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CHAPTER 1

COORDINATION COMPOUNDS

- 1.1 Structure of the Coordination Compounds. The A. Werner's Coordination Theory.
- 1.2 Classification of Coordination Compounds.
- 1.3 Nomenclature of Coordination Compounds.
- 1.4 Coordinate bonds. Geometry (shape) of the Complex Ion. Isomers.
- 1.5 Coordination Compounds in Medicine.

1.1 Structure of the Coordination Compounds. The A. Werner's Coordination Theory

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

The theory of 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.

Round 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**.

The number of ligands, which coordinate around the central atom (ion), is called the **coordination number**.

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

The ions not entering the inner sphere form the **outer sphere** are shown in figure 1.1.

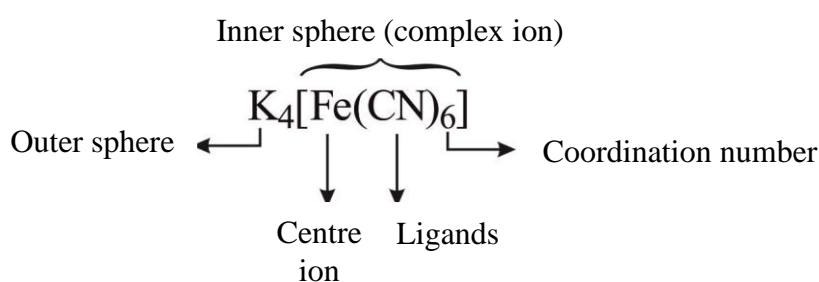


Figure 1.1 – Structure of the Coordination Compounds

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

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

Central atom (ion). The most inclination for complexing is shown by d-elements (transition elements) ions (Pt, Pd, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg). Most of the transition element complexes have coordination number of 2, 4 or 6.

Table 1.1 – Relationship between oxidation state of the central ions and their coordination number

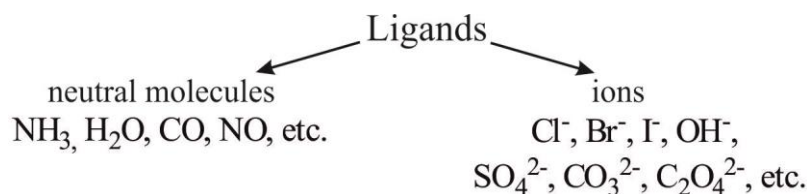
Oxidation state of the central ion	Coordination number (CN)	Example	
		ions	complex compound
+1	2, 3	Cu ⁺ , Ag ⁺ , Au ⁺	[Ag(NH ₃) ₂]Cl
+2	3, 4, 6	Cu ²⁺ , Co ²⁺ , Ni ²⁺ , Pd ²⁺ , Pt ²⁺ , Fe ²⁺	[Cu(NH ₃) ₄]Cl ₂ , K ₄ [Fe(CN) ₆]
+3	4, 5, 6	Fe ³⁺ , Cr ³⁺ , Co ³⁺	K ₃ [Co(NO ₂) ₆]
+4	6, 8	Sn ⁴⁺ , Pt ⁴⁺	K ₂ [PtCl ₆], H ₂ [SnCl ₆]

The least inclination for complexing is shown by alkaline and alkaline-earth metals.

The central atom (ion) can be presented by the nonmetals, for example, boron (K[B₄F₄]), silicon (K₂[SiF₆]), phosphorus (K[PF₆]).

The oxidation state of the central atom (ion) may be positive K₃[Fe⁺³(CN)₆], K⁺³[B₄F₄], negative [NH₄]⁻³Cl, zero [Cl₂(H₂O)₄], [Ni(CO)₄]. Oxidation state of the central atom is the main factor affecting the coordination number (table 1.1).

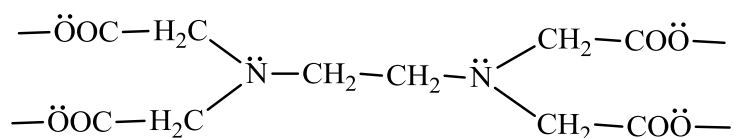
Ligands. The ligands are divided into neutral molecules and ions.



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 NH₃ 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, NH₃, H₂O, Cl⁻, CN⁻, OH⁻, etc.
2. **Bidentate** ligands are ligands that donate two electron pairs. For example, SO₄²⁻, CO₃²⁻, C₂O₄²⁻, H₂N-CH₂-CH₂-NH₂ (ethylenediamine and abbreviated to en).
3. **Polydentate** (or multidentate) ligands donate more than two electron pairs. For example, ethylenediaminetetraacetate EDTA (hexadentate ligands).



The porphyrin ligands in the haem group in hemoglobin are also polydentate.

The polydentate ligands generally form very stable complex and are called 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, Fe^{2+} , is surrounded by six cyanides 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 a complex ion is the cation, there are anions in the outer sphere. $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$; $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$.

If a complex ion is the anion, there are cations in the outer sphere. Cations are usually the cations of alkaline and alkaline-earth metals and an ammonium cation: $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{Na}[\text{Ag}(\text{CN})_2]$, $\text{NH}_4[\text{AuCl}_4]$.

Example 1.1. What is the charge of 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 Co^{+3} and six ligands of chlorides Cl^- ions.

$$[\text{Co}^{+3}\text{Cl}_6]^x: \text{charge (x)} = +3 + 6 \cdot (-1) = -3, [\text{CoCl}_6]^{3-};$$

$$(b) \text{charge (x)} = +3 + 4 \cdot (0) + 2 \cdot (-1) = +1, [\text{Co}^{+3}(\text{NH}_3)_4\text{Cl}_2]^{1+};$$

$$(c) \text{charge (x)} = +2 + 4 \cdot (0) = +2, [\text{Cu}^{+2}(\text{H}_2\text{O})_4]^{2+};$$

$$(d) \text{charge (x)} = +3 + 3 \cdot (0) + 3 \cdot (-1) = 0, [\text{Co}^{+3}(\text{NH}_3)_3\text{Cl}_3]^0.$$

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 1.2. Calculate the oxidation state (OS) 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) $[\text{Cu}^{+2}(\text{CN})_4]^{2-}$.

$$(a) [\text{Co}^x(\text{NH}_3)_5^0(\text{H}_2\text{O})^0]^{3+} \quad x + 5 \cdot (0) + 0 = +3; \quad x = +3; \quad \text{OS of Co} = +3;$$

$$(b) [\text{Co}^x(\text{H}_2\text{O})_4^0\text{Cl}_2^0]^0 \quad x + 4 \cdot (0) + 2 \cdot (-1) = 0; \quad x = +2; \quad \text{OS of Co} = +2;$$

$$(c) [\text{Cu}^{+2}(\text{CN})_4]^{2-} \quad x + 4 \cdot (-1) = -2; \quad x = +2; \quad \text{OS of Cu} = +2.$$

1.2 Classification of Coordination Compounds

According to the **complex-ion** coordination, compounds are divided into neutral coordination compounds, anionic coordination compounds, and cationic coordination compounds.

For example: **neutral complex** is a complex ion which has no charge $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]^0$, $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]^0$.

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

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

According to the **ligands** coordination, compounds are divided into **hydroxocomplexes, acidocomplexes, ammines, and aquacomplexes**.

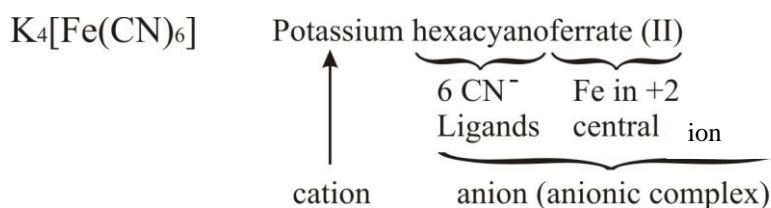
Table 1.2 – Name of the coordination compound type

Ligand	Name of the coordination compound type	Example
Hydroxide ions OH^-	Hydroxocomplexes	$\text{Na}_2[\text{Zn}(\text{OH})_4]$
Anions of the acid residues: CN^- , NO_2^- , Cl^- , I^- , Br^- , etc.	Acidocomplexes	$\text{K}_4[\text{Fe}(\text{CN})_6]$ $\text{K}_2[\text{HgI}_4]$ $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
Neutral molecules: NH_3 , H_2O	Ammines aquacompeexes	$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$

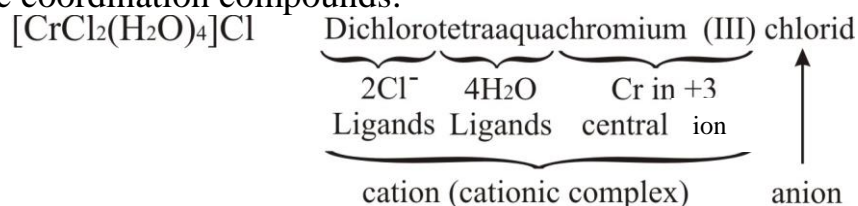
1.3 Nomenclature of Coordination Compounds

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:

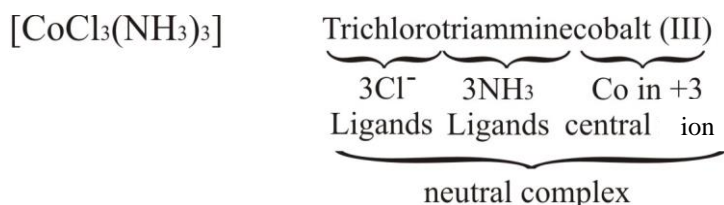
1. Anionic coordination compounds:



2. Cationic coordination compounds:



3. Neutral coordination compounds:



The nomenclature can be summarized as follows:

1. Naming a coordination compound:

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

$\text{K}_3[\text{Fe}(\text{CN})_6]$ potassium hexacyanoferrate (III);

$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$ dichlorotetraaquachromium (III) chlorid;

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

$[\text{CoCl}_3(\text{NH}_3)_3]$ trichlorotriamminecobalt (III).

2. Naming a complex ion in a coordination compound:

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

$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ dichlorotetraaquachromium (III).

3. Naming the ligands in a complex ion:

a) the order of the ligands is anionic, neutral, cationic.

$[\text{PtCl}_2(\text{NH}_3)_4]^{2+}$ dichlorotetraammineplatinum (IV)

- the names of anionic ligands end in - o:

CN^- – cyano;

Cl^- – chloro;

- the names of neutral ligands are the names of the molecules, except NH_3 ,

H_2O , CO , and NO :

NH_3 – ammine;

H_2O – aqua.

Table 1.3 shows the names of some common ligands.

Table 1.3 – Names of some common ligands

Anionic ligand	Ligand name	Neutral ligand	Ligand name
bromide (Br^-)	bromo	ammonia (NH_3)	ammine
chloride (Cl^-)	chloro	water (H_2O)	aqua (aquo)
cyanide (CN^-)	cyano	carbon monoxide (CO)	carbonyl
fluoride (F^-)	fluoro	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	ethylenediamine
hydroxide (OH^-)	hydroxo	$\text{C}_6\text{H}_5\text{N}$	pyridine
sulphate (SO_4^{2-})	sulphato		
amide (NH_2)	amido		
nitrite (NO_2^-)	nitro		
nitrate (NO_3^-)	nitrate		

- b) within each type of ligand (cationic, anionic or neutral).
 - if the number of a particular ligand is more than one, the number is indicated with the appropriate Greek prefix as it is shown in table 1.4.

Table 1.4 – Greek prefix of 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 the central atom (ion) in a complex:

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



Table 1.5 – 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 Latin 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;

- (b) if the complex is cationic or neutral, the name of the metal is unchanged:



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

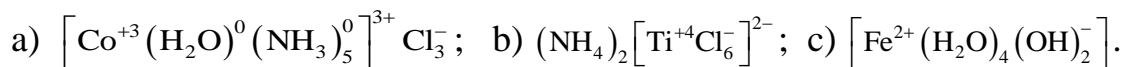
Example 1.3. Name the following compounds:

- (a) $\text{K}_3[\text{Fe}(\text{CN})_6]$; (b) $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$; (c) $[\text{PtCl}_4(\text{NH}_3)_2]$.

Answers: a) potassium hexacyanoferrate (II); b) tetraamminecopper (II) chloride; c) diamminetetrachloroplatium (III).

Example 1.4. Write the formula of the following compounds: a) aquapentamminecobalt (III) chloride; b) ammonium hexachlorotitanate (IV); c) dihydroxotetra aquairon (II).

Answers:



1.4. 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. (figure 1.2)

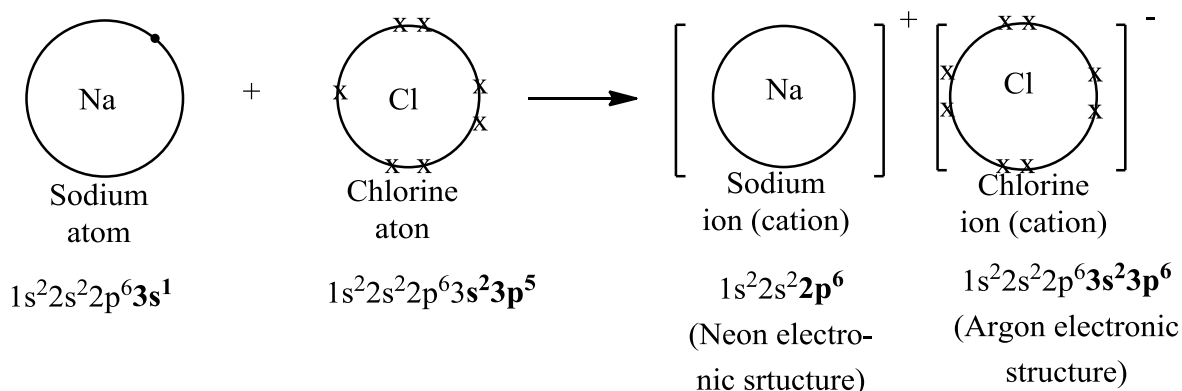


Figure 1.2 – Electron transfer during the reaction between sodium and chlorine

Covalent bond is formed by electron sharing between non-metal elements.

The octet rule states that an atom tries to attain the octet structure through bond formation (figure 1.3).

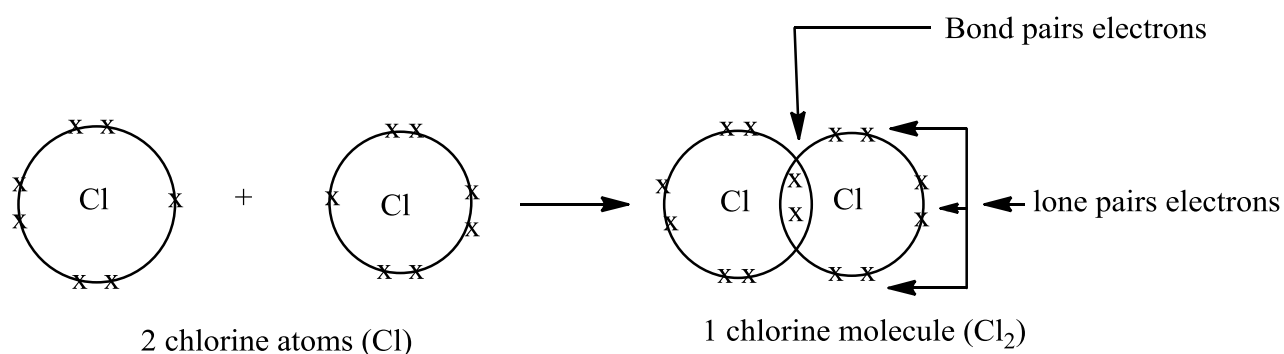


Figure 1.3 – The single covalent bond in a chlorine molecule

In the chlorine molecule, each chlorine atom achieves the stable [Ar] electronic configuration by sharing a pair of electrons. There are three pairs of non-bonding electrons on each atom and they are known as the **lone pairs electrons**.

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

The atom that supplies the shared pair of electrons is known as the donor while the other atom involved in the dative covalent bond is known as the 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 (figure 1.4):

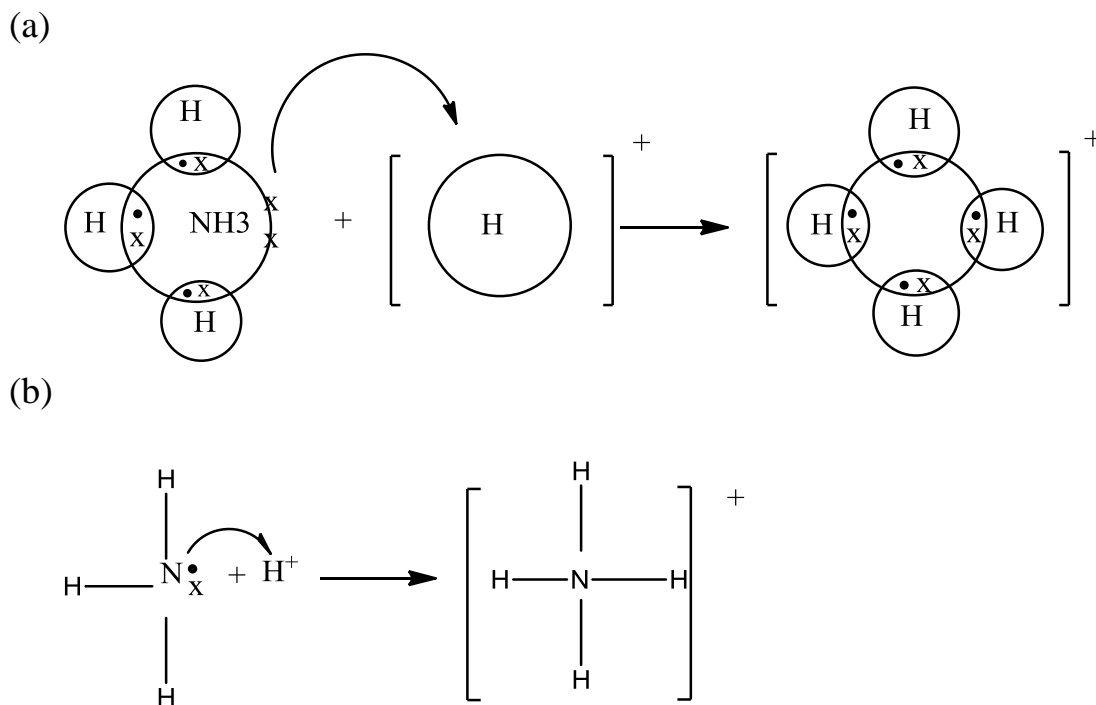


Figure 1.4 – Formation of the dative covalent bond in an NH_4^+ ion: (a) dot and cross diagram; (b) single line representation

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

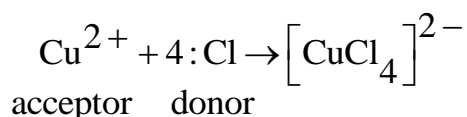


Figure 1.5 – Shows the schematic view of coordination compound molecule of $\text{K}_2[\text{CuCl}_4]$

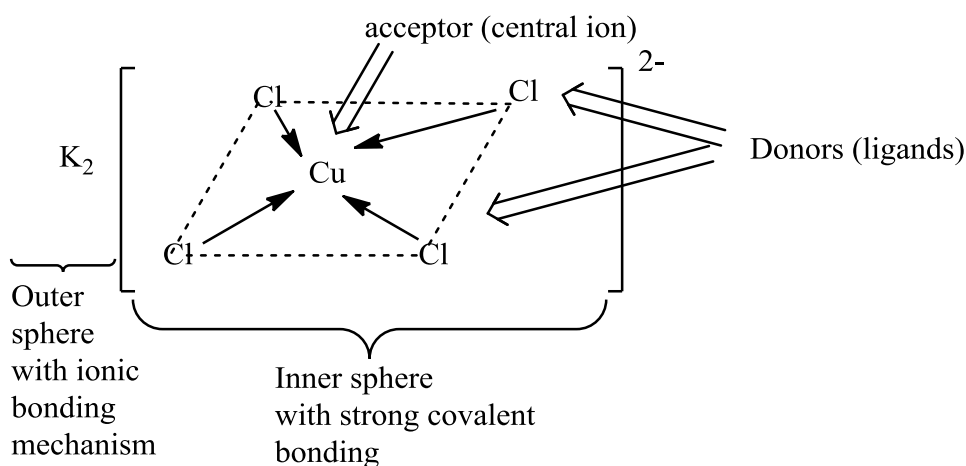


Figure 1.6 – Schematic view of coordination compound $K_2[CuCl_4]$

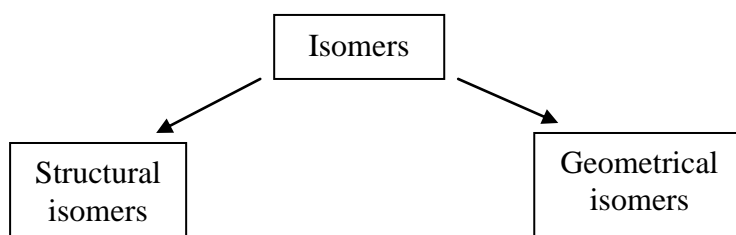
Central ions or atoms with different coordination numbers undergo different hybridizations, giving rise to a number of different empty hybrid orbitals with different shapes (table 1).

Table 1 – Relationship between the coordination numbers, hybridisations, and shapes of complexes

Coordination number	Hybrid orbitals involved	Shape of resulting complex	Example
2	sp	Linear	
4	sp^3	Tetrahedral	$[Zn(NH_3)_4]^{2+}$ $[CoCl_4]^{2-}$
4	dsp^2	Square planar	$[Cu(NH_3)_4]^{2+}$ $[CuCl_4]^{2-}$
6	d^2sp^3 or sp^3d^2	Octahedral	$[Cr(NH_3)_6]^{3+}$ $[Fe(CN)_6]^{3-}$

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

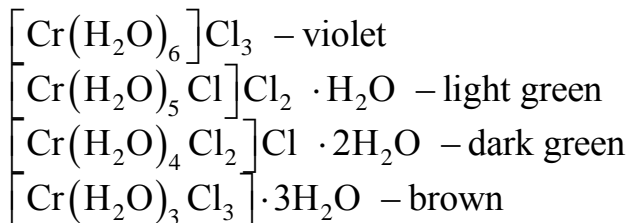
There are two kinds of isomers – structural isomers and geometrical isomers.



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

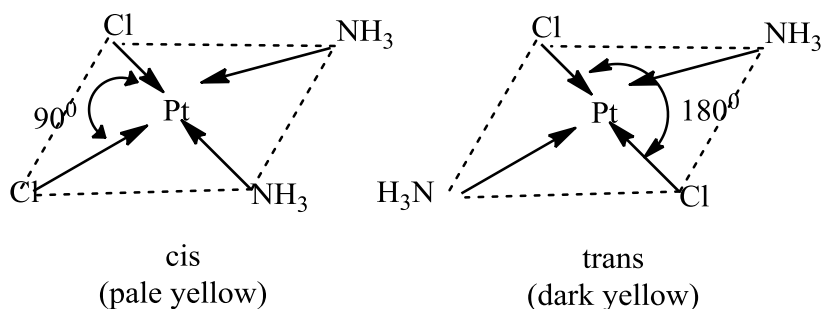
For example, $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} \text{SO}_4^-$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+ \text{Br}^-$ are two structural isomers.

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



Geometrical isomers are isomers in which the composition of the first coordination sphere is the same but the geometrical arrangement of the ligands varies.

Geometrical isomers exist for square planar (4-coordinated) and octahedral (6-coordinated) complexes only. For example, the complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has two isomers differing in colour, solubility, reactivity, and the way of preparation. Chlorine atoms can be diagonally opposite (trans-isomer) or they can be adjacent to each other (cis-isomer).



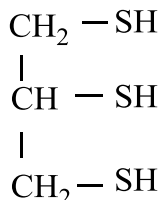
1.5. Coordination Compounds in Medicine

Coordination compounds are present in the minerals and living organisms. Many biologically important compounds are coordination compounds in which complicated organic species are bound to metal ions. Red colour of blood is caused by the presence of hemoglobin, 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 enters the composition of myoglobin, oxidases, peroxidases, cytochromes. More than 60 biologically active substances contain zinc. Cobalt is in composition of vitamin B₁₂ (cyanocobalamin).

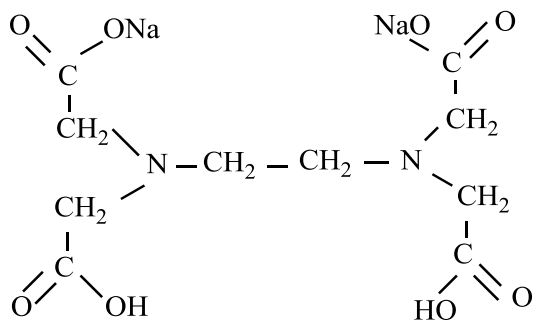
Formation and destruction of biological complexes occur constantly in the organism and metal-ligand homeostasis is maintained at the definite level. Metal-ligand homeostasis can be disturbed due to deficiency or excess of biometals cations, entering of toxic metals cations, and entering or formation 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 metals cations is based on the formation of stable complexes (chelation) between these metals and special ligands.

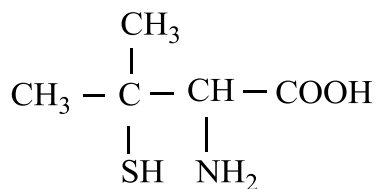
Dimercaprol is an effective antidote for the organic arsenical like lewisite, but can be used for poisoning due to antimony, gold, and mercury. Penicillamine is an effective antidote for the treatment of poisoning by copper, mercury, and lead. Trilon B (bisodium salt of EDTA) is used for treatment of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



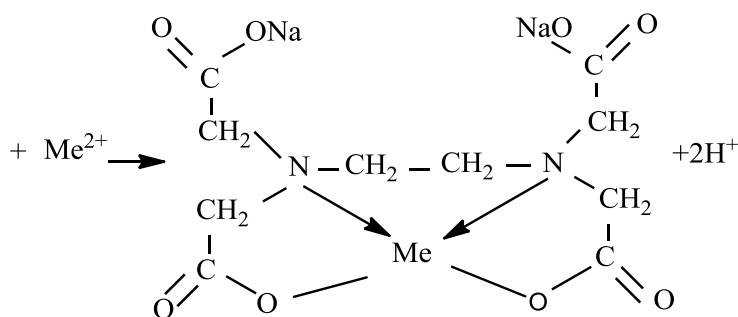
2,3-dimercaptopropan-1-ol
(BAL, dimercaprol)



B Trilon



Penicillamine (dimethylcystein)



CHAPTER 2 SOLUTIONS

- 2.1 Solutions Theory.
- 2.2 Methods of Solutions Concentrations Expression.
- 2.3 Aqueous Solutions Acids, Bases, and Salts.
- 2.4 Dissociation of Water. pH Scale.
- 2.5 Hydrolysis.
- 2.6 Buffer Solutions.
- 2.7 Colligative Properties of Solutions.

2.1 Theory of Solutions

Solutions are of great importance in the life and practical human activities. 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 products of their interaction.

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

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

Solute is a solution component **present** in **lesser quantity** than the solvent.

Solution in which **water** is a **solvent** is called an **aqueous solution**.

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

Types of solution

According to their state solutions can be a **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 CO₂.

All **gaseous mixtures** are **solutions**. The best known example of gaseous solution is air, which consists of N₂, O₂, CO₂, and other gases.

In a **solid solution** the **solvent** is a **solid** substance. The ability to form solid solution is particularly common among metals, and such solid solutions are called **alloys**. For example, an alloy of nickel and copper, an alloy of gold and silver.

Dissolving of the substances in solvent. Solubility

Russian chemist D. I. Mendeleev on the bases of the experiments created the chemical theory of solutions.

Dissolution of substances in solvent is:

1. Destruction of crystalline lattice.
2. Interaction of the solvent with the particles of the solute.

3. Uniform distribution of one substance in the whole volume of another substance.

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 solubility of gases decreases with the temperature raising; solubility of gases increases with pressure raising.

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

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

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

Supersaturated solution is one which holds in solution more solute than can dissolve in presence of the solute at that temperature.

2.2 Methods of Solutions Concentrations Expression

Solution consists of one or more dissolved substances called solutes, and the medium in which the solutes are uniformly distributed in the form of molecules or ions, called the solvent.

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

Mass percent. Percent concentration

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

The solution contains 5 g of NaCl and $100 - 5 = 95$ g of H₂O.

Percent concentration is defined by equation:

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

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

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

Example 2.1. 50 g of glucose were dissolved in 450 g of water. Calculate the mass percent of the glucose.

Answer: 1. Calculate the mass of solution:

$$\text{mass of solution} = \text{mass of solvent} + \text{mass of solute} = 450 \text{ g} + 50 \text{ g} = 500 \text{ g}$$

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 2.2. How would you prepare 100 g of a 10% aqueous solution of NH_4Cl ?

Answer:

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

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

The mass of solute = 10 g. The mass of H_2O = $100 - 10 = 90 \text{ g}$.

Example 2.3. How many grams and moles of NaCl are contained in 220 g of a 25% NaCl solution?

Answer:

$$1) \quad 25\% = \frac{x}{220} \cdot 100\%, \quad \text{mass of } \text{NaCl} = \frac{25 \cdot 220}{100} = 55 \text{ g } \text{NaCl};$$

$$2) \quad \text{number of moles}(\text{NaCl}) = \frac{\text{mass of } (\text{NaCl})}{\text{molar mass of } (\text{NaCl})} = \frac{55 \text{ g}}{58.5 \text{ g/mol}} = 0.94 \text{ mol}.$$

Example 2.4. Calculate the mass percent of NaOH if 500 ml of solution contains 25 g of NaOH .

Density is the amount of mass per unit volume 25 g of NaOH , density of solution is 1.024 g/ml.

Answer:

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

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

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

2)

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

$$\text{mass percent} = \frac{25 \text{ g}}{512 \text{ g}} \cdot 100\% = 4.88\%,$$

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:

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

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

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

Example 2.5. How would you prepare 0.5 M aqueous solution of NH_4Cl ?

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

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

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

Example 2.6. How many moles of solute are contained in 3.0 L of 1.8 M solution?

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

Example 2.7. What volume of 2.0 M solution will contain 0.5 mol of solute?

$$\text{Answer: } 2 = \frac{0.5}{\text{no.L soln}}, \quad \text{no.L soln} = 0.25 \text{ L.}$$

Example 2.8. What will be the molarity of a NaCl solution in which 175.5 g of NaCl is dissolved in 750 mL of solution?

Answer: Since molarity is defined as moles per liter, we must first calculate the number of moles in 175 g of NaCl, then convert 750 mL to liters, and finally calculate C_M :

$$\text{Molar mass of NaCl} = 58.5 \text{ g,}$$

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

$$750\text{mL} = 0.75 \text{ L,}$$

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

Example 2.9. Calculate the molar concentration of a solution where the mass percent of HNO_3 is 25% and the density of the solution is 1.151 g/ml.

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

1. Calculate the mass of solution:

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

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

2. Calculate the mass of solute 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 solute (HNO_3):

$$\text{no. of moles of solute} = \frac{\text{mass of HNO}_3}{\text{molar mass of HNO}_3},$$

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

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

4. Calculate the molarity (C_M):

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

Molal concentration (molality)

Molality (C_m) is a concentration of a solution expressed as number of moles of solute per kilogram of solvent.

Molal concentration is defined by equation:

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

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

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

Example 2.10. How would you prepare 0.5 m aqueous solution of NH_4Cl ?

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

Normality (molar concentration of the equivalent)

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

N is defined by equation:

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

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

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

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

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

Basicity is a number of displaceable H^+ ions from one molecule of the acid.

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

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

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

Acidity is the number of displaceable OH^- ions from one molecule of the base.
For example,

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

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

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

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

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

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

Example 2.11. 500 ml of solution contain 9.8 g of H_2SO_4 . Calculate the normality (molar concentration of the equivalent).

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

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

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

For any neutralization reaction, the following relationship holds:

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

Example 2.12. Calculate normality of 21% H_2SO_4 solution with the density of 1.150 g/ml, mass of solution equal 1000 g.

Answer:

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

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

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

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

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

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

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

Mole fraction

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

If solutions n_1 and n_2 contain the number of moles of solvent and the solute respectively, then:

$$\text{mole fraction of solute} = \frac{\text{no. of moles of solute (n}_2\text{)}}{\text{no. of moles of solute (n}_2\text{)} + \text{no. of moles of solvent (n}_1\text{)}};$$

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

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

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

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

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

Example 2.13. 4.41 g of $\text{K}_2\text{Cr}_2\text{O}_7$ were dissolved in 200 g of water, density of solution is 1.015 g/ml. Calculate: (a) the mass percent of $\text{K}_2\text{Cr}_2\text{O}_7$; (b) the molarity; (c) the molality; (d) normality; (e) mole fraction.

Answer:

(a) mass of solution = mass of solvent + mass of solute;

$$\text{mass of solution} = 200 \text{ g} + 4.41 \text{ g} = 204.41 \text{ g,}$$

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

$$\text{mass percent} = \frac{4.41 \text{ g}}{204.41} \cdot 100\% = 2.2\%;$$

(b) volume of solution = mass of solution / density,

$$\text{volume of solution} = \frac{204.41 \text{ g}}{1.015 \text{ g/ml}} = 201.48 \text{ ml} = 0.201 \text{ L,}$$

molar mass of $\text{K}_2\text{Cr}_2\text{O}_7 = 2 \cdot 39 + 2 \cdot 52 + 7 \cdot 16 = 294 \text{ g/mol}$,

$$\text{no. of mol solute} = \frac{\text{mass of } \text{K}_2\text{Cr}_2\text{O}_7}{\text{molar mass of } \text{K}_2\text{Cr}_2\text{O}_7} = \frac{4.41 \text{ g}}{294 \text{ g/mol}} = 0.015 \text{ mol},$$

$$\text{molarity} = \frac{\text{no. of mol solute}}{\text{volume of solution}} = \frac{0.015 \text{ mol}}{0.2014 \text{ L}} = 0.074 \text{ mol/L};$$

$$\text{(c) molality} = \frac{\text{no. of mol. solute}}{\text{mass of solvent}} = \frac{0.015 \text{ mol}}{0.20 \text{ kg}} = 0.075 \text{ mol/kg};$$

$$\text{(d) eq. mass of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{molar mass of } \text{K}_2\text{Cr}_2\text{O}_7}{2} = 147 \text{ g/mol},$$

$$\text{moles of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ equivalent} = \frac{\text{mass of } \text{K}_2\text{Cr}_2\text{O}_7}{\text{Eq. mass of } \text{K}_2\text{Cr}_2\text{O}_7} = \frac{4.41 \text{ g}}{147 \text{ g/mol}} = 0.03 \text{ mol},$$

$$\text{normality} = \frac{\text{moles of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ equivalent}}{\text{volume of solution}} = \frac{0.03 \text{ mol}}{0.2014 \text{ L}} = 0.148 \text{ mol/L};$$

$$\text{(e) mole fraction of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{no. of moles } \text{K}_2\text{Cr}_2\text{O}_7}{\text{no. of moles of solute} + \text{no. of moles of solvent}},$$

molar mass (H_2O) = $2 \cdot 1 + 16 = 18 \text{ g/mol}$,

$$\text{no. of solvent mol} = \frac{\text{mass of solvent } (\text{H}_2\text{O})}{\text{molar mass of } \text{H}_2\text{O}} = \frac{200 \text{ g}}{18 \text{ g/mol}} = 11.111 \text{ mol},$$

$$\text{mole fraction of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{0.015}{0.015 + 11.111} = 0.0014.$$

2.3 Aqueous Solutions Acids, Bases, and Salts

The first theory of acid and bases was proposed by Svante Arrhenius. His idea was that **acids** were substance which produced hydrogen ions, H^+ , in aqueous solution. **Bases** were substance which produced hydroxide ions, OH^- , when dissolved in water.



Bronsted-Lowry acid is a hydrogen ion donor (proton donor). 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, $\text{AlCl}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{Cl}^-$

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

Substances decomposing in solutions or melts into ions are called **electrolytes**. They include salts, acids and bases. Electrolytes conduct electric current.

S. Arrhenius introduced the concept of the degree of dissociation.

The degree of dissociation (α) 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 the dissociation is designated by the Greek letter α and is customarily expressed either in fractions of unity or as a percentage.

Electrolytes are divided into two groups: strong and weak. In strong electrolyte solution α is 1. For weak electrolyte, for example, 0.1 N solution of CH_3COOH , $\alpha = 0.013$ (or 1.3%).

Salts are strong electrolytes. Salts are 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 are completely dissociated 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 is completely dissociated in aqueous solution to form H^+ and Cl^- .

There are only a few strong acids and bases. These are listed below.

Names and Formulas of all strong Acids and Bases

HClO_4 Perchloric acid.

HNO_3 Nitric acid.

H_2SO_4^* Sulfuric acid.

HCl Hydrochloric acid.

HBr Hydrobromic acid.

HI Hydroiodic acid.

LiOH Lithium hydroxide.

NaOH Sodium hydroxide.

KOH Potassium hydroxide.

RbOH Rubidium hydroxide.

CsOH Cesium hydroxide.

$\text{Ca}(\text{OH})_2$ 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 dissociation, HSO_4^- , is a weak acid.

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

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

For example, $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$. NH_4OH is a weak base. When dissolved in water it produces OH^- ions, but OH^- concentration is considerably less than NH_4OH concentration.

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

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

In the case of weak acid, for example, acetic acid, CH_3COOH , 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

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

Dissociation process for the weak base NH_4OH is written $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

and the equilibrium constant expression is $K_b = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_4\text{OH}]}$.

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.

Dissociation constants must be determined by experiment.

$$\text{CH}_3\text{COOH } K_a = 1.8 \cdot 10^{-5}$$

$K_{\text{CH}_3\text{COOH}}$ greater than K_{HCN} .

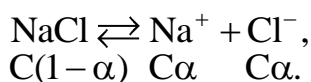
$$\text{HCN hydrocyanic } K_a = 4 \cdot 10^{-10}$$

(HCN less acid than CH_3COOH).

CH_3COOH stronger than HCN.

The value of K depends on the nature of the electrolyte and solvent and also on the temperature, but does not depend on the concentration of the solution.

If we denote the concentration of electrolyte (NaCl) dissociating into two ions (Na^+ and Cl^-) by C and the degree of its dissociation in given solution by α , 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

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

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

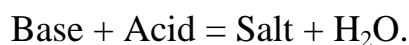
$$K \approx \alpha^2 C \quad \text{or} \quad \alpha \approx \sqrt{\frac{K}{C}}$$

This equation clearly shows the relationship existing between the concentration of a weak electrolyte and the degree of its dissociation: the degree of dissociation increases upon dilution of a solution. The value of the dissociation constant for electrolytes are given in table 2.1.

Table 2.1 – Dissociation constant for selected electrolytes in aqueous solutions at 25 °C

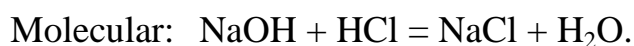
Electrolyte	Dissociation of compound	Dissociation constant (K)
Acetic acid	$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$	$1.8 \cdot 10^{-5}$
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH} \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^- + \text{H}^+$	$6.4 \cdot 10^{-5}$
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	$\text{CH}_3\text{CH}(\text{OH})\text{COOH} \rightleftharpoons \text{CH}_3\text{CH}(\text{OH})\text{COO}^- + \text{H}^+$	$1.38 \cdot 10^{-4}$
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 ₂ O water	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$1.8 \cdot 10^{-16}$
NH ₄ 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	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$ $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$K_1 = 1000$ $K_2 = 10^{-2}$
Permanganic acid	$\text{HMnO}_4 \rightleftharpoons \text{MnO}_4^- + \text{H}^+$	200

The reaction between acids and bases is called **neutralization reaction**.



Bases react with acid to produce salt and water.

Equations for acid - base neutralization reactions can be written in molecular, ionic, and net ionic form.



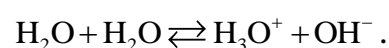
Neutralization reaction simply involves the combination of hydrogen and hydroxide ions to form water.

2.4 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 H₂O is $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-.$

In water solution H⁺ exists as hydronium ion H₃O⁺.



In this process, H₂O molecule transfers a proton to another H₂O molecule.

The equilibrium constant expression for this process is

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

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

$K_w.$

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

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

The ion-product of water has value of 1.0×10^{-14} at 25 °C.

Acid solutions have concentrations of hydronium ions greater than 1.0×10^{-7} mol/L; basic solutions have concentrations less than 1.0×10^{-7} mol/L.

These concentrations are extremely small numbers. It is often inconvenient to work with them. In 1909 the chemist Sorensen proposed pH scale. If a solution has $[H^+] = 10^{-x}$, $pH = x$. On this scale, a concentration of 1×10^{-7} mol of H^+ per liter of solution becomes a pH of 7. The table 2.2 shows the relationship between pH and the concentration of H^+ .

pH is the negative of the logarithm of $[H^+]$

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

Example 2.14. What is pH of a solution that has a H^+ concentration of 1×10^{-5} M?

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

Table 2.2 – Relationship between pH and concentration of H^+

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

Table 2.3 – pH of some common solution.

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 ware	7
Blood	7.35–7.45
Fresh egg white	7.6–8.0
Bile	7.8–8.6

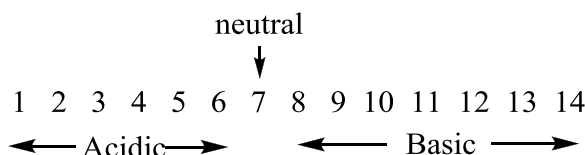
Example 2.15. What is the concentration of H^+ ions in a solution that has a pH of 4?

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

Example 2.16. Calculate the concentration of H^+ ions in Coca Cola if its pH is 2.5.

Answer:

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



A pH of 7 represents a neutral solution. If the pH less than 7, the solution is acidic; the pH greater than 7 indicates that the solution is basic.

The pOH is defined in an analogous way to pH:

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

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

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

$$\text{p}K_w = \text{pH} + \text{pOH} = 14,$$

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

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

During the medico-biological researches it is necessary to differentiate well total and active acidities, 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 equals the total acidity for strong electrolytes, because strong acid is completely (100%) dissociated in solution to form H^+ .



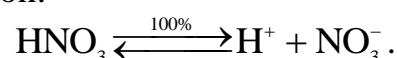
Concentration of H^+ equals the concentration of HCl.

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

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

Example 2.17. Calculate $[H^+]$ and $[NO_3^-]$ of 0.175 M solution of nitric acid HNO_3 .

Answer: HNO_3 is a strong acid and is therefore 100% dissociated in aqueous solution:



$$\text{Therefore, } [HNO_3] = [H^+] = [NO_3^-] = 0.175 \text{ M.}$$

Example 2.18. Calculate $[OH^-]$ and $[Ca^{2+}]$ of 0.01 M solution of $Ca(OH)_2$.

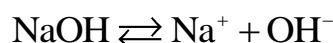
Answer: $\text{Ca}(\text{OH})_2$ is a strong base and is therefore 100 percent dissociated in aqueous solution. Since there are 2 mol of hydroxide ion per mol of $\text{Ca}(\text{OH})_2$, $[\text{OH}^-] = 2 \cdot [\text{Ca}(\text{OH})_2] = 2 \cdot 0.01 = 0.02 \text{ M}$ and $[\text{Ca}^{2+}] = [\text{Ca}(\text{OH})_2] = 0.01 \text{ M}$.

Example 2.19. What is the pH of 0.001 M solution of HCl?

Answer: HCl is strong acid, therefore
 $\text{pH} = -\log[\text{H}^+] = -\log C = \log[1 \cdot 10^{-3}] = 3$.

Example 2.20. Calculate pH solution, if 500 ml solution contains 2 g of NaOH.

Answer: NaOH is strong electrolyte and it is 100% dissociated in aqueous solution.



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

$$\text{Molarity } C_M = \frac{\text{mass of NaOH}}{\text{Molar mass of NaOH} \cdot \text{Volume}};$$

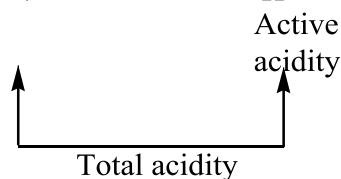
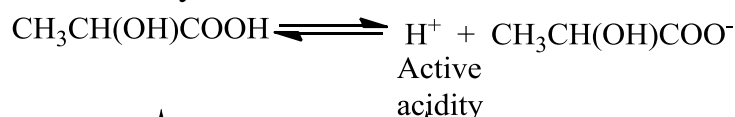
Molar mass (NaOH) = 23 + 16 + 1 = 40 g/mol;

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

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

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

Weak electrolyte is partial by dissociated in water. For example, acetic acid is a weak acid. When dissolved in water it produces H^+ ions, but the H^+ concentration is considerably less than the common concentration of acid:



To calculate pH of weak acid solution it is necessary to know either the degree of dissociation (α), or the dissociation constant (K_a) besides the concentration:

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

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

For the weak base solution:

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

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

where α is a degree of dissociation (ionization) of the base, K_b is the base dissociation (ionization) constant, C is the molarity.

Example 2.21. What is the pH of 0.1M solution of CH₃COOH? K_a CH₃COOH = $1.8 \cdot 10^{-5}$.

Answer: CH₃COOH is weak electrolyte, therefore

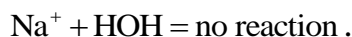
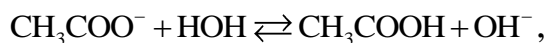
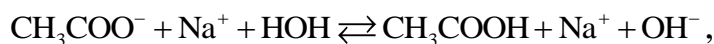
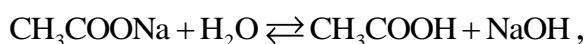
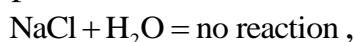
$$\text{pH} = -\log \sqrt{K_a \cdot C},$$

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

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

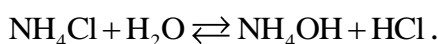
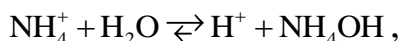
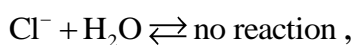
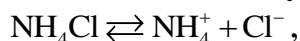
2.5 Hydrolysis

In pure water $[H^+] = [OH^-] = 1 \cdot 10^{-7}$. When NaCl is added to water, the solution remains neutral. When CH₃COONa is added to pure water, the solution becomes basic. When NH₄Cl is added to pure water, the solution becomes acidic.



Water reacts with CH₃COO⁻ to produce OH⁻. Solution of CH₃COONa has pH > 7.

Solution of NH₄Cl has pH < 7. The NH₄⁺ ion hydrolyzes to produce H⁺:



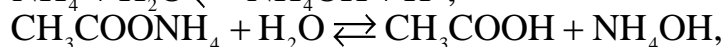
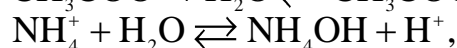
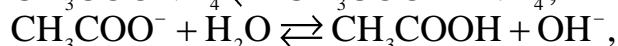
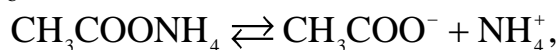
The reaction, in which water reacts with ionic species in solution, is called **hydrolysis**.

Salts of strong acids and strong bases (for example, NaCl) do not hydrolyze PH=7.

Salts of weak acids and strong bases (for example, CH₃COONa) hydrolyze, producing basic solution: pH > 7.

Salts of strong acids and weak bases (for example, NH₄Cl) hydrolyze, producing acidic solution: pH < 7.

Salts of weak acids and weak bases (for example, CH₃COONH₄) hydrolyze, but whether the resulting solution is neutral, acidic, or basic depends on the relative values of K_a and K_b .



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

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

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

2.6 Buffer Solution

Adding acid or base to a solution usually changes the value of its pH greatly. If 0.01 mol of NaOH is dissolved in 1L 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 resist attempts to change their 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 CH₃COOH and 0.1 mol of CH₃COONa, the pH changes from 4.76 to 4.84.

There are two types of buffers:

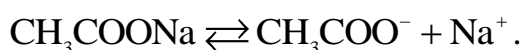
Acidic buffer is prepared by mixing a weak acid and its salt of a strong base, e.g., ethanoic acid and sodium ethanoate. The solution is acidic and is used to resist pH changes in an acidic medium.

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

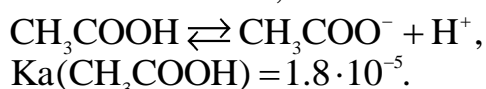
Buffer solution maintain optimum pH values for the biochemical processes taking place in living systems. The enzymes (biological catalysts) that enable biochemical reactions to take place can function only within a narrow range of pH. Human blood pH is stable in the range of 7.35–7.45, saliva pH – in 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?

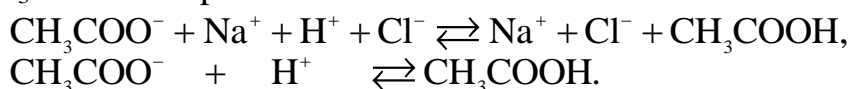
Take a buffer solution with equal concentrations of ethanoic acid and sodium ethanoate (acidic buffer) as an example. Sodium ethanoate is completely dissociated in water.



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



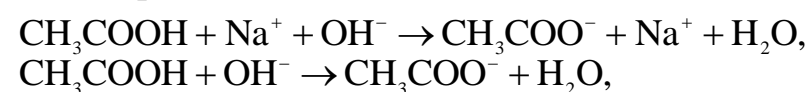
If an acid, for example, (HCl) is added to the system, H⁺ ions will react with the CH₃COONa to produce weak acid.



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, OH⁻ ions will react with the CH₃COOH to produce salt and H₂O.



From buffer ADDED.

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

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

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

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

where pK_a – $(-\log)$ of acid dissociation constant (K_a).

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

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

where pK_b – $(-\log)$ of base dissociation constant (K_b).

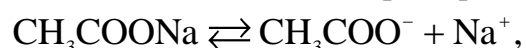
$$\text{pH} = 14 - \text{pOH} \text{ or}$$

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

Example 2.22. A buffer is prepared by adding 4.1 g of sodium ethanoate to 1 dm³ 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 g mol⁻¹)

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



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

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

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

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

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

Example 2.23.

1. Calculate the change in pH when 1 cm³ of 0.25 M NaOH is added to:

- (a) 25 cm³ of pure water;
- (b) 25 cm³ of 0.1 M CH₃COOH;
- (c) 25 cm³ of 0.1 M CH₃COOH containing 0.002 moles CH₃COO⁻Na⁺.
($\text{K}_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$)

2. Comment on the results obtained.

Answer:

(a) pH of pure water = 7

$$\text{Number of moles of NaOH} = 0.25 \cdot \frac{1}{1000} = 2.5 \cdot 10^{-4} \text{ mol};$$

$$\text{Concentration of NaOH after dilution} = 2.5 \cdot 10^{-4} \div \frac{1+25}{1000} = 9.62 \cdot 10^{-3} \text{ M};$$

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

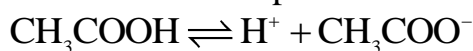
$$1 \cdot 10^{-14} = [\text{H}^+] \cdot 9.62 \cdot 10^{-3},$$

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

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

The change in pH = 11.98 – 7 = 4.98.

(b) **Part 1.** Calculation on the pH of the 25 cm³ of 0.1 M CH₃COOH:



At eqm: (0.1-x) mole x mole x mole (in 1 dm³)

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

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

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

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

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

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

Part 2. Calculation on the pH when 1 cm³ of 0.25 M NaOH is added.

Number of moles of OH⁻ in 1 cm³ of 0.25 M NaOH = 0.25 · 1 · 10⁻³ = 2.5 · 10⁻⁴ mol;

Number of moles of CH₃COOH originally present = 0.1 · 25 · 10⁻³ = 2.5 · 10⁻³ mol.

As the number of moles of OH⁻ added will react with the same number of moles of CH₃COOH, the number of moles of CH₃COOH left = 2.5 · 10⁻³ – 2.5 · 10⁻⁴ = 2.25 · 10⁻³ mol. The number of moles of sodium ethanoate formed = 2.5 · 10⁻⁴ mol.

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

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

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

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

The change in pH = 3.81 – 2.88 = 0.93.

(c) **Part 1.** Calculation on the pH of 25 cm³ of 0.1 M CH₃COOH containing 0.002 moles CH₃COO⁻Na⁺.

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

Number of moles of salt $2 \cdot 10^{-3}$ mol;

Number of moles of acid = $2.5 \cdot 10^{-3}$ mol.

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

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

Part 2. Calculation on the pH when 1 cm^3 of 0.25 M NaOH is added to the buffer.

Answer:

Number of moles of OH^- in 1 cm^3 of 0.25 M

NaOH = $0.25 \cdot 1 \cdot 10^{-3} = 2.5 \cdot 10^{-4}$ mol.

As the number of moles of OH^- added will react with CH_3COOH present in the buffer system,

number of moles of salt present = $2 \cdot 10^{-3} + 2.5 \cdot 10^{-4} = 2.25 \cdot 10^{-3}$ mol;

number of moles of acid present = $2.5 \cdot 10^{-3} - 2.5 \cdot 10^{-4} = 2.25 \cdot 10^{-3}$ mol.

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

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

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

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

The change in pH = $4.76 - 4.66 = 0.10$.

2. A drastic pH change (4.98 units) is shown when 1 cm^3 of 0.25 M NaOH is added to 25 cm^3 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 2.24. How many grams of ammonium chloride would you add to 100 cm^3 of 0.1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ to prepare a basic buffer of pH 9.0?

($K_b(\text{NH}_3) = 1.74 \cdot 10^{-5} \text{ mol dm}^{-3}$; molar mass of $\text{NH}_4\text{Cl} = 53.5 \text{ gmol}^{-1}$)

Answer:

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

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

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

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

$$x = 0.174.$$

$$\text{Number of moles of } \text{NH}_4\text{Cl used} = 0.174 \cdot \frac{100}{1000} = 0.0174 \text{ moles.}$$

$$\text{Mass of } \text{NH}_4\text{Cl used} = 0.0174 \cdot 53.5 = 0.93 \text{ g.}$$

Example 2.25. The dissociation constant of H_2PO_4^- in water, K_a , is

$$6.2 \cdot 10^{-8} \text{ mol} \cdot \text{dm}^{-3} \text{ at } 298 \text{ K, where } K_a = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{[\text{H}_2\text{PO}_4^-]}.$$

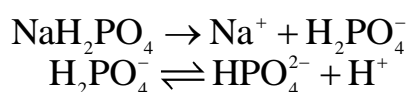
Calculate the pH at 298 K of:

- an aqueous solution of 0.10 M NaH_2PO_4 ;
- an aqueous solution of 0.05 M NaH_2PO_4 and 0.05 M Na_2HPO_4 .

(It may be assumed that the concentrations of H_3PO_4 and PO_4^{3-} are negligible in these solutions.)

Answer:

a)



At eqm: $(0.1 - x)$ mole x mole x mole (in 1 dm^3)

$$6.2 \cdot 10^{-8} = \frac{x^2}{0.1 - x}.$$

$$x^2 = 6.2 \cdot 10^{-8} (0.1 - x).$$

$$x^2 + 6.2 \cdot 10^{-8} x - 6.2 \cdot 10^{-9} = 0.$$

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

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

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

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:

$$\text{Buffer capacity on acid} = \frac{\text{normality of added acid} \cdot \text{volume of added acid}}{\text{volume of buffer} \cdot \text{changing of pH}}$$

$$\text{Buffer capacity on base} = \frac{\text{normality of added base} \cdot \text{volume of added base}}{\text{volume of buffer} \cdot \text{changing of pH}}$$

The more the initial concentrations of components of buffer system are, the more its buffer capacity is.

Example 2.26. 14 ml of sodium hydroxide solution with molarity with 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 of blood.

Answer:

$$\text{Buffer capacity on base} = \frac{\text{normality of added base} \cdot \text{volume of added base}}{\text{volume of buffer} \cdot \text{changing of pH}}$$

Changing of PH = 9.36 – 7.36 = 2.

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

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

1. Bicarbonate buffer (H_2CO_3 – acid, NaHCO_3 – salt).
2. Phosphate buffer (NaH_2PO_4 – acid, Na_2HPO_4 – salt).
3. Amino acid and protein buffer.
4. Haemoglobinous buffer ($\text{HHb} + \text{KHb}$).
5. Oxyhemoglobinous buffer ($\text{HHbO}_2 + \text{KHbO}_2$).

The major buffers of blood are bicarbonate and hemoglobin.

2.7 Colligative Properties of Solutions

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

The important colligative properties are:

1. Relative depression of the saturated vapour pressure of a solvent over a solution (the first Raoult's law).
2. Elevation in the boiling point of the solution compared with that of the pure solvent (the second Raoult's law).
3. Depression in freezing point of the solution compared with that of the pure solvent (the second Raoult's law).
4. Osmotic pressure.

Vapour pressure of solutions. The Raoult's law

At a given temperature, the pressure of the saturated vapour over every liquid is a constant quantity. The saturated vapour pressure of the solvent over a solution is always lower than that over the pure solvent at the same temperature. The difference between these quantities is called **the vapour pressure depression over the solution**.

The Raoult's law: The relative depression of the saturated vapour pressure of a solvent over a 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,

$$\frac{n_2}{n_1 + n_2} - \text{mole fraction.}$$

Example 2.27. An aqueous solution of sucrose is made by dissolution 13.66 g of sucrose ($C_{12}H_{22}O_{11}$) in 90 g of water at 65°C . If the vapour pressure of pure water at 65°C is 25.0 kPa, what will be the vapour pressure of the solution? (Molar mass of $C_{12}H_{22}O_{11} = 342 \text{ g/mol}$.)

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

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

$$n_1 = \frac{\text{mass of } H_2O}{\text{molar mass of } H_2O} = \frac{90 \text{ g}}{18 \text{ g/mol}} = 5 \text{ mol,}$$

$$n_2 = \frac{\text{mass of } C_{12}H_{22}O_{11}}{\text{molar mass of } C_{12}H_{22}O_{11}} = \frac{13.66 \text{ g}}{342 \text{ g/mol}} = 0.0399 \text{ mol,}$$

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

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

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

Vapour pressure of the solution is 24.8 kPa.

Freezing and boiling of solutions

Individual substances are characterized by strictly definite temperatures of their transitions from one state of substance to another (the boiling point and the melting or freezing point). For example, water at standard atmospheric pressure (101.3 kPa, 1 atm, 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 of the pure solvent is called the **elevation of the boiling point of the solution** (ΔT).

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

The amount of boiling point elevation is given by the equation

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

where ΔT_b – the elevation of the boiling point of the solution (K),

E – the ebullioscopic constant characteristic of the solvent (for water
E = 0.52 kg·K/mol, for benzene E = 2.57 kg·K/mol),

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

The difference between the freezing point of the pure solvent and that of the solution is called the **depression of the freezing point of the solution** (ΔT_f).

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

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

$$\Delta T_f = K \cdot C_m .$$

where ΔT_f – the depression of the freezing point of the solution (K),

K – the cryoscopic constant characteristic of the solvent (for water
K = 1.86 kg·K/mol, for benzene K = 5.12 kg·K/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.

Example 2.28. 54 g of glucose were dissolved in 0.9 L of H₂O. Calculate the boiling point and freezing point. M(glucose) = 180 g/mol.

Answer:

$$\Delta T_b = E \cdot C_m , \quad \Delta T_f = K \cdot C_m .$$

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

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

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

$$\Delta T_b = 0.52 \times 0.33 = 0.17^\circ,$$

$$\Delta T_f = K \cdot C_m = 1.86 \times 0.33 = 0.62^\circ,$$

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

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

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

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

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

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

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

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

Example 2.29. Calculate the osmotic pressure of 0.01 M solution of cane-sugar at 27 °C.

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

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

$$\Pi = C_M RT = 0.01 \cdot 8.314 \cdot 300 = 24,942$$

Example 2.30. 18 g of glucose were dissolved in 500 ml of water at 27 °C. Calculate the osmotic pressure. $M(\text{C}_6\text{H}_{12}\text{O}_6) = 180 \text{ g/mol}$

Answer:

$$\pi = C_M RT;$$

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

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

$$\pi = 0.2 \cdot 8.314 \cdot (27 + 273) = 488.4$$

Example 2.31. A solution containing 63.3 g/L of hemoglobin has an osmotic pressure 243.4 kPa at 20 °C. Calculate the molar mass of hemoglobin.

Answer:

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

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

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

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

Molar mass of hemoglobin = 633 g.

Example 2.32. 100g of H₂O contains 4.57 g C₁₂H₂₂O₁₁. Density of solution = 1 g/ml. Calculate:

(a) the osmotic pressure at 293 K;

(b) the boiling point; $E_{\text{H}_2\text{O}} = 0.52$, $T_b(\text{H}_2\text{O}) = 100^\circ\text{C}$;

(c) the freezing point; $K_{\text{H}_2\text{O}} = 1.86$, $T_f(\text{H}_2\text{O}) = 0^\circ\text{C}$;

(d) the vapour pressure of the solution at 293 K, if the vapour pressure of pure water at 293 K is 2.337 kPa.

Answer:

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

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

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

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

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

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

$$(b) \Delta T_b = E \cdot C_m,$$

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

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

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

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

$$(c) \Delta T_f = K \cdot C_m,$$

$$\Delta T_f = 1.86 \cdot 0.134 = 0.25^\circ,$$

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

$$(e) \frac{P_o - P_s}{P_o} = \frac{n_2}{n_1 + n_2},$$

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

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

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

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

$$2.337 - P_s = 0.005,$$

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

Osmosis and osmotic pressure

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

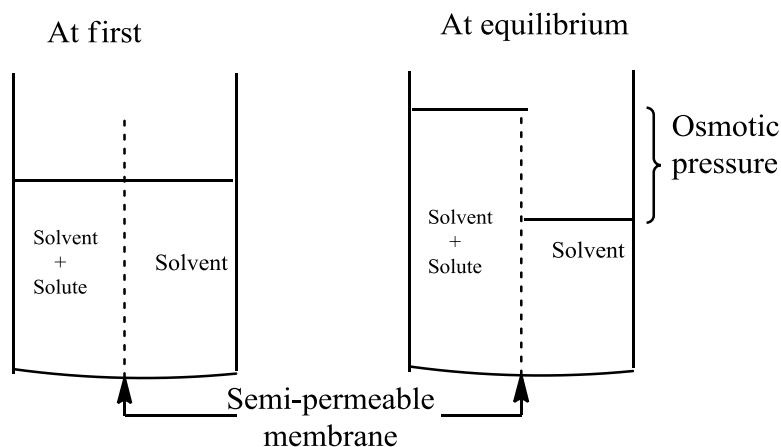


Figure 3 – Osmosis process

Osmotic pressure (π) is the pressure that must be applied to a solution, when separated from a more dilute solution by semi-permeable membrane, in order to prevent the inflow of solvent.

In 1886, J. Van't Hoff showed that for solutions of non-electrolytes 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: π is the osmotic pressure, Pa;

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

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

T is the temperature, K.

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

The osmotic pressure of human blood is 700–800 kPa. Solutions having the identical osmotic pressure (and equal molar concentrations, of course) are called isotonic solutions. NaCl 0.9% solution 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 the water molecules will pass from the cell to the more concentrated solution and the cell becomes smaller (shrink). In hypotonic solution **hamolysis** 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 non-electrolytes 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 Na^+ and Cl^- . From one mole of NaCl , we get not 6.02×10^{23} particles, but twice this number. Hence, the depression of the freezing point or any other colligative property in a solution of NaCl must be double that in a solution of a non-electrolyte having the same concentration. ΔT_b , ΔT_f , P for electrolyte solutions are so times as much as the number of particles in the electrolyte solution. To determine the above-mentioned values in the electrolyte solution it is used the **isotonic coefficient (i)**. **i** is equal to the quantity of ions the substance dissociated to. For example, **i** for NaCl is 2, for BaCl_2 is 3, for 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:

$$\Delta T_b = i \cdot E \cdot C_m,$$

$$\Delta T_f = i \cdot K \cdot C_m,$$

$$P = i \cdot C_m \cdot R \cdot T,$$

$$i = \alpha(n - 1) + 1,$$

n – number of ions.

CHAPTER 3

CHEMICAL THERMODYNAMICS

- 3.1 Thermodynamics Terminology.
- 3.2 The Law of Thermodynamics.
- 3.3 Internal Energy and Enthalpy.
- 3.4 Thermochemical Equations. Hess's Law.
- 3.5 Spontaneity and Disorder. Entropy.
- 3.6 Gibbs Energy. Criteria of Process Direction.
- 3.7 Application of Thermodynamic Law to Living Systems.

3.1 Thermodynamics Terminology

Thermodynamics is the study of energy transfer and the effects of energy changes.

Thermochemistry is the study of the heat change of chemical reaction.

Universe: In the universe, there is no change in the amount of energy.

The Universe = the system + the surroundings.

Surroundings represent that part of the universe with which a system interacts.

System is any totality of bodies separated from the surroundings by a boundary (real or imaginary) inside which matter and/or energy exchange is possible.

There are several types of system:

Open system: can exchange both matter and energy with the surroundings. A living organism is an open system.

Closed system: can exchange energy but not matter with the surroundings.

Isolated system: exchanges neither matter nor energy with the surroundings.

Homogeneous system is a system consists of one phase only.

Heterogeneous system is a system with more than one phase.

Phase refers to any part of a system which is physically separated from other parts of the system by a distinct boundary. A phase can be a solid, liquid, vapor (gas) or aqueous solution which is uniform in both chemical constitution and physical state (figure 3.1).

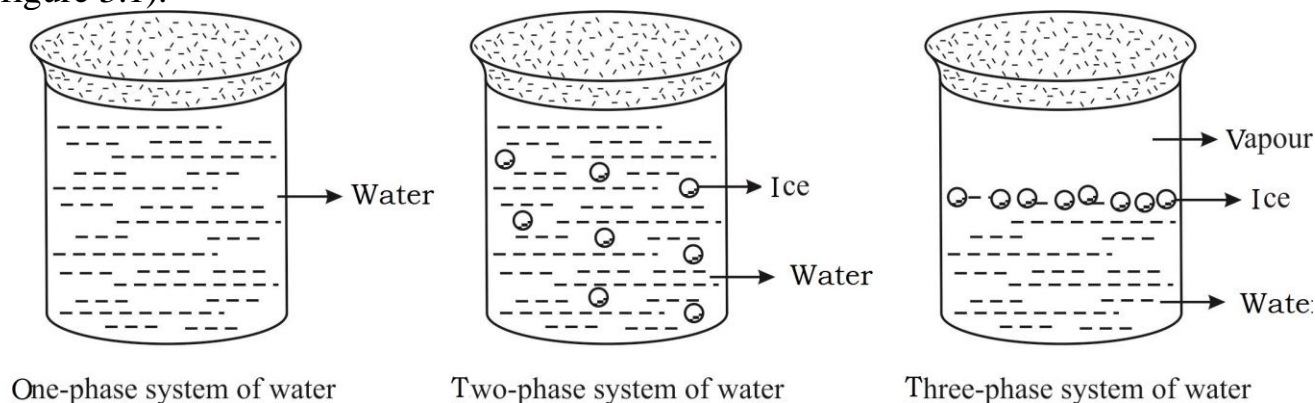


Figure 3.1 – The one-phase, two-phase and three-phase system of water

Thermodynamics distinguishes isochoric, isobaric and isothermal processes.

Isochoric process is the process that takes place at constant volume ($V=\text{const}$).

Isobaric process is the process that takes place at constant pressure ($P=\text{const}$).

Isothermal process is the process that takes place at constant temperature ($T=\text{const}$).

There are exothermic and endothermic processes.

Exothermic process (reaction) is a process that evolves heat to the surroundings.

Endothermic process (reaction) is a process that absorbs heat from the surroundings.

The state of a system is characterized by thermodynamic parameters and state functions.

Thermodynamic parameters are pressure P , temperature T , volume V and concentration.

State function is a property that depends only on the state or present condition of a system and not on how this state is attained.

Some common state functions are internal energy (U), enthalpy (H), entropy (S) and free energy (G).

Example 3.1. For each of the following systems, determine whether it is open, closed or isolated.

1. An ice cube and water in a perfect, stoppered thermos.
2. The same amount of ice and water in an open flask.
3. Water in a sealed glass tube.

Solution:

1. The ice cube and water form the system and are contained in a stoppered, perfectly insulated thermos. This is an isolated system, exchanges neither matter nor energy with the surroundings.

2. If the ice and water are in an open flask, water may escape. The flask may be heated or cooled and the contents will have energy transferred to them or away from them. Because energy and matter may be exchanged with the surrounding, the system is an open system.

3. In a sealed glass tube, matter cannot leave or enter, but energy may be transferred to the system, it is a closed system.

3.2 The Law of Thermodynamics

The first law. Energy is conserved; it can be neither created nor destroyed.

The second law. In an isolated system, natural processes are spontaneous when they lead to the increase in disorder, or entropy.

The third law. The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

3.3 Internal Energy and Enthalpy

Internal energy (U) is the sum of the kinetic and potential energies of the particles that form the system.

A change in internal energy (ΔU) occurs when a system exchanges energy with its surroundings in the form of heat and/or work. This can be represented by the symbols:

$$\Delta U = Q + W$$

change internal energy heat absorbed by the system work done by the system

If the system is gaseous, work done is given by $P\Delta V$, where P – pressure and ΔV – change in volume. The heat absorbed by the system (Q) at constant pressure is equal to the change in **enthalpy** (ΔH).

$$\Delta H = \Delta U + P\Delta V.$$

The above is a mathematical expression of the first law of thermodynamics.

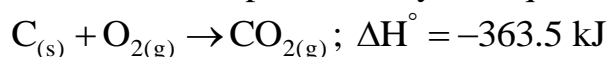
Enthalpy (H) is a term that describes the heat content of a system.

ΔH = heat absorbed by the system at constant pressure.

For a reaction that evolves heat (i.e., heat flows from the system to the surroundings), the sign of ΔH is negative, the sign of Q is positive; $Q = -\Delta H$ (exothermic reaction).

For a reaction that absorbs heat (i.e., heat flows from the surroundings to the system), the sign of ΔH is positive, the sign of Q is negative; $-Q = \Delta H$ (endothermic reaction).

For example, the burning of carbon to form carbon (IV) oxide evolves heat, thus it is an exothermic reaction and represented by the equation:



In a similar way, endothermic reactions are as follows:



Standard enthalpy change of formation of a substance is symbolized as (ΔH_f°) and is the enthalpy change when one mole of the compound is formed from its elements under standard conditions. ΔH_f° is measured in kJmol^{-1} .

Standard state conditions are:

- all substances are in their standard states;
- the pressure is 101.3 kPa (101325 Pa = 1 atm = 760 mm Hg);
- the temperature is 298 K (K = °C + 273).

For example, the standard enthalpy change of formation of sodium chloride is represented as follows:

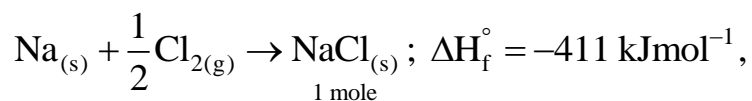


Table 3.1 – Thermodynamic Properties of Substances at T=298.15 K and P=1 atm.

Substance	Enthalpy ΔH° , kJ/mol	Entropy ΔS° , J/mol·K	Gibbs' energy ΔG° , kJ/mol
HCl _(g)	92.2	186.7	-95.3
NaCl _(s)	411.0	72.4	-384.1
O _{2(g)}	0	205.0	0
O _{3(g)}	-142.0	238.8	162.8
H ₂ O _(g)	-241.8	188.7	-226.6
H ₂ O _(l)	-285.8	69.9	-237.2
SO _{2(g)}	296.9	248.5	-300.2
H ₂ S _(g)	20.4	205.6	-33.5
NH _{3(g)}	-46.2	192.5	-16.5
NH _{3(l)}	-80.8		
HCN _(g)	132.0	201.7	121.6
H ₃ PO _{4(s)}	-1281.1	110.5	-1119.2
C _(graphite)	0	5.7	0
C _(diamond)	1.8	2.4	2.8
CO _(g)	-110.5	197.9	-137.1
CO _{2(g)}	-393.5	213.6	-393.4
CO _{2(l)}	-699.6		
H _{2(g)}	0	130.6	
Methane _(g)	-74.8	186.2	-50.8
Ethylene _(g)	52.3	219.4	68.1
Acetylene _(g)	226.7	200.8	20.2
Benzene _(l)	49.0	173.2	-124.4
Ethanol _(l)	-277.8	164.0	-174.1
Glycerin _(l)	-670.7	20.5	-477.1
Acetaldehyde	-166.0	264.2	-132.9
Acetone _(l)	-246.8	198.7	-155.4
Acetic acid _(l)	-487.3	159.8	-398.4
Butyric acid _(l)	-524.3	255.0	-376.7
Fumaric acid _(s)	-811.1	166.1	-653.6
Lactic acid _(l)	-694.0	221.7	
Pyruvic acid _(l)	-607.5		
Glycine _(s)	-524.7	109.2	-366.8
Urea _(s)	-333.2	104.6	-197.1
Urea _(l)	-319.2	173.8	
Glucose _(s)	-1274.4		-919.5
Sucrose _(s)	-2222.0	360.3	-1544.7

ΔH_f° (NaCl) is -411 kJmol^{-1} but not -822 kJ as the definition specifies the formation of 1 mole of the compound.

ΔH° is the heat effect of the reaction.

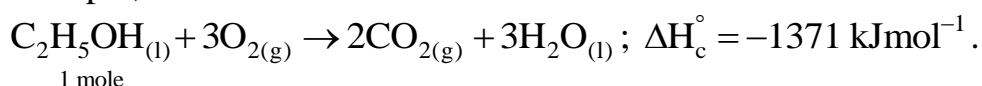
Table 3.1 lists the standard enthalpy changes of formation (ΔH_f°) of some common substances. It should be noted that the absolute enthalpy of substance cannot be determined, only the difference in enthalpies between substances can be measured experimentally.

The standard enthalpy change of formation of an element is equal to zero.

$$\Delta H_f^\circ(\text{Na}_{(s)}) = 0 \text{ kJmol}^{-1}; \Delta H_f^\circ(\text{Cl}_{2(g)}) = 0 \text{ kJmol}^{-1}$$

Standard enthalpy change of combustion (ΔH_c°) is the enthalpy change when one mole of the substance is burnt completely in oxygen under standard conditions.

For example,

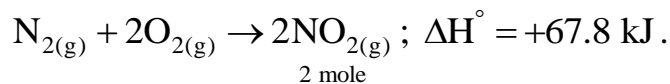


Thermochemistry allows determining standard enthalpy changes of the various reactions, enthalpy of dissolution, melting, neutralization, ionization, atomization, etc.

3.4 Thermochemical Equations. Hess's Law

Thermochemical equations are equations of the reactions in which the physical states of the substances and the values of any thermodynamic function of the state are indicated. The reaction enthalpy in this case is called **heat effect** of the reaction.

For example,



Hess's law: Heat effect of chemical reaction is independent of the route of the reaction and depends only by the initial and final state of the system.

For example, if there are two routes for reactants A and B to form products C and D, the heat effect of the reaction by route 1 is the same as the heat effect of the reaction by route 2 (figure 3.2).

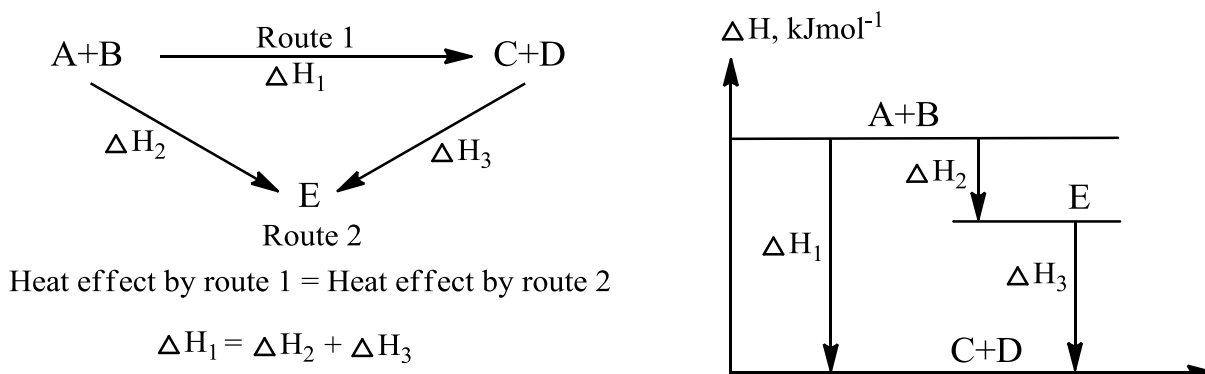
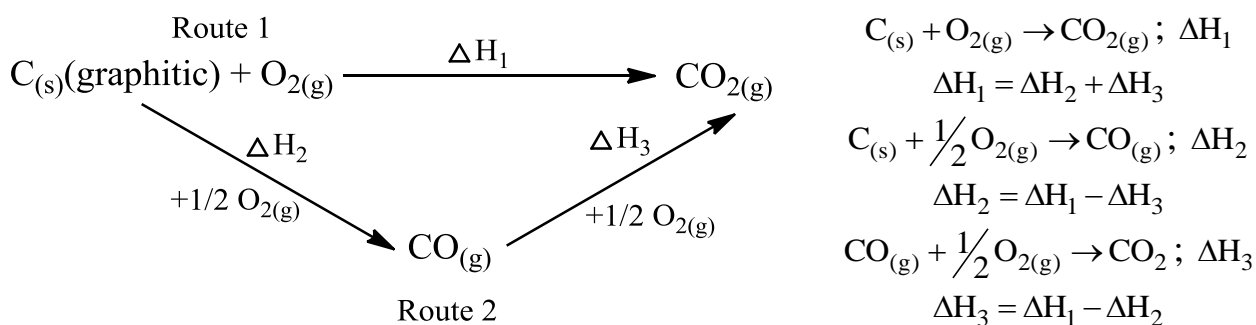


Figure 3.2 – A diagram showing different routes of chemical reaction
Consider the enthalpy change of $\text{CO}_{(g)}$ formation.

It is difficult to measure the heat evolved from the reaction between graphite and O_2 to give CO directly because it is impossible to prevent the combustion of

carbon to form CO_2 . However, making use of Hess's law, $\Delta H_f^\circ(\text{CO}_{2(g)})$ can be determined, as ΔH_1 and ΔH_2 can be obtained directly in a laboratory.



According to Hess's law, the enthalpy change of the reaction from $\text{C}_{(s)}$ and $\text{O}_{2(g)}$ to $\text{CO}_{2(g)}$ is a constant, regardless of the route the reaction takes. Hence, enthalpy change in route 1 is the same as the enthalpy change in route 2.

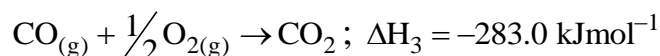
i.e. $\Delta H_3 + \Delta H_2 = \Delta H_1$

$$\Delta H_2 = \Delta H_1 - \Delta H_3$$

ΔH_1 is the standard enthalpy change of $\text{CO}_{2(g)}$ formation.



ΔH_3 is the standard enthalpy change of $\text{CO}_{(g)}$ combustion.



ΔH_2 is the standard enthalpy change of $\text{CO}_{(g)}$ formation.

$$\Delta H_2 = \Delta H_1 - \Delta H_3 = -393.5 - (-283.0) = -110.5 \text{ kJmol}^{-1}$$

The standard enthalpy change of carbon monoxide CO formation is $-110.5 \text{ kJmol}^{-1}$.

After calculation, the enthalpy level diagram for the formation of CO and CO_2 can be drawn (figure 3.3).

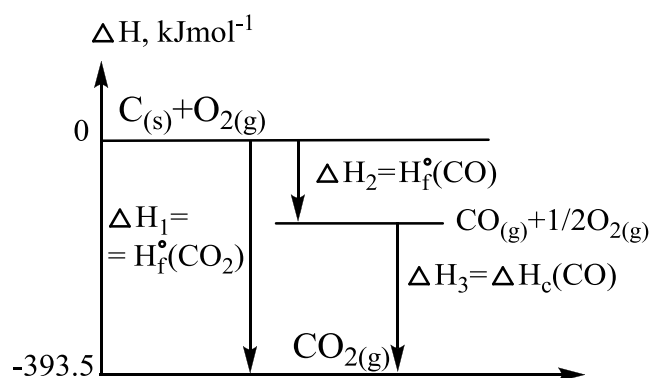


Figure 3.3 – Enthalpy level diagram for determining $\Delta H_f^\circ(\text{CO}_{(g)})$

The consequences of Hess's law are:

1. Heat effect of the forward reaction equals the heat effect of the backward reaction taken with the opposite sign: $\Delta H_{\text{forward}} = -\Delta H_{\text{backward}}$.

For example, $\text{Ca}_{(s)} + \frac{1}{2}\text{O}_{2(g)} \rightleftharpoons \text{CaO}_{(s)}; \Delta H_r^\circ = -635 \text{ kJmol}^{-1}$

$\text{CaO}_{(s)} \rightleftharpoons \text{Ca}_{(s)} + \frac{1}{2}\text{O}_{2(g)}; \Delta H_r^\circ = +635 \text{ kJmol}^{-1}$

2. Heat effect also called enthalpy change of the reaction (ΔH_r°) equals the sum of the enthalpies of the products formation minus the sum of the enthalpies of the reactants formation with the account of stoichiometric coefficients.

$$\Delta H_r^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \cdot$$

3. Heat effect enthalpy change of the combustion reaction (ΔH_c°) equals the sum of the heats of the reactants combustion minus the sum of the heats of the products combustion.

$$\Delta H_c^\circ = \sum \Delta H_c^\circ(\text{reactants}) - \sum \Delta H_c^\circ(\text{products}) \cdot$$

For the reaction $aA + bB = cC + dD$ the heat effects equal:

$$\Delta H_r^\circ = (c\Delta H_f^\circ C + d\Delta H_f^\circ D) - (a\Delta H_f^\circ A + b\Delta H_f^\circ B),$$

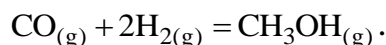
$$\Delta H_c^\circ = (a\Delta H_f^\circ A + b\Delta H_f^\circ B) - (c\Delta H_f^\circ C + d\Delta H_f^\circ D).$$

For example, for the reaction $\text{CO}_{(g)} + 2\text{H}_{2(g)} = \text{CH}_3\text{OH}_{(g)}$,

$$\Delta H_r^\circ = \Delta H_f^\circ \text{CH}_3\text{OH}_{(g)} - (\Delta H_f^\circ \text{CO}_{(g)} + 2\Delta H_f^\circ \text{H}_{2(g)}),$$

$$\Delta H_c^\circ = (\Delta H_c^\circ \text{CO}_{(g)} + 2\Delta H_c^\circ \text{H}_{2(g)}) - \Delta H_c^\circ \text{CH}_3\text{OH}_{(g)}.$$

Example 3.2. Given the following information, find the heat effect of the reaction (ΔH_r°) and heat effect of the combustion reaction (ΔH_c°) for the reaction



	$\text{CO}_{(g)}$	$\text{H}_{2(g)}$	$\text{CH}_3\text{OH}_{(g)}$
$\Delta H_f^\circ, \text{kJmol}^{-1}$	-110.5	0	-237
$\Delta H_c^\circ, \text{kJmol}^{-1}$	-238.0	-285.8	-715.0

Answer:

Use the consequences of Hess's law

$$\Delta H_r^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \cdot$$

$$\Delta H_r^\circ = -237 - (-110.5 + 2 \cdot 0) = -237 + 110.5 = -126.5 \text{ kJ}.$$

$$\Delta H_c^\circ = \sum \Delta H_c^\circ(\text{reactants}) - \sum \Delta H_c^\circ(\text{products}) \cdot$$

$$\Delta H_c^\circ = (-283.0 + 2(-285.8)) - (-715) = -283.0 - 571.6 + 715 = -854.6 + 715 = -139.6 \text{ kJ}.$$

3.5 Spontaneity and Disorder. Entropy

Spontaneous change is change that has a natural tendency to occur, causes a system to move from a less stable state to a more stable state.

For example, energy always flows from a hot object to a cooler one. The reverse never occurs spontaneously (see the second law of thermodynamics). This concept is illustrated in figure 3.4.



Figure 3.4 – Energy always flows spontaneously from hot to cold, never the reverse

Another way to look at the second law is in terms of disorder. The quantitative measure of the disorder of a system is entropy, which is symbolized by S (Fig. 3.5).

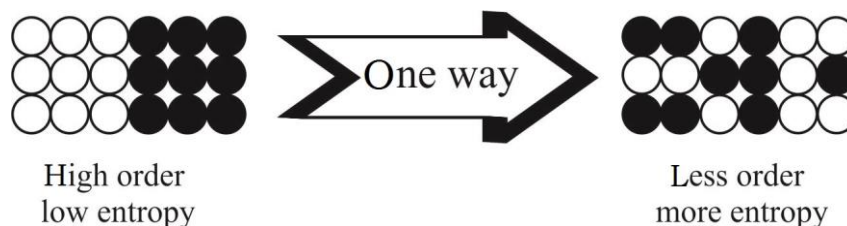


Figure 3.5 – The more mixed up a system is the higher its entropy

Entropy (S) is a function of the state, the changes depend only on the initial and final state of the system. S is measured in $\text{Jmol}^{-1}\text{K}^{-1}$.

There are two definitions of entropy, one is based on statistics and the other – on heat transfer.

The first definition is given by the Boltzmann equation, which describes the relationship between entropy and the amount of disorder in a system:

$$S = K \ln W,$$

where K is Boltzmann's constant ($K = 1.3807 \times 10^{23} \text{J} \cdot \text{K}^{-1}$), W is a thermodynamic probability, i.e., the number of equally probably microscopic states by means of which the given macroscopic state of a system can be achieved.

It follows from Boltzmann's law that entropy of a perfect crystal at absolute zero is equal to zero (the third law of thermodynamics). For it $W = 1$, $S = K \ln 1 = 0$. This is its most order system. In any other system the value of W is very large, and $S > 0$. The greater disorder of the system, the greater its entropy.

The other definition the entropy change is related to the heat absorbed by the equation:

$$\Delta S = \frac{Q}{T}; \text{ units: } \text{J} \cdot \text{K}^{-1},$$

where Q is the amount of heat absorbed by the system in an isothermal reversible process, and T is the absolute temperature (in Kelvin).

The product $T\Delta S$ is called «unfree energy».

The entropy depends on:

- phase $S_{(g)} > S_{(L)} > S_{(s)}$ (figure 3.6);
- temperature (entropy increases with increasing temperature);
- mass of particles of substance (the greater the mass the greater the S);
- degree of dispersion (the greater the dispersion the greater S);

- type of bond ($S_{\text{covalent b.}} < S_{\text{metallic b.}}$);
- pressure (entropy decreases with increasing pressure).

S also changes when chemical processes occur. These changes are especially great in reactions leading to a change in the number of molecules of gases: S increases with increasing the number of gas molecules.

In any spontaneous process the entropy of the universe increases: $\Delta S_{\text{universe}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) > 0$ (this statement is the second law of thermodynamics).

The total change of entropy of human body always is positive.

If the entropy change of the universe is less than zero ($\Delta S_{\text{universe}} < 0$), the process is not spontaneous, but the reverse process is spontaneous.

If the entropy change of the universe is zero ($\Delta S_{\text{universe}} = 0$), the process described is at equilibrium.

Entropy changes in chemical reactions are calculated by the same method as the enthalpy change because entropy is a state function:

$$\Delta S_r = \sum S_f^0(\text{products}) - \sum S_f^0(\text{reactants}) .$$

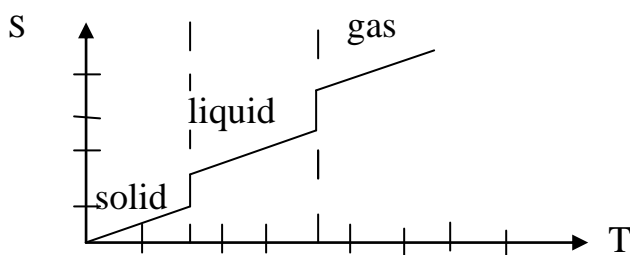
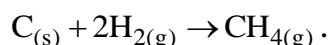


Figure 3.6 – Entropy of substance as a function of temperature.

Example 3.3. Given the following information, find the entropy changes in the reaction:



Substance	$C_{(s)}$	$H_{2(g)}$	$CH_{4(g)}$
$S^\circ, J \cdot mol^{-1} \cdot K^{-1}$	5.74	130.574	186.16

Answer:

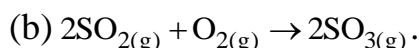
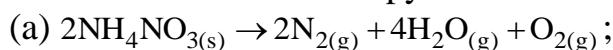
$$\Delta S_r = \sum S_f^0(\text{products}) - \sum S_f^0(\text{reactants}) ,$$

$$\Delta S_r = S^\circ(CH_4) - (S^\circ(C) + 2S^\circ(H_2)) ,$$

$$\Delta S_r = 186.16 - (5.74 + 2 \cdot 130.574) = -80.73 \text{ J} \cdot \text{K}^{-1} .$$

$\Delta S_r < 0$. The entropy change for this process is negative, showing that the entropy of the system decreases as reactants are converted to products.

Example 3.4. Predict whether each of the following processes involves an increase or decrease in entropy:



Answer:

(a) entropy increases. The disorder of the system increases because the number of particles increases as 2 moles of solid reactant yield 5 moles of gas product;

(b) three moles of gaseous reactants produce 2 moles of gaseous product. The number of particles in the system decreases, the disorder decreases. Entropy decreases.

3.6 Gibbs Energy. Criteria of Process Direction

Gibbs energy G (or free energy, isobaric potential, isobaric and isothermal potential) was introduced for isothermal reactions proceeding at a constant pressure.

The free energy change of a reaction is a **measure** of the **spontaneity** of the reaction. The more negative the free energy change, the more spontaneous the reaction.

The free energy is related to the enthalpy, entropy, and temperature by the equation

$$G = H - TS.$$

Absolute values of the free energy are not determined, instead the free energy change, ΔG , is used:

$$\Delta G = \Delta H - T\Delta S.$$

Gibbs energy is a function of the state, it is measured in $\text{kJ}\cdot\text{mol}^{-1}$.

The sign of this function change in a reaction can be a criterion of the possibility of the reaction to proceed spontaneously.

$\Delta G < 0$ – the process is spontaneous;

$\Delta G > 0$ – the process is not spontaneous. The reverse process will be spontaneous;

$\Delta G = 0$ – the process is at equilibrium.

The following table summarizes how the ΔG is affected by temperature for the different possibilities of the signs of ΔH and ΔS (table 3.2).

Table 3.2 – Different possibilities of the signs

Sign of			Conclusion	Example
ΔH°	ΔS°	ΔG°		
+	–	+	The process is not spontaneous	photosynthesis
+	+	+	The process is not spontaneous at low temperature	melting (s – L); evaporation (L – g)
–	–	–	The process is spontaneous at low temperature	Condensation
–	+	–	The process is spontaneous	combustion of organic compounds
–	–	+	The process is not spontaneous at high temperature	$2\text{H} \rightarrow \text{H}_2$
+	+	–	The process is spontaneous at high temperature	$\text{Br}_2 \rightarrow 2\text{Br}$

The free energy change in chemical reactions can be calculated either by using standard free energy of formation (ΔG_f°), or ΔH and ΔS :

$$\Delta G = \sum \Delta G_{f(\text{products})}^0 - \sum \Delta G_{f(\text{reactants})}^0 ,$$

$$\Delta G = \Delta H - T\Delta S .$$

The standard free energy of formation of a substance (ΔG_f°), is the free energy change when one mole of the compound is formed from the elements under standard conditions.

Table 3.1 lists the standard free energy of formation of some common substances.

Example 3.5. Calculate the free energy for the reaction: $\text{CH}_2\text{CH}_{2(\text{g})} + \text{HCl}_{(\text{g})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightarrow \text{CH}_2\text{CHCl}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$ under standard conditions.

Thermodynamic data for the reactants and products are summarized in the following table.

Substance	$\Delta G_f^\circ(\text{KJ} \cdot \text{mol}^{-1})$	$\Delta H_f^\circ(\text{KJ} \cdot \text{mol}^{-1})$	$S^\circ(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
$\text{CH}_2\text{CH}_{2(\text{g})}$	81.3	36.36	122.17
$\text{HCl}_{(\text{g})}$	-95.3	-92.31	186.80
$\text{O}_{2(\text{g})}$	0	0	205.03
$\text{CH}_2\text{CHCl}_{(\text{g})}$	51.9	35.56	263.88
$\text{H}_2\text{O}_{(\text{g})}$	-241.8	-228.591	188.71

Answer: The ΔG_r will be calculated by two methods.

Using standard free energies of formation: this method is faster if you only need ΔG_r at 298 K.

$$\Delta G = \sum \Delta G_{f(\text{products})}^0 - \sum \Delta G_{f(\text{reactants})}^0$$

$$\Delta G^\circ = (\Delta G_f^\circ(\text{H}_2\text{O}) + \Delta G_f^\circ(\text{CH}_2\text{CHCl})) - (\Delta G_f^\circ(\text{CH}_2\text{CH}_2) + \Delta G_f^\circ(\text{HCl}) + \frac{1}{2}\Delta G_f^\circ(\text{O}_2)) =$$

$$= (-241.8 + 51.9) - (81.3 + (-95.3) + 1/2 \cdot 0) = -162.7 \text{ kJ}.$$

Using ΔH_r and ΔS_r is necessary for estimating ΔG_r at temperature other than 298 K.

Calculate the ΔH_r and ΔS_r

$$\Delta H_r = \sum \Delta H_{f(\text{products})}^0 - \sum \Delta H_{f(\text{reactants})}^0 .$$

$$\Delta H_r = (-228.59 + 35.56) - (36.36 + (-92.31) + 1/2 \cdot 0) = -150.3 \text{ kJ}.$$

$$\Delta S_r = \sum \Delta S_{(\text{products})}^\circ - \sum \Delta S_{(\text{reactants})}^\circ .$$

$$\Delta S_r = (188.71 + 263.88) - (122.17 + 186.8 + 1/2 \cdot 205.03) = 41.1 \text{ J} \cdot \text{K}^{-1} = 41.1 \cdot 10^{-3} \text{ kJ} \cdot \text{k}^{-1}$$

$$\Delta G_r = \Delta H_r - T\Delta S_r .$$

At standard temperature (298 K)

$$\Delta G_r = -150.3 - 298 \cdot 41.1 \cdot 10^{-3} = -162.7 \text{ kJ}.$$

Example 3.6. The equation of reaction for reforming methane is $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$.

1. Calculate the free energy change for this reaction at standard conditions.
2. Estimate the temperature at which the process becomes spontaneous.

Substance	CH _{4(g)}	H ₂ O _(g)	CO _(g)	H _{2(g)}
ΔH _f ^o (KJ·mol ⁻¹)	-75	-241.8	-110.5	0
S ^o (J·mol ⁻¹ ·K ⁻¹)	186	188.7	197.9	131

Answer:

1. ΔH_r and ΔS_r is calculated by methods already described above using the values of ΔH_f^o and ΔS^o listed in the table.

$$\Delta H_r = (\Delta H_f^o(\text{CO}) + 3\Delta H_f^o(\text{H}_2)) - (\Delta H_f^o(\text{H}_2\text{O}) + \Delta H_f^o(\text{CH}_4))$$

$$\Delta H_r = (-110.5 + 3 \cdot 0) - (-241.8 + (-75)) = 206 \text{ kJ.}$$

$$\Delta S^o = (S^o(\text{CO}) + 3S^o(\text{H}_2)) - (S^o(\text{H}_2\text{O}) + S^o(\text{CH}_4))$$

$$\Delta S^o = (197.9 + 3 \cdot 131) - (188.7 + 186) = 216 \text{ J} \cdot \text{K}^{-1} = 0.216 \text{ kJ} \cdot \text{K}^{-1}.$$

At standard conditions (298 K):

$$\Delta G_r = \Delta H_r - T\Delta S_r = 206 - 298 \cdot 0.216 = 142 \text{ kJ.}$$

$$\Delta G = 142 \text{ kJ, } \Delta G > 0.$$

2. Because ΔG > 0, the process is not spontaneous.

When ΔG = 0, ΔG^o = 0 = ΔH - TΔS

$$\Delta H = T\Delta S \text{ or } T = \frac{\Delta H}{\Delta S} = \frac{206}{0.216} = 954 \text{ K.}$$

The reaction will become spontaneous when the temperature is greater than 954 K.

3.7 Application of Thermodynamic Law to Living Systems

The reactions that living organisms carry out to obtain the energy they need and to synthesize the compounds they require are commonly known as **metabolism**. Metabolism can be divided into two parts: **catabolism** and **anabolism**. **Catabolism reactions** break down complex nutrient molecules to provide energy and simple precursor molecules for synthesis. **Anabolism reactions** require energy and result in the synthesis of complex biomolecules from simple precursor molecules.

Catabolism: complex molecules → simple molecules + *energy*

Anabolism: simple molecules + *energy* → complex molecules

A living organism is an open system. The total change of entropy of human body always is positive.

Biochemical reactions accompanied by reduction in Gibbs energy (ΔG < 0) are called **exergonic** and, respectively, **endergonic** at ΔG > 0.

The energy used by the living body is obtained from the biological combustion of food. The three main classes of foods used by people are carbohydrates, fats, and proteins. For proper nutrition, our diet should consist of balanced proportions of all three types of foods (60–70 g of fats – 20–25% of energy; 100–140 g of proteins – 15–20% of energy; and 55–60% of energy of carbohydrates per day), plus vitamins, minerals, and water.

The SI unit of heat is kilojoule (kJ). For measuring the energy content of foods calorie or kilocalorie (kcal) is sometimes used.

$$1\text{kcal}=1000\text{cal}=4184\text{J}=4.184\text{ kJ}.$$

The accurate determination of heat of combustion of a substance is carried out by using bomb calorimeter.

Example 3.6.

Calculate caloricity of 200 g of nuts containing 16% of proteins, 67% of fats and 10% of carbohydrates. Caloricity of proteins is 18 kJ/g, fats – 39 kJ/g, carbohydrates – 18 kJ/g.

Answer: Calculate the mass of proteins, fats, and carbohydrates.

$$\begin{array}{l} 100\text{ g nuts} - 16\text{ g proteins} \\ 200\text{ g} \quad - x \end{array} \quad x = \frac{16 \cdot 200}{100} = 32\text{ g};$$

$$\begin{array}{l} 100\text{ g nuts} - 67\text{ g fats} \\ 200\text{ g} \quad - x\text{ g} \end{array} \quad x = \frac{67 \cdot 200}{100} = 134\text{ g};$$

$$\begin{array}{l} 100\text{ g nuts} - 10\text{ g proteins} \\ 200\text{ g} \quad - x\text{ g} \end{array} \quad x = \frac{10 \cdot 200}{100} = 20\text{ g}.$$

Calculate the caloricity.

$$32 \cdot 18\text{ kJ/g} = 576\text{ kJ}$$

$$134\text{ g} \cdot 39\text{ kJ/g} = 5226\text{ kJ}$$

$$20\text{g} \cdot 18\text{ kJ/g} = 360\text{ kJ}$$

Caloricity of 200 g of nuts is $576 + 5226 + 360 = 6162\text{ KJ}$.

Example 3.7. A student requires about 15000 kJ of energy to exercise a normal vital activity. Calculate the amount of bread, butter, and eggs promoting this amount of energy. Caloric value of wheat bread is 9.91 kJ/g, butter – 30.41 kJ/g, eggs – 6.12 kJ/g.

Answer:

$$\begin{array}{l} 1\text{ g bread} - 9.91\text{ kj} \\ x\text{ g} - 15000\text{ kj} \end{array} \quad x = \frac{1 \cdot 15000}{9.91} = 1513.62\text{ g} = 1.514\text{ kg};$$

$$\begin{array}{l} 1\text{ g butter} - 30.4\text{ kj} \\ x\text{ g} - 15000\text{ kj} \end{array} \quad x = \frac{1 \cdot 15000}{30.4} = 493.42\text{ g} = 0.493\text{ kg};$$

$$\begin{array}{l} 1\text{ g eggs} - 6.12\text{ kj} \\ x\text{ g} - 15000\text{ kj} \end{array} \quad x = \frac{1 \cdot 15000}{6.12} = 2450.98\text{ g} = 2.451\text{ kg}.$$

CHAPTER 4

CHEMICAL KINETICS

- 4.1 The Main Concepts of Chemical Kinetics.
- 4.2 Factors Affecting the Reaction Rate.
- 4.3 Chemical Equilibrium.
- 4.4 Le Chatelier's Principle States.

4.1 The Main Concepts of Chemical Kinetics

Chemical kinetics is the study of the rates of chemical reaction, the factors affecting the rates of the reactions and the mechanism by which the reactions proceed.

The description of the step-by-step process by which reactants are changed into products is called the **mechanism** of the reaction.

Chemical reaction rate is the change in the concentration of any of the reactions or products per unit time (for homogeneous reaction).

$$\text{Rate of reaction} = \frac{\text{Decrease in the concentration of a reactant}}{\text{Time interval}},$$
$$\text{or} = \frac{\text{increase in the concentration of a product}}{\text{Time interval}}.$$

For any reaction of the type $A + B \rightarrow C + D$.

$$\text{Rate of reaction} = -\frac{\Delta C_A}{\Delta t} = -\frac{\Delta C_B}{\Delta t} = +\frac{\Delta C_C}{\Delta t} = +\frac{\Delta C_D}{\Delta t}.$$

The unit of the rate of reaction is $\text{mol/L}\cdot\text{s}$ ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$).

We can consider the minus signs as indicating the decrease in reactant concentration, and the + signs as indicating the increase in concentration of the product.

For heterogeneous reactions:

$$\text{Rate of reaction} = \frac{\text{Change in amount of a substance}}{\text{Surface area of the reactants} \cdot \text{Time interval}}.$$

Example 4.1. In studying the reaction between acetone and bromine, it was found that 0.025 mol of bromine disappeared in 34.5 sec. What was the rate of the reaction?

Answer: The rate of the reaction is defined as moles of bromine disappearing per unit time. Therefore

$$\text{Rate} = \frac{0.025 \text{ mol}}{1 \text{ L} \cdot 34.5 \text{ s}} = 0.07 \text{ mol/L}\cdot\text{s}.$$

4.2 Factors Affecting the Reaction Rate

The main factors affecting the reaction rate are concentration, temperature, nature of the reacting substances, and catalyst presence.

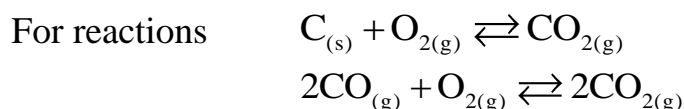
Concentration of the reactants. The greater is the concentration of the reactants, the faster is the reaction.

The concentration effect is described by the Law of Mass Action, formulated in 1867 by Norwegians K. Guldberg and P. Waage: at a constant temperature the rate of the chemical reaction at each moment is directly proportional to the concentration of the reacting substances.

For reaction $aA + bB \rightarrow dD$ dependence of a homogeneous reaction on the concentration of reacting substances can be represented as:

$$\text{Rate} = kC_A^a \cdot C_B^b, \text{ where } k \text{ is a reaction rate constant.}$$

which equals the rate of the chemical reaction when the concentrations of all reaction substances equals 1 mol/L. This equation is called **kinetic**. In kinetic equations only concentration of substances in gaseous or liquid form are written, because concentrations of solid substances are constant, thus, as included in the reaction rate constant.



Kinetic equations are as follows:

$$\text{rate} = kC_{O_2}$$

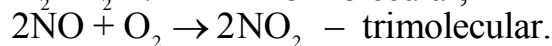
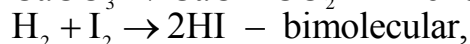
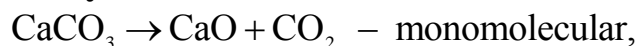
$$\text{rate} = kC_{CO}^2 C_{O_2}$$

Example 4.2. Given the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$. $K = 0.16 \text{ L/mol}\cdot\text{s}$, $C_{H_2} = 0.04 \text{ mol/L}$, $C_{I_2} = 0.05 \text{ mol/L}$. What is chemical reaction rate?

Answer: $\text{Rate} = 0.16 \cdot 0.04 \cdot 0.05 = 3.2 \cdot 10^{-4} \text{ mol/L}\cdot\text{s}$.

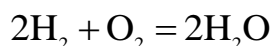
The above kinetic reactions being an analytical expression of the law of mass action are applicable only to ideal systems, in which the stoichiometric equation reflects the reaction mechanism.

In practice the stoichiometric equation does not reflect the reaction mechanism. Only a few chemical reactions are accomplished in one stage. The majority are accomplished in several elementary stage, in which one, two, three molecules may take place. The number of molecules which react simultaneously at the moment of collision accomplishing the act of chemical interaction is called the reaction **molecularity**.



The probability of simultaneous collision of three molecules is 1000 times less than collision of two molecules. Elementary stages of any chemical reaction can be presented as mono- or bimolecular interactions. The rate of multistage reactions is mediated by the rate of its slowest stage.

Thus the observed rate of the reaction:



Does not correspond to the rate predicted by the equation:

$$W = K[H_2]^2[O_2]$$

Experiments have shown that this reaction is rather complicated. It is accomplished in several stages following the chain mechanism.

The exponents of power in a kinetic equation are determined using special methods, they are called reaction order for the respective substance. General order of the reaction equals the sum of power exponents in the equation of chemical reaction rate. For a reaction $aA + bB \rightarrow C$, rate is given by the equation $W = K[A]^x[B]^y$ in which K is the rate constant, $[A]$ and $[B]$ represent concentrations of reactants A and B respectively, and x and y represent orders of reaction with respect to A and B respectively. General order of reaction = $x+y$.

Temperature. The rate of reaction increases with increase of temperature. This can be explained by increased chaotic movement of the molecules which causes increase in the collision number. In 1879 Van't-Hoff formulated an empirical rule:

with temperature elevation by 10 degrees the rate of the chemical reaction increases 2–4 times:

$\text{Rate}_{T_2} = \text{Rate}_{T_1} \cdot \gamma^{\frac{T_2 - T_1}{10}}$, where Rate_{T_2} and Rate_{T_1} – the reaction rate at temperatures T_2 and T_1 respectively, γ – temperature coefficient showing how many times the rate increases at temperature elevation by 10 degrees.

The nature of the reacting substances. The decisive is the type of the chemical bond. For organic substances, main types of bonds are nonpolar or low-polar covalent σ and π -bonds. The reaction with the substances having σ bonds are slower than with those having π -bonds. Inorganic substances which have ionic or polar covalent bond react faster.

Surface area of the reactants. For a reaction involving a solid reactant or catalyst, the smaller is the particle size, the greater is the surface area, the faster is the reaction.

Pressure. For reactions involving gases, increasing of a gas pressure increases its concentration. A given volume contains a greater amount in moles of the gas.

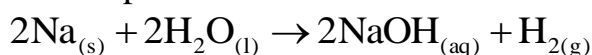
Presence of Catalyst. Catalyst is a substance that increases the rate of a chemical reaction without itself undergoing a permanent change. In case of reversible reactions, catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.

4.3 Chemical Equilibrium

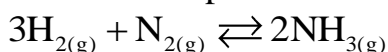
Chemical equilibrium is a state in which the concentrations of reactants and products remain constant over time.

Chemical equilibrium is dynamic in nature in which the forward reaction proceeds at the same rate as the backward reaction.

Reactions that go to completion are **irreversible**.



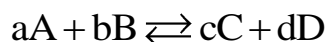
Reactions that do not proceed to completion are **reversible**.



The sign \rightleftharpoons represents the reversibility of a reaction. The reaction from left to right (\rightarrow) is called the **forward** reaction while the reaction from left to right (\leftarrow) is called the **backward** reaction (**reverse**).

A mathematical relationship derived from experiment and verified by theory which describes the equilibrium state is called the **equilibrium constant** expression.

For a reversible reaction at equilibrium:



in which A and B are reactants, C and D are products, and a, b, c, d are the stoichiometric coefficients.

The equilibrium constant is written as:

$$K_{\text{eq}} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}.$$

For the reaction $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$

$$K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]},$$

$$W_f = K_f [\text{H}_2]^3 [\text{N}_2],$$

$$W_b = K_b [\text{NH}_3]^2,$$

$$W_f = W_b = K_f [\text{H}_2]^3 [\text{N}_2] = K_b [\text{NH}_3]^2,$$

$$K_{\text{eq}} = \frac{K_f}{K_b} = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]}.$$

4.4 Le Chatelier's Principle States

When a change is introduced into a chemical system at equilibrium, the system will shift in the direction that counteracts that change.

The changes of pressure influence the equilibrium of the reactions accompanied by changes in the volume. For gas reactions, changes of pressure are equivalent to the changes in the concentration. During the process of ammonium synthesis $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$ which takes place with volume reduction, pressure increase will increase the concentration of the initial substances in greater extent than that of the products. The reaction will shift to the reaction products that are to smaller volume.

At heating the system equilibrium will shift to the side of the endothermic process, at cooling – exothermic.

Catalysts do not shift chemical equilibrium as they accelerate both forward and backward (reverse) reactions. In this case equilibrium will be achieved faster.

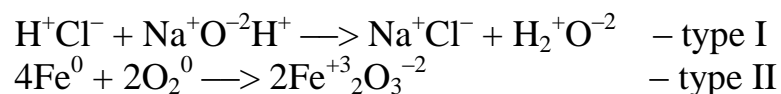
CHAPTER 5

OXIDATION-REDUCTION REACTIONS

- 5.1 Oxidation States (OS).
- 5.2 Oxidation-Reduction: Some Definitions.
- 5.3 Balancing Oxidation-Reduction Equations.

5.1 Oxidation States

The chemical reactions can be divided into two general types: type I reactions, in which the valence shells of the reactants remain unchanged after conversion to products, and type II reactions, in which the valence shells of the reactants are modified by the gain or loss of electrons. Type II reactions are oxidation-reduction or redox reactions.



0, +3, –2 are oxidation states (oxidation numbers).

The oxidation state of an atom is the apparent or real charge that an atom has when all bonds between atoms of different elements are assumed to be ionic.

Rules for determining oxidation state.

1. The oxidation state (oxidation number) of an atom in a free (uncombined) element is zero.
2. The total of the oxidation states of all the atoms in a molecule or formula unit is zero. For an ion this total is equal to the charge on the ion, both in magnitude and sign, and regardless of whether the ion consists of a single atom (monatomic) or two or more atoms (polyatomic).
3. In their compounds the alkali metals (group IA of the periodic table) have an oxidation state of +1, the alkaline earth metals (IIA), +2, and the metals of group III, +3.
4. In its compounds the oxidation state of hydrogen is +1; that of fluorine is –1.
5. In its compounds oxygen has an oxidation state of –2. Exception is $\text{H}_2^{+1}\text{O}_2^{-1}$.
6. In their binary compounds with metals, elements of group VIIA have an oxidation state of –1; those of group VIA, –2; and those of group VA, –3 (binary compounds are comprised of two elements, e.g., KI, MgBr_2 , BaS).

Example 5.1. What is the oxidation state of the underlined atom in each of the following? (a) $\underline{\text{P}}_4$; (b) $\underline{\text{Al}}_2\text{O}_3$; (c) $\underline{\text{Mn}}\text{O}_4^-$; (d) $\text{H}_2\underline{\text{O}}_2$; (e) $\text{K}\underline{\text{O}}_2$.

Answer:

(a) P_4 . This formula represents a molecule of the element phosphorus. For an atom of a free element the oxidation state is 0 (rule 1). The oxidation state of P in P_4 is 0;

(b) Al_2O_3 . The total of the oxidation numbers of all the atoms in a formula unit is 0 (rule 2). The oxidation state of O is –2 (rule 5). The total for three O atoms is –6. The total for two Al atoms is +6. The oxidation state of Al is +3. $3(-2) + 2x = 0$ $x=3$;

(c) MnO_4^- . The total of the oxidation numbers of all the atoms in this ion must be -1 (rule 2). The total of the oxidation numbers of the four O atoms is -8 . The oxidation state of Mn is $+7$;

(d) H_2O_2 . Rule 4, stating that H has an oxidation state of $+1$. The sum of the oxidation number of the two H atoms is $+2$ and that of the two O atoms is -2 . The oxidation state of O in H_2O_2 is -1 ;

(e) KO_2 . The oxidation state of K = $+1$. The sum of the oxidation state of the two O atoms is -1 . The oxidation state of each O atom in KO_2 is $-\frac{1}{2}$.

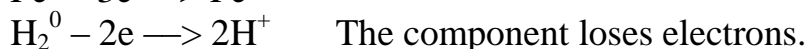
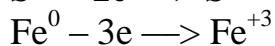
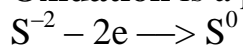
5.2 Oxidation-Reduction: Some Definitions

When an iron object is exposed to the atmosphere, it rusts. A simplified equation is $4\text{Fe}^0 + 3\text{O}_2^0 \longrightarrow 2\text{Fe}_2^+3\text{O}_3^{-2}$.

In this reaction iron combines with oxygen. This is oxidation-reduction reaction.

Reaction in which electrons lost by one of the reaction components are gained by another component are known as **oxidation-reduction or redox reactions**.

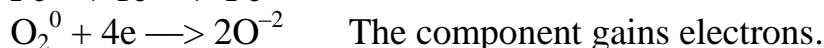
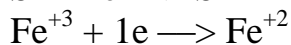
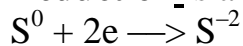
Oxidation is a process in which the oxidation state of some element increases.



The component supplying the electrons is called the **reducing agent** (reductant) (figure 5.1).

Reducing agent (reductant) is a substance that causes reduction and is itself oxidized.

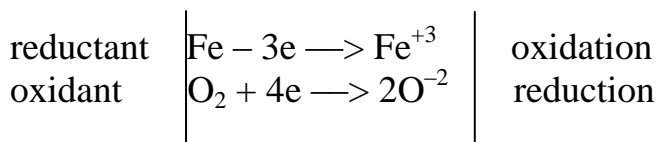
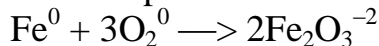
Reduction is a process in which the oxidation state of some element decreases.

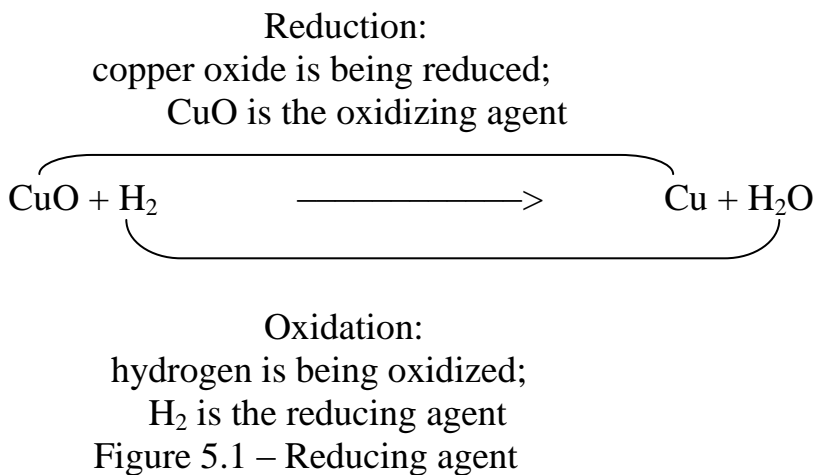
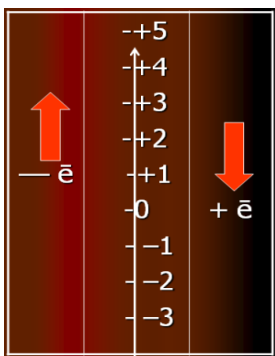


The component receiving the electrons is called the **oxidizing agent** (oxidant).

Oxidizing agent (oxidant) is a substance that causes oxidation and is itself reduced.

The two processes – oxidation and reduction – always occur together.





5.3 Balancing Oxidation-Reduction Equations

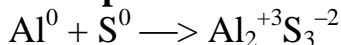
Balancing redox reactions have all the requirements of balancing other types of chemical reactions: mass must be conserved in the transformation. This requires:

1. Atoms of all elements must be conserved.
2. Electrons must be conserved.
3. Total electric charge must be conserved (follows from electrons being conserved).
4. All coefficients must be integers.

For charge to be conserved,

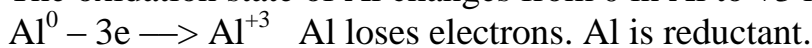
the number of electrons lost in the oxidation must equal the number of electrons gained in the reduction.

Example 5.2. Balance the following equation.



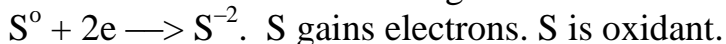
1. Calculate the oxidation state of all elements in the equation.
2. Identify the oxidation and reduction process and write them separately:

The oxidation state of Al changes from 0 in Al to +3 in Al⁺³.



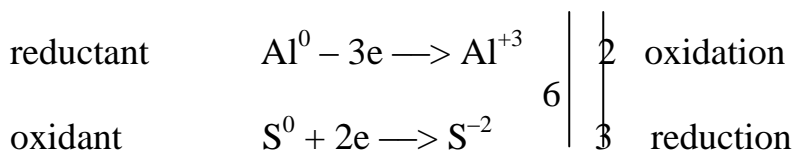
This is a process oxidation.

The oxidation state of S changes from 0 in S to -2 in S⁻².



This is a process reduction.

Write the oxidation and reduction process

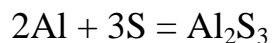


3. The number of e lost in the oxidation must equal the number of e gained in the reduction.

Al⁰ loses 3 electrons. S gains 2 electrons.

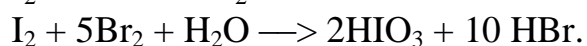
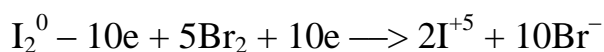
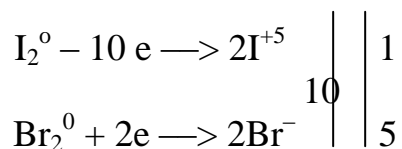
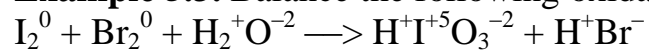
6 is the least common multiple.

2 and 3 are coefficients of Al and S.



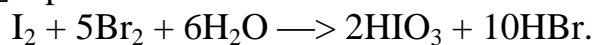
This method is called the **oxidation state change method**.

Example 5.3. Balance the following oxidation-reduction expression.



The remaining coefficient (that of H_2O) is determined by inspection.

There are 12 H atoms on the right and only 2 on the left. The coefficient “6” for H_2O produces a balance of H atoms.



REFERENCES

1. Zavgorodniy I. V. Acid-base equilibrium and complex formation in biological liuids : methodical instruction. – Module 1 / I. V. Zavgorodniy, N. M. Tkachuk, E. K. Grabovetskaya, V. A. Vekshin – Kharkiv : KSMU, 2007. – 152 p.
2. Zavgorodniy I. V. Equilibrium in biological systems at a phase interface : methodical instruction. – Module 2 / I. V. Zavgorodniy, N. M. Tkachuk, E. K. Grabovetskaya, V. A. Vekshin – Kharkiv : KSMU, 2007. – 152 p.
3. Wong Y. C. University General Chemistry. Inorganic and Physical / C. T. Wong, S. O. Onyirukas, L. E. Akpanisi – Manhattan Press (n.k.) LTD. In association with Africana – Fep PublishersLTD, 2002. – 776 p.