trans-isomer), and in the other one they are adjacent to each other (cis-isomer).



## 2.5 Coordination Compounds in Medicine

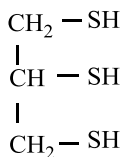
Coordination compounds are present in minerals, and living organisms. Many biologically important compounds are coordination compounds in which complicated organic species are bound to metal



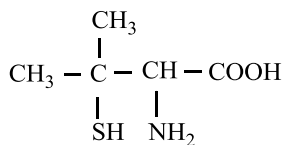
ions. The red color of blood is caused by the presence of hemoglobin – a coordination compound containing Fe(II). Chlorophyll, which is found in plants, is a coordination compound similar in structure to hemoglobin but containing Mg(II) instead of Fe(II). Iron is a part of the composition of myoglobin, oxidases, peroxidases, cytochromes. More than 60 biologically active substances contain zinc. Cobalt is in composition of vitamin B<sub>12</sub> (cyanocobalamin).

Formation and destruction of biological complexes occur constantly in the organism, and metal-ligand homeostasis is maintained on the definite level. Metal-ligand homeostasis can be disturbed due to deficiency or excess of biometal cations, entering of toxic metal cations, entering or formation of alien ligands. Toxicity of d-metals in many cases is explained by the stability of biological complexes, formed by them. Complexing agents are used for removal of metal poisoning. Antidote therapy of poisonings, caused by heavy metal cations, is based on the formation of stable complexes (chelation) between these metals and special ligands.

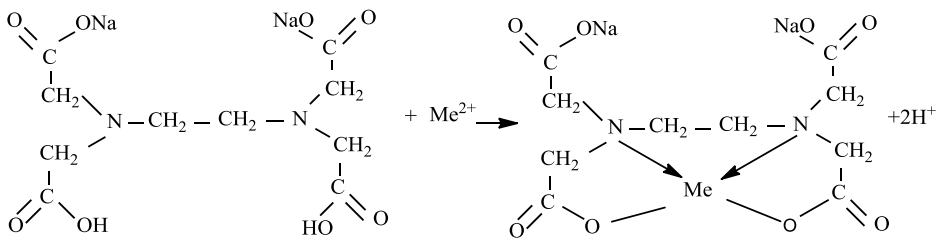
Dimercaprol is an effective antidote against the organic arsenic like lewisite, but can be used for poisoning due to antimony, gold and mercury. Penicillamine is an effective antidote the treatment of poisoning by copper, mercury and lead. Trilon B (bisodium salt of EDTA) is used for treatment of hypercalcemia, poisoning by calcium compounds.



2,3-dimercaptopropan-1-ol  
(BAL, dimercaprol)



Penicillamine (dimethylcystein)



B Trilon

### Examples of exercise solution

**Example 2.1.** What is the charge on the complex ion in the following:

- a)  $[\text{Co}^{+3}\text{Cl}_6]^x$ , b)  $[\text{Co}^{+3}(\text{NH}_3)_4\text{Cl}_2]^x$ , c)  $[\text{Cu}^{+2}(\text{H}_2\text{O})_4]^x$ , d)  $[\text{Co}^{+3}(\text{NH}_3)_3\text{Cl}_3]^x$  ?

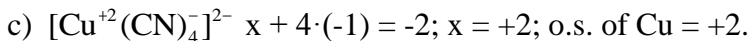
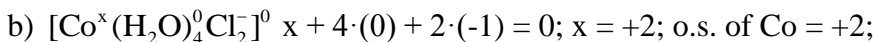
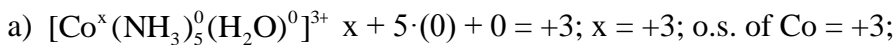
**The charge on the complex ion is always the sum of the charges on the ions or molecules that form the complex:**

- a) the charge of  $[\text{Co}^{+3}\text{Cl}_6]^x$  is equal to the sum of charges of central ion  $\text{Co}^{+3}$  and six ligands of chloride  $\text{Cl}^-$  ions.  
 $[\text{Co}^{+3}\text{Cl}_6]^x$  : charge (x) =  $+3 + 6 \cdot (-1) = -3$ .  $[\text{CoCl}_6]^{3-}$  ;
- b) the charge (x) =  $+3 + 4 \cdot (0) + 2 \cdot (-1) = +1$ ,  $[\text{Co}^{+3}(\text{NH}_3)_4\text{Cl}_2]^{1+}$  ;
- c) the charge (x) =  $+2 + 4 \cdot (0) = +2$ ,  $[\text{Cu}^{+2}(\text{H}_2\text{O})_4]^{2+}$  ;
- d) the charge (x) =  $+3 + 3 \cdot (0) + 3 \cdot (-1) = 0$ ,  $[\text{Co}^{+3}(\text{NH}_3)_3\text{Cl}_3]^0$  .

Knowing the charge of the complex ion, we can calculate the oxidation state of the central atom (ion), which will be used while writing the names of compounds.

- Example 2.2.** Calculate the oxidation state (o.s.) of the central ion in the following: a)  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  ;  
 b)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]^0$  ; c)  $[\text{Cu}^{+2}(\text{CN})_4]^{2-}$  .

Ans.:



**Example 2.3.** Name the following compounds:

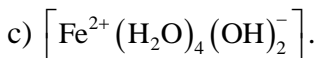
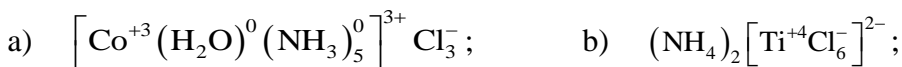


Ans.: a) potassium hexacyanoferrate (II); b) tetraamminecopper (II) chloride; c) diamminetetrachloroplatinum (III).

**Example 2.4.** Write the formula of the following compounds:

a) aquapenta-amminecobalt (III) chloride; b) ammonium hexachloro titanate (IV); c) dihydroxotetra aquairon (II).

Ans.:



### Questions for class work

1. What are coordination compounds?
2. Give the definitions of ligand, central ion, coordination number, inner sphere, outer sphere, complex ion.
3. Give the classification of complexes.
4. Give the examples of biocomplexes.

### Exercises for classwork and independent work

1. What is the charge on the complex ion in the following:
  - a)  $[\text{Ni}^{+2}(\text{CN})_6]^x$ ;
  - b)  $[\text{Co}^{+3}\text{Cl}_6]^x$ ;
  - c)  $[\text{Ti}^{+3}(\text{H}_2\text{O})_6]^x$ ;
  - d)  $[\text{Fe}^{+2}(\text{H}_2\text{O})_6]^x$ ;
  - e)  $[\text{Pd}^{+2}\text{Br}_4]^x$ .
2. Calculate the oxidation state of the central ion in the following:

- a)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ;                      d)  $\text{K}_2[\text{PbCl}_4]$ ;  
b)  $\text{Na}_2[\text{Cu}(\text{OH})_4]$ ;                        e)  $\text{Na}_2[\text{PtBr}_6]$ .  
c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$ ;
3. Determine the type of the following compounds:  
a)  $\text{K}_2[\text{Cu}(\text{OH})_4]$ ;                        d)  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ ;  
b)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ;                      e)  $\text{K}[\text{Au}(\text{CN})_2]$ .  
c)  $\text{Na}_2[\text{PbBr}_4]$ ;
4. Name the following compounds:  
a)  $\text{K}_4[\text{Ni}(\text{CN})_6]$ ;                        e)  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ ;  
b)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ;                      f)  $\text{K}_2[\text{PtCl}_6]$ ;  
c)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ ;                        g)  $\text{Na}[\text{Au}(\text{CN})_2]$ .  
d)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$ ;
5. Write the formula of the following compounds:  
a) aquapentaammineferrum (III) bromide;  
b) ammonium hexabromotitanate (IV);  
c) dihydroxotetraaquacobalt (II).

### Questions for self-testing

For each of questions 1 through 20, choose one correct lettered answer.

1. What is the oxidation state of the central metal ion in the compound:  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$  ?  
a) +2        b) +3        c) +4        d) 0
2. What is the oxidation state of the central metal ion in the compound:  $\text{K}_2[\text{PtCl}_6]$  ?  
a) +2        b) +4        c) +7        d) 0
3. What is the oxidation state of the central metal ion in the compound:  $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$  ?  
a) +2        b) +4        c) +9        d) 0

4. What is the oxidation state of the central metal ion in the compound:  $\text{Na}_2[\text{PdBr}_4]$ ?  
 a) +2      b) +5      c) 0      d) +6
5. What is the oxidation state of the central metal ion in the compound:  $\text{K}[\text{Au}(\text{CN})_2]$ ?  
 a) +2      b) +3      c) 0      d) +5
6. What is the central metal ion in the compound:  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ ?  
 a) Fe      b)  $\text{H}_2\text{O}$       c)  $\text{Cl}_2$       d) O
7. What is the central metal ion in the compound:  $\text{K}_2[\text{PtCl}_6]$ ?  
 a) K      b) Pt      c) Cl      d) Na
8. What is the central metal ion in the compound:  $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$ ?  
 a) Cu      b)  $\text{NH}_3$       c) Cl      d) N
9. What is the central metal ion in the compound:  $\text{Na}_3[\text{CoBr}_6]$ ?  
 a) Na      b) Co      c) Br      d) K
10. What is the central metal ion in the compound:  $\text{K}[\text{Au}(\text{CN})_2]$ ?  
 a) K      b) Au      c) CN      d) C
11. What is the name of the compound:  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ ?  
 a) hexaaquaferrum (II) chloride  
 b) chloropentaamminecobalt (III) chloride  
 c) ammonium hexachlorotitanate (IV)  
 d) tribromotriaquacobalt (III)
12. What is the name of the compound:  $\text{K}_2[\text{PtCl}_6]$ ?  
 a) hexaammineferrum (II) chloride  
 b) potassium hexachloroplatinate (IV)  
 c) trichlorotriaquacobalt (III) bromide  
 d) hexaaquaferrum (III) hydroxide
13. What is the name of the compound:  $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$ ?  
 a) chloropentaamminecobalt (III) chloride  
 b) hexaaquaferrum (II) hydroxide  
 c) tetraamminecopper (II) chloride  
 d) ammonium hexachlorotitanate (IV)
14. What is the name of the compound:  $\text{Na}_3[\text{CoBr}_6]$ ?

- a) sodium hexabromocobaltate (III)  
 b) ammonium hexachlorotitanate (IV)  
 c) chloropentaammincobalt (III) chloride  
 d) potassium hexachloroplatinate (IV)
15. What is the name of the compound:  $\text{K}[\text{Au}(\text{CN})_2]$  ?  
 a) potassium dicyanoaurate (III)  
 b) podium hexabromocobalte (III)  
 c) chloropentaammincobalt (III) chloride  
 d) potassium hexachloroplatinate (IV)
16. What is the formula of the compound potassium tetracyanonickelate (II)?  
 a)  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$   
 b)  $\text{K}_2[\text{Ni}(\text{CN})_4]$   
 c)  $\text{Na}_2[\text{PtCl}_6]$   
 d)  $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$
17. What is the formula of the compound sodium hexachlorocobaltate (III)?  
 a)  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}$   
 b)  $\text{K}_2[\text{Ni}(\text{CN})_4]$   
 c)  $\text{Na}_3[\text{CoCl}_6]$   
 d)  $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$
18. What is the formula of the compound tetraamminecopper (II) chloride?  
 a)  $[\text{Fe}(\text{NH}_3)_6]\text{Br}_2$   
 b)  $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$   
 c)  $\text{Na}_2[\text{PtCl}_6]$   
 d)  $\text{K}[\text{Ag}(\text{CN})_2]$
19. What is the formula of the compound potassium hexachloroplatinate (IV)?  
 a)  $\text{Na}_2[\text{PtCl}_6]$   
 b)  $\text{K}_2[\text{PtCl}_6]$   
 c)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$   
 d)  $\text{K}_3[\text{CoBr}_6]$
20. What is the formula of the compound hexaaquaferrum (II) bromide?  
 a)  $\text{K}_2[\text{PtCl}_6]$   
 b)  $[\text{Co}(\text{NH}_3)_3\text{Br}_3]$   
 c)  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Br}_2$   
 d)  $[\text{Cu}(\text{NH}_3)_4]\text{Br}_2$

## LABORATORY WORK

### Coordination compounds

**Materials and equipment:** test-tubes,

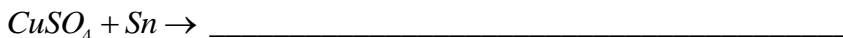
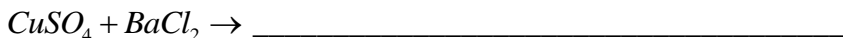
$\text{CuSO}_4$ ,  $\text{NH}_4\text{OH}$ ,  $\text{BaCl}_2$ ,  $\text{Sn}$ ,  $\text{NaOH}$ ,  $\text{AlCl}_3$ ,  $\text{ZnSO}_4$ ,  $\text{Cr}_2(\text{SO}_4)_3$

### The operation process

#### Experiment 1. *Preparation and properties of complex compound of copper*

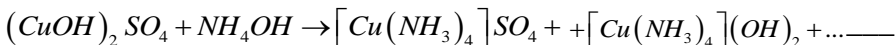
1) Test for copper (II) sulfate.

Take two test-tubes. Place 4-8 drops of copper (II) sulfate  $\text{CuSO}_4$  solution into each test-tube. Add 2-3 drops of barium chloride  $\text{BaCl}_2$  to the first test-tube. Observe the formation of white precipitate. Place the piece of tin  $\text{Sn}$  in the second test-tube. Tin dissolves gradually, and red-brown copper appears. Write down the reaction equations:



2) Preparation of tetraamminecopper (II) complex.

Place 10-15 drops of  $\text{CuSO}_4$  solution in a clean test-tube. Add a few drops of ammonia solution  $\text{NH}_4\text{OH}$ . At first, we observe the formation of blue-green precipitate of  $(\text{CuOH})_2\text{SO}_4$  which dissolves in excess of  $\text{NH}_4\text{OH}$  with the formation of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion, which are blue. Write down the reaction equations and balance them.

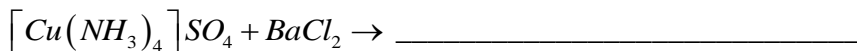


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3) Properties of coordination compound of copper.

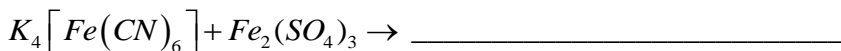
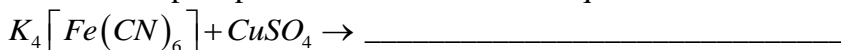
Divide solution of tetraamminecopper (II) complex into two equal parts. Add 2-3 drops of  $\text{BaCl}_2$  to the first test-tube and 2-3 drops of  $\text{Sn}$  to the second one. Observe the formation of white

precipitate in the first test-tube and absence of free copper in the second one.



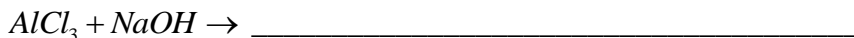
### Experiment 2. Coordination compound in the exchange reactions

Take two test-tubes. Place 4-5 drops of  $K_4[Fe(CN)_6]$  solution into each test-tube. Add 4-5 drops of  $CuSO_4$  solution to the first test-tube. To the second test-tube, add 4-5 drops of  $FeSO_4$ . Observe the formation of precipitate. Write the reaction equations.

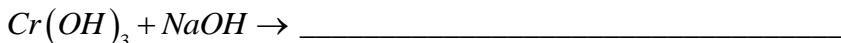
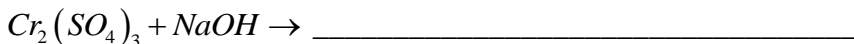
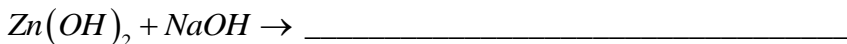


### Experiment 3. Preparation of hydroxo complexes

1) Place 8-10 drops of  $AlCl_3$  solution in a test-tube. Add a few drops of  $NaOH$ . Observe the formation of white precipitate of aluminium hydroxide  $Al(OH)_3$  which is amphoteric and dissolves in excess of  $NaOH$ . Write down the reaction equations.



2) Repeat similar experiments with solutions of  $ZnSO_4$  and  $Cr_2(SO_4)_3$ . Write down the reaction equations.



### Conclusions



### 3. SOLUTIONS

#### **Characteristic of the subject**

Solutions are of great importance in the life and practical activities of a man. All biological liquids – blood, lymph, intercellular lymph, gastric juice, etc. – are solutions. All biochemical processes in organism occur in aqueous solutions. Good knowledge of theory of solutions is necessary to explain physical and chemical essence of such phenomena as diffusion, osmosis, dissolution, hydrolysis and others, which are the basis of metabolism in nature.

#### **Goals:**

1. To be able to characterize quantitative composition of solutions.
2. To be able to prepare solutions of given concentration.
3. To make conclusions about acidity of biological liquids on the basis of pH.
4. To explain the mechanism of buffer action and ability of buffers to maintain acid-base equilibrium.
5. To analyze correlation between colligative properties and of concentration solutions.

#### **Objectives**

- 1 Theory of solutions.
- 2 Methods of expressing concentration of solutions.

#### **Practical skills**

After studying the subject you should be able:

1. To describe the process of dissolving of substances in a solvent.
2. To characterize the influence of different factors on the solubility.
3. To express a solution concentration in mass percent, molarity, molality, normality, and mole fraction.
4. To prepare solution of given concentration.

## Theoretical Material

### 3.1 Theory of Solutions

Solutions are of great importance in the life and practical activities of a man. All the biological liquids – blood, lymph, intercellular lymph, gastric juice, etc. – are solutions. All biochemical processes in organism occur in aqueous solutions.

**Solutions** are homogeneous systems consisting of two or more components and the products of their interaction.

Compulsory components of the solution are the solvent and the **solute**.

The **solvent** is the solution component which is **present in greatest quantity** or the component that determines the state of matter in which the solution exists.

The **solute** is the solution component which is **present in lesser quantity** than the solvent.

A solution in which **water** is the **solvent** is called an **aqueous solution**.

A solution containing a relatively large quantity of a solute is called to be **concentrated**. If the quantity of solute is small, the solution is **dilute**.

#### Types of solution

According to their state solutions can be **liquid**, **solid** and **gaseous**.

In a **liquid solution** the **solvent** is a **liquid** substance. For example: gasoline is a mixture of a number of liquid hydrocarbons. Seawater is an aqueous solution of sodium chloride and other ionic solids. Carbonated water is an aqueous solution of  $\text{CO}_2$ .

All **gaseous mixtures** are **solutions**. The best known example of a gaseous solution is an air, which consists of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and other gases.

In a **solid solution** the **solvent** is a **solid** substance. The ability to form solid solution is particularly common to metals; and

such solid solutions are called **alloys**. For example: an alloy of nickel and copper, an alloy of gold and silver.

### **Dissolving of substances in a solvent. Solubility**

Russian chemists D.I. Mendeleev, on the basis of his experiments, created the chemical theory of solutions.

Dissolving of substances in a solvent is:

1. The destruction of the crystal lattice.
2. The interaction of the solvent with the particles of the solute.
3. The uniform distribution of one substance in the whole volume of another substance.

The heat can be evolved or absorbed during this process.

**Solubility** is the ability of the substance to uniformly distribute in the whole volume of another substance.

There are **soluble** and **insoluble** substances.

Solubility depends on the nature of substances, temperature and pressure. For example, solubility of solid substances increases and of gases decreases with the raising of temperature. Solubility of gases increases with raising of pressure.

There are **saturated** and **unsaturated** solutions.

A solution, in which under the certain temperature the solute cannot be dissolved any more, is called a **saturated** solution.

A solution, in which under the certain temperature more solute can be dissolved, is called an **unsaturated** solution.

**A supersaturated** solution is one which holds in a solution more of the solute, than can dissolve in presence of the solute at that temperature.

### **3.2 Methods of expression of solution concentration**

A solution consist of a mixture of two substances: the solute, the one in a smaller amount, dissolved in the solvent, the component in a larger amount.

**Concentration** is a measure of the amount of the solute, which is dissolved in a given amount of the solvent.

## Mass percent. Percent concentration

The statement “5% aqueous solution of NaCl” has the following meaning: the solution contains 5g of NaCl in 100g of solution.

The solution contains 5g of NaCl and  $100-5=95$ g of H<sub>2</sub>O.

Percent concentration is defined by equation:

$$\text{Mass percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \cdot 100 \%, \quad \%$$

$$\text{Mass of Solution} = \text{Mass of Solute} + \text{Mass of Solvent.}$$

Mass percent (percent concentration, %) shows how many grams of solute are dissolved in 100 g of solution.

## Molar concentration (Molarity)

**Molar concentration (Molarity)** is a concentration of a solution expressed as number of moles of solute per liter of solution.

Molar concentration is defined by equation:

$$\text{Molar concentration } (C_M) = \frac{\text{Number of moles of solute}}{\text{Number of liters of solution}}, \quad \text{mol/L or M,}$$

$$C_M = \frac{\text{No.mol solute}}{\text{No.L sol.}}$$

A solution in which 1 mol of NaCl is dissolved in 1L (1000mL) of solution is described as a 1 molar solution and is designated by the symbol 1M NaCl.

## Molal concentration (Molality)

**Molality (C<sub>m</sub>)** is a concentration of a solution which is expressed as a number of moles of solute per kilogram of solvent.

Molal concentration is defined by equation:

$$\text{Molal concentration } (C_m) = \frac{\text{Number of moles of solute}}{\text{Number of kilograms of solvent}}, \text{ mol/kg or m,}$$

$$C_m = \frac{\text{No. mol solute}}{\text{No. kg solvent}}.$$

A solution, in which 1 mol of NaCl is dissolved in 1000g of water, is described as a 1 molal solution and is designated by the symbol 1m NaCl.

### **Normality (equivalent concentration)**

**Normality (N)** – is defined as the number of equivalents of solute per liter of solution.

N is defined by equation:

$$\text{Normality(N)} = \frac{\text{Number of equivalents of solute}}{\text{Volume of solution}}; \frac{\text{Equiv}}{\text{L}}; \text{mol.eq / L.}$$

This means that 1N solution contains 1 equivalent of solute per liter of solution. Further we will use the term **equivalent concentration**  $C_E$ . These are the same terms, because  $C_E$  is the number of equivalent moles of a substance per one liter of solution.

1N solution contains 1 equivalent (or 1 mol of equivalent) of solute per liter of solution, this means that  $C_E = 1 \text{ mol/L}$ .

$$C_E = \frac{\text{Mass of substance}}{\text{Equivalent mass of substance} \cdot \text{Volume of solution}}$$

$$\text{or } C_E = \frac{\text{Moles of solute equivalent}}{\text{Volume of solution}}.$$

### **Equivalent mass**

**Equivalent mass** of an **element** is the mass of the element which combines with or displaces 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen.

$$\text{Eq. mass of an element} = \frac{\text{Atomic mass of the element}}{\text{Valency of the element}}.$$

$$\text{For example, Eq.mass (O)} = \frac{16}{2} = 8.$$

$$\text{Eq. mass of an acid} = \frac{\text{Mol.mass of the acid}}{\text{Basicity of the acid}}.$$

Basicity is the number of replaceable  $\text{H}^+$  ions in a molecule of an acid.

$$\text{For example, Eq. mass (HNO}_3) = \frac{63}{1} = 63\text{g / mol};$$

$$\text{Eq. mass(H}_2\text{SO}_4) = \frac{98}{2} = 49\text{g / mol}.$$

$$\text{Eq.mass of a base} = \frac{\text{Mol.mass of the base}}{\text{Acidity of the base}}.$$

Acidity is the number of replaceable  $\text{OH}^-$  ions in a molecule of a base.

For example,

$$\text{Eq. mass(NaOH)} = \frac{40}{1} = 40\text{g / mol};$$

$$\text{Eq. mass(Ca(OH)}_2) = \frac{74}{2} = 37\text{g / mol}.$$

$$\text{Eq. mass of a salt} = \frac{\text{Mol. mass of the salt}}{\text{Total valency of the metal atoms}}.$$

$$\text{For example, Eq. mass (AlCl}_3) = \frac{133.5}{3} = 66.7\text{g / mol};$$

$$\text{Eq. mass (Al}_2\text{(SO}_4)_3) = \frac{342}{6} = 57\text{g / mol}.$$

$$\text{Eq. mass of an oxidizing/reducing agent} = \frac{\text{Mol. mass or At. mass}}{\text{No. of electrons, lost or gained by one molecule of the substance}}.$$

### Mole fraction

**Mole fraction** is the ratio of the number of moles of a substance to the total number of moles of all substances in the solution.

If, in a solution  $n_1$  and  $n_2$  are the numbers of moles of solvent and the solute respectively, then

$$\begin{aligned} \text{mole fraction of solute} &= \\ &= \frac{\text{No. of moles of solute } (n_2)}{\text{No. of moles of solute } (n_2) + \text{No. of moles of solvent } (n_1)}; \end{aligned}$$

$$\text{mole fraction of solvent} = \frac{n_1}{n_2 + n_1}.$$

For example, if a solution contains 4 moles of alcohol and 6 moles of water, then

$$\text{mole fraction of alcohol} = \frac{4}{4 + 6} = 0.4$$

$$\text{and mole fraction of water} = \frac{6}{4 + 6} = 0.6.$$

The sum of mole fraction of all constituents of a solution is always equal to 1.0.

### Example of exercise solution

**Example 3.1.** How would you prepare a 0.5 m aqueous solution of  $\text{NH}_4\text{Cl}$ ?

Ans. Weigh out 26.75 g of salt (0.5 mol) and dissolve it in 1 kg (1000 g) of solvent (water).

**Example 3.2.** 50 g of glucose were dissolved in 450 g of water. Calculate the mass percent of glucose.

Ans.: 1) Calculate the mass of solution:

$$\begin{aligned} \text{mass of solution} &= \text{mass of solvent} + \\ &+ \text{mass of solute} = 450 \text{ g} + 50 \text{ g} = 500 \text{ g}. \end{aligned}$$

2) Calculate the mass percent:

$$\text{mass percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \cdot 100 \%;$$

$$\text{mass percent} = \frac{50 \text{ g}}{500 \text{ g}} \cdot 100 \% = 10 \%.$$

**Example 3.3.** How would you prepare 100 g of a 10 % aqueous solution of  $\text{NH}_4\text{Cl}$ .

$$\text{Ans.: } \% = \frac{\text{mass of } \text{NH}_4\text{Cl (solute)}}{\text{mass of } \text{NH}_4\text{Cl (solute)} + \text{mass of } \text{H}_2\text{O (solvent)}} \cdot 100\%,$$

$$10\% = \frac{\text{mass of } \text{NH}_4\text{Cl}}{100 \text{ g}} \cdot 100 \%, \quad \text{Mass of } \text{NH}_4\text{Cl} = \frac{10\% \cdot 100 \text{ g}}{100\%}.$$

The mass of solute = 10 g ; the mass of  $\text{H}_2\text{O}$  = 100 – 10 = 90 g.

**Example 3.4.** How many grams and moles of  $\text{NaCl}$  are contained in 220 g of a 25 %  $\text{NaCl}$  solution?

$$\text{Ans.: } 1) 25 \% = \frac{x}{220} \cdot 100 \%,$$

$$\text{mass of } \text{NaCl} = \frac{25 \cdot 220}{100} = 55 \text{ g } \text{NaCl}.$$

$$\text{number of moles}(\text{NaCl}) = \frac{\text{mass of } (\text{NaCl})}{\text{molar mass of } (\text{NaCl})} =$$

$$2) = \frac{55 \text{ g}}{58,5 \text{ g/mol}} = 0.94 \text{ mol}.$$



**Example 3.5.** Calculate the mass percent of NaOH if 500 ml of solution contain 25 g of NaOH; density of solution is 1.024 g/ml.

**Density** is the amount of mass per unit volume.

Ans.:

$$1) \text{ density} = \frac{\text{mass of solution}}{\text{volume of solution}},$$

$$\text{mass of solution} = \text{density} \cdot \text{volume of solution},$$

$$\text{mass of solution} = 1.024 \cdot 500 \text{ ml} = 512 \text{ g}.$$

2)

$$\text{mass percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \cdot 100 \%,$$

$$\text{mass percent} = \frac{25 \text{ g}}{512 \text{ g}} \cdot 100 \% = 4,88 \%$$

**Example 3.6.** How would you prepare a 0.5 M aqueous solution of  $\text{NH}_4\text{Cl}$ ?

Ans.: 0.5 M solution is a 0.5 molar solution and its molarity is 0.5 mol/L.

$$\begin{aligned} \text{Mass of } 0.5 \text{ mol } \text{NH}_4\text{Cl} &= \text{molar mass } \text{NH}_4\text{Cl} \times 0.5 \text{ mol} = \\ &= 53.5 \text{ g/mol} \times 0.5 \text{ mol} = 26.75 \text{ g}. \end{aligned}$$

Weigh out 26.75 g (0.5 mol) of salt, and dissolve it in a sufficient amount of water so, that the final volume of solution is one litre. The dilution is done in a calibrated volumetric flask to contain 1000 mL.

**Example 3.7.** How many moles of solute are contained in 3.0 L of a 1.8 M solution?

$$\begin{aligned} \text{Ans.:} \quad C_M &= \frac{\text{No. mol solute}}{\text{No. L soln}}, & 1.8 &= \frac{\text{No. mol solute}}{3.0}, \\ \text{No. mol solute} &= 5.4 \text{ mol}. \end{aligned}$$

**Example 3.8.** What volume of a 2.0 M solution will 0.5 mol of solute contain?

Ans.:  $2 = \frac{0.5}{\text{No. L soln}}$ ,      No. L soln = 0.25 L.

**Example 3.9.** What will be the molarity of a NaCl solution in which 175.5 g of NaCl is dissolved in 750 mL of solution?

Ans.: Since molarity is defined as the number of moles per litre of solution, we must first calculate the number of moles in 175 g of NaCl, then convert 750 mL to litres, and finally calculate  $C_M$ :

$C_M$ :

Molar mass of NaCl = 58.5g,

number of moles =  $175:58.5 = 3 \text{ mol NaCl}$ ,

750 mL = 0.75 L,

$$C_M = \frac{3 \text{ mol}}{0.75 \text{ L}} = \frac{4 \text{ mol}}{\text{L}} = 4 \text{ M.}$$

**Example 3.10.** Calculate the molar concentration of a solution where the mass percent of  $\text{HNO}_3$  is 25 % and the density of the solution is 1.151 g/ml.

Ans.: Since the volume was not given, you can start with any volume you wish. The molarity will be the same both for 1 ml and 1000 ml.

1) Calculate the mass of solution:

mass of solution = volume of solution · density of solution;

$$\text{mass of solution} = 100 \text{ ml} \cdot 1.151 \text{ g/ml} = 1151 \text{ g.}$$

2) Calculate the mass of solute  $\text{HNO}_3$ :

$$\text{mass of solute} = \frac{\text{mass percent} \cdot \text{mass of solution}}{100 \%};$$

$$\text{mass of solute (HNO}_3) = \frac{25 \% \cdot 1151 \text{ g}}{100 \%} = 287.5 \text{ g.}$$

3) Calculate the number of moles of  $\text{HNO}_3$  solute:

$$\text{No. of mol solute} = \frac{\text{mass of HNO}_3}{\text{molar mass of HNO}_3};$$

$$\text{molar mass (HNO}_3) = 1 + 14 + 16 + 3 = 63 \text{ g / mol,}$$

$$\text{No. of mol solute} = \frac{287.5 \text{ g}}{63 \text{ g / mol}} = 4.57 \text{ mol.}$$

4) Calculate the molarity ( $C_M$ ):

$$C_M = \frac{4.57 \text{ mol}}{1 \text{ L}} = 4.57 \text{ mol / L.}$$

**Example 3.11.** How would you prepare a 0.5 M aqueous solution of  $\text{NH}_4\text{Cl}$ ?

Ans.: Weigh out 26.75 g of salt (0.5 mol), and dissolve it in 1 kg (1000 g) of solvent (water).

**Example 3.12.** 500 ml of solution contains 9.8 g of  $\text{H}_2\text{SO}_4$ . Calculate the normality (the equivalent molar concentration).

$$\text{Eq. mass of H}_2\text{SO}_4 = \frac{98}{2} = 49 \text{ g / mol,}$$

$$\text{Moles of solute equivalent} = \frac{9.8 \text{ g}}{49 \text{ g / mol}} = 0.2 \text{ mol,}$$

$$\text{Normality} = \frac{\text{Moles of solute equivalent}}{\text{Volume of the solution}} = \frac{0.2 \text{ mol}}{0.5 \text{ L}} = 0.4 \text{ mol / L.}$$

For any neutralization reaction, the following relationship is true:

$$\text{Normality of acid} \cdot \text{Volume of acid} = \text{Normality of base} \cdot \text{Volume of base.}$$

**Example 3.13.** Calculate normality of 21 %  $\text{H}_2\text{SO}_4$  solution with the density of 1.150 g/ml, mass of solution equal 1000 g.

Ans.:

$$\text{Mass of solute} = \frac{\text{mass of solution} \cdot \text{mass percent}}{100\%}$$

$$\text{mass of solute} = \frac{1000 \text{ g} \cdot 21\%}{100\%} = 210 \text{ g.}$$

$$\text{Eq. mass of H}_2\text{SO}_4 = \frac{98}{2} = 49 \text{ g / mol},$$

$$\text{moles of solute equivalent} = \frac{\text{mass of H}_2\text{SO}_4}{\text{Eq. mass of H}_2\text{SO}_4},$$

$$\text{moles of solute equivalent} = \frac{210 \text{ g}}{49 \text{ g / mol}} = 4.29 \text{ mol}.$$

$$\text{Volume of solution} = \frac{\text{mass of solution}}{\text{density of solution}} = \frac{1000 \text{ g}}{1.150 \text{ g / ml}} = 869.6 \text{ ml} = 0.869 \text{ L}.$$

$$\text{Normality (C}_E\text{)} = \frac{\text{moles of solute equivalent}}{\text{volume of solution}} = \frac{4.29 \text{ mol}}{0.869 \text{ L}} = 4.94 \text{ mol / L}.$$

### Questions for classwork

1. What is a solution?
2. What components of the solution are compulsory?
3. What is a solvent and a solute? Is water always a solvent for solutions, containing water?
4. What is a concentrated solution and a dilute solution?
5. Give the examples of liquid, solid and gaseous solutions?
6. What processes proceed in dissolution?
7. What is the solubility?
8. Name factors which influence the solubility of substances.
9. What solutions are named: saturated, unsaturated, supersaturated?
10. Give the definitions of the following terms: mass percent, molarity, molality, normality, and mole fraction.
11. What formulas are used for the calculation of the mass percent, molarity, molality, normality, and mole fraction?

## Exercises for classwork and independent-work

- Calculate the mass percent of the following solutions:
  - 40 g  $\text{CaCl}_2$  in 160 g  $\text{H}_2\text{O}$ ;
  - 15 g of ethyl alcohol in 175 g  $\text{H}_2\text{O}$ ;
  - 60 g  $\text{NaCl}$  in 40 g  $\text{H}_2\text{O}$ ;
  - 54 g of glucose in 96 g  $\text{H}_2\text{O}$ .
- How much of each compound is present in the following solutions:
  - 25 g of a 4.5 % solution of glucose ;
  - 125 g of a 5 % solution of ammonium sulfate ;
  - 63 g of a 1.2 % solution of insulin.
- How much 5 %  $\text{NaCl}$  solution can be prepared from 5 g of  $\text{NaCl}$ ?
- Given are 200 g of 5 % solution of  $\text{NaCl}$ . Add 250 g of 2 % solution of  $\text{NaCl}$ . Calculate mass percent of  $\text{NaCl}$ .
- How would you prepare the following aqueous solutions:
  - 50 g of 10 % ethanol solution;
  - 250 g of 85 % solution.
- How many grams and moles of  $\text{KCl}$  are contained in 25 g of a 3 %  $\text{KCl}$  solution?
- Calculate the number of moles of glucose, contained in 55 g of 12 % aqueous solution.
- Calculate the molarity of the following solutions:
  - 0.25 mol  $\text{H}_2\text{SO}_4$  in 1.2 L ;
  - 0.12 mol  $\text{NaCl}$  in 0.65 L ;
  - 2.3 mol  $\text{NaHCO}_3$  in 1.8 L ;
  - 0.175 mol  $\text{HCl}$  in 0.084 L ;
  - 3.5 g  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1.2 L of solution ;
  - 152 g  $\text{C}_6\text{H}_{12}\text{O}_6$  in 750 ml ;
  - 48 g  $\text{BaCl}_2$  in 3 L of solution .

9. Calculate the number of moles in each of the following solutions:
- 35 ml of 1.5 M  $\text{CaCl}_2$  solution ;
  - 1.2 L of 0.56 M  $\text{KNO}_3$  solution ;
  - 0.435 L of 0.45 M  $\text{LiCl}$  solution ;
  - 74.2 ml of 0.252 M  $\text{NaHCO}_3$  solution .
10. Calculate the grams of solute, which is present in each of the following solutions:
- 2.5 L of 0.5 M  $\text{NaCl}$  ;
  - 425 ml of 0.65 M  $\text{Mg}(\text{NO}_3)_2$  ;
  - 600 ml of 1.6 M  $\text{K}_2\text{CO}_3$  .
11. How would you prepare a 0.5 M aqueous solution of  $\text{NH}_4\text{Cl}$  ?
12. What is the mass of 124 ml of a solution which has a density of 1.13 g/ml?
13. A commercial concentrated sulfuric acid is 94 %  $\text{H}_2\text{SO}_4$  and has density of 1.831 g/ml. What is the molarity of this solution?
14. Calculate the molality of the following solutions:
- 0.5 mol glucose in 0.5 kg  $\text{H}_2\text{O}$  ;
  - 9.4 g  $\text{C}_6\text{H}_5\text{OH}$  in 200 g  $\text{H}_2\text{O}$  ;
  - 11.5 g  $\text{C}_2\text{H}_5\text{OH}$  in 125 g  $\text{H}_2\text{O}$  ;
  - 200 g  $\text{NaCl}$  in 2.0 kg  $\text{H}_2\text{O}$  .
15. How many grams of iodine,  $\text{I}_2$ , must be dissolved in 125 ml of carbon tetrachloride,  $\text{CCl}_4$ , (density 1.595 g/ml) to produce a 0.158 m  $\text{I}_2$  solution?
16. An aqueous solution of hydrofluoric acid 30 % HF by mass, and has a density of 1.101 g/ml. What are the molality and molarity of HF in this solution?

17. A solution contains 1g of naphthaline,  $C_{10}H_8$ , in 44g of benzene,  $C_6H_6$ . What is the mass percent  $C_{10}H_8$  in this solution?
18. Calculate the molarity and normality of a solution containing 9.8g of  $H_2SO_4$  in 250 ml of the solution.
19. Calculate the mole fraction of ethanol and water in a sample of rectified spirit which contains 95% of ethanol by mass.
20. Calculate the molality and mole fraction of the solute in aqueous solution containing 3g of urea (mol.mass=60g/mol) per 250 g of water.
21. A solution contains 22g  $CH_3COOH$  and 118g  $H_2O$ , a density is 1.014g/ml. calculate the mass percent, molarity, molality, normality, mass fraction of  $CH_3COOH$ .

### Questions for self-testing

For each of questions 1 through 20, choose one correct lettered answer.

1. A solution is 15.0 % by mass magnesium nitrate ( $Mg(NO_3)_2$ ). Calculate how many grams of  $Mg(NO_3)_2$  are dissolved in 250 g of solution.  
 a) 37.5                      b) 0.06                      c) 16.7                      d) 15
2. 10 g of magnesium nitrate ( $Mg(NO_3)_2$ ) are dissolved in 200 g of a solution. Calculate mass percent of this solution.  
 a) 10                      b) 5                      c) 20                      d) 15
3. A solution is 10.0 % by mass of sodium hydroxide ( $NaOH$ ). Calculate how many grams of  $NaOH$  are dissolved in 150 g of the solution.  
 a) 10                      b) 20                      c) 15                      d) 30
4. 100 g of hydrochloric acid ( $HCl$ ) are dissolved in 500 g of a solution. Calculate mass percent of this solution.  
 a) 10                      b) 100                      c) 0.2                      d) 20

5. A solution is 20.0 % by mass nitric acid ( $\text{HNO}_3$ ). Calculate how many grams of  $\text{HNO}_3$  are dissolved in 250 g of the solution.  
a) 50                      b) 20                      c) 25                      d) 10
6. 10 g of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) are dissolved in 50 g of a solution. Calculate mass percent of this solution.  
a) 10                      b) 20                      c) 60                      d) 0.5
7. A solution is 38.0 % by mass of hydrochloric acid ( $\text{HCl}$ ). Calculate how many grams of  $\text{HCl}$  are dissolved in 200 g of the solution.  
a) 38                      b) 19                      c) 76                      d) 7.6
8. 5 g of sodium chloride ( $\text{NaCl}$ ) are dissolved in 100 g of a solution. Calculate mass percent of this solution.  
a) 10                      b) 0.5                      c) 15                      d) 5
9. A solution is 25.0 % by mass of calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ). Calculate how many grams of  $\text{Ca}(\text{NO}_3)_2$  are dissolved in 200g of the solution.  
a) 50                      b) 25                      c) 8                      d) 0.125
10. 15 g of potassium hydroxide ( $\text{KOH}$ ) are dissolved in 150 g of a solution. Calculate mass percent of this solution.  
a) 10                      b) 20                      c) 0.15                      d) 15
11. How many moles of the solute are present in 5 liters of a 0,5 M solution?  
a) 2.5                      b) 0.5                      c) 5                      d) 1
12. How many moles of the solute are present in 3 liters of a 0,3 M solution?  
a) 1                      b) 0.9                      c) 0.3                      d) 3
13. 98 g of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) are dissolved in 1 litre of a solution. Calculate molarity of this solution (molar mass of  $\text{H}_2\text{SO}_4$  is 98 g/mol)  
a) 2                      b) 0.5                      c) 1                      d) 98
14. 40 g of sodium hydroxide ( $\text{NaOH}$ ) are dissolved in 2 liters of a solution. Calculate molarity of this solution (molar mass of  $\text{NaOH}$  is 40 g/mol)



- a) 1                      b) 40                      c) 2                      d) 0.5
15. 36.5 g of hydrochloric acid (HCl) are dissolved in 1 litre of a solution. Calculate molarity of this solution (molar mass of HCl is 36.5 g/mol)
- a) 1                      b) 2                      c) 0.5                      d) 36.5
16. The molarity of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution is 1 M. Calculate mass of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in 1 litre of the solution (molar mass of H<sub>2</sub>SO<sub>4</sub> is 98 g/mol)
- a) 49                      b) 98                      c) 1                      d) 2
17. The molarity of sodium hydroxide (NaOH) solution is 2 M. Calculate the mass of sodium hydroxide (NaOH) in 2 litres of the solution (molar mass of NaOH is 40 g/mol)
- a) 40                      b) 20                      c) 80                      d) 10
18. The molarity of nitric acid (HNO<sub>3</sub>) solution is 1 M. Calculate the mass of nitric acid (HNO<sub>3</sub>) in 0.5 litre of the solution (molar mass of HNO<sub>3</sub> is 63 g/mol)
- a) 63                      b) 126                      c) 6.3                      d) 31.5
19. The molarity of potassium hydroxide (KOH) solution is 1 M. Calculate the mass of potassium hydroxide (KOH) in 1 litre of the solution (molar mass of KOH is 56 g/mol)
- a) 56                      b) 112                      c) 28                      d) 14
20. 98 g of sulfuric acid H<sub>2</sub>SO<sub>4</sub> are diluted to a volume of 2 litres. Determine the molar concentration of the acid in the solution (molar mass of H<sub>2</sub>SO<sub>4</sub> is 98 g/mol)
- a) 1                      b) 2                      c) 4                      d) 0.5

## LABORATORY WORK

**Materials and equipment:** the potassium dichromate, water, balance, measuring cylinder, beaker, aerometer.

### The process

How would you prepare 50 g of ...% solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>?

1. Calculate the mass of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, contained in the solution.
2. Calculate the volume of water ( $\rho_{\text{H}_2\text{O}} = 1 \text{ g/ml}$ ).

### 3. Put the data into the table

Mass of solution, g	Mass percent, %	Mass of solute m ( $K_2Cr_2O_7$ ), g	Mass and volume of water m ( $H_2O$ ), V ( $H_2O$ )	Density, g/ml	Molar concentration $C_M$ , Mol/L	Molal concentration $C_m$ , Mol/kg	Normality $C_N$ , Mol/L
50g							

4. Weigh out a beaker.
5. Weigh out  $K_2Cr_2O_7$  into the beaker.
6. Take distilled water in the graduated cylinder and pour it into the beaker with  $K_2Cr_2O_7$ . Dissolve the salt in water in the breaker.
7. Pour the solution from the beaker into the cylinder.
8. Measure the density of the solution by aerometer.
9. Calculate the molarity, molality and normality of this solution.

### 3.3 Aqueous Solutions of Acids, Bases and Salts. Dissociation of Water. The pH Scale. Hydrolysis

#### Objectives

1. Define acids and bases.
2. The theory of electrolytic dissociation.
  - a) the degree of dissociation;
  - b) the dissociation (ionization) constant.
3. Weak and strong electrolytes.
4. The W. Ostwald's dilution law.
5. The ion product of water. The pH scale.
6. Hydrolysis.

#### Practical skills

After studying the subject you should be able:

1. To write the equation for the dissociation of the acids, bases

and salts.

2. To write the dissociation constant for the dissociation of weak acids and bases.
3. To make the pH calculation in the solution of acids, bases and salts.
4. To determine the concentration of hydrogen ions according to the pH value.
5. To use the knowledge of this subject for the estimation of medium acidity of biological solution (blood, gastric juice, urine, ect.).
6. To write the hydrolysis reactions for salts.

### Theoretical materials

The first theory of acids and bases was proposed by Svante Arrhenius. His idea is that **acids** are substance which produce hydrogen ions,  $H^+$ , in aqueous solutions. **Bases** are substances which produce hydroxide ions,  $OH^-$ , when dissolved in water.



A Bronsted-Lowry acid is a hydrogen ion donor (proton donor). A Bronsted-Lowry base is a hydrogen ion acceptor (proton acceptor). According to the theory of electrolytic dissociation (S. Arrhenius, 1887), when electrolytes dissolve in water, they decompose (dissociate) into positively charged ions (cations) and negatively charged ions (anions).

For example,  $AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$ .

Compounds whose aqueous solutions do not conduct electricity are called **nonelectrolytes**.

Aqueous or molten substances, that will conduct an electric current and are decomposed into ions are called **electrolytes**. They include salts, acids and bases.

S. Arrhenius introduced the concept of the degree of

dissociation.

**The degree of dissociation ( $\alpha$ )** of an electrolyte is the ratio of the number of its molecules that have broken up into ions in the given solution to the total number of its molecules in the solution.

The degree of dissociation is designated by the Greek letter  $\alpha$  and is customarily expressed either in unit fractions or as a percentage.

Electrolytes are divided into two groups: strong and weak ones. In a strong electrolyte solution  $\alpha = 1$ . For a weak electrolyte, for example, 0.1 N solution of  $\text{CH}_3\text{COOH}$ ,  $\alpha = 0.013$  (or 1.3 %).

Salts are strong electrolytes. Salts always completely dissociated in water. For example,  $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$ ,  $\text{Al}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{Al}^{3+} + 3\text{SO}_4^{2-}$ .

Acids and bases that completely dissociate in water are called strong acids or bases (**strong electrolytes**).

For example,  $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$ . HCl is the strong acid, which completely dissociate in aqueous solution to form  $\text{H}^+$  and  $\text{Cl}^-$ .

There are only a few strong acids and bases. They are listed in the table.

#### Names and Formulas of all strong Acids and Bases

$\text{HClO}_4$ – Perchloric acid	$\text{LiOH}$ – Lithium hydroxide
$\text{HNO}_3$ – Nitric acid	$\text{NaOH}$ – Sodium hydroxide
$\text{H}_2\text{SO}_4^*$ – Sulfuric acid	$\text{KOH}$ – Potassium hydroxide
$\text{HCl}$ – Hydrochloric acid	$\text{RbOH}$ – Rubidium hydroxide
$\text{HBr}$ – Hydrobromic acid	$\text{CsOH}$ – Cesium hydroxide
$\text{HI}$ – Hydroiodic acid	$\text{Ca}(\text{OH})_2$ – Calcium hydroxide
	$\text{Sr}(\text{OH})_2$ – Strontium hydroxide
	$\text{Ba}(\text{OH})_2$ – Barium hydroxide

\*Note: Only the first proton in sulfuric acid is completely dissociable. The first product of the dissociation,  $\text{HSO}_4^-$ , is a weak acid.

All inorganic acids that are not listed above are weak acids. All organic acids (RCOOH) are weak acids.

Acids and bases that partially dissociate in water are called weak acids or bases (**weak electrolytes**).

For example,  $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ .  $\text{NH}_4\text{OH}$  is a weak base. When dissolved in water it produces  $\text{OH}^-$  ions, but the  $\text{OH}^-$  concentration is considerably lower than the  $\text{NH}_4\text{OH}$  concentration.

For the weak acids and bases dissociation is the reversible process and can be characterized by the **equilibrium constant**.

The equilibrium constant corresponding to the dissociation of a weak electrolyte is known as **the dissociation (or ionization) constant**.

In case of the weak acid, for example, acetic acid,  $\text{CH}_3\text{COOH}$ , the equilibrium constant is called the **acid dissociation constant  $K_a$** , and for the dissociation reaction  $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$  the equilibrium constant expression

$$\text{is } K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}.$$

The dissociation process for the weak base  $\text{NH}_4\text{OH}$  is written as  $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$  and the equilibrium constant expression is

$$K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]}.$$
 The term  **$K_b$**  is called the **base dissociation constant**.

The values of  $K_a$ 's and  $K_b$ 's indicate the extents of dissociation of weak acids and bases. The larger the constants, the stronger the acids or bases.

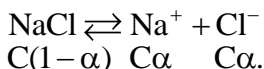
The dissociation constants must be determined experimentally.

$$\text{CH}_3\text{COOH } K_a = 1.8 \cdot 10^{-5}, \quad K_{\text{CH}_3\text{COOH}} \text{ is higher than } K_{\text{HCN}},$$

$\text{HCN}$  hydrocyanic  $K_a = 4 \cdot 10^{-10}$ , ( $\text{HCN}$  is a weaker acid than  $\text{CH}_3\text{COOH}$ ),  $\text{CH}_3\text{COOH}$  is stronger than  $\text{HCN}$ .

The value of  $K_a$  depends on the nature of the electrolyte and the solvent as well as on the temperature, but does not depend on the concentration of the solution.

If we denote the concentration of the electrolyte (NaCl), dissociating into two ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ) by  $C$ , and the degree of its dissociation in given solution by  $\alpha$ , then the concentration of each of the ions will be  $C\alpha$ , and the concentration of the undissociated molecules will be  $C(1-\alpha)$ :



The equation of the dissociation constant has the form

$$K = \frac{(C\alpha) \times (C\alpha)}{C(1-\alpha)} = \frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}.$$

This equation expresses W. Ostwald's **dilution law**.

For solutions, in which the dissociation of an electrolyte is very small, the equation of Ostwald's law is simplified. Since in these cases  $\alpha \ll 1$ , it has the form:

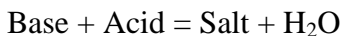
$$K \approx \alpha^2 C \quad \text{or} \quad \alpha \approx \sqrt{\frac{K}{C}}.$$

This equation clearly shows the relationship existing between the concentration of a weak electrolyte and the degree of its dissociation: the dissociation degree increases upon the dilution of a solution. The values of the dissociation constant for electrolytes are given in Table 3.1.

Table 3.1 – Dissociation constant for selected electrolytes in aqueous solutions at 25 °C

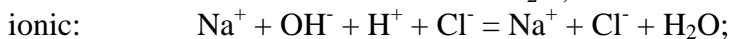
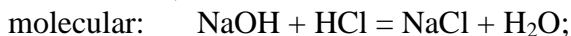
Electrolyte	Dissociation of a compound	Dissociation constant (K)
Acetic acid	$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$	$1.8 \cdot 10^{-5}$
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH} \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^- + \text{H}^+$	$6.4 \cdot 10^{-5}$
Carbonic acid	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ , $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	$K_1 = 4.5 \cdot 10^{-7}$ $K_2 = 4.7 \cdot 10^{-11}$
Hydrocyanic acid	$\text{HCN} \rightleftharpoons \text{CN}^- + \text{H}^+$	$6.2 \cdot 10^{-10}$
Lactic acid	$\text{CH}_3\text{CH}(\text{OH})\text{COOH} \rightleftharpoons$ $\rightleftharpoons \text{CH}_3\text{CH}(\text{OH})\text{COO}^- + \text{H}^+$	$1.38 \cdot 10^{-4}$
Citric acid	$\text{HOOCCH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{COOH}$	$7.5 \cdot 10^{-5}$
Nitrous acid	$\text{HNO}_2 \rightleftharpoons \text{NO}_2^- + \text{H}^+$	$4 \cdot 10^{-4}$
H <sub>2</sub> O (water)	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$1.8 \cdot 10^{-16}$
NH <sub>4</sub> OH	$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$1.74 \cdot 10^{-5}$
Hydrochloric acid	$\text{HCl} \rightleftharpoons \text{Cl}^- + \text{H}^+$	$10^7$
Nitric acid	$\text{HNO}_3 \rightleftharpoons \text{NO}_3^- + \text{H}^+$	43.6
Sulfuric acid	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$ , $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$K_1 = 1000$ $K_2 = 10^{-2}$
Permanaganic acid	$\text{HMnO}_4 \rightleftharpoons \text{MnO}_4^- + \text{H}^+$	200

The reaction of acids and bases is called a **neutralization reaction**.



Bases react with acids to form salts and water.

Equations for acids-base neutralization reactions can be written in molecular, ionic and net ionic forms:

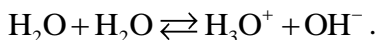


A neutralization reaction simply involves the combination of hydrogen and hydroxide ions to form water.

### 3.4 Dissociation of water. The pH scale

Water is a very poor electrical conductor; yet the fact that it does conduct electric current feebly indicates that some ions are present.

The equation of dissociation of  $\text{H}_2\text{O}$  is  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ ; in water solution  $\text{H}^+$  exists as hydronium ion  $\text{H}_3\text{O}^+$ .



In this process,  $\text{H}_2\text{O}$  molecule transfers a proton to another  $\text{H}_2\text{O}$  molecule.

The equilibrium constant expression for this process is

$$K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-] \text{ or } K_w = [\text{H}^+] \times [\text{OH}^-].$$

This equilibrium constant also has a special name: the **ion-product of water**,  $K_w$ .

In pure water at  $25^\circ\text{C}$ :  $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$ ,

$$K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-7} \times 10^{-7} = 1.0 \times 10^{-14}.$$

The ion-product of water has value of  $1.0 \times 10^{-14}$  at  $25^\circ\text{C}$ .

Acid solutions have higher concentration of hydronium ions than  $1.0 \times 10^{-7}$  mol/L; basic solutions have lower concentration than  $1.0 \times 10^{-7}$  mol/L.

These concentrations are extremely small numbers. It is often inconvenient to work with them. In 1909 the chemist Sorensen proposed the pH scale. If a solution has  $[\text{H}^+] = 10^{-x}$ ,  $\text{pH} = x$ .



According to this scale, a concentration of  $1 \times 10^{-7}$  mol of  $H^+$  per litre of the solution is expressed a pH of 7. The table 3.2 shows the relationship between the pH and the concentration of  $H^+$ .

**The pH is the negative of the logarithm of**

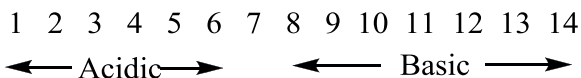


$$pH = -\log[H^+]$$

Concentration of $H^+$ (moles per liter)	pH
$1 \times 10^0$	0
$1 \times 10^{-1}$	1
$1 \times 10^{-2}$	2
$1 \times 10^{-3}$	3
$1 \times 10^{-4}$	4
$1 \times 10^{-5}$	5
$1 \times 10^{-6}$	6
$1 \times 10^{-7}$	7
$1 \times 10^{-8}$	8
$1 \times 10^{-9}$	9
$1 \times 10^{-10}$	10
$1 \times 10^{-11}$	11
$1 \times 10^{-12}$	12
$1 \times 10^{-13}$	13
$1 \times 10^{-14}$	14

Solution	pH
Gastric juices	1.6 – 1.8
Lemon juice	2.3
Vinegar	2.4 – 3.4
Soft drinks	2.0 – 4.0
Milk	6.3 – 6.6
Urine	5.5 – 7.0
Saliva	6.2 – 7.4
Pure water	7
Blood	7.35 – 7.45
Fresh egg	7.6 – 8.0
Bile	7.8 – 8.6

neutral



A pH of 7 is neutral. A pH less than 7 is acidic. A pH greater than 7 is basic.

The pOH is defined in a similar way to pH:

$$\mathbf{pOH = -\log[H^-]} \text{ or } [\text{OH}^-] = 10^{-\text{pOH}} .$$

We can write the equilibrium constant for water in a new way:

$$-\log K_w = -\log[H^+] - \log[OH^-] = -\log[1 \times 10^{-14}] ,$$

$$\mathbf{pK_w = pH + pOH = 14,}$$

$$\mathbf{pH + pOH = 14 .}$$

A pH value – is the measure of the active acidity of the medium.

During the medico-biological researches total and active acidities must be well differentiated, as the nondissociated molecules of acids and hydrogen ions possess different physiological activity. For example, gastric juice contains many acids of different strength, but its acidity is defined only by hydrogen ions. Therefore, the results of the pH measurements and the titration of gastric juice will be quite different.

The total acidity can be defined by titration. The active acidity is equal to the total acidity for strong electrolytes, because strong acid completely (100%) dissociated in solution to form  $H^+$ .

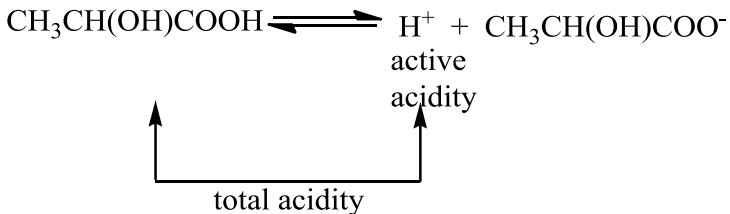
For example,  $HCl \rightleftharpoons H^+ + Cl^-$ .

The concentration of  $H^+$  is equal to the concentration of HCl.

$$\mathbf{pH = -\log[H^+] = -\log C,} \text{ where } C \text{ is the molarity.}$$

For the strong base solution:  $\mathbf{pOH = -\log[OH^-] = -\log C.}$

Weak electrolyte partially dissociates in water. For example, acetic acid is a weak acid. When dissolved in water it produces  $H^+$  ions, but the  $H^+$  concentration is considerably lower than the common concentration of an acid:



To calculate a pH of weak acid solution it is necessary to know besides the concentrations either the degree of the dissociation ( $\alpha$ ), or the dissociation constant ( $K_a$ ):

$$\text{pH} = -\log C \cdot \alpha, \text{ or}$$

$$\text{or : pH} = -\log \sqrt{K_a \times C}.$$

For the weak base solution:

$$\text{pOH} = -\log C \times \alpha, \text{ or}$$

$$\text{pH} = -\log \sqrt{K_b \times C},$$

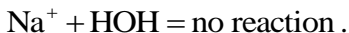
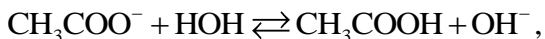
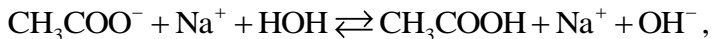
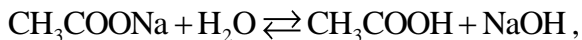
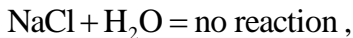
where  $\alpha$  is the degree of dissociation (ionization) of the base;

$K_b$  is the base dissociation (ionization) constant;

$C$  is the molarity.

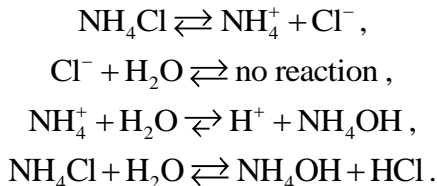
### 3.5 Hydrolysis

In pure water  $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$ . When NaCl is added to water, the solution remains neutral. When  $\text{CH}_3\text{COONa}$  is added to pure water, the solution becomes basic. When  $\text{NH}_4\text{Cl}$  is added to pure water, the solution becomes acidic:



Water reacts with  $\text{CH}_3\text{COO}^-$  to produce  $\text{OH}^-$ . A solution of  $\text{CH}_3\text{COONa}$  has a  $\text{pH}>7$ .

A solution of  $\text{NH}_4\text{Cl}$  has a  $\text{pH}<7$ . The  $\text{NH}_4^+$  ion hydrolyzes to produce  $\text{H}^+$ :



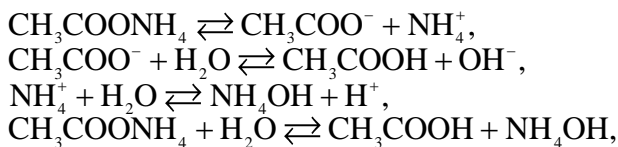
This reaction, in which water reacts with ionic species in solution, is called **hydrolysis**.

Salts of strong acids and strong bases (for example,  $\text{NaCl}$ ) do not hydrolyze:  $\text{pH}=7$ .

Salts of weak acids and strong bases (for example,  $\text{CH}_3\text{COONa}$ ) hydrolyze, producing a basic solution:  $\text{pH}>7$ .

Salts of strong acids and weak bases (for example,  $\text{NH}_4\text{Cl}$ ) hydrolyze, producing an acidic solution:  $\text{pH}<7$ .

Salts of weak acids and weak bases (for example,  $\text{CH}_3\text{COONH}_4$ ) will hydrolyze, but the acidity or basicity depends on the equilibrium constants of  $K_a$  and  $K_b$ . If the  $K_a$  value is greater than the  $K_b$  value, the resulting solution will be acidic and vice versa.



$$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5} ,$$

$$K_b(\text{NH}_4\text{OH}) = 1.74 \times 10^{-5} ,$$

$$K_a \approx K_b, \text{ neutral } \text{pH}=7 .$$

### Examples of exercise solution.

**Example 3.14.** What is the pH of a solution that has a  $H^+$  concentration of  $1 \times 10^{-5} M$ ?

Ans.:  $[H^+] = 10^{-5}$ ,  $pH = -\log[10^{-5}] = -(-5) = 5$ .

**Example 3.15.** What is the concentration of  $H^+$  ions in a solution that has a pH of 4?

Ans.: The pH value is the negative exponent of 10, so  $[H^+] = 1 \cdot 10^{-4}$ ,  $[H^+] = 10^{-4} M$ .

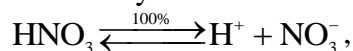
**Example 3.16.** Calculate the concentration of  $H^+$  ions of Coca-Cola if its pH is 2.5.

Ans.:

$$\begin{aligned} pH &= -\log[H^+], & 2.5 &= -\log[H^+], \\ [H^+] &= 10^{-2.5}, & [H^+] &= 3.16 \times 10^{-3} M. \end{aligned}$$

**Example 3.17.** Calculate  $[H^+]$  and  $[NO_3^-]$  of a 0.175 M solution of nitric acid  $HNO_3$ .

Ans.:  $HNO_3$  is a strong acid and, therefore, it dissociates in aqueous solution by 100%:



Therefore,  $[HNO_3] = [H^+] = [NO_3^-] = 0.175 M$ .

**Example 3.18.** Calculate  $[OH^-]$  and  $[Ca^{2+}]$  of a 0.01 M solution of  $Ca(OH)_2$ .

Ans.:  $Ca(OH)_2$  is a strong base and therefore, it dissociates in aqueous solution by 100%. Since, there are 2 mols of hydroxide ion per mol of  $Ca(OH)_2$ ,

$$\begin{aligned} [\text{OH}^-] &= 2 \times [\text{Ca}(\text{OH})_2] = 2 \times 0.01 = 0.02 \text{ M and } [\text{Ca}^{2+}] = \\ &= [\text{Ca}(\text{OH})_2] = 0.01 \text{ M.} \end{aligned}$$

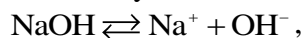
**Example 3.19.** What is the pH of 0.001 M solution of HCl?

Ans.: HCl is a strong acid, therefore,

$$\text{pH} = -\log[\text{H}^+] = -\log C = \log[1 \cdot 10^{-3}] = 3.$$

**Example 3.20.** Calculate a pH of a solution, if 500 ml of solution contain 2 g of NaOH.

Ans.: NaOH is strong electrolyte and it dissociates in aqueous solution by 100 %.



therefore  $[\text{NaOH}] = [\text{Na}^+] = [\text{OH}^-] = C_M$  (molarity),

$$\text{molarity } C_M = \frac{\text{mass of NaOH}}{\text{Molar mass of NaOH} \cdot \text{Volume}},$$

molar mass (NaOH) = 23 + 16 + 1 = 40 g/mol,

$$C_M = \frac{2 \text{ g}}{40 \text{ g/mol} \cdot 0.5 \text{ L}} = 0.1 \text{ mol/L},$$

$$[\text{OH}^-] = C_M = 0.1 \text{ mol/L},$$

$$\text{pOH} = -\lg[\text{OH}^-] = -\lg 0.1 = 1, \text{ pH} = 14 - \text{pOH} = 14 - 1 = 13.$$

**Example 3.21.** What is the pH of 0.1 M solution of  $\text{CH}_3\text{COOH}$ ?  $K_a$   $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ .

Ans.:  $\text{CH}_3\text{COOH}$  is a weak electrolyte, therefore,

$$\text{pH} = -\log \sqrt{K_a \times C},$$

$$\text{pH} = -\log \sqrt{1.8 \times 10^{-5} \times 0.1} = -\log \sqrt{1.8 \times 10^{-6}} = -\log(1.34 \times 10^{-3}),$$

$$\text{pH} = 3 - \log 1.34 = 2.88.$$

### Questions for classwork

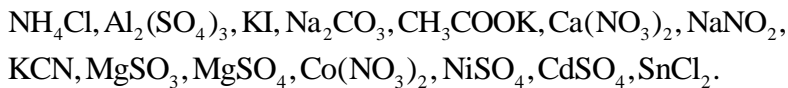
1. What is an acid? Give the examples.
2. What is a base? Give the examples.
3. What is an electrolyte?

4. What is called “the strong acid or base”? Give the examples.
5. What is called “the weak acid or base”? Give the examples.
6. What is the neutralization reaction?
7. Give the definition of the degree of the dissociation and dissociation constant.
8. Write the equation that expresses W. Ostwald’s dilution law.
9. What is pH? Write formula for pH calculation in acidic and basic solutions.
10. What is the hydrolysis?

### Exercises for class work and independent work

1. Write the equations for the dissociation of the following substances:  
 $\text{HCl}, \text{KOH}, \text{HNO}_3, \text{H}_2\text{SO}_4, \text{Fe}(\text{OH})_2, \text{H}_3\text{PO}_4, \text{Ba}(\text{OH})_2, \text{K}_3\text{PO}_4,$   
 $\text{Ca}(\text{NO}_3)_2, \text{KCN}, \text{CH}_3\text{COONa}, \text{MgSO}_3, \text{H}_2\text{S}.$
2. Write the dissociation constant of the following substances:  
 $\text{HCN}, \text{Fe}(\text{OH})_2, \text{H}_3\text{PO}_4, \text{CH}_3\text{COOH}, \text{H}_2\text{S}.$
3. Write the molecular, ionic and net ionic equations of the following reactions:  
 $\text{Ba}(\text{OH})_2 + \text{HNO}_3 =$   
 $\text{Ca}(\text{OH})_2 + \text{HCl} =$
4. Calculate  $[\text{H}^+]$  and  $[\text{Br}^-]$  of a 0.05 M solution of HBr acid.
5. Calculate the pH values of the following solutions:
  - a) 0.001 M HCl;
  - b) 0.05 M NaOH;
  - c) 0.05 M  $\text{Ba}(\text{OH})_2$ ;
  - d) 0.002 M  $\text{H}_2\text{SO}_4$ ;
  - e) 0.5 M HCN,  $K_a = 4 \times 10^{-4}$ ;
  - f) 0.01 M HF,  $K_a = 6.7 \times 10^{-4}$ .
6. Calculate the concentration of hydrogen ions in the blood if  $\text{pH} = 7.35$ .
7. Calculate the  $[\text{OH}^-]$  in the solution of KOH if  $\text{pH} = 12.0$ .

8. Write the hydrolysis reactions for salts which undergo hydrolysis in the ionic and molecular forms:



Predict whether aqueous solutions of these salts are acidic, neutral, or basic.

### Questions for self-testing

For each of 10 questions choose the one correct the one lettered answer.

- Calculate  $[\text{H}^+]$  in 0.01 M  $\text{HNO}_3$ .  
a) 0.01            b) 0.1            c) 0.02            d) 0.005
- Calculate  $[\text{H}^+]$  in 0.01 M  $\text{H}_2\text{SO}_4$ .  
a) 0.01            b) 0.02            c) 0.005            d) 0.03
- Calculate  $[\text{OH}^-]$  in 0.1 M  $\text{NaOH}$ .  
a) 0.2            b) 0.3            c) 0.1            d) 0.05
- Calculate  $[\text{OH}^-]$  in 0.1 M  $\text{Ca}(\text{OH})_2$ .  
a) 0.1            b) 0.2            c) 0.3            d) 0.4
- What is the  $\text{H}^+$  concentration of a solution that has a pH of 3?  
a) 3            b) 11            c)  $10^{-11}$             d)  $10^{-3}$
- What is the  $\text{H}^+$  concentration of a solution that has a pH of ?  
a)  $10^{-9}$             b)  $10^{-5}$             c) 9            d) 5
- What is the  $\text{H}^+$  concentration of a solution that has a pH of 4?  
a) 4            b)  $10^{-4}$             c)  $10^{-10}$             d) 10
- Calculate the pOH of a 0.01 M solution of  $\text{KOH}$ .  
a) 12            b) 14            c) 2            d)  $10^{-2}$
- Calculate the pH of a 0.01 M solution of  $\text{HCl}$ .  
a) 12            b) 14            c) 2            d)  $10^{-2}$
- Calculate pH of a solution that contains 0.00001 M  $\text{HNO}_3$ .  
a) 9            b)  $10^{-9}$             c)  $10^{-4}$             d) 5



## 3.5 Buffer Solution

### Objectives

1. Buffer solution, types of buffer.
2. Mechanism of action of buffer.
3. pH calculation of buffer solutions. Henderson – Hasselbalch equation.
4. Buffer systems of the organism.

### Practical skills

After studying the subject you should be able to:

1. To characterize the mechanism of buffer action.
2. To calculate the pH value of buffer solution.
3. To determine the change in pH of buffer solution after addition of strong acids or base.
4. To calculate the buffer capacity.

### Theoretical material

Adding acid or base to a solution the value of its pH usually changes greatly. If 0.01 mol of NaOH dissolves in 1 L of distilled water, the pH changes from 7 to 12.

**Buffer solution** is a solution that tends to resist changes in pH when a small amount of acid or base is added to it.

Buffer solution resists the attempts to change the pH by the addition of acid or base. If 0.01 mol of NaOH is added to 1 L of solution containing 0.1 mol of  $\text{CH}_3\text{COOH}$  and 0.1 mol of  $\text{CH}_3\text{COONa}$ , the pH changes from 4.76 to 4.84.

There are two types of buffers:

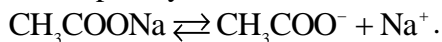
**Acidic buffer** is prepared by mixing a weak acid and a salt of conjugate base, e.g. ethanoic acid and sodium ethanoate. The solution is acidic and is used to resist pH changes in an acidic medium.

**Basic buffer** is prepared by mixing a weak base and a salt of a conjugate acid, e.g. aqueous ammonia and ammonium chloride. The solution is basic and is used to resist pH changes in a basic medium.

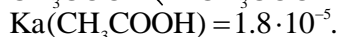
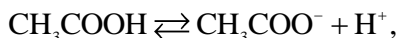
Buffer solution maintain optimum pH values for the biochemical processes taking place in living systems. The enzymes (biological catalysts) that enable biochemical reactions can function only within a narrow range of pH. Human blood pH is stable in the range of 7.35–7.45, saliva pH – in the range of 6.35–6.85, gastric juice pH – in the range of 1.5–3.0, urine pH – in the range of 4.8–7.5. The pH out of this range is fatal to human life.

How does a buffer act? How does it resist changes in pH when an acid or base is added to it?

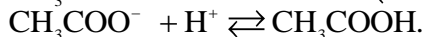
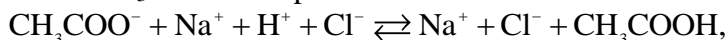
Take a buffer solution with equal concentration of ethanoic acid and sodium ethanoate (acidic buffer) as an example. Sodium ethanoate completely dissociates in water:



On the other hand, ethanoic acid is only slightly dissociate.



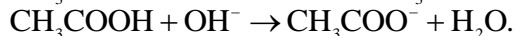
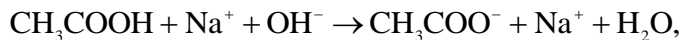
If an acid, (e. g. HCl) is added to the system,  $\text{H}^+$  ions will react with the  $\text{CH}_3\text{COONa}$  to produce weak acid.



From Buffer ADDED.

A strong acid is substituted by a weak acid, and the pH changes very little.

If a base (NaOH) is added to the buffer,  $\text{OH}^-$  ions will react with  $\text{CH}_3\text{COOH}$  to produce a salt and  $\text{H}_2\text{O}$ :



From Buffer ADDED.

A strong base is substituted by a salt, and the pH changes very little.

pH of a buffer solution can be estimated according to the Henderson-Hasselbalch equation.

$$\text{For acidic buffer: } \text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} \text{ or}$$

$$\text{pH} = \text{pK}_a + \log \frac{\text{molarity of a salt solution} \times \text{volume of salt solution}}{\text{molarity of an acid solution} \times \text{volume of acid solution}},$$

where  $\text{pK}_a$  –  $(-\log)$  of acid dissociation constant ( $\text{K}_a$ ).

$$\text{For basic buffer: } \text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]} \text{ or}$$

$$\text{pOH} = \text{pK}_b + \log \frac{\text{molarity of salt solution} \times \text{volume of salt solution}}{\text{molarity of base solution} \times \text{volume of base solution}},$$

where  $\text{pK}_b$  –  $(-\log)$  of base dissociation constant ( $\text{K}_b$ ).

$$\text{pH} = 14 - \text{pOH} \text{ or}$$

$$\text{pH} = 14 - \text{pK}_b - \log \frac{[\text{salt}]}{[\text{base}]}.$$

Buffer solutions are vitally important to living organisms. Buffer systems of the organism:

1. Bicarbonate buffer ( $\text{H}_2\text{CO}_3$  - the acid,  $\text{NaHCO}_3$  - the salt).
2. Phosphate buffer ( $\text{NaH}_2\text{PO}_4$  - the acid,  $\text{Na}_2\text{HPO}_4$  - the salt).
3. Amino acid and protein buffer.
4. Hemoglobin buffer ( $\text{HHb} + \text{KHb}$ ).
5. Oxyhemoglobin buffer ( $\text{HHbO}_2 + \text{KHbO}_2$ ).

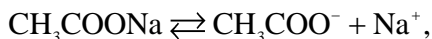
The major buffers of blood are bicarbonate and hemoglobin.

### Examples of exercise solutions

**Example 3.22.** A buffer is prepared by adding 4.1 g of sodium ethanoate to  $1 \text{ dm}^3$  of 0.01 M ethanoic acid. What is the pH of the buffer?

( $\text{K}_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$ ; molar mass of sodium ethanoate =  $82 \text{ g mol}^{-1}$ ).

$$\text{Ans.: } \text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]},$$



$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}.$$

$$\text{Number of moles of } \text{CH}_3\text{COONa} = \frac{4.1}{82} = 0.05 \text{ mol},$$

$$[\text{CH}_3\text{COO}^-] = [\text{salt}] = \frac{0.05}{1} = 0.05 \text{ mol},$$

$$[\text{CH}_3\text{COOH}] = [\text{acid}] = 0.01 \text{ M},$$

$$\text{pH} = -\log(1.74 \times 10^{-5}) + \log \frac{0.05}{0.01} = 4.76 + 0.70 = 5.46$$

### Example 3.23

1. Calculate the change in pH when 1 cm<sup>3</sup> of 0.25 M NaOH is added to

- 25 cm<sup>3</sup> of pure water;
- 25 cm<sup>3</sup> of 0.1 M CH<sub>3</sub>COOH;
- 25 cm<sup>3</sup> of 0.1 M CH<sub>3</sub>COOH containing 0.002 moles CH<sub>3</sub>COO<sup>-</sup>Na<sup>+</sup>.

$$(\text{K}_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5} \text{ mol dm}^{-3})$$

2. Comment on the obtained results.

Ans.:

a) pH of pure water = 7

$$\begin{array}{ccccccc} \text{Number} & & \text{of} & & \text{moles} & & \text{of} & & \text{NaOH} \\ = & = & 0.25 \times & \frac{1}{1000} & = & 2.5 \times 10^{-4} & \text{mol} \cdot \end{array}$$

$$\begin{array}{ccccccc} \text{Concentration} & & \text{of} & & \text{NaOH} & & \text{after} & & \text{dilution} \\ = & = & 2.5 \times 10^{-4} \div & \frac{1+25}{1000} & = & 9.62 \times 10^{-3} & \text{M} \end{array}$$

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

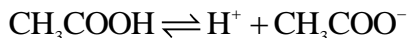
$$1 \times 10^{-14} = [\text{H}^+] \times 9.62 \times 10^{-3},$$

$$[\text{H}^+] = 1.04 \times 10^{-12} \text{ M},$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.04 \times 10^{-12}) = 11.98.$$

The change in pH is  $11.98 - 7 = 4.98$

b) **Part 1.** Calculation of pH of the  $25 \text{ cm}^3$  of  $0.1 \text{ M CH}_3\text{COOH}$ :



Number of moles at equilibrium:  $(0.1-x)$  mole  $\times$  mole  $\times$  mole (in  $1 \text{ dm}^3$ ),

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]},$$

$$1.74 \times 10^{-5} = \frac{x \times x}{0.1 - x},$$

$$x^2 = 1.74 \times 10^{-5} (0.1 - x),$$

$$x^2 + 1.74 \times 10^{-5} - 1.74 \times 10^{-6} = 0,$$

$$x = 1.31 \times 10^{-3} \text{ or } -1.33 \times 10^{-3} \text{ (rejected),}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.31 \times 10^{-3}) = 2.88.$$

**Part 2.** Calculation of pH when  $1 \text{ cm}^3$  of  $0.25 \text{ M NaOH}$  is added.

Number of moles of  $\text{OH}^-$  in  $1 \text{ cm}^3$  of  $0.25 \text{ M NaOH}$   
 $= 0.25 \times 1 \times 10^{-3} = 2.5 \times 10^{-4} \text{ mol}.$

Number of moles of  $\text{CH}_3\text{COOH}$  originally present  
 $= 0.1 \times 25 \times 10^{-3} = 2.5 \times 10^{-3} \text{ mol}.$

As the number of moles of  $\text{OH}^-$  added will react with the same number of moles of  $\text{CH}_3\text{COOH}$ , the number of moles of  $\text{CH}_3\text{COOH}$  left  
 $= 2.5 \times 10^{-3} - 2.5 \times 10^{-4} = 2.25 \times 10^{-3} \text{ mol},$  the number of moles of sodium ethanoate formed  
 $= 2.5 \times 10^{-4} \text{ mol}:$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]},$$

$$[\text{salt}] = [\text{CH}_3\text{COO}^-] = \frac{2.5 \times 10^{-4}}{(25+1) \times 10^{-4}} = 9.62 \times 10^{-3} \text{ M},$$

$$[\text{acid}] = [\text{CH}_3\text{COOH}] = \frac{2.25 \times 10^{-3}}{(25+1) \times 10^{-3}} = 0.0865 \text{ M},$$

$$\text{pH} = -\log(1.74 \times 10^{-5}) + \log \frac{9.62 \times 10^{-3}}{0.0865} = 4.76 - 0.95 = 3.81.$$

The change in  $\text{pH} = 3.81 - 2.88 = 0.93$ .

c) **Part 1.** Calculation of pH of  $25 \text{ cm}^3$  of  $0.1 \text{ M CH}_3\text{COOH}$  containing  $0.002$  moles  $\text{CH}_3\text{COO}^- \text{Na}^+$ :

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]},$$

the number of moles of salt  $= 2 \times 10^{-3} \text{ mol}$ ,

the number of moles of acid  $= 2.5 \times 10^{-3} \text{ mol}$ ,

$$[\text{CH}_3\text{COO}^-] = \frac{2 \times 10^{-3}}{25 \times 10^{-3}} = 0.08 \text{ M},$$

$$\text{pH} = -\log(1.74 \times 10^{-5}) + \log \frac{0.08}{0.1} = 4.76 - 0.10 = 4.66.$$

**Part 2.** Calculation of pH when  $1 \text{ cm}^3$  of  $0.25 \text{ M NaOH}$  is added to the buffer.

Ans.:

Number of moles of  $\text{OH}^-$  in  $1 \text{ cm}^3$  of  $0.25 \text{ M NaOH} = 0.25 \times 1 \times 10^{-3} = 2.5 \times 10^{-4} \text{ mol}$

As the number of moles of  $\text{OH}^-$  added will react with  $\text{CH}_3\text{COOH}$  present in the buffer system,

$$\begin{aligned} \text{the number of moles of salt present} &= 2 \times 10^{-3} + 2.5 \times 10^{-4} = \\ &= 2.25 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{the number of moles of acid present} &= 2.5 \times 10^{-3} - 2.5 \times 10^{-4} = \\ &= 2.25 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]},$$

$$[\text{salt}] = [\text{CH}_3\text{COO}^-] = \frac{2.25 \times 10^{-3}}{(25+1) \times 10^{-3}} = 0.0865 \text{ M},$$

$$[\text{acid}] = [\text{CH}_3\text{COOH}] = \frac{2.25 \times 10^{-3}}{(25+1) \times 10^{-3}} = 0.0865 \text{ M},$$

$$\text{pH} = -\log(1.74 \times 10^{-5}) + \log \frac{0.0865}{0.0865} = 4.76 + 0 = 4.76.$$

The change in pH = 4.76 - 4.66 = 0.10.

2. A drastic pH change (4.98 units) is shown when 1 cm<sup>3</sup> of 0.25 M NaOH is added to 25 cm<sup>3</sup> of water as there is no buffering effect. There is also a significant change in pH (0.92 unit) for the ethanoic acid solution which is not a good buffer without the presence of sodium ethanoate. However, the change is insignificant (0.10 unit) when the same amount of NaOH is added to the solution with buffering effect. It could be seen that a buffer solution can resist the change in pH when a small amount of acid (or base) is added to it.

**Example 3.24.** To prepare a basic buffer with pH of 9.0, how many grams of ammonium chloride would you add to 100 cm<sup>3</sup> of 0.1 M NH<sub>3</sub> × H<sub>2</sub>O ?

(K<sub>b</sub>(NH<sub>3</sub>) = 1.74 × 10<sup>-5</sup> mol dm<sup>-3</sup>; molar mass of NH<sub>4</sub>Cl = 53.5 gmol<sup>-1</sup>)

Ans.:

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}.$$

Let x M be the concentration of ammonium chloride in the buffer system. Then:

$$14 - 9 = -\log(1.74 \times 10^{-5}) + \log \frac{x}{0.1},$$

$$5 = 4.76 + \log \frac{x}{0.1},$$

$$x = 0.174.$$

The number of moles of NH<sub>4</sub>Cl used = 0.174 ×  $\frac{100}{1000}$  = 0.0174 moles.

The mass of NH<sub>4</sub>Cl used = 0.0174 × 53.5 = 0.93g.

**Example 3.25.** The dissociation constant of  $\text{H}_2\text{PO}_4^-$  in water,  $K_a$ , is  $6.2 \times 10^{-8} \text{ mol} \times \text{dm}^{-3}$  at 298 K, where

$$K_a = \frac{[\text{HPO}_4^-][\text{H}^+]}{[\text{H}_2\text{PO}_4^-]}.$$

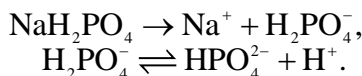
Calculate the pH at 298 K:

- of an aqueous solution of 0.10 M  $\text{NaH}_2\text{PO}_4$ ;
- of an aqueous solution of 0.05 M  $\text{NaH}_2\text{PO}_4$  and 0.05 M  $\text{Na}_2\text{HPO}_4$ .

(It may be assumed that the concentrations of  $\text{H}_3\text{PO}_4$  and  $\text{PO}_4^{3-}$  are negligible in these solutions.)

Ans.:

a)



The number of moles at equilibrium:

(0.1-x) mole    x mole    x mole (in 1  $\text{dm}^3$ ).

$$6.2 \times 10^{-8} = \frac{x^2}{0.1-x},$$

$$x^2 = 6.2 \times 10^{-8} (0.1-x),$$

$$x^2 + 6.2 \times 10^{-8} x - 6.2 \times 10^{-9} = 0,$$

$$x = 7.87 \times 10^{-5} \text{ or } -7.88 \times 10^{-5} \text{ (rejected),}$$

$$\text{pH} = -\log(7.87 \times 10^{-5}) = 4.10.$$

$$\text{b) } [\text{H}^+] = \frac{K_a \times [\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]}.$$

Taking negative logarithm on both sides,

$$-\log[\text{H}^+] = -\log K_a - \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]},$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = -\log(6.2 \times 10^{-8}) + \log \frac{0.05}{0.05} = 7.21.$$



There is a limit to how much a buffer system can resist change. Ability of a buffer solution to keep the assigned pH rate is quantitatively characterized by the buffer capacity.

**Buffer capacity** is a number of moles of a strong acid or a strong base that is needed to be added to 1 L of buffer solution in order to change its pH for 1 unit. The formula for calculating is:

$$\text{Buffer capacity for an acid} = \frac{\text{normality of the adding acid} \times \text{volume of the adding acid}}{\text{volume of buffer} \times \text{changing of pH}},$$

$$\text{Buffer capacity for a base} = \frac{\text{normality of the adding base} \times \text{volume of the adding base}}{\text{volume of buffer} \times \text{changing of pH}}.$$

The higher is the initial concentration of the components of the buffer system, the higher is its buffer capacity.

**Example 2.26.** 14 ml of sodium hydroxide solution molarity 0,1 mol/L were added to 100 ml of blood resulting in the pH change from 7.36 to 9.36. Calculate the buffer capacity off blood.

Ans.

$$\text{Buffer capacity for a base} = \frac{\text{normality of the adding base} \times \text{volume of the adding base}}{\text{volume of buffer} \times \text{changing of pH}}.$$

$$\text{Changing of pH} = 9.36 - 7.36 = 2$$

$$\text{Buffer capacity for a base} = \frac{0.1 \text{ mol/L} \times 14 \cdot 10^{-3} \text{ L}}{100 \cdot 10^{-3} \text{ L} \times 2} = \frac{14 \cdot 10^{-4}}{2 \cdot 10^{-1}} = 7 \cdot 10^{-3} \text{ mol/L}$$

### Questions for classwork

1. What are buffer solutions?
2. How does a buffer act? How does a buffer regulate pH? When an acid or base is added to buffer solution?
3. What is the Henderson-Hasselbalch equation for the calculation of pH of buffer solutions?

4. What is buffer capacity?
5. Name the most important buffer system of the organism.

### Exercises for classwork and independent work

1. To change the pH value from 7.36 to 7.00 it is necessary to add 35 ml of HCl with normality 0.05 mol/L to 100 ml of blood. Calculate the buffer capacity of blood.
2. Calculate the volumes of 0.2 mol/L  $\text{CH}_3\text{COOH}$  and 0.2 mol/L  $\text{CH}_3\text{COONa}$  which ought to be mixed in order to obtain 400 ml of buffer solution where  $\text{pH} = 5.24$  if  $K_a(\text{CH}_3\text{COOH}) = 1.8 \cdot 10^{-5}$ .
3. Calculate the volumes of 0.02 mol/L  $\text{NaH}_2\text{PO}_4$  and 0.02 mol/L  $\text{Na}_2\text{HPO}_4$  which ought to be mixed in order to obtain 200 ml of buffer solution where  $\text{pH} = 6.8$  if  $\text{p}K(\text{H}_2\text{PO}_4^-) = 6.8$ .
4. Calculate the pH value of a buffer mixture prepared of 150 ml of  $\text{CH}_3\text{COOH}$  solution with concentration 0.1 mol/L and 250 ml of 0.2 mol/L  $\text{CH}_3\text{COONa}$  solution if  $\text{p}K(\text{CH}_3\text{COOH}) = 4.75$ .
5. Calculate the pH of a buffer solution prepared by mixing  $30 \text{ cm}^3$  of 0.1 M ethanoic acid and  $20 \text{ cm}^3$  of 0.08 M sodium ethanoate. ( $K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5} \text{ moldm}^{-3}$ ).
6. Calculate the pH value of a buffer solution obtained by mixing 300 ml of 0.1 mol/L  $\text{NH}_4\text{Cl}$  solution with 150 ml of 0.2 mol/L  $\text{NH}_3 \times \text{H}_2\text{O}$  solution.  $K(\text{NH}_3 \times \text{H}_2\text{O}) = 1.8 \cdot 10^{-5}$ .
7. What will be the change of the pH value of buffer which consists of 100 ml of 0.3 mol/L  $\text{CH}_3\text{COOH}$  solution and 100 ml of 0.2 mol/L  $\text{CH}_3\text{COONa}$  solution at the addition of 200 ml of 0.05 mol/L HCl solution if  $K(\text{CH}_3\text{COOH}) = 1.8 \cdot 10^{-5}$ ?
8. Choose the buffer systems:
  - a) HCl;  $\text{NH}_4\text{Cl}$ ;
  - b)  $\text{H}_2\text{CO}_3$ ;  $\text{KHCO}_3$ ;

- c)  $\text{H}_2\text{CO}_3$ ;  $(\text{NH}_4)_2\text{CO}_3$ ;  
d)  $\text{NH}_4\text{OH}$ ;  $\text{NH}_4\text{Cl}$ .
9. A buffer solution is made by adding 75.0 g of sodium ethanoate to 500.0 cm<sup>3</sup> of 0.64 M solution of ethanoic acid. Assuming there is no volume change during dissolution, calculate the pH of the final solution? ( $K_b(\text{NH}_3) = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$ ).
10. A buffer solution is made by adding 50.0 g of ammonium chloride to 1.00 litre of 0.75 M solution of  $\text{NH}_3$ . Assuming there is no volume change during dissolution, calculate the pH of the final solution. ( $K_b(\text{NH}_3) = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$ ).
11. Calculate the change in pH after 0.01 mole of gaseous HCl being added to 250.0 cm<sup>3</sup> of a solution containing 0.05 M and 0.15 M  $\text{NH}_4\text{Cl}$ . ( $K_b(\text{NH}_3) = 1.7 \cdot 10^{-5} \text{ mol dm}^{-3}$ ).
12. Calculate the change in pH after 2 cm<sup>3</sup> of 0.02 M NaOH is added to 200.0 cm<sup>3</sup> of a solution containing 0.10 M  $\text{CH}_3\text{COOH}$  and 0.08 M  $\text{CH}_3\text{COONa}$ . ( $K_a(\text{CH}_3\text{COOH}) = 1.7 \cdot 10^{-5} \text{ mol dm}^{-3}$ ).

### 3.6 Colligative Properties of Solutions

**Colligative properties** are the properties of solutions that depend only on the number of particles of a solute in a definite amount of the solvent and do not depend on the nature of the solute.

#### Objectives

1. Relative lowering of the saturated vapour pressure of a solvent above a solution (the first Raoult's law).
2. Elevation in boiling point of the solution as compared with that of the pure solvent (the second Raoult's law).

3. Depression in freezing point of the solution as compared with that of the pure solvent (the second Raoult's law).
4. Osmotic pressure.

### Practical skills

1. To calculate relative lowering of vapour pressure.
2. To calculate elevation in boiling point and depression in freezing point of the solution.
3. To calculate osmotic pressure.
4. To predict processes that take place in a cell when placing it in the hypotonic, isotonic or hypertonic solution.

### Theoretical material

#### Vapour pressure of solutions. Raoult's law

At a certain temperature, the pressure of the saturated vapour above any liquid is constant. The saturated vapour pressure of the solvent above the solution is always lower than that above the pure solvent at the same temperature. The difference between these values is called **the vapour pressure lowering over the solution**.

**The Raoult's law:** The relative depression of the saturated vapour pressure of the solvent above the solution equals the mole fraction of the solute.

The mathematical expression of the first Raoult's law is:

$$\frac{P_o - P_s}{P^o} = \frac{n_2}{n_1 + n_2},$$

Where  $P^o$  – vapour pressure of the solvent;

$P_s$  – vapour pressure of the solution;

$n_2$  – number of moles of the solute;

$n_1$  – number of moles of the solvent;

$\frac{n_2}{n_1 + n_2}$  – mole fraction.

## Freezing and boiling of solutions

Individual substances are characterized by strictly definite temperatures of their transitions from one state to another (the boiling point and the melting or freezing point). For example, water at a standard atmospheric pressure (101.3 kPa, 1 tm, 760 mm of Hg) freezes at a temperature of 0 °C and boils at 100 °C. The presence of a solute raises the boiling point and lowers the freezing point of the solvent.

The difference between the boiling point of a solution and that one of the pure solvent is called the elevation in boiling point of the solution ( $\Delta T_b$ ):

$$\Delta T_b = T_{b \text{ solution}} - T_{b \text{ solvent}}$$

The extent of the boiling point elevation is given by the equation

$$\Delta T_b = E \times C_m,$$

where  $\Delta T_b$  – the temperature value of the boiling point rise in degrees Kelvin;

E – the ebullioscopic constant characteristic of the solvent, (for water  $E = 0.52 \text{ kg}\cdot\text{K}/\text{mol}$ ;

for benzene  $E = 2.57 \text{ kg}\cdot\text{K}/\text{mol}$ );

$C_m$  – the molar concentration (the molality), mol/kg.

The difference between the freezing point of the pure solvent and that one of the solution is called the **of the freezing point depression of the solution** ( $\Delta T_f$ ):

$$\Delta T_f = T_{f \text{ solvent}} - T_{f \text{ solution}}$$

The extent of freezing point depression is given by the equation.

$$\Delta T_f = K \times C_m,$$

where  $\Delta T_f$  – the freezing point depression of the solution (K);

$K$  – the cryoscopic constant characteristic of the solvent, (for water  $K = 1.86 \text{ kg}\cdot\text{K}/\text{mol}$ ; for benzene  $K = 5.12 \text{ kg}\cdot\text{K}/\text{mol}$ );

$C_m$  – the molar concentration (the molality), mol/kg.

**The second Raoult's law** For dilute solutions of non-electrolytes, the elevation of the boiling point and the depression of the freezing point are proportional to the molar concentration of the solution.

### Osmosis and osmotic pressure

When two solutions of different concentrations are separated by a **semipermeable membrane** (a membrane which allows the solvent molecules to pass through, but not the solute particles), it is found that the solvent flows through the membrane from the dilute solution to the more concentrated solution until two concentrations become equal. This process known as *osmosis* is shown in Figure 3.

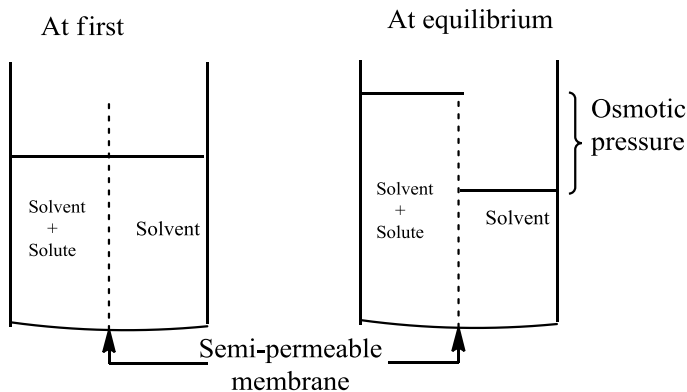


Figure 3

**Osmotic pressure ( $\pi$ )** is the pressure that must be applied to a solution when separated from a more dilute solution by semipermeable membrane, in order to prevent the inflow of a solvent.

In 1886, J. H. Van't Hoff showed that for solutions of nonelectrolytes with moderate concentrations the dependence of the osmotic pressure on the concentration and temperature of the solution is expressed by the equation:

$$\pi = C_M RT,$$

where  $\pi$  – the osmotic pressure, Pa;

$C_M$  – the molar concentration (molarity), mol/L;

R – the molar gas constant,  $8.314 \times 10^3 \text{ L} \cdot \text{Pa} / \text{mol} \times \text{K}$   
( $8.314 \text{ J} / \text{mol} \cdot \text{K}$ );

T – the temperature, K.

The phenomenon of osmosis plays a very important role in the life of animal and vegetable organisms. The cell envelopes may be defined as the cell membranes that are permeable for water, but almost impermeable for the substances which dissolve in the liquid inside the cells.

The osmotic pressure of a human blood is 700–800 kPa. Solutions that have the identical osmotic pressure (and equal molar concentrations, of course) are called isotonic solutions. 0,9 % solution of NaCl and 5 % solution of glucose are isotonic regarding blood. Solutions with a high osmotic pressure are **hypertonic**, and those having a low osmotic pressure are called **hypotonic**.

If placing a living cell to the isotonic solutions it will not change, as the osmotic pressure inside and outside of it will be the same. **Plasmolysis** will occur if we place a cell to the hypertonic solution as water molecules will pass from the cell to the more concentrated solution and the cell becomes smaller (shrinks). In hypotonic solution **hemolysis** of the cells takes place, since water molecules pass from the external solution to the cell as a result of osmosis. The cells grow, swell, and can be destroyed.

Electrolytes have a more pronounced effect on colligative properties than nonelectrolytes do. This is because electrolyte's molecules decompose into ions so that the total number of particles in solution grows. And since the colligative properties depend on the

number of solute particles per unit volume of the solution, when this number increases, they also grow. For example, Sodium chloride passes into a solution in the form of the ions  $\text{Na}^+$  and  $\text{Cl}^-$ . From one mole of  $\text{NaCl}$ , we get twice number of  $6.02 \times 10^{23}$  particles. Hence, the depression freezing point or any other colligative property of a  $\text{NaCl}$  solution must be double, as compared to a solution of a nonelectrolyte having the same concentration.  $\Delta T_b$ ,  $\Delta T_f$ ,  $P$  for electrolyte solutions are so many times as much as the number of particles in the electrolyte solution. To calculate the above-mentioned values in the electrolyte solution the **isotonic coefficient (i)** is used. **i** is equal to the quantity of ions, which the substance dissociated to. For example, **i** for  $\text{NaCl}$  is 2, for  $\text{BaCl}_2$  is 3, for  $\text{AlCl}_3$  is 4, for  $\text{C}_6\text{H}_{12}\text{O}_6$  is 1, as glucose is non-electrolyte.

So, for the electrolyte solutions:

$$\begin{aligned}\Delta T_b &= i \times E \times C_m, \\ \Delta T_f &= i \times K \times C_m, \\ P &= i \times C_m \times R \times T, \\ i &= \alpha(n-1) + 1, \\ n &= \text{numbers of ions.}\end{aligned}$$

### Examples of exercises solution

**Example 3.27.** An aqueous solution of sucrose is made by dissolving 13.66 g of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) in 90 g of water at  $65^\circ\text{C}$ . If the vapour pressure of pure water at  $65^\circ\text{C}$  is 25.0 kPa, what would be the vapour pressure of the solution? (Molar mass of  $\text{C}_{12}\text{H}_{22}\text{O}_{11} = 342\text{g/mol}$ ).

$$\text{Ans.: } \frac{P_o - P_s}{P_o} = \frac{n_2}{n_1 + n_2},$$

$$P_o = 25 \text{ kPa,}$$



$$n_1 = \frac{\text{mass of H}_2\text{O}}{\text{molar mass of H}_2\text{O}} = \frac{90 \text{ g}}{18 \text{ g/mol}} = 5 \text{ mol},$$

$$n_2 = \frac{\text{mass of C}_{12}\text{H}_{22}\text{O}_{11}}{\text{molar mass of C}_{12}\text{H}_{22}\text{O}_{11}} = \frac{13.66 \text{ g}}{342 \text{ g/mol}} = 0.0399 \text{ mol},$$

$$\frac{25 - P_s}{25} = \frac{0.0399}{5 + 0.0399}, \quad \frac{25 - P_s}{25} = 0.0079,$$

$$25 - P_s = 0.0079 \times 25,$$

$$P_s = 25 - 0.1975 = 24.8 \text{ kPa}.$$

Ans.: The vapour pressure of the solution is 24.8 kPa.

### Example 3.28

54 g of glucose were dissolved in 0.9 L of H<sub>2</sub>O. Calculate the boiling point and the freezing point, if M(glucose) = 180 g/mol.

Ans.:  $\Delta T_b = E \times C_m$ ,  $\Delta T_f = K \times C_m$ ,

$$E(\text{H}_2\text{O}) = 0.52^\circ\text{C} \times \text{kg/mol}, \quad K(\text{H}_2\text{O}) = 1.86^\circ\text{C} \times \text{kg/mol},$$

$$m(\text{H}_2\text{O}) = V(\text{H}_2\text{O}) = 0.9 \text{ kg},$$

$$C_m = \frac{v}{m(\text{solvent})} = \frac{m(\text{glucose})}{M \times m(\text{solvent})} = \frac{54 \text{ g/mol}}{180 \text{ g/mol} \times 0.9 \text{ kg}} = 0.33 \text{ mol/kg},$$

$$\Delta T_b = 0.52 \times 0.33 = 0.17^\circ\text{C},$$

$$\Delta T_f = K \cdot C_m = 1.86 \times 0.33 = 0.62^\circ\text{C},$$

$$T_b(\text{H}_2\text{O}) = 100^\circ\text{C} = 373 \text{ K},$$

$$T_f(\text{H}_2\text{O}) = 0^\circ\text{C} = 273 \text{ K},$$

$$\Delta T_b = T_{b \text{ solution}} - T_{b \text{ solvent}},$$

$$0.17 = T_{b \text{ solution}} - 373,$$

$$T_{b \text{ solution}} = 373 + 0.17 = 373.17 \text{ K} = 100.17^\circ\text{C},$$

$$\Delta T_f = T_{f \text{ solution}} - T_{f \text{ solvent}},$$

$$0.62 = 273 - T_{f \text{ solution}},$$

$$T_{f \text{ solution}} = 273 - 0.62 = 272.38 \text{ K} = -0.62^\circ\text{C}.$$

**Example 3.29**

Calculate the osmotic pressure of 0.01 M solution of cane-sugar at 27 °C.

$$\text{Ans.: } C_M = 0.01 \text{ mol/L, } T = 273 + 27 = 300 \text{ K,}$$

$$R = 8.314 \text{ kPa,}$$

$$\Pi = C_M RT = 0.01 \times 8,314 \times 300 =$$

**Example 3.30**

18 g of a glucose were dissolved in 500 ml of water at 27 °C. Calculate the osmotic pressure.  $M(\text{C}_6\text{H}_{12}\text{O}_6) = 180 \text{ g/mol}$ .

Ans.:

$$\pi = C_M RT,$$

$$C_M = \frac{v}{V} = \frac{m}{M \cdot V},$$

$$C_M = \frac{18 \text{ g}}{180 \text{ g/mol} \times 0.5 \text{ L}} = 0.2 \text{ mol/L,}$$

$$\pi = 0.2 \times 8.314 \times (27 + 273) =$$

**Example 3.31**

A solution containing 63.3 g/L of hemoglobin has an osmotic pressure of 243.4 kPa at 20 °C. Calculate the molar mass of hemoglobin.

Ans.:

$$\pi = C_M RT \Rightarrow C_M = \frac{\pi}{RT},$$

$$C_M = \frac{243.4}{8.31 \times 293} = 0.1 \text{ mol/L,}$$

$$C_M = \frac{v}{V} = \frac{m}{M \cdot V},$$

$$M = \frac{m \cdot V}{C_M} = \frac{63.3 \cdot 1}{0.1} = 633 \text{ g.}$$

Molar mass of hemoglobin = 633 g.

### Example 3.32

100 g of  $\text{H}_2\text{O}$  contains 4.57 g of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . Density of solution = 1 g/ml. Calculate:

- the osmotic pressure at 293 K;
- the boiling point, if  $E_{\text{H}_2\text{O}} = 0.52$ ,  $T_b(\text{H}_2\text{O}) = 100^\circ\text{C}$ ;
- the freezing point, if  $K_{\text{H}_2\text{O}} = 1.86$ ,  $T_f(\text{H}_2\text{O}) = 0^\circ\text{C}$ ;
- the vapour pressure of the solution at 293 K, if the vapour pressure of pure water at 293 K is 2.337 kPa.

Ans.:

a)

$$\pi = C_M RT; \quad C_M = \frac{v}{V} = \frac{m(\text{C}_{12}\text{H}_{22}\text{O}_{11})}{M(\text{C}_{12}\text{H}_{22}\text{O}_{11}) \times V}; \quad M(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 342 \text{ g/mol.}$$

$$V_{\text{solution}} = \frac{m}{\rho}, \quad m_{\text{solution}} = m(\text{H}_2\text{O}) + m(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 100 + 4.57 = 104.57 \text{ g};$$

$$V_{\text{solution}} = \frac{104.57 \text{ g}}{1 \text{ g/ml}} = 104.57 \text{ ml} = 0.105 \text{ L.}$$

$$\pi = \frac{m(\text{C}_{12}\text{H}_{22}\text{O}_{11})RT}{M(\text{C}_{12}\text{H}_{22}\text{O}_{11})V},$$

$$\pi = \frac{4.57 \times 8.31 \times 293}{342 \times 0.105} = 309.8 \text{ kPa.}$$

b)

$$\Delta T_b = E \times C_m;$$

$$C_m = \frac{v}{m(\text{solvent})} = \frac{m(\text{C}_{12}\text{H}_{22}\text{O}_{11})}{M(\text{C}_{12}\text{H}_{22}\text{O}_{11}) \times m(\text{solvent})},$$

$$C_m = \frac{4.57 \text{ g}}{342 \text{ g/mol} \times 0.1 \text{ kg}} = 0.134 \text{ mol};$$

$$\Delta T_b = 0.52 \times 0.134 = 0.069 = 0.07^\circ\text{C},$$

$$T_b = 100 + 0.07 = 100.07^\circ\text{C}.$$

c)

$$\Delta T_f = K \times C_m,$$

$$\Delta T_f = 1.86 \times 0.134 = 0.25 \text{ } ^\circ\text{C},$$

$$T_f = 0 \text{ } ^\circ\text{C} - 0.25 - 0.25 \text{ } ^\circ\text{C}.$$

d)

$$\frac{P_o - P_s}{P_o} = \frac{n_2}{n_1 + n_2};$$

$$n_1(\text{H}_2\text{O}) = \frac{100 \text{ g}}{18 \text{ g/mol}} = 5.556 \text{ mol};$$

$$n_2(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = \frac{m}{M} = \frac{4.57 \text{ g}}{342 \text{ g/mol}} = 0.013 \text{ mol},$$

$$\frac{2.337 - P_s}{2.337} = \frac{0.013}{0.013 + 5.556},$$

$$\frac{2.337 - P_s}{2.337} = 0.002,$$

$$2.337 - P_s = 0.005,$$

$$P_s = 2.337 - 0.005 = 2.33 \text{ kPa}.$$

### Question for classwork

1. What determines the colligative properties? Name them.
2. Give the definition of the osmotic pressure.
3. What is Raoult's law? Give its mathematical expression.

### Exercises for classwork and independent work

1. What is the boiling point of 10 %  $\text{C}_6\text{H}_{12}\text{O}_6$  solution.  
 $K_b(\text{H}_2\text{O}) = 0.52 \text{ } ^\circ\text{C kg/mol}.$
2. What is the freezing point of an aqueous solution containing 20 g in 400 g of water .

3. What mass of  $\text{CH}_3\text{OH}$  must be added to 5.00 kg of water to lower the freezing point to  $-3$ .  $\text{CH}_3\text{OH}$  is a nonelectrolyte;  $K_b(\text{H}_2\text{O}) = 1.86 \text{ }^\circ\text{C} \cdot \text{kg/mol}$ .
4. Depression in freezing point of nonelectrolyte solution containing 29.5 g of substance in 100 g of water is 1.6 K. Calculate the molar mass of the substance.
5. Calculate the molar mass of hemoglobin, if the osmotic pressure of hemoglobin in water containing 124 g/L of a substance equals 4.4 kPa at  $17 \text{ }^\circ\text{C}$ .
6. What is the osmotic pressure of a 0.9 % solution of NaCl at  $25 \text{ }^\circ\text{C}$ .
7. Calculate the osmotic pressure at  $0 \text{ }^\circ\text{C}$  of an aqueous solution containing 18.4 g of  $\text{C}_3\text{H}_8\text{O}_3$  in 1 L of water.
8. Calculate the osmotic pressure at 25 of an aqueous solution containing 18 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 500 ml of water.
9. What is the expected vapor pressure at  $25 \text{ }^\circ\text{C}$  for a solution prepared by dissolving 158 g of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) in 1800 g of water? At  $25 \text{ }^\circ\text{C}$  vapor pressure of pure water is 3168 Pa.
10. What is the boiling point of an aqueous solution containing 468 g of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) in 350 g of water? ( $K_b(\text{H}_2\text{O}) = 0.52 \text{ }^\circ\text{C kg/mol}$ , normal boiling of water =  $100 \text{ }^\circ\text{C}$ ).

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