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# **GENERAL CHEMISTRY**

## **Training manual**

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О 28

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compiled in accordance with the Federal State Educational Standard within the  
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This training manual sets out theoretical material covering the main sections  
of the general chemistry course for medical schools, provides the necessary  
reference materials and provides a dictionary of the most important physical and  
chemical terms.

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## PREFACE

The book provides an introduction into the General Chemistry. It is necessary for foreign students who are going to pass the Chemistry exam into the ФГБОУ ВО «Майкопский государственный технологический университет» in English.

This textbook is intended for use in one-semester or full-year course in medical universities. The principles of general chemistry are presented from the viewpoint of their application to chemical and biochemical systems.

The chapters follow a generally accepted sequence. Chapter 1 studies the laws of thermodynamics and deals with thermochemical calculations. Chapters 2 and 3 present the laws of chemical kinetics and discuss the main features of enzymatic reactions. Chapter 4 presents chemical equilibrium, while chapter 5 take up the introduction into volumetric analysis. As a group, chapters 6–7 deal with physical properties of solutions, emphasizing acid-base and electrochemical equilibria in aqueous solutions, chapter 8 take up the electrochemistry.

At the end of each chapter, we provide material designed to engage you in active learning. The end of chapter exercises consist of questions and problems.

At the end of the textbook involves data about physiochemical properties of chemical substances that are required to do problems and discuss processes. Then, at the end of the textbook, there is a Glossary where each of the key terms is defined.

# CHAPTER 1. CHEMICAL THERMODYNAMICS

**After studying this section, you will**

- define energy, heat, work and three types of thermodynamic systems;
- understand the difference between state and path functions;
- be able to define the first law of chemical thermodynamics for isolated, opened and closed systems;
- ready to calculate standard enthalpies of chemical reactions using the Hess law;
- define the second law of chemical thermodynamics; give thermodynamical and statistical definition for entropy;
- describe spontaneous and nonspontaneous process;
- calculate free Gibbs energy changes for different types of processes;
- discuss the main problems of bioenergetics.

## *1.1 Main definitions of chemical thermodynamics*

Chemical thermodynamics is a branch of chemistry studying energy, heat and work transformation in the process of chemical reactions. It's a theoretical base for bioenergetics, thermochemistry, thermophysiology and other sciences dealing with energy exchange between biosystems and their surroundings.

**Energy (E)** is defined as a capacity to do work or to produce changes. The main types of Energy are: (a) potential - energy of position; (b) kinetic - energy of motion. According to the types of useful work Energy can be classified as electrical, mechanical, chemical, surface energy and some others.

**Heat (Q)** is a process in which energy is transferred from one system to another as a result of temperature difference between them.

**Work (A)** in mechanics is by times distance:

$$A = f \times dl \quad 1.1$$

In thermodynamics work becomes a more subtle concept; it encompasses a broader range of processes, including surface work, electrical work, work of magnetization, and so on (table 1.1)

All types of work except work of gas expansion are assumed to be useful **work (A)**. The most common forms of useful work done in a human body are:

- mechanical work of muscles;
- osmotic work of kidneys;
- electrical work of nerve tissue.

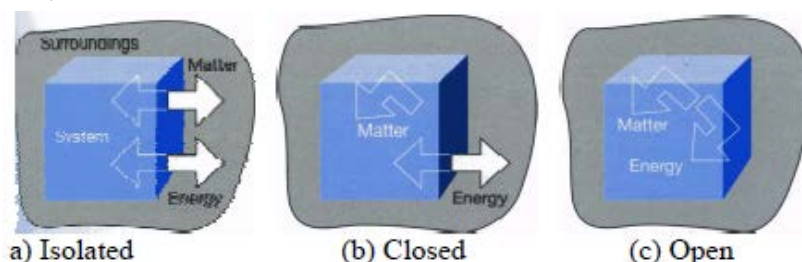
**Table 1.1 — Different types of Work**

| Type of Work       | Expression*        | Meaning of symbols  |
|--------------------|--------------------|---|
| Mechanical work    | $f \times dl$      | f: force; dl: distance traveled                               |
| Surface work       | $\sigma \times dA$ | $\sigma$ : surface tension; dA: change in area                |
| Electrical work    | $E \times dQ$      | E: potential difference; dQ: electric charge                  |
| Gravitational work | $mg \times dh$     | m: mass; g: acceleration due to gravity; dh: change in height |
| Expansion work     | $P \times dV$      | P: pressure; dV: change in volume                             |

\* The work done in each case corresponds to an infinitesimal process, as indicated by the d symbol.

**Thermodynamic systems** are the objects of thermodynamic investigations. They are defined as a part of Universe separated from its surroundings by a thermodynamics cover (real or abstract). There are three types of systems:

- **isolated systems**, which can exchange neither energy nor matter with their surroundings (fig. 1.1-a);
- **closed systems** can exchange energy with the surroundings, but they cannot exchange matter, e.g. ampoule with a drug (fig. 1.1-b).
- **open systems** can exchange matter and energy with their surroundings. A human body, a living cell and other biological systems are bright examples of open systems. For example, for 40 years a person consumes about 40 tons of water, approximately 12 millions litres of oxygen and about 10 thousand bars of chocolate. He also drops 69 L of tears (fig. 1.1-c).



**Figure 1.1 — Thermodynamic systems**

The descriptions of a system include:

- a set of ***thermodynamic parameters***, such as temperature, pressure, volume, mass and others;
- a set of ***thermodynamic functions***, which characterize energy of a system and its ability to do work. There are two types of functions:

Thermodynamic functions are:

(a) ***state functions***. Their changes depend upon the energy state of reactants and products and don't depend upon a number of intermediate steps.

(b) ***path functions***. Their changes depend upon a number of intermediate steps. For example: heat -  $Q$  or work -  $A$ .

The most important ***state functions*** of a system are:

- ***internal energy*** ( $U$ ) - the total energy of a system composed of kinetic and potential energy of all its structural units;
- ***enthalpy*** or ***heat content*** ( $H$ ) - a part of system's internal energy that can be converted into heat;
- ***Gibbs free energy*** ( $G$ ) - a part of system's internal energy that can be converted into useful work;
- ***entropy*** ( $S$ ), which characterizes on one hand characterizes the heat that cannot be converted into useful work, and on the other hand, randomness and disorder in the system.

## ***1.2 The First Law of chemical thermodynamics***

***Helmholts*** formulated ***the First Law of thermodynamics in 1847***: «*The total quantity of energy in the universe is assumed to remain constants*».

This statement is generally known as the law of energy conservation. In other words, energy is neither created nor destroyed in any process, although it may be transferred from one body to another or converted from one form into another. The First Law can't be proved theoretically but it was confirmed by all experience of people humanity. For example, ***perpetual motion machine*** of the first type is impossible (it is a machine which fulfills work due to energy absorption from the surroundings).

Let's review the analytical description for the First Law for three types of thermodynamic systems:

1. The internal energy of an *isolated system* is constant:

$$U = \text{const}, \Delta U = 0 \quad 1.2$$

2. Heat absorbed by a *closed system* increases its internal energy and is used to do work:

$$Q = \Delta U + A \quad 1.3$$

or

$$Q = \Delta U + A' + p\Delta V \quad 1.4$$

where  $Q$  - is the heat absorbed by a system, kJ;  $A'$  - is a useful work produced in a system, kJ;  $p\Delta V$  - the work of gas expansion, kJ.

When a process is isobaric ( $p = \text{const}$ ) and useful work is not produced ( $A'=0$ ) the equation (1.1) may be rearranged as follows:

$$Q = \Delta U + p\Delta V \quad 1.5$$

where

$$\Delta H = \Delta U + p\Delta V \quad 1.6$$

Hence  $Q = \Delta H$ , thus change in the enthalpy ( $\Delta H$ ) *has a sense of heat of an isobaric chemical reaction*.

3. Internal energy of an *open system* is increased by heating and adding some amount of a substance into it:

$$\Delta U = Q \pm \mu\Delta v - A \quad 1.7$$

where  $\mu$  - proportionality coefficient named chemical potential;  $\Delta v$  - change in chemical amount of substances, mol.

### 1.3 Thermochemistry

Thermochemistry is a branch of chemical thermodynamics dealing with *the heat of chemical reactions*. The heat of a reaction can be defined as the heat change in the transformation of reactants at some temperature and pressure to products at the same temperature and pressure. For an isobaric process, the heat of a reaction is equal to the enthalpy change of the reaction  $\Delta_r H$ , where the subscript  $r$  denotes reaction.

The heat of reactions may be determined experimentally or calculated on the base of ***the Hess's law (1840): the heat of an isobaric chemical reaction does not depend upon a number of intermediate steps, but depends upon the energy state of reactants and products.***

Application of ***the Hess's Law:***

**(a) *The reaction enthalpy in terms of enthalpies of formation***

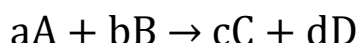
***The standard molar enthalpy of formation of the substance*** ( $\Delta_f H^0_{298}$ ) is the standard reaction enthalpy for the formation of one mole of a compound from its elements in their reference state. The reference state of an element is the most stable state at the specified temperature 298K and pressure 101.3 kPa. For elements at their stable state standard enthalpy of formation is assumed to be zero.

In general, the enthalpy change of a chemical reaction can be thought of as the total enthalpy of products' formation minus the total enthalpy of reactants' formation:

$$\Delta_r H = \sum v \Delta_f H_{(\text{products})} - \sum v \Delta_f H_{(\text{reactants})} \quad 1.8$$

where  $v$  - is a stoichiometric coefficient.

For a hypothetical chemical reaction:



the standard enthalpy of a reaction ( $\Delta_r H^0_{298}$ ) can be calculated as follows:

$$\Delta_r H = c \times \Delta_f H(C) + d \times \Delta_f H(D) - a \times \Delta_f H(A) + b \times \Delta_f H(B)$$

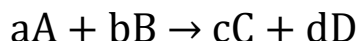
**(b) *The reaction enthalpy in terms of enthalpies of combustion***

***The standard molar enthalpy of combustion of a substance*** ( $\Delta_{\text{com}} H^0_{298}$ ) is a standard reaction enthalpy of one mole of the substance oxidation in pure oxygen up to the highest oxides. In general, the enthalpy change of a chemical reaction can be thought of as the total enthalpy of reactants' combustion minus the total enthalpy of products' combustion:

$$\Delta_r H = \sum v \Delta_{\text{com}} H_{(\text{reactants})} - \sum v \Delta_{\text{com}} H_{(\text{products})} \quad 1.9$$

where  $v$  - is a stoichiometric coefficient.

For a hypothetical chemical reaction:

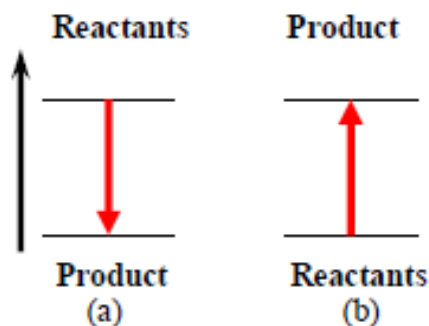


the enthalpy of a reaction ( $\Delta_r H$ ) can be calculated as follows:

$$\Delta_r H_{298}^0 = a \times \Delta_{\text{com}} H(A) + b \times \Delta_{\text{com}} H(B) - c \times \Delta_{\text{com}} H(C) + d \times \Delta_{\text{com}} H(D)$$

When  $\Delta_r H < 0$ , the reaction is exothermic (heat is released by a system), when  $\Delta_r H > 0$ , the reaction is endothermic (heat is absorbed by a system) (fig. 1.2).

Thermochemistry is a theoretical base for dietology. Thermochemical properties of foods are discussed in terms of their *specific enthalpy*, the magnitude of the enthalpy of combustion per gram of matter. The specific enthalpy of carbohydrates, which are the main source of energy for a human body, is about 16.7 kJ/g.



**Figure 1.2 — Enthalpy changes for (a) an exothermic reaction, (b) an endothermic reaction**

The specific enthalpy of lipids is much greater, of about 37.6 kJ/g. Lipids are commonly used as an energy store, to be used only when more readily accessible carbohydrates have fallen into short supply.

Proteins are also used as a source of energy, but their components, amino acids, are often too valuable to squander in this way, and are used to contract other proteins instead. When proteins are oxidized to urea, the equivalent specific enthalpy is comparable to that of carbohydrates.

Various foods have different compositions and hence different energy contents (table 2). Many labels on food packages show the caloric content of the food. The calorie (cal) is a non-SI unit of energy where 1 cal = 4.184 J.

Daily Requirements in Energy depend upon muscle activity of a person:

- easy muscle work - 2500 kcal;
- average muscle work (students, doctors and some others) - 3500 kcal;
- hard muscle work - 4500 kcal;
- especially hard muscle work (sportsmen) — 7000 kcal.

High muscle activity increases energy requirements by 30-50 %. They are also increased by serious diseases of patients. Thus rheumatoid arthritis increases in energy requirements up to 10 %. High mental activity doesn't require increase in energy. Brain constantly oxidizes 5-6 g of glucose.

**Table 1.2 — Fuel values of food products**

| Food product | Content, % |        |               |                  | Heat content kJ/kg |
|--------------|------------|--------|---------------|------------------|--------------------|
|              | proteins   | lipids | carbohydrates | H <sub>2</sub> O |                    |
| Bread        | 6.3        | 1.3    | 46.1          | 43.9             | 9500               |
| Noodle       | 11.0       | 0.9    | 74.2          | 13.6             | 14980              |
| Sugar        | -          | -      | 99.9          | 0.1              | 17150              |
| Butter       | 0.5        | 83.0   | 0.5           | 16.0             | 32470              |
| Beaf         | 18         | 10.5   | -             | 71.3             | 7150               |
| Potatoes     | 2.0        | -      | 21.0          | 76               | 3930               |
| Apples       | 0.4        | -      | 11.3          | 87               | 2130               |

Increase in the energy of food products and decrease in physical activity are responsible for obesity. Obesity is a noninflectional epidemic of the 21 century. 300 million people in the world suffer from obesity. In highly developed countries their number is 30 % of the total population. Obesity increases the risk of heart and oncological diseases, diabetes mellitus.

### ***1.4 The Second Law of chemical thermodynamics***

***The Second Law*** of thermodynamics deals with the spontaneity of processes in nature:

- ***spontaneous processes*** proceed without absorbing energy from the surroundings; they run up to the equilibrium state. They are dissolving, diffusion, osmosis, all types of explosion and many other reactions and processes.

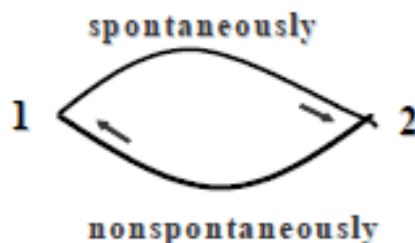
- ***nonspontaneous processes*** proceed by absorbing energy from the surroundings. They are photosynthesis, electrolysis and some other.

***Thermodynamic equilibrium*** is a state of a system characterized by constant thermodynamic parameters ( $T$ ,  $p$ ,  $V$  and others) in all the points of its volume. The system in equilibrium state is not able to produce useful work.

Equilibrium state is maintained only in isolated and closed systems. It can't be achieved in open systems because of permanently changing outer conditions.

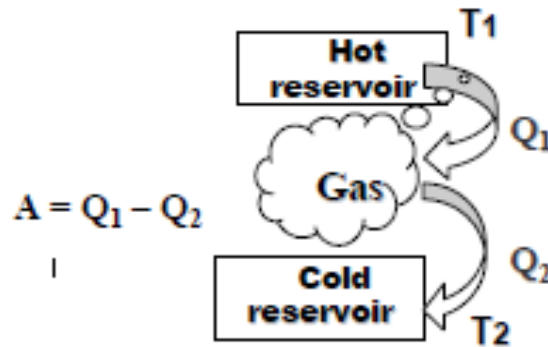
***Stationary state*** of an open system is an analogue for its equilibrium state. Stationary system is characterized by thermodynamic parameters which remain constant for a long period of time with simultaneous ability to produce useful work. The balanced flow of heat and substances inside and outside a system is responsible for stationarity of an open system. All biological systems, including human body, are defined as open systems at their stationary state.

The main feature of processes in nature is their asymmetry: they run spontaneously only in one direction. When a forward process proceeds spontaneously, a reverse process runs nonspontaneously:



A lump of sugar spontaneously dissolves in a cup of coffee, but dissolved sugar does not spontaneously reappear in its original form. Water runs downhill but never up spontaneously. A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas. However, hydrogen gas and sodium hydroxide do not interact to form water and sodium. We witness many of these spontaneous processes in everyday life. A type of a process (spontaneous or nonspontaneous) can be predicted within the Second Law of Chemical Thermodynamics.

The Second Law was developed by French physicist Sadi Carnot when he studied heat engine work. Heat engines are machines that convert heat energy into mechanical work. Steam locomotives, steam turbines and internal combustion engines in automobiles play an essential role in our technological society.



**Figure 1.3 — A scheme of an ideal heat engine**

An ideal heat engine is composed of a hot reservoir with the temperature  $T_1$ , a cold reservoir with the temperature  $T_2$  and gas or vapor referred to as a working body. When the heat engine is working the gas is reversibly heated and then cooled. A step of gas expansion is followed by a step of its compression, thus the working body fulfills mechanical work.

### ***Carnot's Theorems***

1) The heat engines' efficiency depends upon temperatures of hot and cold reservoirs and doesn't depend upon the nature of gas.

2) The efficiency of heat engines can't exceed unity. Carnot's Equation is:

$$\text{Efficiency} = \frac{A}{Q_h} \leq \frac{T_1 - T_2}{T_1} \quad 1.10$$

Since  $T_2 \neq 0$ , (absolute zero can't be achieved), efficiency  $< 1$

The efficiency of modern heat engines is rather low: for steam locomotives it is about 20 %, for internal combustion engines in automobiles ~30 %. It was proved experimentally that the efficiency of the chemical energy of food conversion in a human body is approximately 25 %, the efficiency of ATP conversion into muscle work ~50%, the efficiency of healthy heart ~43%.

***The Second Law may be defined in several ways:***

***- it is impossible to extract the amount of heat from a hot reservoir and use it all to do work. Some amount of heat must be exhausted to the cold reservoir*** (Kelvin-Planck's statement);

***- it is impossible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow*** (Clausius's statement);

***- a perpetual motion machine of the second type is impossible*** (it is a heat engine of which efficiency is equal to unity).

The mathematical description of the Second Law involves a state ***function named Entropy (S, J/K)***. The term «Entropy» was invented by Clausius in 1865.

Clausius defined entropy as heat absorbed by a system, divided by the absolute temperature of the system at the time the heat was absorbed:

$$s = \frac{Q}{T} \quad 1.11$$

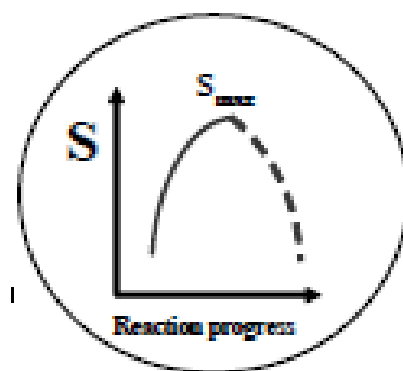
Entropy is the only state function which can be defined in two different ways: (a) thermodynamical, (b) statistical.

***Thermodynamic definition of entropy is:*** «Entropy is a quantitative measure of the amount of thermal energy not available to do work». In other words entropy is a measure for «**waste energy**» which dissipates to the surroundings and is not available to produce useful work. The higher entropy is, the lower the efficiency of a process is.

The Clausius inequality is considered to be the mathematical description of the ***Second Law***:

$$s \geq \frac{Q}{T} \quad 1.12$$

Isolated systems do not absorb energy ( $Q = 0$ ), hence  $\Delta S \geq 0$  thus entropy of an isolated system constantly increases up to its maximum value (fig. 1.4).

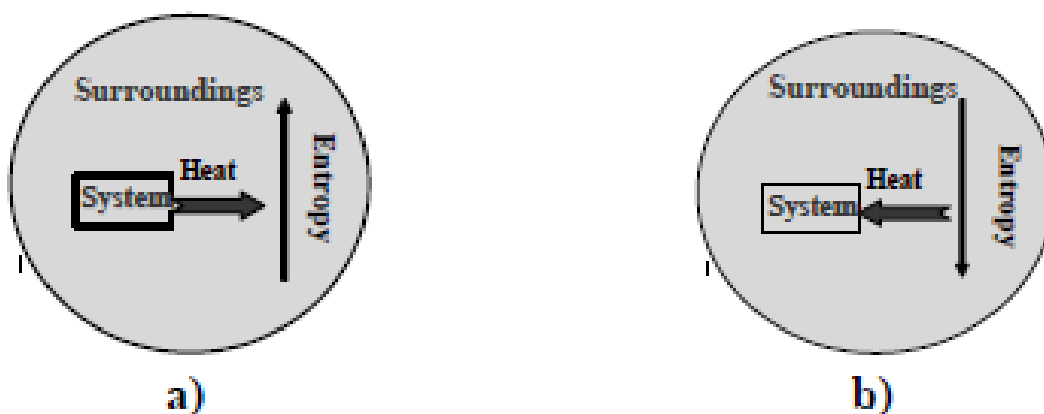


**Figure 1.4 — Change in entropy in isolated systems**

Assuming that the Universe is an isolated system Clausius gave the following combined definition for *the first and second laws of thermodynamics*: «*The energy of the universe is constant, the entropy increases toward the maximum*».

In such a way Clausius postulated the *Entropy death* of the Universe: it will be destroyed not being able to produce useful work; its efficiency will become zero.

Closed and open systems do not tend to entropy maximum because they exchange entropy with their surroundings (fig. 1.5).



**Figure 1.5 — (a) In an exothermic process heat is transferred from the system to the surroundings and as a result the entropy of the surrounding increases.**

**(b) In an endothermic process heat is absorbed from the surroundings and thereby the entropy of the surroundings decreases**

One of the most profound and original treatments of entropy is that of the nobel prize-winning chemist Ilya Prigogine. He studied thermodynamics of open systems and came to the belief that open stationary systems are attracted to the state of minimum entropy

production, i.e. The state where the smallest amount of disorder is produced and the least amount of energy is wasted (Prigogine's theorem).

In other words, all changes in stationary systems proceed slowly. Prigogine's theorem gives reason for homeostasis: constant parameters of a human body. This statement is not applicable to babies because changes in their bodies are rather fast.

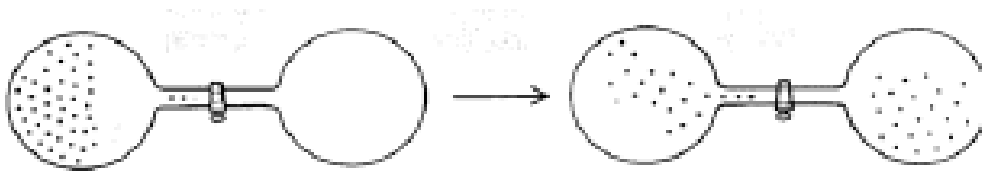
Statistical definition of entropy was proposed by the great Austrian physicist Ludwig Boltzmann in 1904. ***Entropy is a measure of disorder or randomness in a system.*** It's a negative concept, this time the opposite of organization.

**Statistical thermodynamics** derives energy state of a system from energy state of its structural units. ***Boltzmann's equation*** is considered to be another mathematical description of the second law:

$$S = k \times \ln W \quad 1.13$$

where  $k$  - the Boltzmann's coefficient ( $k = 1.38 \times 10^{-23} \text{ j/k}$ );  $W$  - thermodynamics probability or a number of microstates a system can be described. A microstate is an energy state of a structural unit of a system. The greater the number of microstates is, the higher disorder or randomness in a system is.

Consider a cylinder filled with compressed air and connected to an evacuated vessel (fig. 1.6).

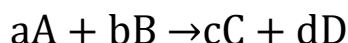


**Figure 1.6 — Spontaneous processes**

When the valve of the cylinder is opened, gas will pour from it and distribute itself evenly throughout the volume of the vessel, so that the system changes from a more ordered state to a less ordered one. This experiment proves the boltzmann's statement for the second law of thermodynamics: «total disorder increases in any spontaneous process».

As all statistical laws, the second law is not available for systems which contain a small and a huge number of structural units. The deviations from this law are known as fluctuations.

The entropy change for a chemical reaction ( $\Delta_r S, \text{J/K}$ ) may be calculated on the base of the Hess law, using *the standard molar entropy* of reactants and products ( $S, \text{J/mol}\times\text{K}$ ). For a hypothetical chemical reaction:



the change in entropy ( $\Delta_r S$ ) can be calculated in the following way:

$$\Delta_r S = c \times S(C) + d \times S(D) - a \times S(A) + b \times S(B) \quad 1.14$$

### 1.5 Calculating free energy changes

Two tendencies operate simultaneously during chemical reactions: (a) a tendency for particles to unite into more complicated systems which reduces enthalpy ( $H \rightarrow \min$ ); (b) a tendency for particles to separate, which increases entropy ( $S \rightarrow \max$ ). The total effect of these two opposing tendencies in processes taking place at constant temperature and pressure is reflected by a state function known as Gibbs free energy (Gibbs potential or isobaric isothermal potential):

$$G = H - TS \quad 1.15$$

The combined review of the first and second laws gives opportunity to calculate free energy change in a closed system:

$$\begin{cases} Q = \Delta U + p\Delta V + A' \\ \Delta S = \frac{Q}{T} \end{cases}$$

Rearrange this to get:

$$A' = T\Delta S - \Delta U - p\Delta V = T\Delta S - (\Delta U + p\Delta V)$$

where

$$\Delta U + p\Delta V = \Delta H$$

Thus

$$A' = -(\Delta H - T\Delta S)$$

that is why

$$\Delta H - T\Delta S = \Delta G \quad 1.16$$

Hence  $A' = -\Delta G$ , and free energy change has a sense of useful work fulfilled by a system or under a system.

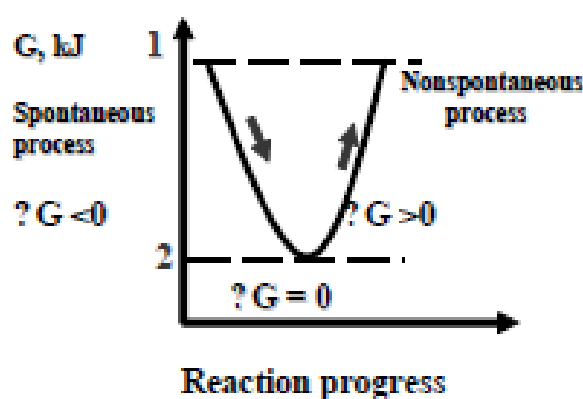
The sign of  $\Delta G$  is a criterion for reactions' spontaneity.

Spontaneous process:  $A' > 0$ ,  $\Delta G < 0$

Equilibrium state:  $A' = 0$ ,  $\Delta G = 0$

Nonspontaneous process:  $A' < 0$ ,  $\Delta G > 0$

Thus, we can make a conclusion that all spontaneous processes run with the decrease of free energy of a system. This statement can be represented in a graph form (fig. 1.7).



**Figure 1.7 — Energy profile of spontaneous and nonspontaneous processes**

Sometimes it is possible to change the character of a reaction by altering thermodynamic parameters of a system: temperature, pressure, concentration of substances. The effect of temperature on spontaneity of different processes is given in table 1.3.

**Table 1.3 — Temperature effect on  $\Delta G$  of a reaction**

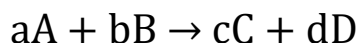
| $\Delta H$ | $\Delta S$ | $\Delta G$   |
|------------|------------|--|
| +          | +          | Positive at low temperatures; negative at high temperatures. Reaction spontaneous at high temperatures |
| +          | -          | Positive at all temperatures. Reaction nonspontaneous at all temperatures                              |
| -          | +          | Negative at all temperatures. Reaction spontaneous at all temperatures                                 |
| -          | -          | Negative at low temperatures; positive at high temperatures. Reaction spontaneous at low temperatures  |

When calculating  $\Delta G$ , we can determine:

- the direction of a spontaneous process;
- the amount of useful work produced by a system in the result of a spontaneous process.

***There are several methods to calculate Gibbs free energy changes:***

1. Calculating free energy change of chemical reactions ( $\Delta_r G$ ) on the base of the Hess law, using the standard molar free energy of formation ( $\Delta_f G$ , kJ/mol). For a hypothetical chemical reaction:



the change in free energy ( $\Delta_r G$ ) can be calculated in the following way:

$$\Delta_r G = c \times \Delta_f G(C) + d \times \Delta_f G(D) - a \times \Delta_f G(A) + b \times \Delta_f G(B) \quad 1.17$$

2. Calculating free energy change of chemical reactions ( $\Delta_r G$ ) on the base of the equation 1.16.

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

3. Calculating free energy change of chemical reactions ( $\Delta_r G$ ), using the equation referred to as an isotherm of a chemical reaction.

- for reactions running in liquid solutions:

$$\Delta_r G = \Delta_r G^0 + R \times T \times \ln \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \quad 1.18$$

where [A] and [B] - molarity of reactants, [C] and [D] - molarity of products, mol/L.

- for reactions running in gaseous phases:

$$\Delta_r G = \Delta_r G^0 + R \times T \times \ln \frac{P^c(C) \times P^d(D)}{P^a(A) \times P^b(B)} \quad 1.19$$

where P - partial pressure of a gas in a mixture.

4. Calculating free energy change in processes of substances transporting against their concentration gradient:

$$\Delta_r G = v \times R \times T \times \ln \frac{[A]_{ph2}}{[A]_{ph1}} \quad 1.20$$

where [A] ph2 and [A] ph1 are molarity of a substance in different phases.

$$[A]_{ph2} > [A]_{ph1}$$

Calculating free energy change is essential for biosystems since makes it possible to understand deeply the sense of biochemical reactions. For example equation (20) can be applied to calculate osmotic work produced by kidneys.

## 1.6 Bioenergetics

**Bioenergetics** is thermodynamics of biological systems. It deals with energy, heat and work exchange in plants, animals and human bodies. A human body is an open stationary system. Its main source of energy is chemical energy of food products (99 %). Carbohydrates are responsible for 55-60 %, lipids - 20-25 %, and proteins - 15-20 % of energy.

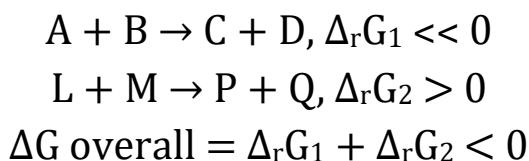
In general efficiency of food chemical energy conversion in a human body is approximately 25 %. Thus waste energy dissipated into surroundings is 75 %. 20 liters of water can be boiled if focused daily waste energy of one person.

Biochemical reactions are chemical reactions which proceed *in vivo*. They are:

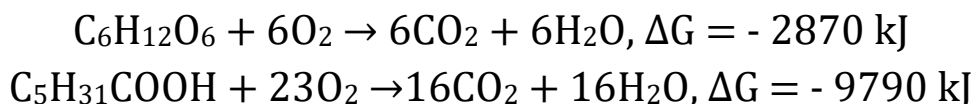
- exergonic (spontaneous)  $\Delta_r G < 0$
- endergonic (nonspontaneous)  $\Delta_r G > 0$

Many biochemical reactions are endergonic, but in some cases they can be carried out to an appreciable extent by coupling them with an exergonic reaction.

A coupled reaction is a process in which an endergonic reaction is made to proceed by coupling it to an exergonic reaction. Biologically coupled reactions are usually mediated with the aid of one enzyme. A scheme of a coupled reaction can be represented as follows:



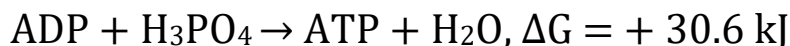
Carbohydrates and lipids metabolism involves highly spontaneous oxidation reactions:



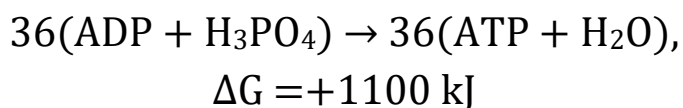
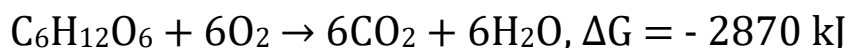
Some of this energy is released as heat that maintains constant body temperature. Another portion is stored in high- energy molecules that a body uses as «power sources» for numerous reactions that occur within cells. The most immolecules is adenosine triphosphate (ATP).

Adenosine triphosphate (ATP) is a high - energy triphosphate ester used in living systems to provide chemical energy for metabolic needs.

The synthesis of ATP molecules from ADP and phosphoric acid is nonspontaneous under physiological conditions:



In cells ATP production is coupled with glucose oxidation. One molecule of glucose can convert as many as 36 ADP molecules into ATP molecules as it is oxidized to  $\text{CO}_2$  and water:



---

$$\Delta G_{\text{overall}} = - 2870 + 1100 = - 1770 \text{ kJ}$$

Although 1100 kJ of energy is stored in this coupled process, 1770 kJ of energy is «wasted». Efficiency of the process is:  $e = 1100/2870 = 0.38$  or 38 %.

Thus cells harness 38 % of the chemical energy stored in glucose to drive the biochemical machinery of metabolism. The remaining 62 % of energy is dissipated as heat.

### ***1.7 Exercises for the self-control***

#### **Discussion questions:**

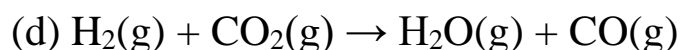
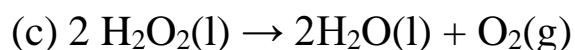
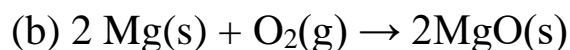
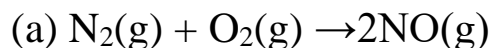
1. Provide definitions of energy, heat and work.
2. Compile a list of as many state functions as you can identify.
3. The evolution of life requires the organization of a very large number of molecules into biological cells. Does the formation of living organisms violate the Second Law of thermodynamics? State your conclusion clearly and present arguments to support it.
4. Each of the following statements is false. Rewrite that each makes a correct statement about free energy:
  - (a) In any process at constant T and P, the free energy of the universe decreases.
  - (b) When T changes during the process, the free energy of the system always decreases.
  - (c)  $\Delta_r G > 0$  for any spontaneous process.

(d)  $\Delta_r G = \Delta_r H + T \times \Delta_r S$ .

5. A certain reaction is known to have  $\Delta_r G$  value of -122 kJ. Will the reaction necessarily occur if reactants are mixed together?

6. According to the second law of thermodynamics, the entropy of an irreversible process in an isolated system must always increase. On the other hand, it is well known that the entropy of living systems remains small. (For example, the synthesis of protein molecules from individual amino acids is a process that leads to a decrease in the entropy.) Is the second law invalid for living systems? Explain.

7. Without referring to any table, predict whether the entropy change is positive, nearly zero, or negative for each of the following reactions:



## CHAPTER 2. THE RATES OF CHEMICAL REACTIONS. ENZYME KINETICS.

**After reading this chapter, you should be able to:**

- define rates of homogeneous and heterogeneous reactions;
- describe mechanism and molecularity of chemical reactions;
- discuss rate laws and rate constants;
- describe temperature dependence of the reactions rate.
- define catalysis and its general principles;
- describe the characteristics of enzymatic reactions from the viewpoint of energy and equilibrium;
- discuss enzyme kinetics based on the Michaelis-Menten equation and the significance of the Michaelis constant;
- define enzyme activity or turnover number;
- describe the factors affecting enzymatic reactions.

### *2.1 Rate and mechanism of chemical reactions*

Chemical kinetics is a branch of chemistry dealing with the rates and mechanisms of chemical reactions. Kinetic method of investigation is widely used for studying natural processes.

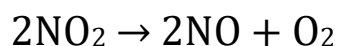
Average rate *of homogeneous reactions* (reactions proceeding in a uniform medium) is defined as the change in the concentration of reactants or products per unit time:

$$\text{Rate}(\theta) = \pm \frac{[A] - [A]_0}{\tau} \quad 2.1$$

where  $\tau$  - time, s., min., hours;  $[A]_0$  - initial molar concentration, mol/l;  $[A]$  - final molar concentration.

A negative sign appears in the equation to make the rate positive, even though substance A concentration decreases with time.

For a chemical reaction



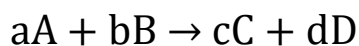
the rate ( $\nu$ ) of  $\text{NO}_2$  consumption is equal to

$$\nu = - \frac{[\text{NO}_2] - [\text{NO}_2]_0}{\tau}$$

The rate of  $\text{O}_2$  production can be calculated as

$$\nu = \frac{[\text{O}_2] - [\text{O}_2]_0}{\tau}$$

In general, for the chemical reaction



the rate is given by

$$\text{Rate}(\vartheta) = -\frac{1}{a} \frac{d[A]}{d\tau} = -\frac{1}{b} \frac{d[B]}{d\tau} = \frac{1}{c} \frac{d[C]}{d\tau} = \frac{1}{d} \frac{d[D]}{d\tau} \quad 2.2$$

where the expressions in brackets refer to the concentrations of the reactants and products at time  $\tau$  after the start of the reaction.

For *heterogeneous reactions* (reactions proceeding in nonuniform medium) an average rate is defined as a change in moles of reactants and products per unit time per unit area of an interface surface:

$$\text{Rate}(\vartheta) = \pm \frac{\vartheta(A) - \vartheta_0(A)}{\tau \times S} \quad 2.3$$

where  $\tau$  - time, s., min., hours;  $\vartheta_0(A)$  - initial amount of a substance, mol.;  $\vartheta(A)$  - final amount of a substance, mol.;  $S$  - an interface surface,  $m^2$ .

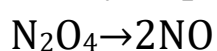
The rate of chemical reactions depends upon:

- nature of reactants;
- their physical state;
- nature of solvents (for reactions in solutions);
- concentration of reactants;
- pressure (for gaseous reactants);
- temperature;
- catalyst;
- some other external factors.

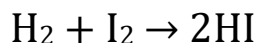
The rates of chemical processes in vivo differ greatly. The time of the total renewal of bone tissue is 4-7 years, the time of a half proteins renewal - 70 days, chemical reactions responsible for neural activity run instantly.

Each reaction involves a huge number of collisions among molecules of reactants. An elementary step is a collision of reactants' particles which produce molecules of a product. A *reaction mechanism* is a sequence of elementary steps that leads to product formation. Each step in such a sequence is called an elementary reaction. *Elementary reactions can be:*

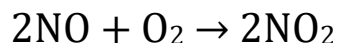
(a) *unimolecular*: an elementary step involves one molecule



(b) **bimolecular**: an elementary step involves two molecules



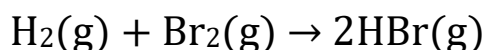
(c) **termolecular**: an elementary step involves three molecules



A number of molecules involved in elementary step is defined as molecularity. **Molecularity** can't exceed three since probability of four particles collision is negligibly low.

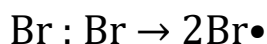
If a reaction mechanism involves only one elementary reaction it is known as simple, but most reactions involve several elementary reactions (they are complex). The largest number of steps is involved in **chain** or **radical reactions** which generate free radicals as intermediates. Free radicals are particles with unpaired electron. They are generated in case of photolysis, thermolysis and oxidation-reduction reactions.

One of the best known gas-phase chain reactions involve is the formation of hydrogen bromide from molecular hydrogen and bromine between 230°C and 300°C:

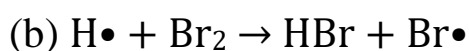
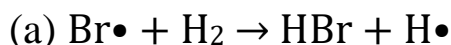


We assume the following mechanism for a process:

1) Chain initiation (unimolecular step)



2) Chain propagation (involves two bimolecular steps):



3) Chain termination (involves three bimolecular steps):



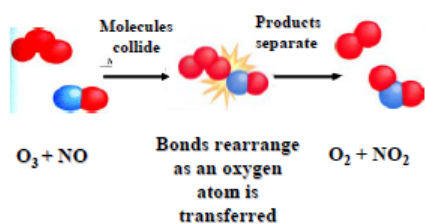
Radical reactions proceed in vivo under the affect of different free radicals  $\text{OH}\bullet$ ,  $\text{HOO}\bullet$ ,  $\text{ROO}\bullet$ ,  $\text{O}_2\bullet$  and some ones. Scientists came to the belief that accumulation of free radicals in intracellular fluids is one of the reasons for aging.

Rate of radical reactions can be increased greatly under the influence of radiation. Even small dozes of radiation can accelerate generation of free radicals. Free radicals cause the destruction of cell

membranes, suppress immune system of people, and cause different diseases. Radical reactions can be retarded by antioxidant substances: vitamins A, E, C and selenium compounds.

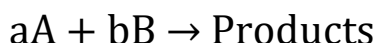
## 2.2 Rate Laws and rate constants

The rate of homogeneous reaction depends on a number of collisions of the reacting particles per unit time. The number of collisions, in turn, is directly proportional to the concentration of the reactants (fig. 2.1).



**Figure 2.1 — The reaction between ozone and NO is believed to occur by a mechanism that consists of the single bimolecular step shown here in a molecular view**

Thus the rate of a reaction is directly proportional to the reactants' concentration raised to a power. For a hypothetical chemical reaction



the rate can be expressed as

$$\text{Rate}(\theta) = k \times [A]^x \times [B]^y \quad 2.4$$

This equation, known as the **rate law**, tells us that the rate of a reaction is not constant; its value at any time (x) is proportional to the concentrations of A and B raised to a power. These powers are the orders of a reaction by reactants. The sum of powers is called the **overall reaction order (n)**:  $n = x + y$ .

The order of a reaction can be determined experimentally. Only for simple reactions their order coincides with coefficients in chemical equations,  $k$  is a **rate constant** which depends upon temperature and nature of substances and doesn't depend upon their concentrations.

**Zero-order reactions.** The Rate Law for a zero-order reaction of the type



is given by

$$-\frac{d[A]}{dt} = k \times [A]^0 = k \quad 2.5$$

The quantity  $k$  ( $\text{mol} \times \text{l}^{-1} \times \text{s}^{-1}$ ) is the zero-order rate constant. It can be calculated as

$$k = \frac{[A]_0 - [A]}{\tau} \quad 2.6$$

As you can see, the rate of the reaction is independent of the reactant concentration (fig. 2.2). Photochemical, catalytic and enzymatic reactions run as the zero-order reactions.



Figure 2.2. — Zero-order reaction

**First-order reactions.** A first-order reaction is one in which the rate of the reaction depends only on the concentration of the reactant raised to the first power:

$$\text{Rate}(\vartheta) = -\frac{d[A]}{d\tau} = k \times [A] \quad 2.7$$

where  $k$  ( $\text{s}^{-1}$ ) is the first-order rate constant. It can be calculated as follows:

$$k = \frac{1}{\tau} \times \ln \frac{[A]_0}{[A]} \quad 2.8$$

A measure of considerable practical importance in kinetic studies is the **halflife** ( $\tau_{1/2}$ ) of a reaction. The half-life of a reaction is defined as the time it takes for the concentration of the reactant to decrease by half of its original value.

For the first-order reactions the half-life is calculated as:

$$\tau_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad 2.9$$

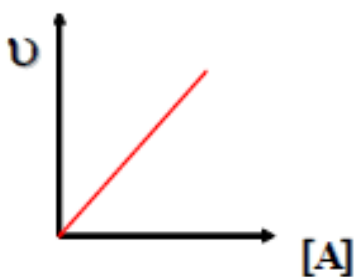


Figure 2.3 — First-order reaction

Radioactive decay and many other natural processes fit first-order kinetics. Half-lives of radioactive isotopes which are the main factors of the Chernobyl zone's contamination are:

$$I^{131} = 8 \text{ days}$$

$$Sr^{90} = 27 \text{ years}$$

$$Cs^{137} = 26.6 \text{ years}$$

**Second-order reactions.** We consider two types of second-order reactions here. In one type, there is just one reactant. This type is represented by the general reaction



and that rate is

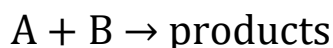
$$\text{Rate}(\vartheta) = k \times [A]^2 \quad 2.10$$

where

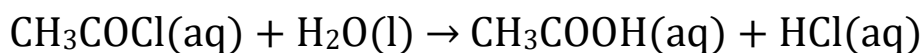
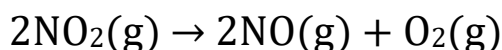
$$k = \frac{1}{\tau} \times \frac{[A]_0 - [A]}{[A]_0 \times [A]}$$

$$\tau^{1/2} = \frac{1}{k[A]_0} \quad 2.11$$

The second type involves two different reactants. It is represented by



This reaction is the first order in A, first order in B, and second order overall. Below are a few examples of a second-order reactions:



Hydrolysis of proteins, carbohydrates, lipids and other bioactive compounds run the second-order kinetics.

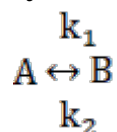
### ***2.3 The kinetics of complex reactions***

Many reactions take place by a mechanism that involves several elementary steps. They are named complex reactions. Among them chain reactions considered in chapter 1 are distinguished by extremely large number of elementary steps. Other types of complex reactions are:

- reversible;
- parallel;

- consecutive.

**Reversible reactions.** Most reactions are reversible to a certain extent, and we must consider both the forward and reverse rates. For the reversible reaction that proceeds by two elementary steps:

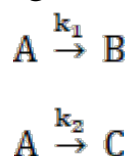


where  $k_1$  and  $k_2$  - are rate constants of forward and reverse reactions respectively.

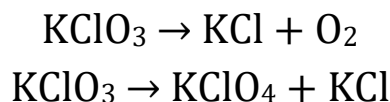
The rate law for a reversible reaction is

$$\vartheta = k_1[A] - k_2[B]$$

**Parallel reactions.** Parallel Reactions run simultaneously in several directions thus a conversion of a reactant results in several different products according to the scheme given below:



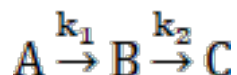
For example, the thermal decomposition of potassium chlorate can be represented as follows:



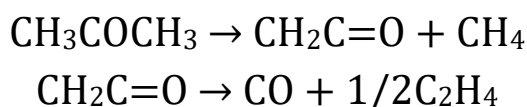
The rate law for a parallel reaction is

$$\vartheta = k_1([A]_0 - [B]) - k_2([A]_0 - [C])$$

**Consecutive reactions.** A consecutive reaction is one in which the product from the first step becomes a reactant for the second step and so on. For a two-step consecutive reaction we have:



The thermal decomposition of acetone in the gas phase is an example:



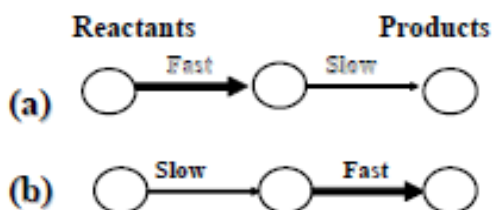
If we assume that the first step is much faster than the second one, the overall rate is controlled by the rate of the second step, which is

aptly called the rate-determining step (fig.4). The **rate determining step** is the slowest step in the sequence of steps leading to the formation of products. It governs the rate of the overall chemical reaction:

$$\vartheta = k_2[B]$$

If we assume that the second one is much faster than the first step, the overall rate is controlled by the rate of the first step:

$$\vartheta = k_1[B]$$



**Figure 2.4 — In these diagrams of reaction schemes, heavy arrows represent fast steps and light arrows represent slow steps**

Kinetics of complex reactions is summarized in table 2.1

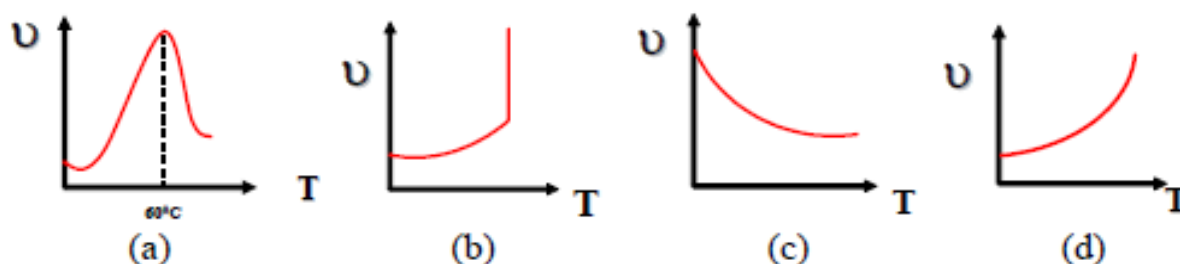
**Table 2.1 — Kinetics of complex reactions**

| №<br>п/п | Type of a<br>reaction    | A Scheme   | A Rate Law   |
|----------|--------------------------|--|--|
| 1.       | Reversible<br>reactions  | $  \begin{array}{c}  k_1 \\  A \leftrightarrow B \\  k_2  \end{array}  $             | $\vartheta = k_1[A] - k_2[B]$  |
| 2.       | Parallel reactions       | $  \begin{array}{c}  A \xrightarrow{k_1} B \\  A \xrightarrow{k_2} C  \end{array}  $ | $\vartheta = k_1([A]_0 - [B]) - k_2([A]_0 - [C])$  |
| 3.       | Consecutive<br>reactions | $A \xrightarrow{k_1} B \xrightarrow{k_2} C$  | The rate determining step governs the rate of the overall chemical reaction:<br>$\vartheta = k_2[B]$ |

## 2.4 The temperature dependence of reaction rates

Figure 2.5 shows four types of temperature dependence for reaction rate constants. Type (a) represents normal reactions whose rates increase with increasing temperature. Type (b) shows a rate that initially increases with temperature, reaches a maximum, and finally decreases with further temperature rise. It is typical for enzyme-catalyzed reaction. When the enzyme is in the native state, the reaction rate does increase with temperature. At higher temperatures, the enzyme molecule may

undergo denaturation, thereby losing its effectiveness as a catalyst. Type (c) shows a steady decrease of rate with temperature. It corresponds to termolecular reactions. The behavior shown in (d) corresponds to a chain reaction. At first, the rate rises gradually with temperature. At a particular temperature, the chain propagation reactions become significant, and the reaction is literally explosive.



**Figure 2.5 — Four types of temperature dependence for reaction rate constants**

The normal reactions obey the Van't Hoff's rule: for every  $10^0$  of temperature elevation, the rate of most reactions increases from 2 to 4 times.

$$k_2 = k_1 \times \gamma^{\frac{T_2 - T_1}{10}} \quad 2.12$$

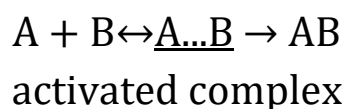
where  $\gamma$  - is the temperature coefficient of the chemical reaction,  $2 \leq \gamma \leq 4$  for most reactions and  $1.5 \leq \gamma \leq 3.0$  for biochemical reactions.

The more accurate description of how reactions' rates depend upon temperature is given in the Arrhenius equation:

$$k = k_0 \times e^{\frac{-E_a}{RT}} \quad 2.13$$

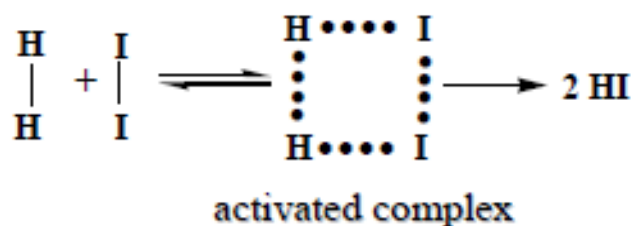
where  $k_0$  - pre-exponential factor;  $E_a$  - activation energy, kJ/mol.

We can define **activation energy** in terms of the theory of activated complex, which represents a pathway of a chemical reaction in the following way:



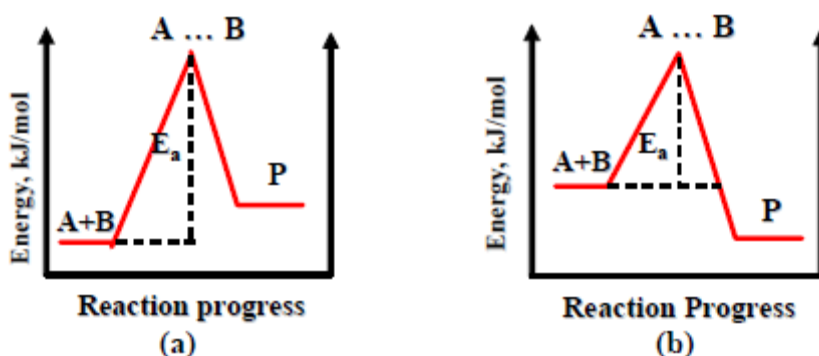
Before reactants turn into products an activated complex is generated. **Activated complex** is an energetically excited state that is intermediate between reactants and products in a chemical reaction. In

activated complexes the chemical bonds in reactants' molecules are partly broken and new bonds are partly formed. For example:



The theory of activated complex defines activated energy as the minimum amount of energy required to initiate a chemical reaction. We may think of activation energy as a barrier that prevents less energetic molecules from reacting.

The following graph represents the pathways of chemical reactions (fig. 2.6):



**Figure 2.6 — Potential energy profiles of (a) an exothermic reaction, (b) an endothermic reaction**

Activation energy depends upon nature of reactants and doesn't depend upon temperature in the narrow range. Normally, only a small fraction of the reacting molecules has enough kinetic energy to exceed the activation energy. The higher the temperature rises, the greater the kinetic energy of reacting molecules is and the larger a fraction of active molecules is in a mixture. Thus increase in temperature accelerates most chemical reactions.

If we know rate constants at two different temperatures we may use them to calculate activation energy according to the formula:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{T_1 - T_2}{T_1 \times T_2} \right) \quad 2.14$$

## 2.5 General principles of catalysis

Catalysis is a field of chemistry that deals with the change in chemical reactions in the presence of special substances named catalysts.

The general principles of catalysis are:

- a catalyst is a substance that changes the rate of a reaction without itself being consumed by the process. A reaction in which a catalyst is involved is a catalyzed reaction, and a process is called catalysis;
- a small quantity of a catalyst should be able to affect the rate of a reaction for a large amount of reactants;
- catalysts do not change the equilibrium constant of chemical reactions.

From the point of view of *activated complex theory* catalysts change the rate of chemical reactions through changing their pathways.

Without a catalyst  $A + B \leftrightarrow A...B \rightarrow AB$

With a catalyst:  $A + B + C \leftrightarrow A...C...B \rightarrow AB + C$

**Positive catalysts** decrease activation energy of a reaction (fig. 2.7).

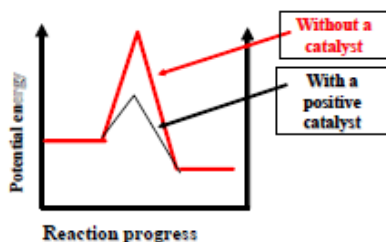


Figure 2.7 — Positive catalysts

Positive catalysts increase a fraction of active molecules in a mixture of reactants at a constant temperature. As a result the rate of reactions increases.

**Negative catalysts** increase activation energy of a reaction (fig. 2.8).

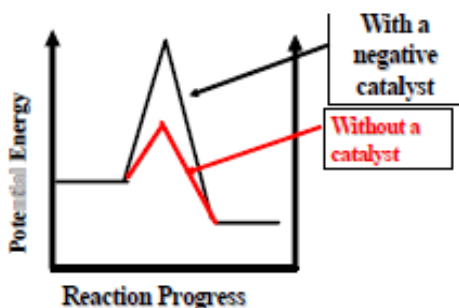
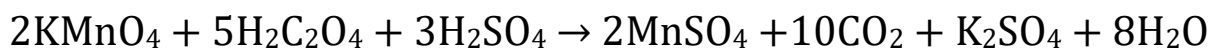


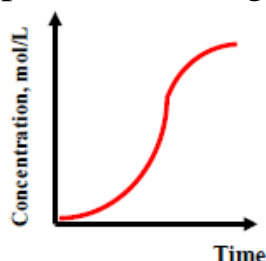
Figure 2.8 — Negative catalysts

Negative catalysts decrease a fraction of active molecules in a mixture of reactants at a constant temperature. As a result the rate of reactions decreases.

**An autocatalysis** is a process when a product of a reaction acts as a catalyst. An example of an autocatalytic reaction is:



Catalyst:  $\text{Mn}^{2+}$ . The kinetic curve of autocatalytic reaction is represented in figure 2.9.



**Figure 2.9 — Kinetic curve of autocatalytic reaction**

The phenomenon of enzyme catalysis usually results in a very large increase in reaction rate and high specificity.

Catalysts are vital in the chemical industry. The market for catalysts in the USA is about 2 billion \$. Catalysts are immensely beneficial in industry, but accidental catalysis in the atmosphere can be highly detrimental. The destruction of ozone layer is an example of homogeneous catalysis, which proceeds in atmosphere under the influence of freons.

The ozone layer acts to protect life on the Earth by blocking harmful ultraviolet rays from the sun. The 1985 report of the discovery of an «ozone hole» over Antarctica focused attention on the idea that humans can have a significant impact on the global environment.

Too much ultra-violet light can result in skin cancer, eye damage such as cataracts, immune system damage, reduction in phytoplankton in the oceans that forms the basis of all marine food, damage to the DNA in various life-forms and probably other things that we don't know about at the moment.

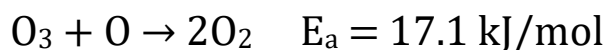
Freons are chloro-fluorocarbons ( $\text{CF}_2\text{Cl}_2$ ), used in a variety of industrial, commercial, and household applications. They are non-toxic, non-flammable, and non-reactive with other chemical compounds. These desirable safety characteristics make them ideal for many applications - as coolants for refrigeration units, aerosol propellants, electronic cleaning solvents, and blowing agents. In atmosphere freons

absorb ultraviolet light from the sun that breaks carbon-chlorine bonds and produces chlorine atoms:

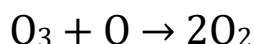
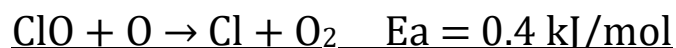
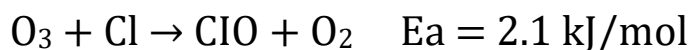


where  $\text{Cl}\bullet$  is a catalyst.

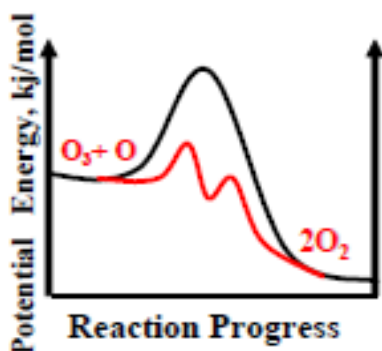
Without a catalyst a reaction proceeds as follows:



Under the effect of a catalyst:



A catalyst decreases the activation energy of a reaction thus increasing its rate (fig. 2.10).



**Figure 2.10 — The energy profile for the reaction between  $\text{O}_3$  and  $\text{O}$ . The direct reaction has a much higher activation energy than the chlorine-catalyzed reaction, so  $\text{Cl}$  atoms are effective catalysts for this reaction**

The potential effects on humans and the environment have led to international resolutions designed to gradually phase out production of ozone-depleting substances.

## ***2.6 The equation of enzyme kinetics***

Almost all biological functions are supported by chemical reactions catalyzed by biological catalysts, enzymes. Efficient metabolism is controlled by orderly, sequential, and branching metabolic pathways. Enzymes accelerate chemical reactions under physiologic conditions:  $37^\circ\text{C}$  and neutral pH. However, an enzyme cannot alter the equilibrium of a concentration, but can only accelerate the reaction rate, by decreasing the activation energy of the reaction.

Enzymes accelerate chemical reactions under physiologic conditions:  $37^\circ\text{C}$  and neutral pH. Nearly all enzymes are proteins,

although some ribonucleic acid molecules, termed ribosome, also have catalytic activity. More than 2,000 enzymes were extracted from living systems; some of them (~150) are applied in medicine as drugs. Enzymes differ from other catalysts by: (a) very high catalytic activity, (b) high selectivity (one enzyme activates only one or two biochemical reactions).

In 1913, the German biochemist Leonor Michaelis and the Canadian biochemist Maud L. Menten proposed a mechanism to explain the dependence of the initial rate of enzyme-catalyzed reactions on concentration. They considered the following scheme, in which ES is the enzyme-substrate complex:



where S - a substrate, E - an enzyme, P - a product of a reaction.

The initial rate of product formation is given by

$$v = k_2[ES] \quad 2.15$$

where  $k_2$  - is a first-order rate constant, known as molar enzyme activity or **turnover number**, expressed in  $\text{min}^{-1}$ . It's the number of substrate molecules processed by an enzyme molecule per second when the enzyme is saturated with the substrate. For most reactions  $k_2$  values are in the range of  $1 \times 10^4 < k_2 < 6 \times 10^6 \text{ min}^{-1}$ .

A concentration of an enzyme-substrate complex [ES] can't be measured experimentally, but can be derived through another experimental data. To derive the expression for the rate in terms of the more easily measurable substrate concentration, Michaelis and Menten assumed that

$$v = \frac{k_2 \times [E]_0 \times [S]}{K_M + [S]} \quad 2.16$$

Substituting equation 2.15 with equation 2.17 yields

$$v = \frac{k_2 \times [E]_0 \times [S]}{K_M + [S]} = \frac{v_{\max} \times [S]}{K_M + [S]} \quad 2.17$$

where  $K_M$  - is the equilibrium constant, known as Michaelis constant.  $K_M$  characterizes stability of enzyme-substrate complexes. The lower  $K_M$  is, the higher stability of a complex is. A multiplication  $k_2 \times [E]_{\text{overall}}$  is

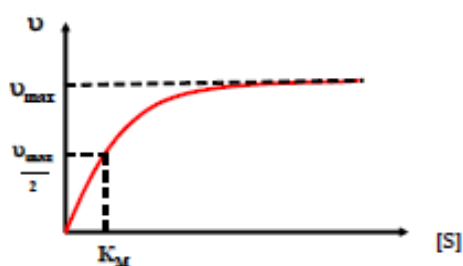
constant and is defined as  $v_{\max}$  (maximum rate). Maximum rate corresponds to the zero-order enzymatic reaction.

Equation (2.16) is a rate law of an enzymatic reaction, which is known as the ***Michaelis-Menten equation***.

At low substrate concentrations ( $[S] \ll K_M$ ) equation (2.17) becomes

$$\theta = \frac{\theta_{\max}}{K_M} \times [S] \quad 2.18$$

It is the first-order reaction in  $[S]$ . This rate law corresponds to the initial linear portion of the plot in figure 2.11.



**Figure 2.11 — Kinetic curve of enzymatic reaction**

At high substrate concentrations ( $[S] \gg K_M$ ), equation (2.17) can be written as

$$\theta = \theta_{\max} \quad 2.19$$

It's a zero order in  $[S]$  and corresponds to the horizontal portion of the plot in figure 2.11. Now consider what happens when  $[S] = K_M$ . From equation 2.17 we find that this condition gives

$$\theta = \frac{\theta_{\max}}{2}$$

so,  $K_M$  equals the concentration of  $S$  when the rate is half its maximum value.

A kinetic curve of an enzymatic reaction is given in figure 2.11. We may use it for graphical determination of  $v_{\max}$  and  $K_M$ .

In many cases, the process involves two or more substrates. The overall picture of a bisubstrate reaction can be represented by



where  $A$  and  $B$  are the substrates and  $P$  and  $Q$  are the products.

The binding of  $A$  and  $B$  to the enzyme can take place in different ways, which can be categorized as a sequential (fig. 2.12) or nonsequential mechanism (fig.2.13).

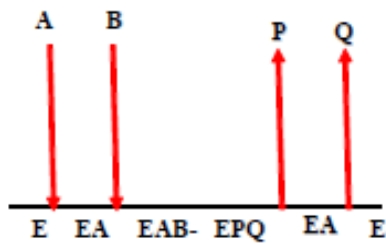


Figure 2.12 — The sequential mechanism.

In this mechanism, one substrate must bind before a second substrate can bind.

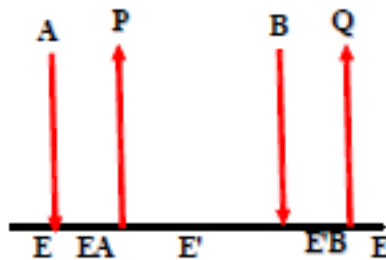


Figure 2.13 — The nonsequential mechanism

In this mechanism, one substrate binds, and one product is released.

Factors affecting enzymatic reactions are:

- temperature;
- acidity and basicity of medium;
- enzyme inhibitors.

Enzymes work best at an optimum pH value, which varies from enzyme to enzyme (fig. 2.14). Most enzymes that are active within cells have a pH optimum fairly close to the range of pH within which cells normally function. For example, the pH optima of two digestive enzymes, pepsin and trypsin, occur at about pH 2 and pH 8 respectively.

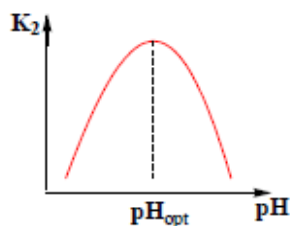


Figure 2.14 — The effect of acidity on enzymes' activity

We consider two forms of inhibition (there are others):

- competitive inhibition;
- noncompetitive inhibition.

**Competitive inhibitors** structurally similar to substrate and bind to active site - keeping out the substrate:

Original (uninhibited)  $v_{\max}$  can be attained by increasing  $[S]$  (competes out the inhibitor).  $K_M$  increases (apparent loss of affinity for a substrate).

**Noncompetitive inhibitors** bind away from the catalytic site but cause a conformational change to be transmitted to the active site.

## ***2.7 Exercises for the self-control***

### **Discussion questions:**

1. What is meant by the rate of a chemical reaction?
2. What are the units of the reaction rate?
3. Can you suggest two reactions that are very slow (take days or longer to complete) and two reactions that are very fast (reactions that are over in minutes or seconds)?
4. Distinguish between reaction order and molecularity/
5. Explain what is meant by the order of a reaction.
6. On which of the following quantities does the rate constant of a reaction depend? (a) concentrations of reactants, (b) nature of reactants or (c) temperature.
7. Use the Arrhenius equation to show why the rate constant of a reaction (a) decreases with increasing activation energy and creasing temperature.
8. For the energy profile presented below, which of the following statements is true?
  - (a)  $E_a$  (forward) =  $E_a$  (reverse).
  - (b) A represents the energy of the starting material.
  - (c)  $E_a$  (forward) = B - C.
  - (d)  $E_a$  of the forward reaction is less than  $E_a$  of the reverse reaction.
9. How does a catalyst increase the rate of a reaction?
10. What are the characteristics of a catalyst?
11. Why does a catalyst must affect the rate of the reaction in both directions
12. A certain reaction is known to proceed slowly at room temperature. Is it possible to make a reaction proceed at a faster rate without changing the temperature?

13. Are enzyme-catalyzed reactions the examples of homogeneous or heterogeneous catalysis? Explain.

14. The concentrations of enzymes in cells are usually quite small. What is the biological significance of this fact?

15. Define the terms (a) a turnover number, (b) the sequential mechanism of enzymatic reactions, (c) the nonsequential mechanism of enzymatic reactions, (d) competitive inhibitors, (e) noncompetitive inhibitors.

16. Discuss the features, advantages, and limitations of the Michaelis-Menten mechanism of enzyme action.

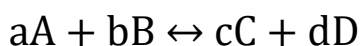
## CHAPTER 3. KINETICS AND THERMODYNAMICS OF CHEMICAL EQUILIBRIUM

**After studying this topic, you should be able to:**

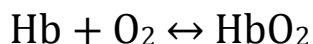
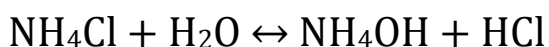
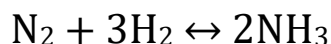
- define reversible reactions and give their examples;
- describe chemical equilibrium from kinetic and thermodynamic points of view;
- discuss different types of equilibrium constants ( $K_c$  and  $K_p$ ) and give their notations; define the Law of mass action
- define Le Chatelier's Principle; describe effect of temperature, pressure changes and as well as, changes in reactant or product concentration at equilibrium state;
- understand equilibria in aqueous solutions. Be able to define water ionization equilibrium constant ( $K_w$ ), acid ionization equilibrium constant ( $K_a$ ) and base ionization equilibrium constant ( $K_b$ );
- describe salt hydrolysis and be able to calculate the hydrolysis equilibrium constants.

### *3.1 Chemical equilibrium*

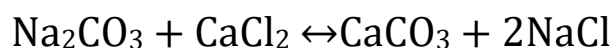
Few chemical reactions proceed in only one direction. Most are, at least to some extent, reversible. Reversible reactions proceed spontaneously both in forward and reverse directions. An equation for a hypothetical reversible reaction can be represented by



For example:



We can thank Napoleon for bringing the concept of reaction reversibility to Chemistry. Napoleon recruited the eminent French chemist Claude Louis Berthollet to accompany him as a scientific advisor on the expedition to Egypt in 1798. Once in Egypt, Berthollet noticed deposits of sodium carbonate around the edges of some salt lakes found there. He was already familiar with the reaction:



Reversible reactions tend to chemical equilibrium. **Chemical equilibrium** is a state of a reversible process characterized by equal rates of forward and reverse reactions (fig. 3.1).

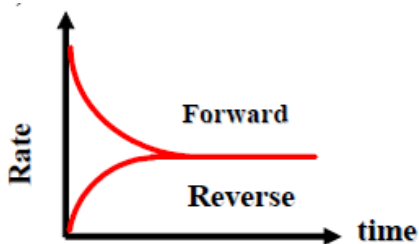


Figure 3.1 — Kinetic curves of forward and reverse reactions

When chemical equilibrium is maintained concentrations of all the components become constant; they do not change with time. Such concentrations are known as **equilibrium concentrations**; they are denoted as  $[\bar{A}]$ , mol/l. Equilibrium concentrations can be figured in a graph form (fig. 3.2).

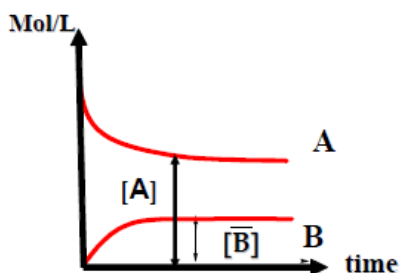


Figure 3.2 — Kinetic curves of a reversible reaction:  $aA \leftrightarrow bB$

Norwegian chemists (and brothers-in-law) Cato Guldberg and Peter Waage developed the **Law of mass action** (1864): *the rate of the reaction in either direction is proportional to the reactants concentration.*

At equilibrium state rates of forward and reverse reaction is

$$v_f = k_f [\bar{A}]^a \times [\bar{B}]^b \quad 3.1$$

$$v_r = k_r [\bar{C}]^c \times [\bar{D}]^d \quad 3.2$$

where  $v_f$  and  $v_r$  are the rates of forward and reverse reaction respectively; the proportionality coefficients  $k$  are called **rate constants**, and the quantities in square brackets represent concentrations, mol/L.

Since  $v_f = v_r$ , we can rearrange equations (3.1) and (3.2) in a following way:

$$\frac{k_f}{k_r} = \frac{[\bar{C}]^c \times [\bar{D}]^d}{[\bar{A}]^a \times [\bar{B}]^b} \quad 3.3$$

The relation of constant quantities is also constant, thus the relation of forward and reverse rate constants is equal to the *equilibrium constant* (K):

$$\frac{k_f}{k_r} = K \quad 3.4$$

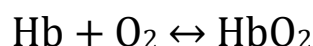
### 3.2 Ways of expressing equilibrium constants

Two types of equilibrium constants can be distinguished: **K<sub>c</sub>** and **K<sub>p</sub>**.

*The notation K<sub>c</sub>* is normally used to denote that the equilibrium constant refers to the expression in which the amounts of substances are expressed in molar concentrations. The Law of mass action for reversible reactions is the following way:

$$K_c = \frac{[\bar{C}]^c \times [\bar{D}]^d}{[\bar{A}]^a \times [\bar{B}]^b} \quad 3.5$$

For example, for a biochemical reaction:



K<sub>c</sub> is equal to

$$K_c = \frac{[\text{HbO}_2]}{[\text{Hb}] \times [\text{O}_2]} = 1300$$

Concentrations of solids are assumed to be 1, and they can be left out of the concentration ratio without altering the value of K.

For example, for the reaction of urea preparing:



K<sub>c</sub> can be calculated as:

$$K_c = \frac{[\text{H}_2\text{O}]}{[\text{CO}_2] \times [\text{NH}_3]^2}$$

Note that K<sub>c</sub> is given without units.

*The notation K<sub>p</sub>* is used when the amounts of materials are expressed as gas pressures.

$$K_p = \frac{\bar{P}_C^c \times \bar{P}_D^d}{\bar{P}_A^a \times \bar{P}_B^b} \quad 3.6$$

A relationship between K<sub>c</sub> and K<sub>p</sub> is given by the equation:

$$K_c = K_p \times (R T)^{(a+b-c-d)} \quad 3.7$$

### 3.3 Predicting the direction of a reaction

When a chemical reaction *is not at equilibrium*, the ratio of concentrations is called the **concentration quotient**, (Q). The concentration quotient has the same form as the equilibrium concentration ratio, but the concentrations are not equilibrium values: consequently, Q can have any value:

$$Q = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \quad 3.8$$

There are not equilibrium concentrations.

The direction in which a reaction proceeds depends on the relationship between Q and K:

- $Q < K$  reaction goes to the right to make products;
- $Q > K$  reaction goes to the left to make reactants.

The relationship between Q and K signals the direction of a chemical reaction. The free energy change,  $\Delta G$ , also signals the direction of a chemical reaction. These two criteria can be compared:

|                             |                     |                            |
|-----------------------------|---------------------|----------------------------|
| Reaction goes<br>right when | Equilibrium<br>when | Reaction goes<br>left when |
| $Q < K$                     | $Q = K$             | $Q > K$                    |
| $\Delta G < 0$              | $\Delta G = 0$      | $\Delta G > 0$             |

The similarities suggest a link among Q, K and  $\Delta G$ . This link is given by the thermodynamical equation of isotherm of a chemical reaction:

$$\Delta G = \Delta G^0 + R \times T \times \ln \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \quad 3.9$$

At equilibrium state  $\Delta G=0$ , and concentrations of all reactants are equilibrium concentrations. Hence

$$\Delta G^0 = -R \times T \times \ln K \quad 3.10$$

We can calculate equilibrium constant applying thermodynamic data:

$$\Delta G^0 = e^{\frac{-G^0}{R \times T}} \quad 3.11$$

The exponential gives a dimensionless number, since ex is always a pure number. However, we assign units to K as required by the

concentration quotient. Remember that the superscript «o» refers to standard conditions that include concentrations of 1 M for solutes and 1 atm partial pressure for gases.

### 3.4 Equilibrium constants and temperature

The effect of temperature on equilibrium constant becomes clear from the combined equations:

$$\begin{cases} \Delta G^0 = \Delta H^0 - T \times \Delta S^0 \\ \Delta G^0 = -R \times T \times \ln K \end{cases}$$

As the result

$$\ln K = -\frac{\Delta H^0}{R \times T} + \frac{\Delta S^0}{R} \quad 3.12$$

If  $\Delta H < 0$ ,  $\Delta H/R > 0$  (the first term is positive). When T increases, K decreases. For exothermic reactions rise in temperature results in equilibrium constant decrease (fig. 3.3-a).

If  $\Delta H > 0$ ,  $-\Delta H/R < 0$  (the first term is negative). When T increases, K also increases. For endothermic reactions rise in temperature results in equilibrium constant increase (fig. 3.3-b).

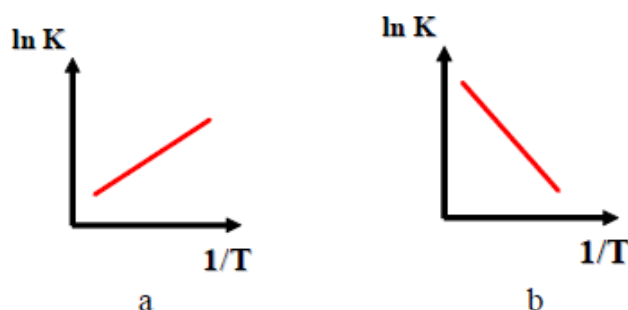


Figure 3.3 — Graphs of  $\ln K$  versus  $1/T$  (a)  $\Delta H > 0$ , (b)  $\Delta H < 0$

### 3.5 Shifts in equilibrium (Le Chatelier's Principal)

Chemical equilibrium represents a balance between forward and reverse reactions. This state of a system is most energy preferable since it is characterized by the lowest level of its Free Energy ( $G_{\min}$ ) (Fig. 3.4).

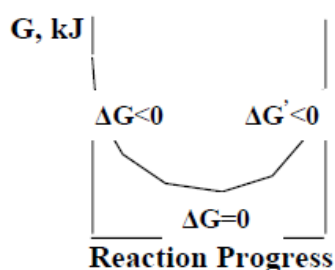
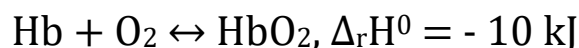


Figure 3.4 — Energy diagram of a reversible reaction

***Le Chatelier's Principle:*** «If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance».

In other words Le Chatelier's principle states, that if an external stress is applied to a system at equilibrium, the system adjusts itself in such a way that the stress is partially offset.

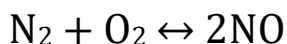
***Effects of temperature changes.*** An increase in temperature always shifts the equilibrium state in the endothermic direction, and a decrease in temperature always shifts the equilibrium state in the exothermic direction. For example, for the biochemical reaction of hemoglobin oxidation into oxyhemoglobin:



an increase in temperature shifts the equilibrium state to the left (blood gives oxygen to tissues), a decrease in temperature shifts the equilibrium state to the right (blood absorbs oxygen).

***Effects of pressure changes.*** Pressure changes affect the equilibrium state only for gaseous reactions, because liquids and solids are virtually incompressible. An increase in pressure always shifts the equilibrium state in the direction of smallest number of gas molecules; a decrease in pressure always shifts the equilibrium state in the direction of a larger number of gas molecules.

Pressure changes do not effect the equilibrium state of gaseous reactions which run without changes in a number of gas molecules:



For the reaction of hemoglobin oxidation into oxyhemoglobin when blood is in lungs under high pressure of  $\text{O}_2$  gas the equilibrium shifts to the right (blood absorbs oxygen). Venus blood is exposed under a low pressure of  $\text{O}_2$ , therefore equilibrium shifts to the left (blood gives oxygen to tissues).

***Change in reactant or product concentration.*** When we add a substance (a reactant or a product) the reaction will shift to reestablish equilibrium by consuming a part of the added substance. Conversely, removal of a substance will result in the reaction moving in the direction

that forms more of the substance. For example, high Hb level in blood shifts equilibrium to the right (blood absorbs oxygen). Low Hb level (anemia) shifts equilibrium to the left (people suffer from oxygen deficiency).

**Effect of catalysts.** Catalysts do not affect the equilibrium constant. Figure 3.5 provides a reminder that a catalyst changes the mechanism of the reaction in a way that reduces the net activation energy barrier, but it does not alter the thermodynamic changes that accompany the reaction. In other words, both the forward activation energy and the reverse activation energy are reduced by a positive catalyst, so the rates of both reactions are increased. The nature of reactants and products are not affected, however, so the free energy change  $\Delta G^0$  does not change, and neither does  $K_{eq}$ . A catalyst allows a reaction to reach equilibrium *more rapidly*, but does not alter the equilibrium position.

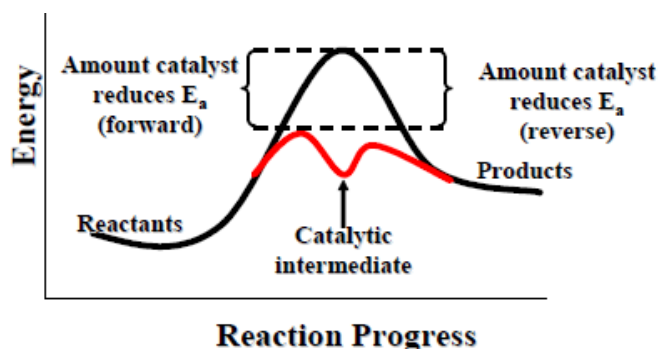
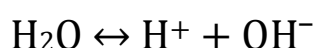


Figure 3.5 — Energy profile of a reversible catalytic reaction

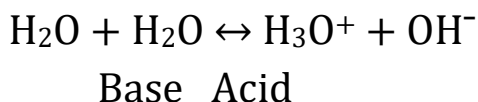
### 3.6 Equilibrium in aqueous solutions

Water is the Earth's most important chemical substance. The oceans and seas cover nearly three quarters of the planet's surface. Water and aqueous solutions (from rainwater to blood) have properties that must be interpreted using the principles of chemical equilibrium. Among them proton transfer equilibria are the most important since they are essential for maintaining cellular life. They are a part of the metabolic processes participating in extra- and intra-cellular fluids.

**Water ionization equilibrium.** The dissociation of water is a particularly important case, because most acid-base reactions occur in aqueous solutions. Water is a weak electrolyte, which undergoes ionization to a small extent:



This reaction is sometimes called the *autoionization of water* thus it is assumed that one H<sub>2</sub>O molecule is an acid (proton's donor) and another is a base (proton's acceptor):



Expressing the hydrated proton as H<sup>+</sup> rather than H<sub>3</sub>O<sup>+</sup>, we can write the equilibrium constant for the autoionization of water:

$$K_c = \frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]} \quad 3.13$$

Since a very small fraction of water molecules are ionized, the concentration of water, that is, [H<sub>2</sub>O], remains virtually unchanged. Therefore we rearrange the equation as

$$K_c[\text{H}_2\text{O}] = K_w = [\text{H}^+] \times [\text{OH}^-] \quad 3.14$$

The «new» *equilibrium constant*, *K<sub>w</sub>*, is called the *ion-product constant* or *water equilibrium constant*.

In pure water at 25<sup>0</sup>C, the concentrations of H<sup>+</sup> and OH<sup>-</sup> ions are equal and found to be [H<sup>+</sup>] = 1.0×10<sup>-7</sup> M and [OH<sup>-</sup>] = 1.0×10<sup>-7</sup> M. Thus, from the Equation (3.14) we can derive:

$$K_w = (1.0 \times 10^{-7}) \times (1.0 \times 10^{-7}) = 10^{-14} \quad 3.15$$

Note that whether we have pure water or a solution of dissolved species, the following relation always holds at 25<sup>0</sup>C:

$$K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-14} \quad 3.16$$

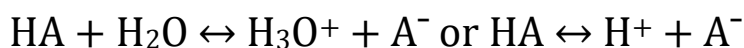
It is important to remember that, because *K<sub>w</sub>* is equilibrium constant, its value changes with temperature.

In pure water and aqueous solutions the concentrations of H<sup>+</sup> and OH<sup>-</sup> can be calculated by:

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} \quad 3.17$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad 3.18$$

**Acid ionization equilibrium.** One of the most important examples of chemical equilibrium is the one that exists when acids and bases are present in a solution. The dissociation of a weak acid, HA, in aqueous solution can be represented by



For example, **acid ionization equilibrium** in acetic acid solution can be expressed as



When we apply the Law of mass action to acid ionization equilibrium the following equation is generated:

$$K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad 3.19$$

where  $K_a$  - is the acid ionization constant. The strength of the acid is indicated by the magnitude of  $K_a$ ; that is, the larger the  $K_a$  value is, the stronger the acids are. Another way to measure the strength of the acid is to calculate its percent dissociation, defined by

$$\text{percent dissociation} = \frac{[\text{H}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100\% \quad 3.20$$

where  $[\text{H}^+]$  is the hydrogen ion concentration at equilibrium and  $[\text{HA}]_0$  is the initial concentration of the acid.

**Base ionization equilibrium.** The treatment of the base dissociation is the same as that for acids. For example, when ammonia dissolves in water, it reacts as follows:



By analogy with the acid-ionization constant, we can write the **the base ionization constant  $K_b$**  as:

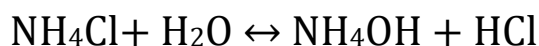
$$K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad 3.21$$

The greater  $K_b$  is, the stronger bases are.

**Hydrolysis** is the reaction of substance decomposition by water which runs in aqueous solutions.

Salts' Hydrolysis is the reaction of an anion or a cation of a salt, or both, with water. Salt hydrolysis usually affects the pH of a solution.

**Hydrolysis of salts which involves a cation of a weak base.** Consider the reaction between ammonium chloride and water:



When we apply the Law of Mass Action to hydrolysis equilibrium the following equation is generated:

$$K_h = \frac{[\text{NH}_4\text{OH}] \times [\text{H}^+]}{[\text{NH}_4^+]} = \frac{[\text{NH}_4\text{OH}] \times K_w}{[\text{NH}_4^+] \times [\text{OH}^-]} = \frac{K_w}{K_b} \quad 3.22$$

where  $K_h$  - is the hydrolysis equilibrium constant. In this case salt hydrolysis is responsible for acidic medium in a solution.

**Hydrolysis of salts which involves an anion of a weak acid.**

Consider the reaction between sodium acetate and water:

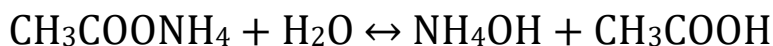


By analogy with the *hydrolysis equilibrium constant of ammonium chloride*, we can write  $K_h$  for sodium acetate as:

$$K_h = \frac{K_w}{K_a} \quad 3.23$$

In this case salt hydrolysis is responsible for basic medium in a solution.

**Salt hydrolysis, which involves both cation and anion.** Consider the reaction between ammonium acetate and water:



Its hydrolysis equilibrium constant is equal to

$$K_h = \frac{K_w}{K_a \times K_b} \quad 3.24$$

Salt property to undergo hydrolysis is characterized by the *hydrolysis percent (h)*:

$$h = \frac{\text{Number of salt's particles, which undergo hydrolysis}}{\text{Initial number of salt's particles in a solution}} \quad 3.25$$

Hydrolysis percent can be calculated as

$$h = \sqrt{\frac{K_h}{C_M}} \quad 3.26$$

The greater hydrolysis equilibrium constant is, the higher the hydrolysis percent.

Salt hydrolysis is a powerful factor that controls acid - base equilibrium in a human body.

### ***3.7 Exercises for the self-control***

#### **Discussion questions:**

1. Define homogeneous equilibrium and heterogeneous equilibrium. Give two examples of each.
2. What do the symbols  $K_c$  and  $K_p$  represent?
3. Taking into consideration the rate constant, explain why the equilibrium constant depends on temperature.
4. List the factors that can shift the position of equilibrium. Does the addition of a catalyst have any effects on the position of equilibrium? Explain.
5. Use the ionization of HCN in water as an example to illustrate the meaning of dynamic equilibrium.
6. Specify which of the following salts will undergo hydrolysis: KF,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_2$ ,  $\text{MgSO}_4$ , KCN,  $\text{C}_6\text{H}_5\text{COONa}$ , RbI,  $\text{Na}_2\text{CO}_3$ , CaCl, HCOOK.
7. Predict the pH(>7, <7, or  $\approx 7$ ) of the aqueous solutions containing the following salts: (a) KBr, (b)  $\text{Al}(\text{NO}_3)_3$ , (c)  $\text{BaCl}_2$ , (d)  $\text{Bi}(\text{NO}_3)_3$
8. A certain salt, MX (containing the  $\text{M}^+$  and  $\text{X}^-$  ions), is dissolved in water, and the pH of the resulting solution is 7.0. What can you say about the strength of the acid and the base from which the salt is derived?

## CHAPTER 4. INTRODUCTION TO VOLUMETRIC ANALYSIS. FUNDAMENTALS OF VOLUMETRIC ANALYSIS

**After studying this section, you will**

- understand the equivalent law and its application in volumetric analysis;
- understand concentration units as the amount of solute present in a given amount of a solution;
- be able to perform typical calculations involving the equivalent law and concentration units;
- understand the principles of volumetric analysis;
- understand the classification of titration methods and types of solutions applied for titration;
- be able to perform typical calculations involving the rules of significant figures;
- understand the principle of acid-base titration;
- understand the role of acid-base indicators and be able to perform typical calculations involving acid-base titrations.
- understand the general concepts of oxidation-reduction processes;
- understand the principles of Redox titration;
- be able to perform typical calculations involving oxidation-reduction titrations.

### ***4.1 The Equivalent Law***

A chemical equivalent is a real or hypothetical particle of a substance, which can interact with one Hydrogen atom in acid-base reactions or with one electron in Redox reactions.

The mass of one mole of chemical equivalents is defined as ***equivalent molar mass*** ( $M_e$ ), g/mol. The equivalent molar mass relates to the molar mass of a substance as follows:

$$M_e = f_e \times M \quad 4.1$$

where  $f_e$  - an equivalent factor.

For the substances involved into ion exchange reactions the equivalent factors can be calculated according to the following formulae:

**For acids:**

$$f_e = \frac{1}{\text{a number of hydrogen atoms substituted in a molecule}} \quad 4.2$$

For monoprotic acids (HCl, HNO<sub>3</sub> and others) the equivalent factor is equal to one ( $f_e = 1$ ); for diprotic acids (H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>CO<sub>3</sub> and others) the equivalent factor takes the values 1 and 1/2 ( $f_e = 1$  and 1/2); for triprotic acids (H<sub>3</sub>PO<sub>4</sub>) the equivalent factor takes the values 1, 1/2 and 1/3 ( $f_e = 1, 1/2$  and 1/3)

**For bases:**

$$f_e = \frac{1}{\text{a number of OH - groups substituted in a molecule}} \quad 4.3$$

For the bases with one hydroxyl group (NaOH, KOH and others) the equivalent factor is equal to one ( $f_e = 1$ ); for the bases with two hydroxyl groups (Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub> and others) the equivalent factor takes the values 1 and 1/2 ( $f_e = 1$  and 1/2); for the bases with three hydroxyl groups (Al(OH)<sub>3</sub> and others) the equivalent factor takes the values 1, 1/2 and 1/3 ( $f_e = 1, 1/2$  and 1/3).

**For salts:**

$$f_e = \frac{1}{\text{a number of metall atoms} \times \text{oxidation number}} \quad 4.4$$

For example:  $f_e(\text{NaCl}) = 1$ ,  $f_e(\text{Na}_2\text{SO}_4) = 1/2$ ,  $f_e(\text{Ca}_3(\text{PO}_4)_2) = 1/6$ .

**For elements:**

$$f_e = \frac{1}{\text{oxidation number}} \quad 4.5$$

For example: the equivalent factor of nitrogen in nitrogen (I) oxide N<sub>2</sub>O is equal to 1/2 ( $f_e = 1/2$ ).

**REMEMBER!!!**

Me (H) - 1 g/mol

Me (O) = 8 g/mol

Me (H<sub>2</sub>O) = 9 g/mol

**The Equivalent Law:** the masses of chemical substances which are involved into a reaction and the masses of its products are directly proportional to their equivalent molar masses.

For a hypothetical reaction



the amounts of equivalents for reactants and products are identical:

$$\vartheta_e(A) = \vartheta_e(B) = \vartheta_e(C) = \vartheta_e(D)$$

where  $\vartheta_e$  - is the amount of an equivalent, mol.

For a substance the amount of an equivalent is a ratio of its mass and its equivalent molar mass:

$$\vartheta_e = \frac{m}{M_e} \quad 4.6$$

where  $m$  - is the mass of a substance, g.

The Equivalent law is applied to do calculations in volumetric analysis.

## 4.2 Concentration units

Quantitative study of a solution requires knowing its concentration, that is, the amount of solute present in a given amount of a solution. Chemists use several different concentration units, each of which has advantages as well as limitations. The choice of concentration unit is generally based on the kind of measurement made of the solution. Let us examine the four most common units of concentration: percent by mass, mole fraction, molarity, and molality.

### Types of concentration units

**Percent by mass ( $\omega$ ).** The percent by mass (also called the percent by weight or the weight percent) is defined as

$$\text{Percent by mass of solution } (\omega) = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \quad 4.7$$

or

$$\text{Percent by mass of solution } (\omega) = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \quad 4.8$$

The percent by mass has no units because it is a ratio of two similar quantities.

**Mole fraction ( $\chi$ ).** The mole fraction of a component in a solution, say, component A, is written  $\chi_A$  and is defined as

$$\text{Mole fraction of component A } (\chi(A)) = \frac{\text{moles of A}}{\text{sum of moles of all components}} \quad 4.9$$

The mole fraction has no units, since it is a ratio of two similar quantities.

**Molality ( $C_m$ ).** Molality is a number of moles of a solute dissolved in 1 kg (1000 g) of solvent - that is

$$\text{Molality } (C_m) = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \quad 4.10$$

For example, to prepare a 1 mol/kg sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) aqueous solution, we need to dissolve 1 mole (142.0 g) of the substance in 1000 g (1 kg) of water. Depending on the nature of the solute-solvent interaction, the final volume of the solution will be either greater or less than 1000 ml. It is also possible, though very unlikely, that the final volume could be equal to 1000 ml.

**Molarity ( $C_M$ ).** Molarity is defined as the number of moles of solute in 1 liter of a solution; that is

$$\text{Molarity } (C_M) = \frac{\text{moles of solute}}{\text{liters of solution}} \quad 4.11$$

Thus, molarity has the units of mol/l or M.

**Normality ( $C_N$ ).** Normality is defined as the number of equivalent moles of a solute in 1 liter of a solution; that is

$$\text{Normality } (C_N) = \frac{\text{equivalent moles of solute}}{\text{liters of solution}} \quad 4.12$$

Thus, normality has the units of mol/l or N.

**Titer (T).** Titer is defined as a mass of a solute in 1 milliliter of a solution. That is

$$\text{Titer}(T) = \frac{\text{mass of solute}}{\text{milliliters of solution}} \quad 4.13$$

Thus, titer has the units of g/ml.

**Concentration units are interconvertible:**

$$\text{Molarity} = \frac{1000 \times T}{\text{molar mass of solute}} \quad 4.14$$

$$\text{Molarity} = \frac{10 \times \text{density of solution} \times \text{percent by mass}(\%)}{\text{molar mass of solute}} \quad 4.15$$

$$\text{Percent by mass of solution } (\%) = \frac{\text{molarity} \times \text{molar mass of solute}}{10 \times \text{density of solution}} \quad 4.16$$

$$\text{Molarity} = C_N \times f_e \quad 4.17$$

$$\text{Normality} = \frac{C_M}{f_e} \quad 4.18$$

$$\text{Normality} = \frac{1000 \times T}{\text{equivalent molar mass of solute}} \quad 4.19$$

### 4.3 Fundamentals of volumetric analysis

**Volumetric analysis (Titration)** is a branch of quantitative analysis which is applied to determine amounts of elements, species or compounds present in a sample. An element, species or compound that is the subject of analysis is known as an analyte.

**Titration** is a common method of determining the amount or concentration of an unknown substance. The method is easy to use if the quantitative relationship between two reacting solutions is known. It is particularly well-suited to acid-base and oxidation-reduction reactions. Titrations are routinely used in clinical and biological studies to test important nutrients, naturally produced chemicals, such as cholesterol, sugars, vitamins and urea, and administered drugs in the body fluids of patients undergoing hospital treatment require monitoring. Titrations permit concentrations of the unknown substance to be determined with a high degree of accuracy.

In a titration experiment, a solution of accurately known concentration, called a titrant, is added gradually to another solution of the unknown concentration, until the chemical reaction between the two solutions is complete. In other words, titration is fulfilled up to the **equivalence** or **endpoint**. Since the stoichiometry of the reaction is known, it is possible to determine the concentration of the unknown substance by performing appropriate calculations in volumetric analysis.

There are two types of titrants in volumetric analyses: **primary standard** and **secondary standard**. The way to prepare primary standard (standard solutions) is to dissolve an accurately massed amount of a substance and dilute it to a measured volume. In this way, the concentration can be calculated exactly. Primary standards are prepared

by dissolving of standard compounds, which should meet the following requirements:

- be easy to obtain and preserve in a high state of purity and of known chemical composition;
- be non-hygroscopic and stable in the air allowing accurate weighing;
- have impurities not normally exceeding 0.02 % by mass;
- be readily soluble in water or another suitable solvent;
- react rapidly with an analyte in solution;
- other than pure elements, to have a high relative molar mass to minimize weighing errors.

The way to obtain a secondary standard (working solution) is to prepare a solution of an approximate molarity and titrate it against a primary titrant of known purity. This analytical procedure is known as standardization.

Chemical reactions applied in volumetric analysis are defined as titrimetric reactions. They should be:

- practically irreversible ( $K > 10^8$ );
- fast (equivalent point ought to be reached within several minutes);
- no by products ought to be prepared;
- there must be a valid method to detect the end-point of titration.

***Titration methods are classified as follows:***

- by a type of chemical reactions;
- by an analytical technique.

***The chemical reactions involved in volumetric analysis are classified as follows:***

- ***acid-base reactions***, where acid donates a proton to the base;
- ***precipitation reactions***, where the reactants form an insoluble product;
- ***complexation reactions***, where a ligand coordinates to an acceptor;
- ***oxidation-reduction reactions***, where the oxidizing agent gains electrons from the reduced species.

***There can be distinguished three variants of analytical technique applied in volumetric analysis are distinguished:***

- ***direct titration***: gradual addition of a titrant to a test solution up to the equivalence point;

- ***back titration***: one adds a known excess of a standard reagent to a solution, then titrates the excess. Back titration is useful if the endpoint of the reverse titration is easier to identify than the endpoint of the normal titration. It is also useful if the reaction between an analyte and a titrant is very slow.

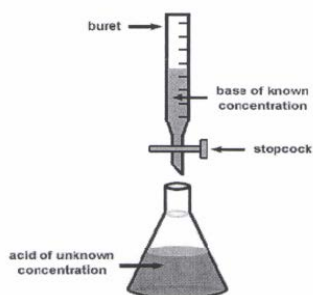
- ***displacement titration***: the excess of a reagent is added to a test solution with later measuring of its product by means of a titration method.

#### ***4.4 The theoretical bases for acid-base titration***

***Acid-base titration*** is one of the titration methods based on a neutralization reaction:



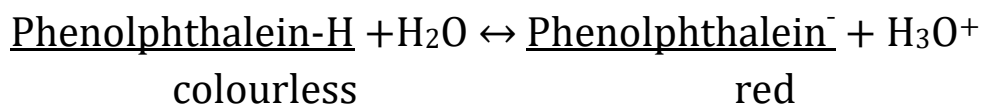
Acid-base titration is observed when we add a base to an acid or an acid to a base until the equivalence point is reached which is when the moles of an acid are equal to the moles of a base. The identification of the acidic solution concentration of unknown normality by means of standard basic solutions is known as ***acidimetry***. The use of standard acid solutions to determine the concentration of basic solutions of unknown normality is called ***alkalimetry***. These methods are applied in clinical practice to analyze solutions of acids, bases and salts, which undergo hydrolysis. It is widely used in medicine to determine acidity of gastric juice and other biological fluids.



**Figure 4.1 — A titration setup**

**Primary standards** applied in acid-base titration are the solutions of sodium tetraborate (borax) ( $\text{Na}_2\text{B}_4\text{O}_7 \times 10\text{H}_2\text{O}$ ), oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \times 2\text{H}_2\text{O}$ ) and succinic acid ( $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$ ). **Secondary standards** are prepared from the solutions of hydrochloric and sulfuric acids, and such hydroxides as NaOH and KOH.

The end point or equivalence point in acid-base titration is signaled by a change in the color of an acid-base indicator. Acid-base indicator is usually a weak organic acid or a base conjugate forms of which have a color different from that of the original compound. One commonly used indicator is phenolphthalein, which is colorless in acidic and neutral solutions but reddish pink in basic solutions:



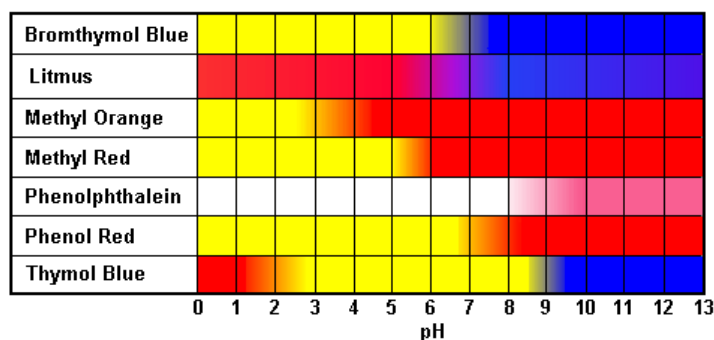
The color changes when a solution contains a 1:1 mixture of the differently colored forms of an indicator.

**Table 4.1 — Some common acid-base indicators**

| Color indicator   | In acid   | In base       | pH rage* | pK <sub>in</sub> |
|-------------------|-----------|---------------|----------|------------------|
| Thymol blue       | Red       | Yellow        | 1.2-2.8  | 1.7              |
| Bromophenol blue  | Yellow    | Bluish purple | 3.0-4.6  | 3.8              |
| Methyl orange     | Orange    | Yellow        | 3.1-4.4  | 4.0              |
| Methyl red        | Red       | Yellow        | 4.2-6.3  | 5.5              |
| Chlorophenol blue | Yellow    | Red           | 4.8-6.4  | 5.6              |
| Bromophenol blue  | Yellow    | Blue          | 6.0-7.6  | 7.0              |
| Cresol red        | Yellow    | Red           | 7.2-8.8  | 7.6              |
| Phenolphthalein   | Colorless | Reddish pink  | 8.3-10.0 | 9.0              |

\* The pH range is defined as a range over which an indicator changes from the acid color to the base color.

Indicators must be carefully chosen so that their color changes take place at the pH values expected for an aqueous solution of the salt produced in the titration (fig. 4.2).



**Figure 4.2 — The change of the color in the deferent media**

The choice of indicator depends upon the reaction to be studied. As a general rule it is noted that the color change takes place over the range:

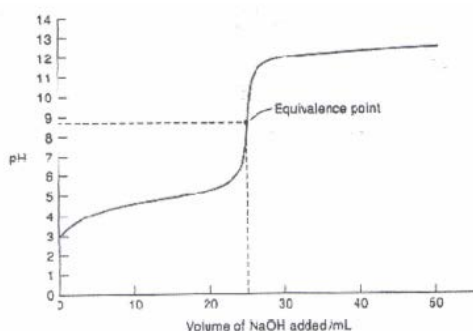
$$\text{pH} = \text{pK}_{\text{in}} \pm 1 \quad 4.20$$

In order to complete titration correctly the concentration at which the indicator changes must match the concentration at the end point.

For example, the  $\text{pK}_{\text{in}}$  value for phenolphthalein is 9.4. Can it be used to monitor the titration of  $\text{CH}_3\text{COOH}$  versus  $\text{NaOH}$ ? From the equation (4.20), we have  $\text{pH} = 9.4 \pm 1$ .

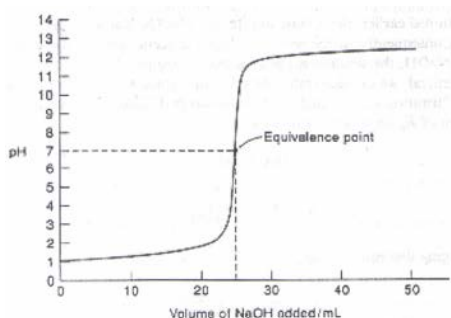
According to this estimate, the color of phenolphthalein begins to change from acid (colorless) at pH 8.4 to the base form (reddish pink) at pH 10.4. Thus, phenolphthalein is a suitable indicator for this titration (fig. 4.3).

We can predict a pH value at the end point of titration with the help of titration curves. A titration curve (or a pH profile of titration) is the plot of pH as a function of titrant added to a test solution.



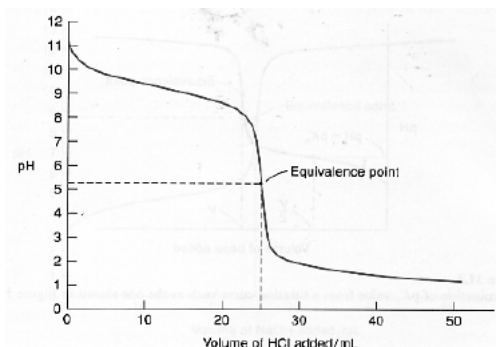
**Figure 4.3 — The pH profile of a weak acid-strong base titration**

For example, the titration of a strong acid with a strong base produces the following pH profile (fig. 4.4). As we can see, pH at the end point of such titration is 7. Thus methyl orange and bromothymol blue can be in analytical practice when strong acids are titrated against strong bases.



**Figure 4.4 — The pH profile of a strong acid-strong base titration**

For example, the pH profile of a weak base-strong acid titration is given in figure 4.5. In accordance with the graph, the pH at the end point is less than 7 thus methyl orange is valid when weak bases are titrated against strong acids, (fig. 4.5).



**Figure 4.5 — The pH profile of a weak base - strong acid titration**

An indicator error of titration appears as a result of applying an indicator the pH range of which does not coincide with the pH of a solution at the endpoint of titration.

#### ***4.5 General concepts of redox reactions***

***Oxidation-reduction reactions (redox reactions)*** are the reactions in which electrons are transferred from one species to another. Electron gain is called ***reduction*** and electron loss is ***oxidation***.

Oxidation-reduction reactions are very much a part of the world around us. They range from combustion of fossil fuels to the action of household bleaching agents. Most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction. Most biochemical processes are the reactions of this type; they fulfill two vital functions *in vivo*:

- synthesis of complex organic molecules;
- the main source of energy for our bodies. Energy is released when high molecular compounds (lipids, carbohydrates and proteins) undergo oxidation in human cells. They give 99 % of energy required for a human body to drive metabolic processes. Lipids and carbohydrates are responsible for 90 % of this energy while proteins give only 10 %.

***Redox reactions*** are processes in which at least one atom changes in oxidation number.

***Oxidation number*** (or oxidation state) is the charge that an atom would have if the compound in which it was found were ionic.

The following rules help us assign the oxidation number of elements:

1. In free elements (that is, in uncombined state), each atom has an oxidation number of zero. Thus each atom in  $\text{H}_2$ ,  $\text{Br}_2$ , Na, Be, K,  $\text{O}_2$ ,  $\text{P}_4$ , and  $\text{S}_8$  has the same oxidation number: zero.

2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus  $\text{Li}^+$  has an oxidation number of +1;  $\text{Ba}^{2+}$  ion, +2;  $\text{Fe}^{3+}$  ion +3; and so on. All alkali metals have an oxidation number of +1, and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum always has an oxidation number of +3 in all its compounds.

3. The oxidation number of oxygen in most compounds (for example,  $\text{MgO}$  and  $\text{H}_2\text{O}$ ) is -2, but in hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and peroxide ions ( $\text{O}_2^{2-}$ ), its oxidation number is -1.

4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is, compounds containing two elements). For example, in  $\text{LiH}$ ,  $\text{NaH}$ , and  $\text{CaH}_2$ , its oxidation number is -1.

5. Fluorine has an oxidation number of -1 in all its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen, for example in oxoacids and oxoanions, they have positive oxidation numbers.

6. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion,  $\text{NH}_4^+$ , the oxidation number of N is -3 and that of H is +1. Thus the sum of the oxidation numbers is  $-3 + 4 \times (+1) = +1$ , which is equal to the net charge of the ion.

### **Fundamentals redox reactions:**

1) Reducing agents (or reductants) are species that lose electrons; this process is referred as oxidation.

2) Oxidizing agents (or oxidants) are species that gain electrons; this process is referred as reduction.

3) Oxidation and reduction always run together in a joint process.

The most important reducing agents are:

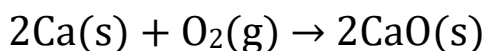
- metals and some nonmetals (H<sub>2</sub>, C);
- some oxides (CO, NO, N<sub>2</sub>O, SO<sub>2</sub>);
- some acids (H<sub>2</sub>S, H<sub>2</sub>SO<sub>3</sub>, HCl, HBr, HI);
- salts of these acids;
- most organic compounds.

The most important oxidizing agents are:

- some nonmetals: O<sub>2</sub>, O<sub>3</sub>, F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>;
- H<sub>2</sub>SO<sub>4</sub> (concentrated), HNO<sub>3</sub>;
- some salts (KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, K<sub>2</sub>CrO<sub>4</sub>, FeCl<sub>3</sub>, CuCl<sub>2</sub>).

### **The types of redox reactions:**

- **Intermolecular reactions:** oxidizing and reducing agents are different substances. For example:



- **Intramolecular reactions:** oxidizing and reducing agents are atoms in a molecule of one substance. For example:

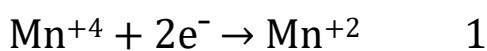
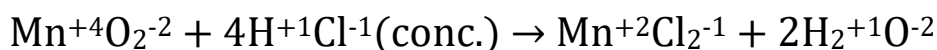


- **Disproportionation reactions:** an element is both oxidized and reduced in a process. For example:



**Balancing oxidation-reduction equations.** Equations representing oxidation-reduction reactions are relatively easy to balance. There are some special techniques for handling these processes. They are known as an *electron balance method* and an *ion-electron (half reaction) method*.

The electron balance method is based on comparison of atoms oxidation numbers in reactants' and products' molecules. It may be used for balancing of any chemical reaction. For example:



The coefficients are used to equalize the number of gained and loosed electrons.

**The equivalent factor** for oxidizing and reducing agents ( $f_e$ ) is calculated as

$$f_e = 1/z \quad 4.21$$

where  $z$  - is an amount of electrons gained or lost by one mole of a substance.

**The ion-electron (half reaction) method** may be applied to balance redox reactions, which run in aqueous solutions.

In this approach, the overall reaction is divided into two half-reactions, one for oxidation and one for reduction. Each half-reaction is balanced separately and then added to produce the overall balanced equation.

**In half-reactions:**

- chemical formulas of strong electrolytes, which are readily soluble in water, are written as ions;

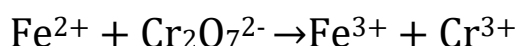
- chemical formulas of weak electrolytes, nonelectrolytes and insoluble electrolytes are written as molecules;

- for reactions in acid medium, add water molecules  $H_2O$  to balance the oxygen O atoms and add protons  $H^+$  to balance the hydrogen H atoms;

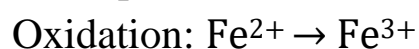
- for reactions in a base medium, add hydroxide ions  $OH^-$  to balance the O atoms and  $H_2O$  molecules to balance the H atoms. As a rule **two hydroxide ions are added to balance one oxygen atom.**

Suppose we are asked to balance the equation showing the oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  ions by dichromate ions ( $Cr_2O_7^{2-}$ ) in an acidic medium.  $Cr_2O_7^{2-}$  is reduced to  $Cr^{3+}$  ions. The following steps will help us accomplish this task.

**Step 1.** Write the basic equation for the reaction in ionic form. Separate them into two half-reactions:



The equations for the two half-reactions are

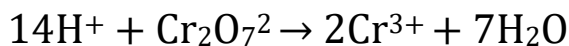


**Step 2.** We begin by balancing the atoms in each half-reaction. The oxidation reaction is already balanced for Fe atoms. For the reduction

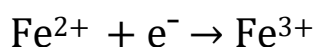
step, we multiply the  $\text{Cr}^{3+}$  by 2 to balance the Cr atoms. Since the reaction takes place in an acidic medium, we add seven  $\text{H}_2\text{O}$  molecules to the right-hand side of the equation to balance the O atoms:



To balance the H atoms, we add fourteen  $\text{H}^+$  ions on the left side:



**Step 3.** Add electrons to one side of each half-reaction to balance the charges. If necessary, equalize the number of electrons in the two half-reactions by multiplying one or both half-reaction by appropriate coefficients. For the oxidation half-reaction we write:



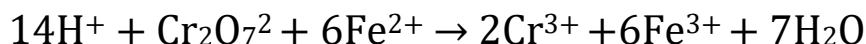
In the reduction half-reaction there are net twelve positive charges on the left-hand side and only six positive charges on the right-hand side. Therefore, we add electrons on the left:



To equalize the number of electrons in both half-reactions, we multiply the oxidation half-reaction by 6:



**Step 4.** Add the two half-reactions together and balance the final equation by inspection. The electrons on both sides must cancel. The two half-reactions are added to give



The electrons in both sides cancel, and we are left with the balanced net ionic equation:

**Step 5.** Verify that the equation contains the same types and numbers of atoms and the same charges on both sides of the equation.

A final check shows that the resulting equation is «atomically» and «electrically » balanced.

We now apply the ion-electron method to balance the equation of a redox reaction in basic medium.

**General classification of redox titration methods.** Oxidation and reduction titration is the quantitative analysis of the amount or concentration of an oxidizing or reducing agent in a sample by observing its reaction with a known amount or concentration of a

reducing or oxidizing agent. Redox titrations may be used to measure many species, especially metals of high and low oxidation states, iodine and iodides, and easily oxidized organic compounds.

*The classification of redox titration methods* is based on the type of a titrant used for analyses. The most applied in medicine are:

- *permanganatometric titration*: Potassium permanganate  $\text{KMnO}_4$  solution is applied as a titrant;

- *iodometric titration*: solutions of iodine  $\text{I}_2$  and sodium thiosulfate  $\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$  are used as titrants;

- *bromatometric titration*: potassium bromate  $\text{KBrO}_3$  solution is used as a titrant.

#### ***4.6 Exercises for the self-control***

##### **Discussion questions:**

1. Define the following terms: (a) titration, (b) equivalence or end point of titration, (c) an analyte.

2. Chemical reactions applied in volumetric analysis are defined as titrimetric reactions. Name the main features of these reactions.

3. Primary standards are prepared by dissolving of standard compounds. What requirements should standard compounds meet?

4. Titration methods are classified by a type of chemical reactions. What types of chemical reactions are applied in volumetric analysis?

5. Define acid-base titration, standard solution, and equivalence point.

6. Describe the basic steps involved in acid-base titration. Why is this technique of great practical value?

7. Explain how an acid-base indicator works in a titration.

8. What are the criteria for choosing an indicator for a particular acid-base titration?

9. The amount of indicator used in acid-base titration must be small. Why?

10. Referring to Table 4.1, specify which indicator or indicators you would use for the following titrations: (a)  $\text{HCOOH}$  versus  $\text{NaOH}$ , (b)  $\text{HCl}$  versus  $\text{KOH}$ , (c)  $\text{HNO}_3$  versus  $\text{NH}_3$ .

11. For each of the following, decide whether the pH at the equivalent point is greater than, less than, or equal to 7:

- (a)  $\text{NaClO}$  (aq) titrated with  $\text{HCl}$  (aq);
- (b)  $\text{HNO}_3$  (aq) titrated with  $\text{KOH}$  (aq);
- (c)  $\text{NaNO}_2$  (aq) titrated with  $\text{HClO}$  (aq);
- (d)  $\text{NH}_4\text{Cl}$  (aq) titrated with  $\text{NaOH}$  (aq).

12. Describe the changes in the pH that take place during the titration of a weak acid with a strong base.

13. Describe the changes in the pH that take place during the titration of a weak base with a strong acid.

14. Describe the changes in the pH that take place during the titration of a strong base with a strong acid.

## CHAPTER 5. PHYSICAL PROPERTIES OF SOLUTIONS

**After reading this chapter, you should be able to:**

- define solutions and their types;
- describe biological functions of water in a human body and its content in different organs and tissues;
- discuss the dissolving process and enthalpy changes at each step of it;
- describe solubility of solids, liquids and gases in water and define thermodynamical factors which can effect their solubility;
- discuss colligative properties of solutions and explain the essential role of osmosis in physiological processes in vivo.

### *5.1 Solutions and solubility*

The study of solutions is of great importance because many interesting and useful chemical and biological processes occur in liquid solutions. Generally, a **solution** is defined as a single-phase system of variable composition consisting at least of two components: a solute and a solvent.

A **solvent** is a component that determines the state of a solution. Normally it is present in the greatest quantity. Solvents can be **polar** (for example,  $\text{H}_2\text{O}$ , concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{N}_2\text{H}_4$ ) and **nonpolar** (for example, benzene, toluene, hexane).

Water is the most important solvent in nature and the most abundant substance in the world. In biosphere the overall volume of water is  $1.5 \times 10^9 \text{ km}^3$ . Living beings contain  $2.3 \times 10^3 \text{ km}^3$  of water. Most of the human body is made up of water (2/3 of the body mass). Different organs and tissues contain a variable amount of water:

- brain is 75 % water and even moderate dehydration or lack of water can cause headaches and dizziness;
- heart and muscles are 75 % water;
- bones are 22 % water;
- lungs and liver are 86 % water;
- kidneys and blood are 83 % water.

The loss of 2/3 volume of intra-cellular fluid may cause death. The excess of water is also dangerous; it may results in cell swelling and edema.

The unique physiochemical properties of water are responsible for its numerous ***biological functions in a human body:***

(a) Water has one of the highest polarities of all liquids. This property makes water an excellent solvent for ionic compounds.

(b) Due to its very high heat capacity water regulates temperature of a cell and protects it from the heat generated by metabolic processes.

(c) Due to its high molar heat of vaporization water protects a human body from overheating.

(d) Water ionization makes it possible to participate in acid-base equilibrium in a human body.

(e) Water is a substrate for numerous biochemical reactions (hydrolysis, hydration).

(f) Water effects enzyme activity thus regulating rates of biochemical reactions.

There is a hypothesis that almost all water is of biological origin since passed through metabolic processes of living systems. A daily consumption of water for people is - 2l.

### **Classification of solutions:**

(a) According to the state of aggregation solutions fall into the three categories:

- gaseous: for example, the Earth's atmosphere is a solution of  $N_2$  and  $O_2$ ;
- liquid: all biological fluids (blood, plasma, lymph, and others);
- solid: metal alloys.

(b) According to the degree of dispersity solutions are:

- molecular or true solutions with the size of solute particles less than  $10^{-9}m$ ;
- colloidal with the size particles ranged between  $10^{-9}$ - $10^{-7} m$ ;
- coarse dispersed with the size of particles ranged between  $10^{-5}$ - $10^{-7}m$ .

**Solutions play essential role in biosphere.** Organic life appeared in the world ocean. Modern animals and human beings inherited mineral content of blood plasma from their ocean ancestors. Salt content of blood is identical to the seawater. Consumption of food components and medicines occurs in a dissolved state. All biochemical reactions proceed in aqueous solutions.

**A dissolving process.** The formation of solutions is governed by the principles of thermodynamics. It's a reversible, spontaneous physical process composed of three main steps:

1) *A destruction of solute's crystal lattice* which proceeds with heat absorption ( $\Delta H_1 > 0$ ).

2) *A formation of solvates or hydrates complexes* which runs with heat releasing ( $\Delta H_2 < 0$ ).

3) *A diffusion of solute particles* throughout a solution ( $\Delta H_3 \approx 0$ ).

Thus the overall heat (enthalpy) of solutions ( $\Delta_{\text{sol}}H$ ) is an integral magnitude which is calculated as

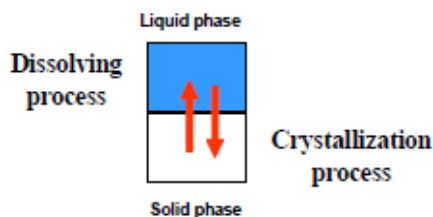
$$\Delta H_{\text{sol}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

**Heat of solution** is defined as a heat amount absorbed or released when one mole of a solute is dissolved in the endless amount of a solvent under the standard conditions.

Dissolving of most solids is endothermic ( $\Delta_{\text{sol}}H > 0$ ) since the amount of heat absorbed in the first step exceeds the amount of heat released in the second step of a process. Dissolving of most gases is exothermic ( $\Delta_{\text{sol}}H < 0$ ) since the first step of a process doesn't occur (gases do not form crystals under normal conditions). Dissolving of one liquid in another liquid is in fact a diffusion of one liquid into another. This process is accompanied by negligibly low heat effect ( $\Delta_{\text{sol}}H \approx 0$ ), since diffusion proceeds without any heat absorption or releasing.

Like all reversible processes a dissolving process runs up to the equilibrium state.

**Saturated solutions** exist at equilibrium state with the excess of a solute. At equilibrium state the rate of desolvation is equal to the rate of crystallization (fig.5.1).



**Figure 5.1 — Saturated solutions exist at equilibrium state with the excess of a solute**

Solutions which concentration is lower than that of saturated are defined as *unsaturated solutions*.

*Supersaturated solutions* contain the greater amount of a solute than saturated solutions. They are unstable.

Generally, *solubility* is defined as an ability of substances to be dissolved in a particular solvent. It's characterized by a solvent content in a saturated solution under the certain temperature. *Solubility* is denoted as «S» and is expressed in g/l, mol/l and, and percent by mass or by volume.

Solubility depends upon nature of substances and thermodynamic parameters of a system. The effect of nature of a solvent and a solute on solubility is described by the following rule: «Like dissolves like». In other words, polar compounds are readily dissolved in polar solvents, while nonpolar compounds are readily dissolved in nonpolar solvents. For example, NaCl exhibits high solubility in water and low solubility in benzene. On the contrary, I<sub>2</sub> exhibits high solubility in benzene and low solubility in water.

**Solubility of gases in water.** Gases dissolution in water may be represented by the following scheme:



In accordance with Le Chatelier's Principle increase in temperature shifts equilibrium to the left, thus decreasing solubility, while decrease in temperature, favors solubility of gases.

**Table 5.1 — Solubility of gases (l/1l H<sub>2</sub>O) at 1 atm**

| Gas             | Temperature, °C |        |        |
|-----------------|-----------------|--------|--------|
|                 | 0               | 20     | 100    |
| N <sub>2</sub>  | 0.0235          | 0.0154 | 0.0095 |
| O <sub>2</sub>  | 0.0489          | 0.0310 | 0.0172 |
| NH <sub>3</sub> | 1150            | 690    | 95     |

In accordance with Le Chatelier's Principle increase in pressure shifts equilibrium to the right, thus increasing solubility, while decrease in produces solubility of gases.

According to **Henry's Law** (1803) the solubility of a gas in a liquid is proportional to the partial pressure of a gas above the solution:

$$S = k \times p \quad 5.1$$

where k - Henry's law constant; S - concentration of a gas in a solution; p - partial pressure of a gas in the vapor phase above a solution.

Henry's Law explains gas exchange between a human body and its surroundings. Thus it gives reason for such a phenomenon as a caisson disease or bend. Deep-sea divers, astronauts and pilots of supersonic planes can suffer this disease. For every 30 feet a diver descends, the pressure increases by 1 atm. As a result, the amount of nitrogen gas dissolved in the diver's blood increases significantly as the diver descends. If a diver returns to the surface too quickly after a deep dive, gas dissolved in the blood may form bubbles in the same way as the CO<sub>2</sub> in a freshly opened carbonated drink. These bubbles interfere with the transmission of nerve impulses and restrict the flow of blood. The mildest result is dizziness, the most serious – paralysis and death. Divers avoid the bends by returning to the surface slowly to allow excess gas to escape from the blood without forming bubbles. It was reported that on June 29, 1971 three Soviet astronauts died from caisson disease, returning to the Earth.

**Sechenov's equation** postulates that solubility of a gas in pure water is higher than in electrolyte solutions:

$$S = S_0 \times e^{-kc} \quad 5.2$$

where S - gas solubility in a solution; S<sub>0</sub> - gas solubility in pure water; e - a base of natural logarithm; c - an electrolyte concentration; k - Sechenov's equation constant.

Sechenov's equation makes clear why gas concentration in blood is lower than in pure water.

**Table 5.2 — Solubility of gases in water and blood plasma at 38°C**

| Gas             | Solubility, percent by volume |                 |
|-----------------|-------------------------------|-----------------|
|                 | In water                      | In blood plasma |
| N <sub>2</sub>  | 0.0263                        | 0.0255          |
| O <sub>2</sub>  | 0.0137                        | 0.0135          |
| NH <sub>3</sub> | 0.387                         | 0.381           |

**Solubility of liquids in other liquids.** Liquids dissolution in water may be represented by the following scheme:



Increase in temperature initiates mutual diffusion of liquids thus increasing their solubility. **Three types of liquids can be distinguished:**

(a) completely soluble in each other (miscible): for example: H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O;

(b) partially soluble in each other: for example C<sub>6</sub>H<sub>6</sub>/H<sub>2</sub>O;

(c) insoluble in each other (immiscible) for example: Hg/H<sub>2</sub>O.

**The Nernst-Shilov's Distributional Law** deals with a heterogeneous equilibrium which is maintained when the third component is added into a system composed of two immiscible liquids. This law is defined in the following way: *when the third component is added into a system of two immiscible liquids, the ratio of its concentrations in both liquids will stay constant at a certain temperature.* (fig. 5.2).

**Phase 1**



**Figure 5.2 — A scheme of two-phase system composed of immiscible liquids, where [A]' and [A] are concentrations of the third component in both phases**

**Phase 2**

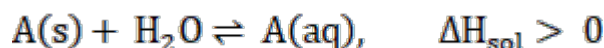
The relationship of the third component concentrations in phases 1 and 2 is a constant value at a given temperature:

$$\frac{[A]'}{[A]} = K \quad 5.3$$

where K - is distributional Equilibrium constant.

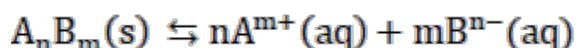
The Nemst-Shilov's Distributional Law is a theoretical base for extraction - a method to separate mixtures into individual components.

**Solubility of solids.** Solids' dissolution in water may be represented by the following scheme:



According to Le Chatelier's principle temperature rise increases solubility of solid substances in water.

A heterogeneous equilibrium between an insoluble electrolyte (salt, hydroxide or an acid) and its ions in a saturated solution may be represented by



Solubility equilibrium which is unique since only the product side of the reaction equation is involved in equilibrium expression is characterized by the *solubility-product constant*  $K_{sp}$ :

$$K_{sp} = [A^{m+}]^n \times [B^{n-}]^m$$

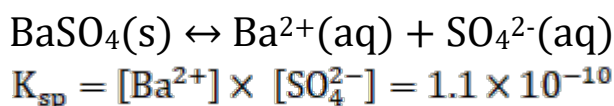
$K_{sp}$  is useful for predicting solubility of insoluble electrolytes:

$$S = \sqrt[n+m]{\frac{K_{sp}}{n^n \times m^m}} \quad 5.4$$

For a binary electrolyte  $n = m = 1$  hence

$$S = \sqrt{K_{sp}} \quad 5.5$$

For example:



$$S = \sqrt{K_{sp}}$$

$$\sqrt{K_{sp}} = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}$$

$K_{sp}$  defines the solubility of a substance: the greater  $K_{sp}$  is, the higher solubility is. On the other hand, the smaller  $K_{sp}$  is, the better crystallization or precipitation of a solid is. Precipitation occurs from saturated and supersaturated solutions and never from unsaturated ones.

In saturated solutions  $[A^+] \times [B^-] = K_{sp}$ .

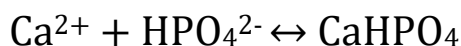
In super saturated solutions  $[A^+] \times [B^-] > K_{sp}$

A theory of heterogeneous equilibrium makes it possible to understand the biological process of bone tissue formation. Bone tissue formation is one of the most important heterogeneous processes in vivo. Hydroxy apatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  is the mineral component of bones (fig. 5.3).



**Figure 5.3 — Hydroxy apatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  is the mineral component of bones**

In blood at pH 7.4 calcium cations  $\text{Ca}^{2+}$  and anions of phosphoric acid  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  are present. The amounts of both anions are approximately equal but  $\text{CaHPO}_4$  ( $K_{\text{sp}} = 2.7 \times 10^{-7}$ ) is less soluble than  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ . ( $K_{\text{sp}} = 1 \times 10^{-3}$ ) thus formation of  $\text{CaHPO}_4$  is proved to be the first step in bone tissue generation:



In the next steps the following salts are produced



Solubility of hydroxy apatite is very low ( $K_{\text{sp}} = 1.0 \times 10^{-58}$ ) thus bones are extremely stable. The excess of  $\text{Ca}^{2+}$  shifts equilibrium to the right, which results in bones calcification.  $\text{Ca}^{2+}$  deficiency shifts equilibrium to the left which results in destruction of bones. Children suffer from rachitis, in adults osteoporosis develops (fig. 5.4).



**(a)**



**(b)**

**Figure 5.4 — Bone tissues (a) Osteoporosis: vertebrae are deformed), (b) Healthy bone tissue: vertebrae are not deformed; bones are dense**

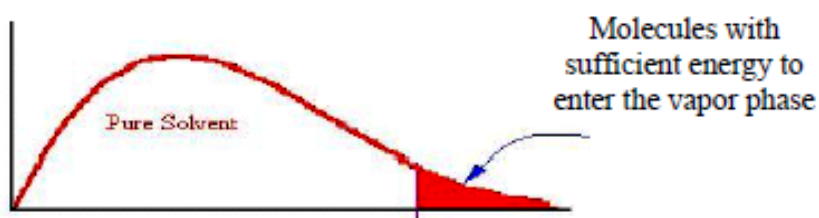
Calcium deficiency leads to incorporation of beryllium and strontium into the bone tissue. Their incorporation results in beryllium and strontium rachitis (bones become fragile and brittle). Incorporation of radionuclide Sr-90 into the bone tissue results in its radioactive irradiation, which may cause leucosis and other oncological diseases. Thus calcium prevents accumulation of radioactive strontium in a human body.

## 5.2 Colligative (collective) properties of solutions

General properties of solutions include vapor- pressure lowering, boiling-point elevation, freezing-point depression and osmotic pressure. These properties are commonly referred to as *colligative* or *collective* properties because they are bound together through their common origin. Colligative properties depend only on the number of solute particles present, not on their size or molar mass of the molecules.

*The first Raoult's Law* deals with the vapor-pressure lowering: *the vapor pressure of solutions containing nonvolatile solutes is always smaller than that of pure solvents.*

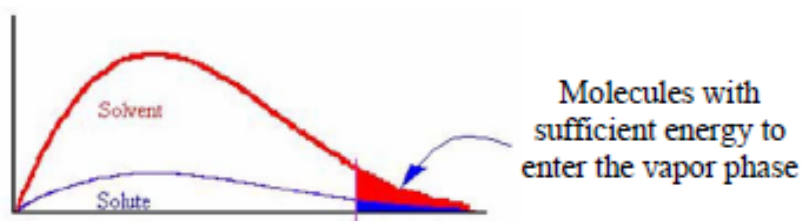
We can explain this phenomenon from the point of view of intermolecular forces which operate between molecules of solvents and solutes. This is most easily illustrated by use of a Boltzman curve (fig. 5.5) in which we assume that only those molecules with energies in excess of some value will be able to break free and go into the vapor phase.



represents the total number of molecules

**Figure 5.5** — The Boltzman's curve illustrates an energy distribution of molecules in a pure solvent. The area under the curve

Nonvolatile solutes bind solvent molecules thus decreasing a fraction of solvent molecules with energies enough to enter the vapor phase (fig. 5.6). Because of this a solution has a lower vapor pressure than a pure solvent.



**Figure 5.6 — The Boltzman's curve illustrates an energy distribution of molecules in a solution of a nonvolatile solute**

The decrease in vapor pressure is proportional to the mole fraction of a solute:

$$\frac{(P_0 - P)}{P_0} = \chi(A) \quad 5.6$$

where  $\chi(A)$  - is a mole fraction of a solute.

For a two-component solution:

$$\frac{(P_0 - P)}{P_0} = \frac{\vartheta(\text{solute})}{\vartheta(\text{solute}) + \vartheta(\text{solvent})} \quad 5.7$$

where  $P_0$  - the vapor pressure of a pure solvent;  $P$  - the vapor pressure of a solution.

To make the equation (5.6) available for electrolyte solutions Van't Hoffs factor ( $i$ ) must be added:

$$\frac{(P_0 - P)}{P_0} = \frac{i \times \vartheta(\text{solute})}{i \times \vartheta(\text{solute}) + \vartheta(\text{solvent})} \quad 5.8$$

Van't Hoffs factor characterizes ionization of electrolytes, and its relationship with percent of ionization is given by

$$\alpha = \frac{(i - 1)}{(n - 1)} \quad 5.9$$

where  $n$  - a number ions contained in a molecule.

***Ebullioscopic Raoult's Law:*** boiling- points of solutions containing nonvolatile solutes are always higher than that of pure solvents.

The boiling-point of a liquid is a temperature under which its vapor pressure equals the external atmospheric pressure:

$$\Delta T_b = K_b \times C_m (\text{for nonelectrolytes}) \quad 5.10$$

$$\Delta T_b = i \times K_b \times C_m (\text{for electrolytes}) \quad 5.11$$

where  $\Delta T_b$  - is boiling-point elevation, which is equal to:

$$\Delta T_b = T_2 - T_1 \quad 5.12$$

where  $T_1$  and  $T_2$  - are boiling-points of a solvent and a solution respectively;  $C_m$  - molality, mol/kg;  $K_b$  - the molar boiling-point elevation constant (0.52 for water).

***Cryoscopic Raoult's Law:*** *freezing points of solutions containing nonvolatile solutes are always lower than that of pure solvents.*

The freezing-point of a liquid is a temperature under which its vapor pressure equals the vapor pressure of solid solvents.

$$\Delta T_f = K_f \times C_m \text{ (for nonelectrolytes)} \quad 5.13$$

$$\Delta T_f = i \times K_f \times C_m \text{ (for electrolytes)} \quad 5.14$$

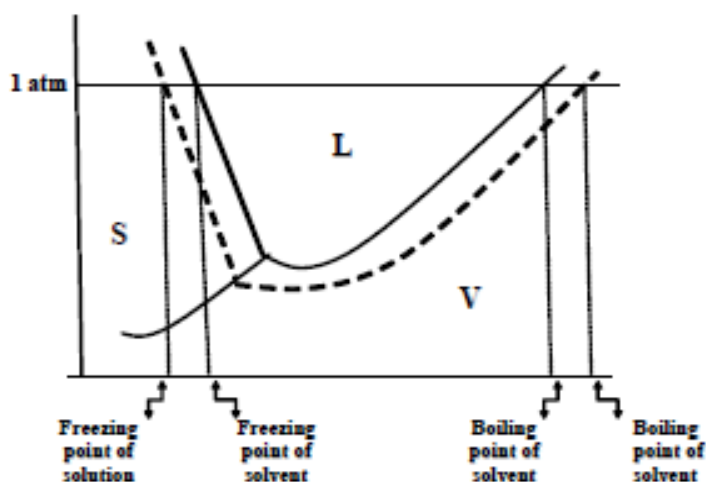
where  $\Delta T_f$  - is freezing point depression, which is equal to:

$$\Delta T_f = T_2 - T_1$$

$T_1$  and  $T_2$  are freezing-points of a solvent and a solution respectively;  $K_f$  - the molar freezing-point depression constant (1.86 for water).

For blood plasma of people  $\Delta T_f$  equals to  $0.56^\circ$ , for blood plasma of mammals  $\Delta T_f$  is a bit higher ( $0.58^\circ$ ).

The freezing point depression and boiling point elevation phenomena can be understood by studying phase diagrams of pure water and of water in an aqueous solution containing a nonvolatile solute (fig. 5.7).



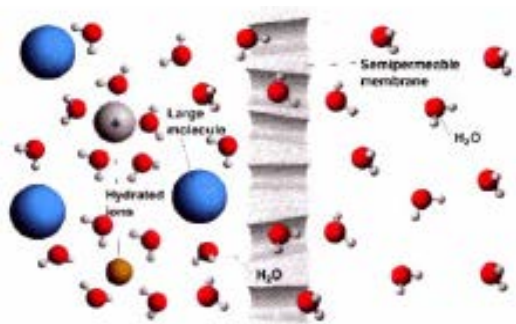
**Figure 5.7 — Phase diagrams of pure water (solid lines) and of water in an aqueous solution containing a nonvolatile solute (dashed lines)**

At 1 atm, the freezing point of a solution lies at the intersection point of the dashed curve (between the solid and the liquid phases) and the horizontal line at 1 atm. Under the same pressure, the boiling point of a solution lies at the intersection point of the dashed curve (between the liquid and the vapor phases) and the horizontal line at 1 atm. We can

use this graph to determine  $\Delta T_f$  and  $\Delta T_b$  of a nonvolatile aqueous solution.

**Cryoscopy** and **ebullioscopy** are experimental methods to determine molar masses of substances. They are wide used in pharmacology to determine molar masses of different medicines. In general, the freezing-point-depression experiment is much easier to carry out.

**Osmosis** is a reversible thermodynamic process of water diffusion through the semipermeable membrane from pure water to a solution, or from a dilute solution into a more concentrated one. Osmosis is driven by a difference in a solute concentration on the two sides of the membrane (fig. 5.8).



**Figure 5.8 — Scheme of the osmosis**

Diffusion of water across a membrane generates pressure called **osmotic pressure** ( $\pi$ , kPa). Osmotic pressure may be calculated by the Van't H off's equations:

$$\pi = R \times T \times C_m \text{ (for nonelectrolytes)} \quad 5.15$$

$$\pi = i \times R \times T \times C_m \text{ (for electrolytes)} \quad 5.16$$

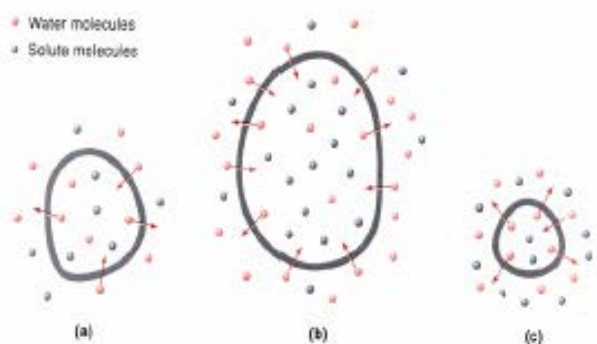
Osmosis plays a key role in biological processes such as absorption of nutrients, elimination of waste products of metabolism, active transport of water.

Normal osmotic pressure of blood plasma is 740-780 kPa; osmotic homeostasis is maintained by useful work of kidneys, lungs and skin. Electrolytes are mainly responsible for high osmotic pressure of blood plasma and other biological fluids. Colloidal particles of proteins not able to pass through cell membranes also contribute into osmotic pressure of blood plasma, but their oncotic pressure is rather low: 3-4 kPa.

Most solutions used in medicine for intravenous injections are **isotonic** (with the same osmotic pressure as blood). Their injection into the blood vessel doesn't disturb osmotic homeostasis of a body. They are (a) 0.9 % by mass NaCl solution and (b) 4.5 % by mass glucose solution.

When a red blood cell is placed in a **hypotonic solution** ( $\pi < 740$  kPa) water tends to move into the cell. The cell swells and eventually burst, releasing hemoglobin and other protein molecules. This phenomenon is known as **hemolysis** - destruction of blood. Its initial step occurs when osmotic pressure becomes equal to  $\sim 360$ -400 kPa, irreversible (total) hemolysis occurs at 260-300 kPa.

When a red blood cell is placed into a **hypertonic solution** ( $\pi > 780$  kPa) the intracellular water tends to remove out of a cell by osmosis to the more concentrated, surrounding solution. This process, known as **plasmolysis**, causes the cell to shrink and eventually cease functioning. Nevertheless some hypertonic solutions are applied in medicine. For example, 10 % by mass NaCl solution is used to heal purulent wounds; and 25 % by mass  $\text{MgSO}_4$  solution is applied to treat hypertonic crises.



**Figure 5.9 — A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c)**

**Osmolarity** and **osmolality** are concentration units, which characterize content of solutes not able to diffuse through the semipermeable membranes.

### **5.3 Problems for the self-control**

#### **Discussion questions:**

1. What is solvation? What are the factors that influence the extent to which solvation occurs?
2. Based on intermolecular force consideration, explain what «like dissolves like» means.

3. Define the following terms: saturated solution, unsaturated solution, supersaturated solution and crystallization.

4. What are colligative properties? What is the meaning of the word «colligative» in this context?

5. How is the lowering in vapor pressure related to a rise in the boiling point of a solution?

6. For intravenous injections great care is taken to ensure that the concentration of solutions to be injected is comparable to that of blood plasma. Why?

7. Explain how colligative properties are used to determine molar mass.

## CHAPTER 6. ELECTROLYTE SOLUTIONS

**After reading this chapter, you should be able to:**

- discuss general features of the Arrhenius theory of electrolytic dissociation;
- define weak electrolytes, give their examples and describe equilibrium which is maintained in their solutions; be able to perform typical calculations involving Ostwald's dilution Law;
- discuss general features of the Debye-Huckel theory of strong electrolyte solution; be able to perform typical calculations of ionic strength, activity, activity coefficient of ions and mean activity coefficients of electrolytes;
- describe specific and equivalent conductivity in electrolytes solutions;
- discuss biological functions of electrolytes in a human body.

### ***6.1 The Arrhenius Theory of electrolytes dissociation***

All biological and many chemical systems are aqueous solutions that contain various ions. The stability of biomacromolecules and the rates of many biochemical reactions are highly dependant on the type and concentration of ions present. It is important to have a clear understanding of the behavior of ions in solutions.

**An electrolyte** is a polar compound that, when dissolved in a solvent (usually water), produces a solution that will conduct electricity. An electrolyte can be an acid, a base, a salt and water itself. **Ionization (dissociation)** is a spontaneous physiochemical process of electrolytes' break down into ions under the influence of water molecules.

***The main statements of the Arrhenius Theory are:***

1. Ionization of electrolytes produces ions which are responsible for solutions' ability to conduct electricity. ***The degree of ionization (ionization percent) ( $\alpha$ )*** can be calculated by the simple relation:

$$\alpha = \frac{\text{a number of ionized molecules}}{\text{a total number of dissolved molecules}} \quad 6.1$$

2. Electrical conductivity of solutions, their osmotic pressure, boiling and melting points depend not only upon their concentration but upon their ionization per cent as well:

$$a = \frac{(i - 1)}{(n - 1)} \quad 6.2$$

where  $i$  - is the Van't Hoffs factor. In dilute solutions  $a$  tends to 1, thus  $i$  tends to  $n$ ;  $n$  - is a number of ions contained in a molecule.

For example, for NaCl  $n$  is 2, for  $\text{Na}_2\text{SO}_4$  - 3 and for  $\text{Na}_3\text{PO}_4$  it equals to 4.

3. According to their ability to dissociate into ions, there can be distinguished two types of electrolytes. They are weak and strong electrolytes. However this classification is not absolute. An electrolyte's ionization percent depends not only upon its nature, but upon the solvent's nature as well. Thus NaCl in water is a strong electrolyte, but when NaCl is dissolved in benzene, there is no dissociation (NaCl remaining as undissociated substance). The nature of the solvent is a crucial factor in ability of substances to dissociate into ions. In this chapter we shall discuss only water solutions of electrolytes.

In his theory Arrhenius did not take into account the interaction of the solute and solvent, but the modern concept of electrolytic dissociation defines the role of a solvent as an instrument to separate ions and prevent their recombination. Most electrolytes are ionic compounds thus water for them is the most effective solvent because of its polarity. Ionization of ionic compounds in water can be represented by the following scheme (fig. 6.1).

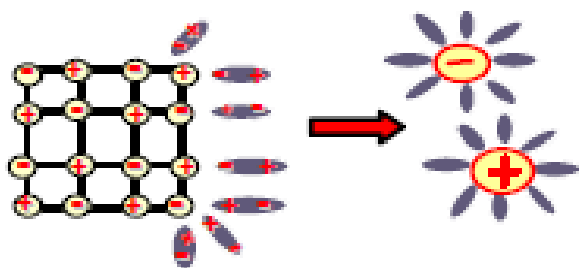


Figure 6.1 — Ionic compound dissociation in water

Each ion in a solution is surrounded by a shell of water molecules. A number of molecules in a shell are defined as a **hydration number**, which can be identified experimentally:

|              |               |               |                 |              |               |               |
|--------------|---------------|---------------|-----------------|--------------|---------------|---------------|
| $\text{H}^+$ | $\text{Li}^+$ | $\text{Na}^+$ | $\text{NH}_4^+$ | $\text{K}^+$ | $\text{Rb}^+$ | $\text{Cs}^+$ |
| 1            | 120           | 66            | 17              | 16           | 14            | 13            |

The role of solvents in a dissociation process can be described by **Coulomb's Law**:

$$F = \frac{q_1 - q_2}{\varepsilon \times r^2} \quad 6.3$$

where F - is the electric force of attraction between a cation and an anion;  $q_1$  and  $q_2$  - electric charges of ions; r - is the distance between ions;  $\varepsilon$  - is the dielectric constant of a solvent, which indicates by how many times a solvent reduces the attractive forces between ions in comparison with vacuum.

For water  $\varepsilon$  is  $\sim 81$ , for ethyl alcohol  $\varepsilon \sim 24$ , for most organic solvents  $\varepsilon$  is in the range at 2-2.5. In water the attractive forces between ions are reduced by 80 times, thus the vibration of ions in a crystal lattice causes their destruction. So water is the most effective solvent for electrolyte ionization.

### 6.2 Weak electrolytes

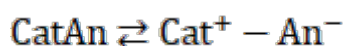
**Weak electrolytes are** polar covalent compounds which undergo reversible ionization in aqueous solutions. **They are:**

(a) most organic and a great amount of mineral acids such as  $H_2S$ ,  $H_2SO_3$ ,  $HNO_2$ ,  $HCN$  and other;

(b) bases with low solubility in water and  $NH_4OH$  (nevertheless it is highly soluble);

(c) some salts, for example  $HgCl_2$  and  $Fe(CNS)_3$ ;

In the solutions of weak electrolytes equilibrium is maintained between ions and molecules of a substance:



Their ionization percent is always much less than one ( $\alpha \ll 1$ ). Such equilibrium is characterized by **ionization equilibrium constants** ( $K_{ion}$ ), which are of several types. According to the Law of Mass Action ionization equilibrium constants are expressed by:

$$K_{ion} = \frac{[Cat] \times [An]}{[CatAn]} \quad 6.4$$

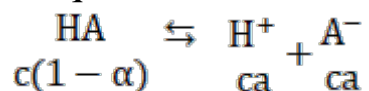
The examples of **ionization equilibrium constants are:**

- the acid ionization constant  $K_a$ ;
- the base ionization constant  $K_b$ ;

- the instability constant  $K_{\text{ins}}$ , and formation constant  $K_f$  that characterize ionization of complex compounds.

Weak electrolytes obey **Ostwald's dilution Law**.

The Ostwald's dilution Law relates ionization percent ( $\alpha$ ) to the molarity of a solution. Let's consider a weak acid HA of the concentration  $c$  (mol/l). At equilibrium, we have



The ionization constant for a weak acid ( $K_a$ ) is given by

$$K_a = \frac{[\text{H}^+] \times [\text{A}^-]}{[\text{HA}]} = \frac{c^2 \times \alpha^2}{c(1-\alpha)} = \frac{c \times \alpha^2}{(1-\alpha)} \quad 6.5$$

For weak electrolytes  $\alpha \ll 1$  thus equation (6.5) can be rearranged as:

$$K_a = c \times \alpha^2 \quad 6.6$$

or

$$\alpha = \sqrt{\frac{K_a}{c}} \quad 6.7$$

The Ostwald's dilution Law is a physical law stating that the degree of ionization for weak electrolytes is proportional to the square root of the dilution. In other words, it states that the dissociation percent of a weak electrolyte grows when the concentration of a solution diminishes.

### 6.3 Strong electrolytes

The **theory of strong electrolytes** was developed in 1923 by Peter Debye and Walter Karl Huckel. **The main statements of this theory are:**

1. Strong electrolytes are mostly ionic compounds completely dissociated into ions in water solutions. They are:

- mineral acids such as HCl, HClO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and others;
- hydroxides of Alkali and Alkaline Earth metals such as NaOH, KOH, Ba(OH)<sub>2</sub>, Ca(OH)<sub>2</sub> and others;
- most salts.

Strong electrolytes' ionization can be represented by a scheme:



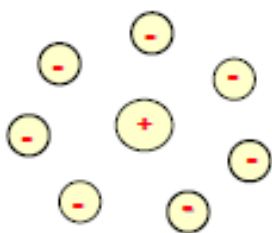
They are 100% dissociated into ions in a solution. The only things present in solutions are ions.

2. All ions in a solution contribute to the ionic strength (I), which characterizes the electric field generated by ions in a solution. It is defined as:

$$I = \frac{1}{2} \sum C_i \times Z_i^2 \quad 6.8$$

where  $C_i$  - is the molarity of ion i, mol/kg;  $Z$  - is the charge number of ion i.

3. Oppositely charged ions attract one another. As a result, anions are more likely to be found near cations in a solution, and vice versa. Overall the solution is electrically neutral, but near any given ion there is an excess of counter ions (ions of appositive charge). A sphere of oppositely charge ions surrounding each ion in an aqueous solution is defined as *ionic atmosphere* (fig.6.2):



**Figure 6.2 — A model of ionic atmosphere**

The density of ionic atmosphere depends upon the concentration of electrolytes in a solution. In outer electric field an ion and its atmosphere migrate in the opposite directions thus retarding the motion of each other. As a result conductivity of a solution becomes lower than that calculated theoretically.



**Figure 6.3 — In a conductance measurement, the movement of a cation toward the cathode is retarded by the electric field exerted by the ionic atmosphere left behind**

The electrostatic forces exerted by ions on one another are enough to cause a deviation from the ideal behavior. It seems that the concentration of ions in a solution is smaller than their true concentrations. The effective concentration of (ions that takes into

account the interaction between them is known as **activity** ( $\alpha$ ). The activity is defined by the formula:

$$a = \gamma \times C_M \quad 6.9$$

where  $\gamma$  - is the activity coefficient of an individual ion (cation or anion), which expresses the deviation of a solution from the ideal behavior.

It relates activity to concentration ( $\gamma < 1$ ). Usually we use activity coefficients of individual ions measured experimentally. They depend upon the ionic strength of a solution and their charge numbers.

A model of ionic atmosphere leads to the result that at very low concentrations the activity coefficient can be calculated from **the Debye-Huckel limiting law**:

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2} \quad 6.10$$

where  $A = 0.509$  for an aqueous solution at  $25^\circ\text{C}$ ,  $\gamma_{\pm}$  is **the mean activity coefficient**, which is the geometric mean of the individual coefficients for cation and anion

$$\gamma_{\pm} = (\gamma_+ \gamma_-)^{1/2} \quad 6.11$$

To describe the real properties of solutions of strong electrolytes we must apply not their true concentration but their effective concentration or activity. Thus, in the vast majority of cases, molarity must be replaced by activity.

#### 6.4 Electrical conduction in solutions

If an aqueous solution conducts electricity, then it must contain ions. Electrolytes solutions conduct electricity due to motion of ions toward electrodes in an external electric field. The type of their conductivity is ionic. They are conductors of the second type.

Any solution, even one containing ions, provides considerable resistance to the flow of current through it. High resistance means low conductivity; low resistance means high conductivity. **Conductivity (C)** is the reciprocal of this resistance:

$$C = \frac{1}{R} = \frac{1A}{\rho \times l} = \frac{A}{\rho l} \quad 6.12$$

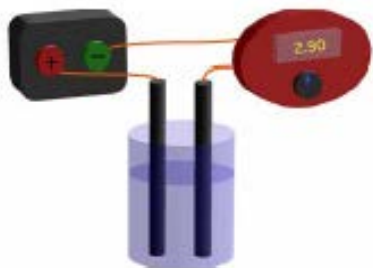
where  $R$  - is the resistance across a particular medium, which is directly proportional to the length ( $l$ ) and inversely proportional to the cross

section area ( $A$ ) of the medium;  $p$  - is the specific resistance or resistivity;  $\kappa$  - is the specific conductance or conductivity equal to  $1/p$ .

Specific conductivity is also defined as the conductivity of  $1\text{ m}^3$  of a solution when a distance between electrodes is  $1\text{ m}$ .

Resistance is measured in ohms ( $\Omega$ ), so conductance is measured in  $\Omega^{-1}$  or Siemens (S). Conductivity has the units  $\Omega^{-1}\text{ cm}^{-1}$ , or  $\Omega^{-1}\text{ m}^{-1}$ .

Chemists measure the conductivity of a solution by using a solution to complete an electrical circuit, usually by inserting a pair of electrodes into the circuit, and immersing the electrodes in the solution (fig. 6.4). The resistance that the solution adds to the circuit is converted into conductivity by a computer chip, and is displayed on a meter.



**Figure 6.4 — A conductance cell**

Electro conductivity of solutions at a constant temperature depends upon

- concentration;
- degree of ionization;
- ionic mobility ( $U$ ), which is defined as ionic velocity per unit of electric field ( $U=v/E$ ).

Conductivity is roughly proportional to the concentration of ions in a solution, but all ions do not conduct equally. Ions that move through a solution easily conduct better. For example, small, fast moving ions like hydrogen ion ( $\text{H}^+$ ) or heavily hydrated ions do, like sulfate ion ( $\text{SO}_4^{2-}$ ).

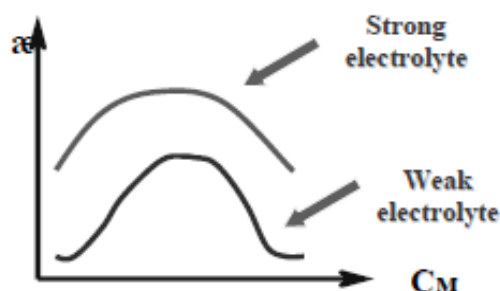
**Table 6.1 — Ionic Mobility of some common ions  
at 298 K,  $10^{-8}\text{ m}^2\text{s}^{-1}\text{V}^{-1}$**

| Ion           | $u_\infty$ | Ion                | $u_\infty$ |
|---------------|------------|--------------------|------------|
| $\text{H}^+$  | 36.3       | $\text{OH}^-$      | 20.50      |
| $\text{Na}^+$ | 5.19       | $\text{Cl}^-$      | 7.91       |
| $\text{K}^+$  | 7.62       | $\text{SO}_4^{2-}$ | 8.29       |

All the factors that effect specific conductance of solutions at a particular temperature are reflected in equation 6.13:

$$\kappa = \alpha \times C_M \times F \times (u_+ + u_-) \times 10^3 \quad 6.13$$

We can use this equation to explain the relationship between conductivity and molarity in dilute and concentrated solutions of strong and weak electrolytes (fig.6.5).



**Figure 6.5 — Specific conductivity of solutions and their concentration**

In dilute solutions increase in both strong and weak electrolytes molarity gives increase in specific conductivity, but in concentrated solutions it falls down rapidly with elevation in molarity. Increase in conductivity can be explained by an increase in a number of ions in solutions, while its decrease has different reason for weak and strong electrolytes. In weak electrolytes solutions increase in their concentration is responsible for decrease in ionization percent (the Ostwald's dilution law) which results in a low conductance. For strong electrolytes a high concentration of ions increases their interaction and decreases their mobility (the Debye-Huckel theory).

Specific conductivity is the important characteristic of the organs and tissues of a human body. The deviations from their physiological magnitudes signal about pathological processes in a body.

**Table 6.2 — Specific conductivity of bio substrates at 37°C**

| Bio substrate | $\kappa, \Omega^{-1} \text{ m}^{-1}$ | Bio substrate | $\kappa, \Omega^{-1} \text{ m}^{-1}$ |
|---------------|--------------------------------------|---------------|--------------------------------------|
| Blood plasma  | 1.47-1.60                            | Muscles       | 0.66                                 |
| Gastric juice | 1.0-1.25                             | Nerve tissue  | $4 \times 10^{-2}$                   |
| Urea          | 1.6-2.3                              | Bone tissue   | $5 \times 10^{-7}$                   |

For example, when a person suffers from kidneys' insufficiency the specific conductivity of urea decreases down to  $0.9\text{-}1.4 \Omega^{-1} \text{ m}^{-1}$  due to low NaCl concentration and high content of proteins. On the contrary

diabetes mellitus is responsible for decrease in urea conductivity because of high content of sugars which are nonelectrolytes.

Physiotherapeutic methods of healing which are wide applied in modern medicine are possible due to electric conductivity of organs and tissues. These methods are: ionophoresis, electrical stimulation, ultra violet therapy.

A more fundamental unit of electrolytic conductance is **molar conductance** ( $\lambda$ ), which can be defined as the value of specific conductance contributed by one mole of ions contained in 1000 cm<sup>3</sup> (1l) of a solvent. It is defined as:

$$\lambda = \frac{\kappa}{C_M} \times 10^{-3} \quad 6.14$$

On the other hand we can write that

$$\lambda = \alpha \times F \times (u_+ + u_-) \quad 6.15$$

Let's assume that the multiplication

$$F \times u_+ = \lambda_+ \text{ and } F \times u_- = \lambda_-$$

where  $\lambda_+$  and  $\lambda_-$  are the molar ionic conductance of cation and anion respectively.

Thus we have

$$\lambda = \alpha \times (\lambda_+ + \lambda_-) \quad 6.16$$

In infinite diluted solutions ( $c \rightarrow 0$ )  $\alpha$  tends to 1, therefore

$$\lambda_\infty = (\lambda_{\infty+} + \lambda_{\infty-}) \quad 6.17$$

where  $\lambda_\infty$  - is molar conductance at infinity dilution;  $\lambda_{\infty+}$  and  $\lambda_{\infty-}$  are the ionic conductances at infinite dilution.

Equation 6.17 is known as **Kolrausch's Law of independent migration**. It means that molar conductance at infinite dilution is made up of independent contributions from cationic and anionic species.

Molar conductivity of solutions is applied for physiochemical investigations. **Degree of ionization** ( $\alpha$ ) and **solubility of electrolytes** ( $S$ ) can be calculated according to electric conductivity data:

$$\alpha = \frac{\lambda}{\lambda_\infty} \quad 6.18$$

$$S = \frac{\kappa - \kappa(H_2O)}{\lambda_\infty} \quad 6.19$$

Molar ionic conductances of some common ions at 298 K are given in table 6.3.

**Table 6.3 — Molar ionic conductances of some common ions at 298 K,**  
 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$

| Ion             | $\lambda_{\infty}$ | Ion                              | $\lambda_{\infty}$ |
|-----------------|--------------------|----------------------------------|--------------------|
| H <sup>+</sup>  | 350                | OH <sup>-</sup>                  | 198                |
| Na <sup>+</sup> | 50                 | Cl <sup>-</sup>                  | 76                 |
| K <sup>+</sup>  | 74                 | CH <sub>3</sub> COO <sup>-</sup> | 41                 |

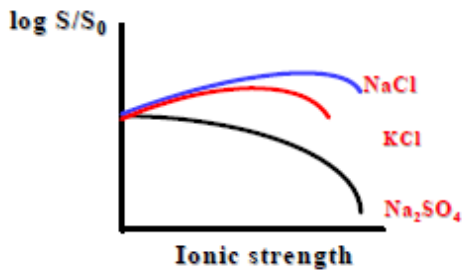
### 6.5 Biological functions of electrolytes

Electrolytes are contained in all organs and tissues of a human body. The content of cations in blood plasma is ~ 154 mmol/l. The bioessential cations are Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>. The content of anions in blood is also ~ 154 mmol/l. The most important for living beings are Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, and macro anions of proteins. Ionic strength of blood plasma is ~0,15 mol/l. Each ion fulfills its specific functions in vivo, but there are common functions of electrolytes in a body.

#### Electrolytes in a human body:

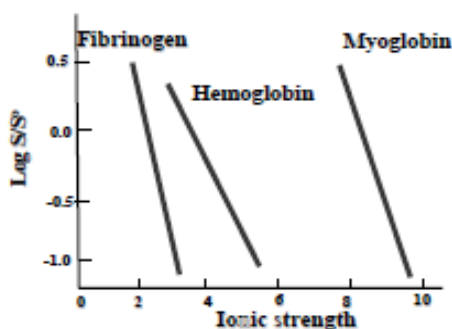
- hold water in tissues as hydrates. For example, 2 grams of NaCl hold 2 l of water;
- maintain osmotic pressure of biological fluids. The gradients in osmotic pressure are responsible for active transport of water in living systems;
- effect solubility of gases, salts, proteins and other bioactive compounds.

In dilute electrolytes solutions the *salting-in effect* occurs - the increase in solubility of substances caused by the increase in ionic strength of a solution. In concentrated solutions of electrolytes the *salting-out effect* takes place - the decrease in solubility of substances with increasing ionic strength of a solution.



**Figure 6.6 — Plots of  $\log (S/S^0)$  versus ionic strength for horse hemoglobin in the presence of various inorganic salts**

The practical value of the salting-out effect is that it allows us to precipitate proteins from solutions. In addition, the effect can also be used to purify proteins. Figure 6.7 shows the range of the salting out phenomenon for several proteins in the presence of ammonium sulfate.



**Figure 6.7 — Plots of  $\log (S/S^0)$  versus ionic strength for several proteins in aqueous ammonium sulfate, demonstrating the salting-out effect**

Although the solubility of proteins is sensitive to the degree of hydration, the strength of binding of water molecules is not the same for all proteins. The relative solubility of different proteins at a particular ionic strength provides a means for selective precipitation. The point is that although a higher ionic strength are needed to salt out proteins, precipitation occurs over a small range of the ionic strength, providing sharp separations.

## ***6.6 Problems for the self-control***

### **Discussion questions:**

1. Define the following terms: electrolyte, nonelectrolyte, and hydration.
2. Water, as we know, is an extremely weak electrolyte and therefore cannot conduct electricity. Yet we are often cautioned not to operate electrical appliances when our hands are wet. Why?
3. Identify each of the following substances as a strong electrolyte, a weak electrolyte, or a nonelectrolyte: (a)  $\text{H}_2\text{O}$ , (b)  $\text{KCl}$ , (c)  $\text{HNO}_3$ , (d)  $\text{CH}_3\text{COOH}$ , (e)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , (f)  $\text{Ba}(\text{NO}_3)_2$ , (g)  $\text{NaOH}$ .

4. Classify each of the following species as a weak or strong base:  
(a) LiOH, (b) H<sub>2</sub>O, (c) NaOH, (d) NH<sub>4</sub>OH, (e) Ba(OH)<sub>2</sub>, (f) Fe(OH)<sub>3</sub>,  
(g) Cu(OH)<sub>2</sub>.

5. Classify each of the following species as a weak or strong acid:  
(a) HNO<sub>3</sub>, (b) HF, (c) H<sub>2</sub>SO<sub>4</sub>, (d) H<sub>2</sub>CO<sub>3</sub>, (e) HCl, (f) HNO<sub>2</sub>, (g) HCN.

6. Predict and explain which of the following systems are electrically conducting: (a) solid NaCl, (b) molten NaCl, (c) an aqueous solution of NaCl.

7. Explain why a solution of HCl does not conduct electricity but in water it does.

8. Discuss the general features of the Debye-Huckel theory of a strong electrolyte solution;

9. Discuss the factors responsible for the magnitude of the activity coefficients of ions in aqueous solutions.

10. Define Kohlrausch's law of independent migration.

## CHAPTER 7. ACID-BASE EQUILIBRIUM

**After reading this chapter, you should be able to:**

- define acids and bases in the terms of Arrhenius, Bronsted and Lewis Theories;
- identify pH and pOH as main characteristics of acidity and basicity in aqueous solutions;
- be able to perform typical calculations of pH and pOH in aqueous solutions of weak acids and bases;
- be able to perform typical calculations of pH and pOH in aqueous solutions of strong acids and bases;
- describe buffer solutions and buffer capacity; define the role of buffers in maintaining acid-base status of a human body;
- be able to perform calculations of pH and pOH in buffer solutions of different types.

Acids and bases form a particularly important class of electrolytes. No chemical equilibria are as widespread as those involving acids and bases. The precise balance of their concentrations or pH in our bodies is necessary for the proper function of enzymes, maintenance of osmotic pressure, and so on.

### *7.1 Development of the acid-base concept*

In 1680, Robert Boyle noted that acids dissolve many substances, that they change the color of certain natural dyes (litmus) from blue to red, and that they lose these characteristic properties after coming in contact with alkalis (bases).

In the eighteenth century acids were recognized to be sour in taste and to react with limestone producing a gaseous substance ( $\text{CO}_2$ ). Neutral substances were noticed to result from their interaction with bases. In 1787 Lavoisier proposed that acids are binary compounds of oxygen, and he considered oxygen to be responsible for the acidic properties of that class of substances. The necessity of oxygen was disproved by Humphry Davy in 1811 when he showed that hydrochloric acid ( $\text{HCl}$ ) contains no oxygen. Davy made a great step forward in the development of the acid-base concept by concluding that hydrogen, rather than oxygen, is the essential constituent of acids.

In 1814 Gay-Lussac concluded that acids are substances which can neutralize alkalis and that these two classes of substances can be defined only in terms of each other. The idea of Davy and Gay-Lussac provide the foundation for our modern concepts of acids and bases in aqueous solution.

**The Arrhenius Theory.** In 1887, a young Swedish chemist, Svante Arrhenius, published a paper about acids and bases. He knew that solutions containing acids or bases conducted an electric current, and he tried to explain why. He concluded that these substances released charged particles when dissolved; he called these charged particles ions (wanderers). He concluded that:

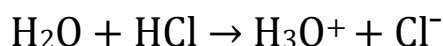
- acids are substances which produce hydrogen ions in a solution;
- bases are substances which produce hydroxide ions in a solution.

For example:



Free hydrogen ions cannot exist in water and cannot be responsible for acidic properties. In fact, they exist as hydrated protons called hydronium ions.

The hydrated proton is usually represented by  $\text{H}_3\text{O}^+$ , so a better representation for the HCl ionization is:



in which a proton is transferred from HCl to the water molecule, where it is bonded to the oxygen atom by a stable coordinate covalent bond.

**The Bronsted-Lowry Theory.** As chemistry developed, knowledge of catalytic and non-aqueous solutions increased, and it became necessary to redefine the terms acid and base. In 1923, an English scientist, T. M. Lowry, and a Danish scientist, J. N. Bronsted independently proposed that:

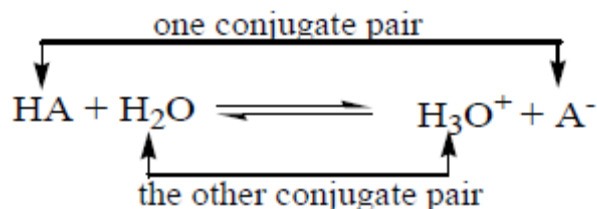
- an acid is a proton (hydrogen ion) donor;
- a base is a proton (hydrogen ion) acceptor.

The Bronsted-Lowry theory does not contradict the Arrhenius theory in any way - it just adds to it. In general, any acid-base reaction is described as:

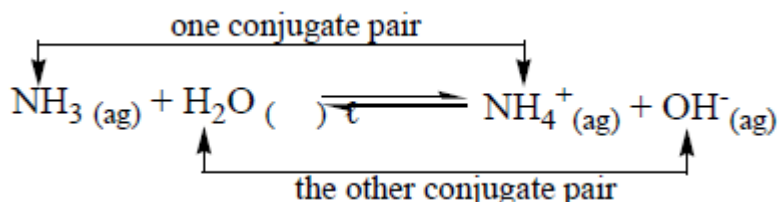


A **conjugate base** of an acid is the remainder of the acid after it has released a proton. A **conjugate acid** of a base is formed when the base acquires a proton from the acid.

For example, interaction of an acid with water can be represented by:

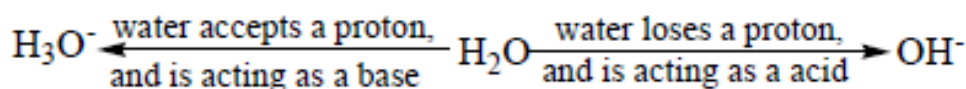


The reaction between ammonia and water also involves two conjugate pairs:



Ammonia is a base because it is accepting hydrogen ions from the water. The ammonium ion is its conjugate acid - it can release that hydrogen ion again to reform the ammonia.

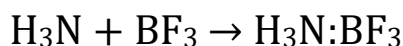
A substance, which can act as either an acid or a base, is described as being amphoteric. For example water is acting as a base, whereas in the other one it is acting as an acid:



**The Lewis Theory.** In 1923, the same year that Bronsted and Lowry proposed their theories, Gilbert Newton Lewis, an American chemist, proposed even broader definition of acids and bases:

- an acid is an electron pair acceptor;
- a base is an electron pair donor.

Lewis focused on electron transfer instead of proton transfer. His definition is more inclusive than the previous one, and is applied to solutions and reactions which do not even involve hydrogen and hydrogen ions. Consider the reaction between ammonia and boron trifluoride:



Note that boron has an empty orbital, and can accept two more electrons in its valence level. Since boron trifluoride can accept an electron pair, it is a Lewis acid. Note that the nitrogen atom has an unshared electron pair, which can be donated to the boron. Ammonia is therefore a Lewis base, because it can donate an electron pair.

None of the preceding theories is incorrect. Each succeeding theory includes that of its predecessors. What is true for the most specialized (the Arrhenius theory) is also true for the most general (the Lewis theory). According to the Arrhenius' theory, ammonia is a base because it produces  $\text{OH}^-$  ion when placed in water. The Bronsted-Lowry theory classifies ammonia as a base because it accepts a proton from  $\text{H}_2\text{O}$ . The Lewis theory classifies  $\text{NH}_3$  as a base because it donates an electron-pair to a proton. What is considered an acid or base in the simplest theory is also considered an acid or base in the more complex theories.

## ***7.2 Acidity and basicity of aqueous solutions***

Acidity and basicity are important characteristics of aqueous solutions, biological fluids, food products, natural waters and other objects. They are identified by ratio of protons ( $\text{H}^+$  or  $\text{H}_3\text{O}^+$ ) and hydroxyl ions ( $\text{OH}^-$ ) concentrations and expressed in pH or pOH units.

$$\text{pH} = -\log \alpha(\text{H}^+) \quad 7.1$$

where  $\alpha(\text{H}^+)$  - is the activity of the  $\text{H}^+$  ions in a solution, given by  $\gamma[\text{H}^+]$ .

Generally, for relatively dilute solutions at the low ionic strength  $\gamma$  tends to 1, so we can use the following approximate equation

$$\text{pH} = -\log [\text{H}^+] \quad 7.2$$

where  $[\text{H}^+]$  is - the concentration of protons, mol/l.

We can also define a pOH scale as follows

$$\text{pOH} = -\log \alpha(\text{OH}^-) \quad 7.3$$

where  $\alpha(\text{OH}^-)$  - is the activity of the  $\text{OH}^-$  ions in a solution, given by  $\gamma[\text{OH}^-]$ .

Respectively for dilute solutions at low ionic strength

$$\text{pOH} = -\log [\text{OH}^-] \quad 7.4$$

where  $[\text{OH}^-]$  - is the hydroxyl ion concentration, mol/l.

Taking negative logarithm of equation for the water ionization constant

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

we get

$$\begin{aligned} -\log K_w &= -\log[\text{H}^+] - \log[\text{OH}^-] \\ \text{p}K_w &= \text{pH} + \text{pOH} \end{aligned} \quad 7.5$$

where  $\text{p}K_w = -\log K_w$ . At  $25^\circ\text{C}$ , equation (7.5) becomes:

$$\text{pH} + \text{pOH} = 14 \quad 7.6$$

In terms of concentrations, we can express the acidity of a solution as follows:

- in neutral medium  $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$ ,  $\text{pH} = -\log [\text{H}^+] = -\log 10^{-7} = 7$ .
- in acidic medium  $[\text{H}^+] > [\text{OH}^-]$ , hence  $\text{pH} < 7$ .
- in basic medium  $[\text{H}^+] < [\text{OH}^-]$ , hence  $\text{pH} > 7$ .

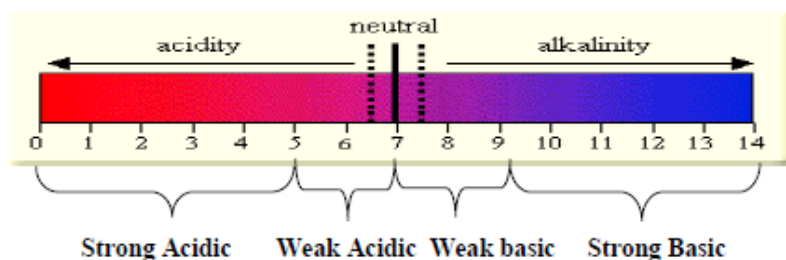
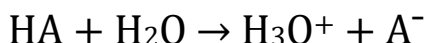


Figure 7.1 — pH Scale

pH of aqueous solutions may be determined experimentally or calculated theoretically.

### 7.3 pH calculating in aqueous solutions of weak acids and bases

The proper understanding of acid-base balance in chemical and biological systems requires a clear understanding of the behavior of weak acids and weak bases. The dissociation of a weak acid, HA, in aqueous solution can be represented by:



or in a simplified form



According to the law of mass action

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad 7.7$$

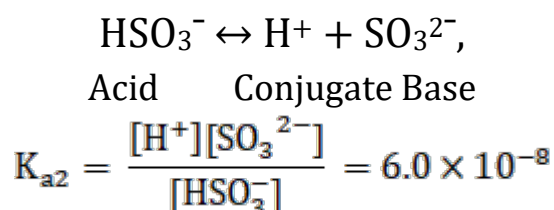
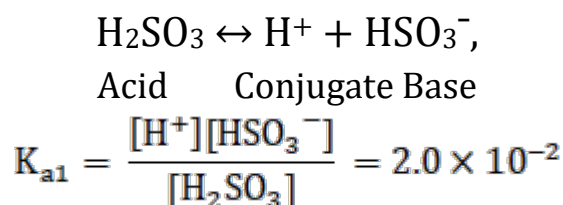
where  $K_a$  - is the acid ionization constant.

Weak acids obey the Ostwald dilution Law, according to which their dissociation percent is:

$$\alpha(\text{acids}) = \sqrt{\frac{K_a}{C_M}} \quad 7.8$$

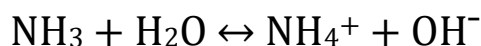
Our discussion so far has focused on monoprotic acids. The treatment of acid-base equilibrium is more complicated for acids that have two or more dissociable protons (diprotic and polyprotic acids). Their dissociation involves several steps and each step is characterized by its own acid ionization constant  $K_a$ .

For example, dissociation of a diprotic sulfurous acid  $\text{H}_2\text{SO}_3$  involves two steps:



Thus the conjugate base for the first dissociation  $\text{HSO}_3^-$  becomes the acid in the second dissociation step.  $K_{a1}$  is greater than  $K_{a2}$  by some six orders of magnitude, thus the acid strength of  $\text{H}_2\text{SO}_3$  is much greater than that of  $\text{HSO}_3^-$ .

The treatment of the dissociation of bases is the same as that of acids. For example, when ammonia dissolves in water, it reacts as follows:



By analogy with the acid ionization constant, we can write the base ionization constant  $K_b$ , as

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

Weak bases obey the Ostwald dilution Law, according to which

$$\alpha(\text{bases}) = \sqrt{\frac{K_b}{C_M}} \quad 7.9$$

where  $\alpha$  - is the ionization degree of weak bases in aqueous solutions.

#### ***7.4 pH calculating in aqueous solutions of strong acids and strong bases***

The pH calculating in strong acids and strong bases solutions involves the main postulates of the Debye-Huckel theory of strong electrolytes. They postulate the following:

- strong acids and bases are completely dissociated into ions in solutions;
- all the ions in solution contribute to the ionic strength (I), which characterizes the electric field of a solution and is defined by

$$I = \frac{1}{2} \sum C_i + Z_i^2 \quad 7.10$$

where  $C_i$  - is the molarity of the ion,  $Z_i$  is its charge.

- the electrostatic forces exerted by ions on one another are enough to cause a deviation from the ideal behavior. Thus, in the vast majority of cases, molarity must be replaced with activity ( $\alpha$ ). The activity is an effective thermodynamic concentration that takes into account a deviation from ideal behavior. Activity is defined by a formula

$$\alpha = \gamma \times C_M \quad 7.11$$

where  $\gamma$  - is the activity coefficient, a characteristic which expresses the deviation of a solution from the ideal behavior. It relates activity to concentration.

#### ***7.5 Acid-base status of a human body***

All biological fluids are characterized by constant pH values (Table 7.1). This phenomenon is defined as acid-base equilibrium or acid-base status; it is regulated by biological buffer systems. A disturbance of acid-base status is rather dangerous for people's health since the pH deviation may cause:

- decrease in hormones' and enzymes' activity;
- change in osmotic pressure;

- alteration in rates of biochemical reactions catalyzed by protons.

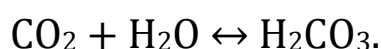
Even a 0.4 pH units deviation from the normal pH value in blood may cause coma or even death of a patient. For babies even 0.1 pH deviations is also very dangerous.

The most dangerous types of acid-base disturbance in blood are:

- **acidosis** — is the increase in blood acidity;
- **alkalosis** — is the increase in blood basicity.

***There can be distinguished two main types of acidosis:***

(a) Respiratory, caused by hypoventilation of lungs and accumulation of carbonic acid in blood



(b) Metabolic, caused by diabetes mellitus and some other diseases responsible for extra production of acids.

The excess of food products with high acidity can lead to acidosis as well.

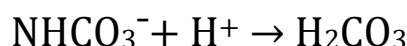
***Alkalosis is initiated by:***

- (a) Hyperventilation of lungs (for example, neurotic paroxysm).
- (b) The excess of food products with high basicity.

**Table 7.1 — pH of some biological fluids**

| Biological fluid    | Average values | Possible deviations |
|---------------------|----------------|---------------------|
| Blood plasma        | 7.36           | 7.25-7.44           |
| Cerebrospinal fluid | 7.6            | 7.35-7.80           |
| Gastric juice       | 1.65           | 0.9-2.0             |
| Urea                | 5.8            | 5.0-6.5             |
| Saliva              | 6.75           | 5.6-7.9             |
| Sweat               | 7.4            | 4.2-7.8             |
| Skin                | 6.8            | 6.2-7.5             |

Acidosis correction is done by intravenous injection of a 4 %  $\text{NaHCO}_3$  solution:



Soda and another antacidic (hypocidic) drugs are substances which reduce acidity of biological fluids. Alkalosis correction is achieved by the injection of 5-15 % ascorbic acid solutions.

Increase in acidity in a mouth is conjugated with food intake (especially sweat). Its gives rise to teeth decay



Addition of acids shifts equilibrium to the right due to decrease in  $F^-$  anions:



### 7.6 Buffer solutions

**Buffer solutions or buffers** are solutions, which have an ability to resist in the pH change upon the addition of small quantities of acids and bases. A mechanism of buffer activity becomes clear on the base of the Bronsted-Lowry acid-base theory. Each buffer solution contains a conjugate pair (an acid and its conjugate base), which is responsible for a solution ability to neutralize acids and bases added to it.

The pH of a buffer solution may be calculated by *the Henderson-Hasselbach equation*:

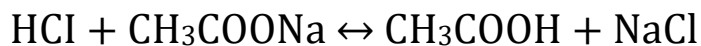
$$pH = pK_a - \log \frac{[acid]}{[conjugate base]} \quad 7.12$$

where  $pK_a = -\log K_a$  ( $K_a$  - acid ionization constant).

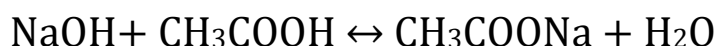
#### Classification of buffer solutions:

1. **Weak acid and its salt.** For example, acetate buffer system:  
 $CH_3COOH/CH_3COONa$

Mechanism of buffer activity:



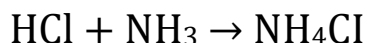
Neutralization of an added acid



Neutralization of an added base

2. **Weak base and its salt.** For example, ammonia buffer system:  
 $NH_3/NH_4Cl$

Mechanism of buffer activity



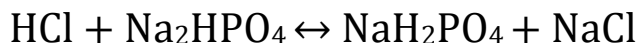
Neutralization of an added acid



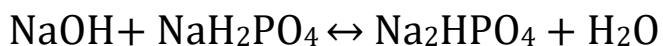
Neutralization of an added base

3. **Two acid salts.** For example, Hydro phosphate buffer system:  
 $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$

Mechanism of buffer activity



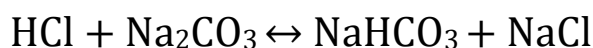
Neutralization of an added acid



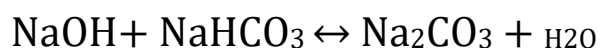
Neutralization of an added base

4. **Acid salt and neutral salt.** For example, carbonate buffer system:  
 $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$

Mechanism of buffer activity



Neutralization of an added acid



Neutralization of an added base

**Buffer capacity** of a solution (B, mmol/l) is the amount of added acids or bases the buffer solution can tolerate without exceeding a specified pH range.

$$B = \frac{C_N \times V}{\Delta\text{pH} \times V_{BS}} \quad 7.13$$

where  $C_N$  - is thenormality of added strong acid or strong base, mol/l;  $V$  - is the volume of an added acid or base, ml;  $\Delta\text{pH}$  - is the change in pH;  $V_{BS}$  - is the volume of a buffer solution, l.

**Buffer capacity depends upon:**

- concentration: the higher is concentration, the greater is buffer capacity of a solution;
- the ratio of components' concentration component 1

$$B = \frac{[\text{component 1}]}{[\text{component 2}]} = 1$$

The greater buffer capacity of a solution is, the higher its activity in supporting acid- base equilibrium is.

Biological buffer systems are characterized by:  $B_A$  - buffer capacity of acids,  $B_B$  - buffer capacity of bases. Buffer capacity of biological

buffers may differ greatly of acids and of bases. Usually  $B_A > B_B$ , because amount of acidic metabolites generated in a human body is much greater than the amount of basic metabolites. The amount of acidic metabolites synthesized daily in a human body is equivalent to 2.5 Z of concentrated HCl.

### 7.7 Buffer systems of blood

The most powerful biological buffer systems are contained in blood. They are subdivided into two categories:

- buffers of plasma;
- buffers of erythrocytes.

The pH of blood plasma is maintained at 7.4 by several buffer systems, the most important of which is  $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ . In the erythrocyte, where the pH is 7.25, the principal buffer systems are  $\text{HCO}_3^-/\text{H}_2\text{CO}_3$  and hemoglobin (fig. 7.2).

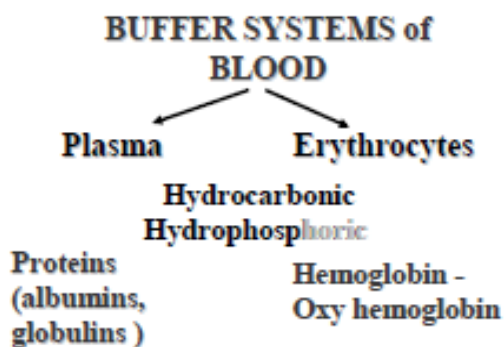
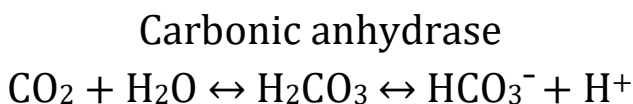


Figure 7.2 — Classification of buffer systems in blood

Let's start the review of buffer systems in blood beginning from the buffers, which are present both on blood plasma and erythrocytes.

**1. Hydrocarbonic buffer system.** This buffer system involves weak carbonic acid and bicarbonate anion:  $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ . The formation of a buffer in biological fluids is represented by:



**The mechanism of buffer activity:**

(a) Neutralization of acids:  $\text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3$

(b) Neutralization of bases:  $\text{OH}^- + \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}_2\text{O}$

In blood plasma the ratio of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  concentrations is

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{40}{1}$$

Thus the excess of bicarbonate anion maintains the ***base reservoir of blood***.

Its buffer capacity of acids is much greater than buffer capacity of bases:

$$B_A = 40 \text{ mmol/l;}$$

$$B_B = 1\text{-}2 \text{ mmol/l.}$$

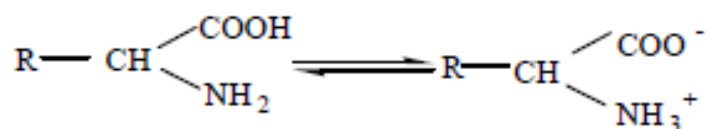
Hydrocarbonic buffer system is contained in all biological fluids of a human body. It acts together with other biological buffers. All alterations which proceed in a body effect the concentration of a carbonic system's components.  $\text{HCO}_3^-$  analysis in blood is an important diagnostical test which signals about respiratory and metabolic diseases.

**2. Hydro phosphoric buffer system.** It is composed of anions of phosphoric acid ( $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ). The mechanism of its buffer activity is given in above.

This buffer exhibits low capacity in blood is due to low concentration of its components:  $B_A = 1\text{-}2 \text{ mmol/l}$  and  $B_B = 0.5 \text{ mmol/l}$ . But hydro phosphoric buffer system is crucial in urea, intracellular fluids and other biological liquids.

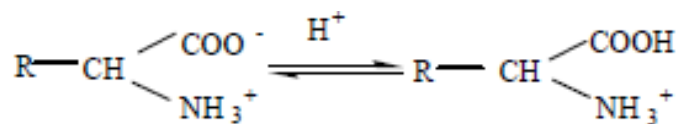
**3. Protein buffer system (albumins, globulins)** is a strong buffer which is present in blood plasma but not in erythrocytes.

Proteins are amphiprotic polyelectrolytes that exist as bipolar ions:

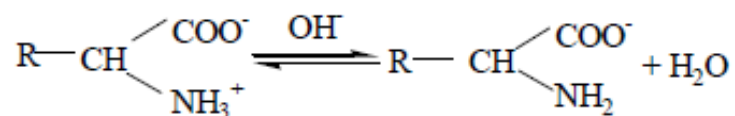


**The mechanism of buffer activity is:**

(a) Neutralization of acids:



(b) Neutralization of bases:

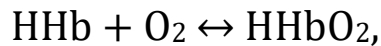


Protein buffer systems are contained not only in blood plasma, but in all biological fluids of a body. Their buffer capacities in blood plasma

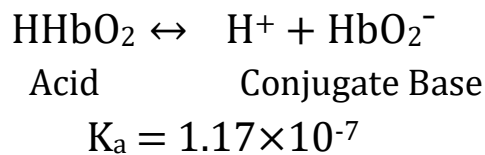
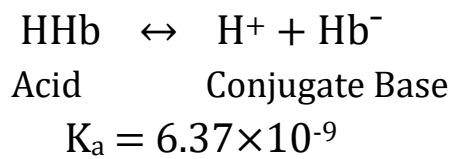
are:  $B_A$  (albumins) = 10 mmol/l and  $B_A$  (globulins) = 3 mmol/l respectively.

4. ***Hemoglobin-oxyhemoglobin buffer system*** is presented in erythrocytes and is responsible for 75 % of blood buffer capacity.

Hemoglobin (HHb) and oxyhemoglobin (HHbO<sub>2</sub>), formed by the combination of oxygen and hemoglobin in the lungs according to the reaction

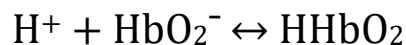
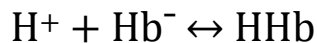


are weak acids although the latter is considerably stronger than the former:

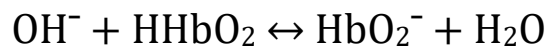
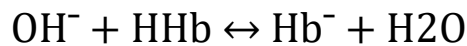


***The mechanism of their buffer activity can be represented as follows:***

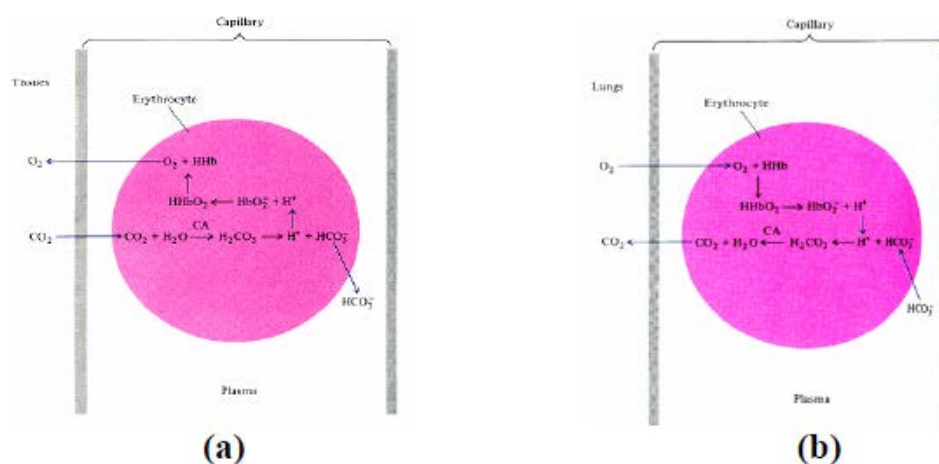
(a) Neutralization of acids:



(b) Neutralization of bases:



Hemoglobin and hydrocarbonic buffer systems are working together to deliver oxygen to tissues and to remove carbon dioxide out of tissues. Using several buffer systems, nature has provided an extremely effective gas exchange (fig. 7.3).



**Figure 7.3 — Oxygen-carbon dioxide is transported and released by blood. (a) In metabolizing tissues, the partial pressure of  $\text{CO}_2$  is higher in the interstitial fluid (fluid in the tissues) than in plasma. Thus,  $\text{CO}_2$  diffuses into the blood capillaries and then into erythrocytes. There it is converted into carbonic acid by the enzyme carbonic anhydrase (CA). The protons provided by the carbonic acid then are combined with the oxyhemoglobin anions to form  $\text{HHbO}_2$ , which eventually dissociates into  $\text{HHb}$  and  $\text{O}_2$ . Because the partial pressure of  $\text{O}_2$  is higher in the erythrocytes than in the interstitial fluid, oxygen molecules diffuse out of the erythrocytes and are carried by the plasma to the lungs. A small portion of  $\text{CO}_2$  binds to hemoglobin to form carbaminohemoglobin; (b) In the lungs, the processes are reversed**

Biological buffer systems maintain acid-base statuses of a human body.

### *7.8 Problems for the self-control*

#### **Discussion questions tell:**

1. What does the ionization constant show in the strength of an acid?
2. Which of the following solutions has the highest pH? (a) 0.40 M  $\text{HCOOH}$ , (b) 0.40 M  $\text{HClO}_4$ , (c) 0.40 M  $\text{CH}_3\text{COOH}$ .
3. Identify the strong and weak acids among the following: (a)  $\text{HNO}_3$ , (b)  $\text{HOC1}$ , (c)  $\text{HOH}$ , (d)  $\text{CH}_3\text{OH}$ .
4. Write all the species (except water) that are present in a phosphoric acid solution. Indicate which species can act as a Bronsted acid, which as a Bronsted base, and which as both a Bronsted acid and a Bronsted base.
5. The  $\text{pK}_a$  of two monoprotic acids HA and HB are 5.9 and 8.1, respectively. Which of the two is the stronger acid?

6. The  $pK_b$  for the bases  $X^-$ ,  $Y^-$ , and  $Z^-$  are 2.72, 8.66 and 4.57, respectively. Arrange the following acids in order of the increasing strength: HX, HY, HZ.

7. Define a buffer solution. What constitutes a buffer solution?

8. Specify which of the following systems can be classified as a buffer system: (a)  $KCl/HCl$ , (b)  $NH_3/NH_4NO_3$ , (c)  $Na_2HPO_4/NaH_2PO_4$  (d)  $KNO_2/HNO_2$ , (e)  $KHSO_4/H_2SO_4$ , (f)  $HCOOK/HCOOH$ .

## CHAPTER 8. ELECTROCHEMISTRY

**After reading this chapter, you should be able to:**

- define the electrochemical reactions and the types of electrochemical cells;
- define reduction potentials and electromotive force of redox reactions;
- be able to perform typical calculations applying the Nemst equation;
- discuss the structure and operation of galvanic cells, identify their types;
- discuss the application of potentiometric investigations for analysis of biological systems.

### ***8.1 Review of electrochemical reaction***

Electrochemistry is an area of chemistry that deals with the interconversion of electrical and chemical energy.

***The electrochemical reaction*** is defined as a chemical reaction that involves the flow of electrons. There are two types of cells in which electrochemical processes are carried out:

- a galvanic cell which uses the energy released from a spontaneous reaction to generate electricity;
- an electrolytic cell, which, on the other hand, uses electrical energy to drive a nonspontaneous chemical reaction (this process is called electrolysis).

There is a convenient difference between electrochemical reactions and chemical reactions: the Gibbs energy change for electrochemical reactions is equivalent to the maximum electrical work done, which can be measured readily.

Because all electrochemical reactions involve the transfer of electrons from one substance to another, their action can be understood in terms of redox reactions.

In ***Redox reactions (oxidation-reduction reactions)*** one species loses electrons and another species gains electrons:

- a process in which a chemical substance loses electrons is called oxidation;

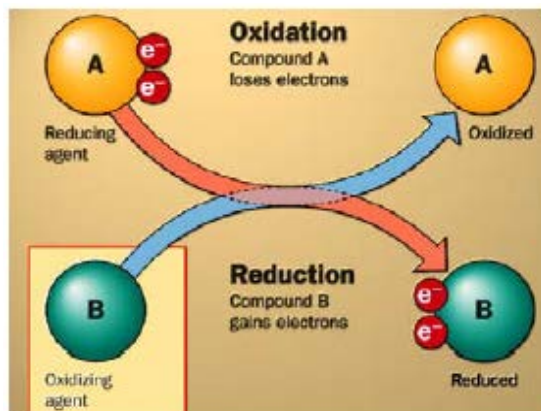
- a process in which a chemical substance gains electrons is called reduction.

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

The species that supplies electron is *a reducing agent (or a reductant)*. The species that removes electron is *an oxidizing agent (or an oxidant)*.

Most biochemical processes are redox reactions. *The vital functions they fulfill in a human body are:*

- *plastic function*: synthesis of complex organic molecules;
- *energetic function*: energy is released when high molecular compounds (lipids, carbohydrates and proteins) undergo oxidation in a human body.



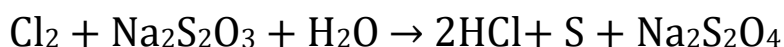
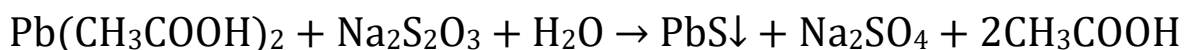
**Figure 8.1 — The electrons' exchange in a Redox reaction**

Thus, 99 % of all energy required for a human body to drive metabolic processes is produced by biochemical oxidation-reduction reactions. 90 % of this energy is released when lipids and carbohydrates undergo oxidation and 10 % - when proteins are oxidized.

Pharmacological activity of some drugs is based on their properties to oxidize or reduce other substances. Most oxidizing agents proved to exhibit antibacterial activity.

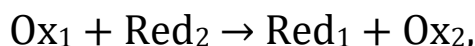
For example,  $I_2$ ,  $H_2O_2$ ,  $O_3$ ,  $KMnO_4$ , and  $HNO_3$  are applied in medicine for disinfection.

$Na_2S_2O_3$  - is an antidote for heavy metals and free halogens:



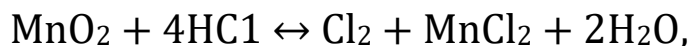
## 8.2 Thermodynamics of electrochemical cells

An equation for an intermolecular Redox reaction may be represented as follows:



where  $\text{Ox}_1/\text{Red}_1$  and  $\text{Ox}_2/\text{Red}_2$  are conjugate pairs of oxidizing and reducing agents.

Thus, for the reaction



the conjugate pairs are:  $\text{MnO}_2/\text{Mn}^{2+}$  and  $\text{Cl}_2/2\text{Cl}^-$ .

To express the strength of oxidizing and reducing agents in aqueous solutions, **reduction potentials** are used ( $\varphi_{\text{Ox/Red}}$ , V). Standard reduction potentials are denoted as  $\varphi^0_{\text{Ox/Red}}$  their values are in the range from -3 V up to +3 V.

The following rule can be used to predict whether oxidizing or reducing agents are weak or strong:

(a) The lower reduction potential is, the stronger a reducing agent is and weaker its conjugate oxidizing agent is. A conjugate pair  $\text{Li}^+ / \text{Li}$  exhibits the minimum standard potential ( $\varphi^0 \text{Li}^+ / \text{Li} = -3.045 \text{ V}$ ), so we come to belief that Li is the strongest reducing agent and  $\text{Li}^+$  is the weakest oxidizing agent in an aqueous solution.

(b) The higher reduction potential is, the stronger an oxidizing agent is and weaker its conjugate reducing agent is. A conjugate pair  $\text{F}_2 / 2\text{F}^-$  exhibits the maximum standard potential (+ 2.87 V), thus  $\text{F}_2$  is the strongest oxidizing agent and  $\text{F}^-$  is the weakest reducing agent in an aqueous solution.

Oxidizing and reducing strength of substances depends upon their:

- electronic structure;
- concentration;
- temperature;
- sometimes acidity of solutions.

**The Nernst equation** named after the German chemist Walter Hermann Nernst (1864-1941), reflects effects of temperature and concentration on redox properties of oxidizing and reducing agents:

$$\varphi_{\text{Ox/Red}} = \varphi^0_{\text{Ox/Red}} + \frac{R \times T}{n \times F} \times \ln \frac{[\text{Ox}]}{[\text{Red}]} \quad 8.1$$

where R - a gas constant (8.31 J/mol K); n - a number of gained or lost electrons; F - the Faraday constant (96500 C/mol).

When  $T = 298 \text{ K}$ ,

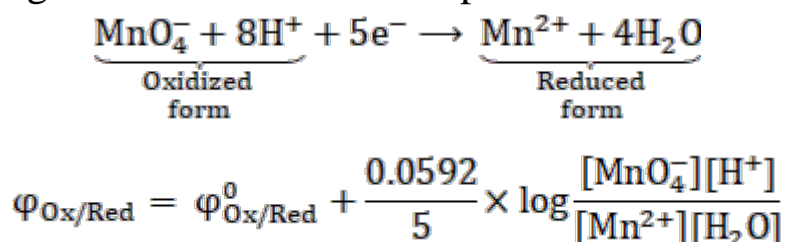
$$2.3 \times \frac{RT}{F} = 0.0592$$

Thus at standard temperature (298 K) the Nemst Equation may be rearranged in the following way:

$$\varphi_{\text{Ox/Red}} = \varphi_{\text{Ox/Red}}^0 + \frac{0.0592}{n} \times \lg \frac{[\text{Ox}]}{[\text{Red}]} \quad 8.2$$

Let us review the effect of concentration and acidity at the reduction potential

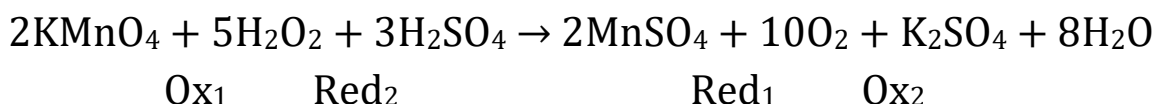
of the following half-reaction. For example:



If a reduction potential characterizes a half-reaction, *the electromotive force* (emf or  $E$ , V) is a characteristics of the overall redox process. It is defined as a difference between reduction potentials of two conjugated pairs, involved into one electrochemical process:

$$E = \varphi_{\text{Ox1/Red2}} - \varphi_{\text{Ox2/Red1}} \quad 8.3$$

For example, for a chemical reaction



the standard reduction potentials for conjugate pairs are:

$$\varphi^0 \text{MnO}_4^-/\text{Mn}^{2+} = + 1.51 \text{ V}$$

$$\varphi^0 \text{O}_2/\text{H}_2\text{O}_2 = + 0.68 \text{ V}$$

Thus emf can be calculated as

$$E^0 = 1.51 - 0.68 = 0.83 \text{ V}$$

Accurate measurements of emf are essential for calculating thermodynamic quantities of electrochemical reactions. Electromotive force of a redox reaction serves as a criterion for its spontaneity because it is related to free energy change ( $\Delta rG$ ). The linkage between free energy and cell potentials can be made quantitative.

The electrical work ( $A_{el}$ ) of electron transferring can be represented as

$$A_{el} = n \times F \times E \quad 8.4$$

On the other hand,  $A_{el}$  is a type of useful work produced by a system and it equals to free energy change

$$A_{el} = -\Delta_r G \quad 8.5$$

Taking together Equations 8.4 and 8.5, we can derive that

$$\Delta G = -n \times F \times E \quad 8.6$$

The equation 8.6 gives the linkage between a free energy change and emf of an electrochemical reaction.

If  $E > 0$ ,  $\Delta_r G < 0$  a reaction is spontaneous;

If  $E < 0$ ,  $\Delta_r G > 0$  a reaction is nonspontaneous.

It is evident that spontaneous Redox reactions generate a positive emf.

The vast majority of oxidation-reduction reactions are reversible; therefore equilibrium constant ( $K$ ) is their important characteristics. Because  $\Delta_r G^0$  is related to the equilibrium constant by the equation

$$\Delta_r G^0 = -R \times T \times \ln K \quad 8.7$$

we have

$$n \times F \times E^0 = R \times T \times \ln K \quad 8.8$$

or

$$K = e^{n \times F \times E^0 / RT} \quad 8.9$$

Thus equilibrium constant of a Redox reaction can be calculated according to the electrochemical data. When a reaction occurs under standard temperature Equation 8.9 can be rearranged as

$$K = 10^{n \times E^0 / 0.0592} \quad 8.10$$

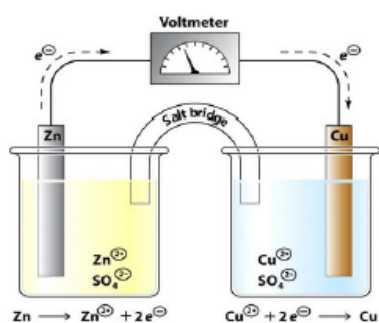
### 8.3 A Galvanic cell

An arrangement that uses redox reactions to generate an electric current is called a **galvanic cell** (figure 8.2). It consists of two electrode compartments (or two electrodes) connected by a salt bridge and an external metallic wire. A **salt bridge** is a concentrated electrolyte

solution in agar jelly that completes the electrical circuit between two electrode compartments.

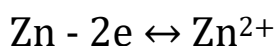
The electrode at which oxidation occurs is called ***the anode***; it gains negative charge when a galvanic cell is functioning. The electrode at which reduction occurs is called ***the cathode***; it gains positive charge when a galvanic cell is functioning. The reduction and oxidation processes, responsible for the overall reaction in a cell, are separated in space: oxidation takes place in one electrode compartment and reduction - in the other compartment. Electrons released in the oxidation at one electrode  $\text{Red}_1 - n\text{e} \rightarrow \text{Ox}_1$  travel through the external wire to another electrode, bringing the reduction:  $\text{Ox}_2 + n\text{e} \rightarrow \text{Red}_2$ .

Let us examine the construction of a Daniel cell. It consists of zinc and copper electrodes, immersed into solutions of their salts.



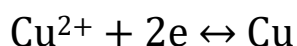
**Figure 8.2 — Scheme of Daniel galvanic cell**

A Zinc bar is an anode; oxidation occurs on its surface:



Electrons, lost by zinc, travel through the external wire to copper electrode, while  $\text{Zn}^{2+}$  cations diffuse into a solution. As a result a solution gains positive charge and a metal electrode - a negative charge.

A Copper bar is a cathode; a reduction occurs on its surface:



$\text{Cu}^{2+}$  cations contained in a solution, gain electrons from external circuit reducing into atoms and precipitate on the electrode. As a result a solution gains a negative charge and the electrode - a positive charge.

Due to such a construction, the reduction and oxidation processes are separate and electrons flow through the external wire from the anode to the cathode.

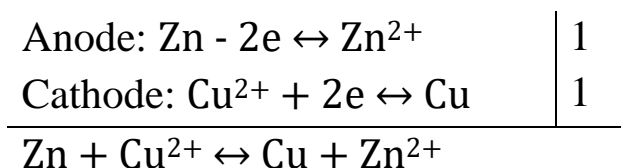
The components of a galvanic cell are represented as cell diagrams. For Daniel cell it may be written as follows:



The single vertical line (/) represents a phase boundary between metal and its solution, and a reduction potential generated at the interface surface.

The double vertical line (//) denotes the salt bridge, and a diffusion potential generated at the interface surface of two solutions.

The overall cell reaction involves the reduction of  $\text{Cu}^{2+}$  ions by Zn metal:



Emf of a galvanic cell is equal to:

$$E = \varphi^0(\text{cathode}) - \varphi^0(\text{anode}) \quad 8.11$$

For Daniel galvanic cell

$$E^\circ = \varphi^0(\text{Cu}^{2+}/\text{Cu}) - \varphi^0(\text{Zn}^{2+}/\text{Zn}) = +0.34 - (-0.76) = 1.1\text{V}.$$

Besides the reduction potentials electricity production in galvanic cells can be driven by the so called **membrane potentials**. The membrane potential appears to respond to the different ionic concentrations across the membrane. The Nernst equation for the membrane potential is

$$\varphi = \frac{R \times T}{n \times F} \times \ln \frac{[\text{X}]_{\text{external}}}{[\text{X}]_{\text{internal}}} \quad 8.12$$

where  $[\text{X}]_{\text{external}}$  and  $[\text{X}]_{\text{internal}}$  - are concentrations of an ion in external and internal media,  $n$  - an electric charge of an ion.

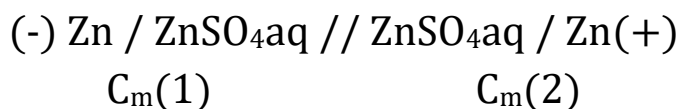
One important example of a system that resembles this description is the biological cell membrane, which is more permeable to  $\text{K}^+$  ions than to either  $\text{Na}^+$  or  $\text{Cl}^-$  ions. The transmembrane potential difference plays an important role in the transmission of nerve impulses.

The **Electrocardiographic method (ECG)** is a powerful tool of identifying heart defects. It is based on measuring of heart muscle biopotentials.

#### ***Classification of Galvanic cells:***

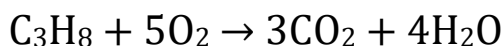
- chemical cells are composed of different electrodes.

- concentration cells consist of two identical electrodes and differ in electrolytes concentrations only:

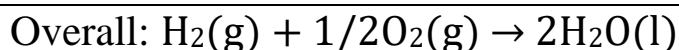
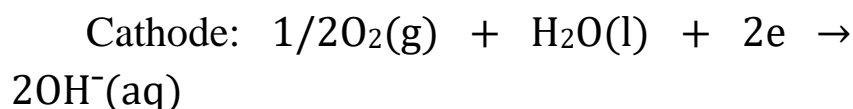
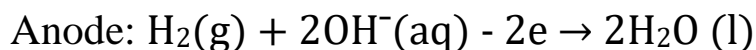


- in fuel cells energy of combustion converts into electrical energy.  
Nowadays

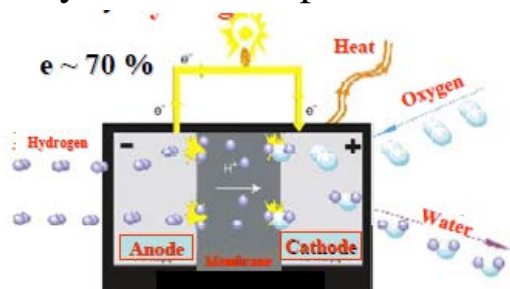
the most applied cells are propane-oxygen ones:



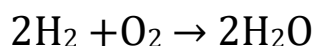
Let us consider the hydrogen-oxygen fuel cell as another example. Such a cell consists of an electrolyte solution, such as sulfuric acid and sodium hydroxide, and two inert electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartments, where the following reactions take place:



The overall reaction is identical to burning hydrogen in oxygen. With proper design, the efficiency of this cell may be as high as 70 %. In addition, fuel cells generate electricity without any noise, vibration, heat transfer, and other problems normally associated with conventional power plants. The advantages are so attractive that fuel cells are most likely to become operational on a large scale in the 21 st century.



**Figure 8.3 — Schematic diagram of a hydrogen-oxygen fuel cell**



Classification of galvanic cells according to their application involves two types of devices:

- the first type is used as chemical sources of electricity;
- the second type is applied to physiochemical analysis of solutions (potentiometry).

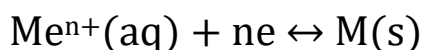
### 8.4 Applications of EMF measurements

Potentiometry is an investigation method based on determination of emf of a specially constructed galvanic cell. Potentiometry can be of two types:

- direct (pH of solutions measuring);
- indirect (potentiometric titration).

**The types of electrodes applied in potentiometry.** Depending on the type of redox reactions that occur in an electrochemical cell, there are many types of electrodes in use. The following electrodes are a few examples.

**(a) Metal electrodes.** A metal electrode consists of a piece of metal immersed in a solution containing cations of the same metal. The electrode reactions are:



For example  $\text{Cu} / \text{Cu}^{2+}(\text{aq})$ ;  $\text{Zn} / \text{Zn}^{2+}(\text{aq})$ .

Their reduction potentials are given by the Nemst's Equation:

$$\varphi = \varphi^0 + \frac{0.0592}{n} \log [\text{Me}^{n+}]$$

where  $\text{Me}^{n+}$  is a potential determining ion

**(b) Metal-insoluble salt electrodes.** Metal-Insoluble Salt Electrodes can be prepared by coating a piece of metal with an insoluble salt of the same metal. Electrode is immersed in a solution containing the anion of the salt. A common example is the silver-silver chloride electrode  $\text{Ag}, \text{AgCl} / \text{KCl}(\text{aq})$ .

The electrode reaction is:  $\text{AgCl} + \text{e}^- \leftrightarrow \text{Ag} + \text{Cl}^-$ .

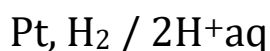


**Figure 8.4 — The silver-silver chloride electrode**

The Nemst's equation is given by

$$\varphi = \varphi^0 - 0.0592 \log [\text{Cl}^-]$$

(c) **Gas electrodes.** An example of a gas electrode is the standard hydrogen electrode (SHE). It is composed of the platinum metal immersed in the solution of sulfuric or hydrogen chloride acid (1 M  $\text{H}^+$  concentration). Hydrogen gas is bubbled into a solution under the pressure of 1 atm. The inert platinum metal has a dual purpose: it acts as a catalyst in the decomposition of  $\text{H}_2$  into atomic hydrogen and as an electrical conductor to the external circuit. The cell diagram is represented as



The electrode reaction is:  $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$

The Nemst's equation is given by:

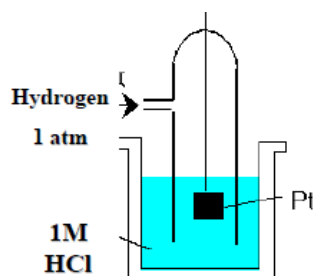
$$\varphi = \varphi^0 + 0.0592 \log [\text{H}^+]$$

or

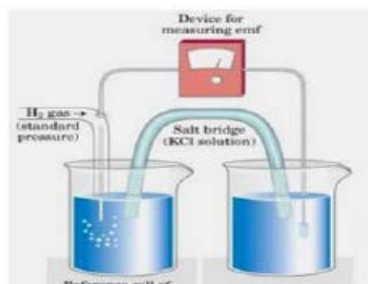
$$\varphi = - 0.0592 \text{ pH}$$

where  $\varphi^0(\text{SHE})$  is assumed to be zero.

The standard hydrogen electrode (figure 8.5) is applied to determine the standard reduction potential of any other electrodes. Figure 8.6 shows a galvanic cell with a test electrode and a SHE electrode. The test half-cell contains 1 M each of the oxidized and reduced species of the substance whose reduction potential is to be determined. The voltmeter across the oxidation-reduction couple measures the electromotive force, or the difference in the reduction potential, between the reference and sample half-reactions. Since the standard reduction potential of the SHE is 0 V, the measured potential is that of the test half-reaction.



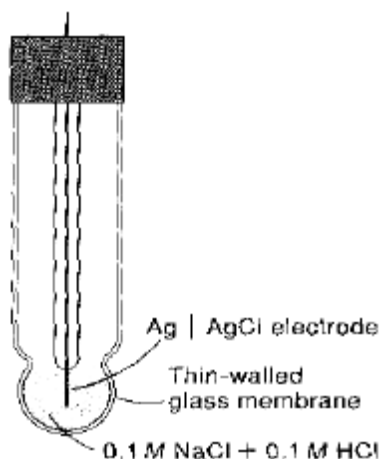
**Figure 8.5 — Gas electrodes**



**Figure 8.6 — A galvanic cell consisting of a test electrode and standard hydrogen electrode**

Every standard reduction potential has a specific sign. When a substance is easier to reduce the hydronium ions under standard conditions, its  $\varphi^0$  is positive. When a substance is more difficult to reduce than hydronium ions under standard conditions, its  $\varphi^0$  is negative.

**The glass electrode.** The glass electrode is an example of widely used ion-selective electrodes, because it is specific for  $H^+$  ions (figure 8.7).



**Figure 8.7 — A glass electrode**

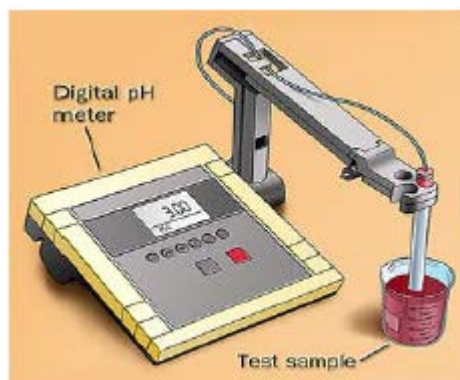
It consists of a very thin bulb or membrane made of a special type of glass that is permeable to  $H^+$  ions. An Ag/AgCl electrode is immersed in 0.1 M HCl solution with constant pH equal to 1.

When the electrode is placed in a solution whose pH is different from 1, the potential difference between the two sides is a measure of the difference in the two pH values. The following equations relate membrane potential of the glass electrode to acidity of a test solution:

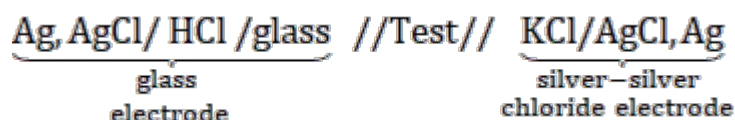
$$\varphi = +0.0592 \log \frac{[H^+]_{ex}}{[H^+]_{in}} \quad 8.13$$

where  $[H^+]_{ex}$  - is the protons' molarity in a test solution, M;  $[H^+]_{in}$  - is the protons' molarity in an internal solution, M.

**Potentiometric pH determination.** Determining pH from emf measurements is a standard technique. The galvanic cell, applied for this purpose, is a combination of the glass electrode (as an indicator electrode) and silver-silver chloride electrode (as a reference electrode). Let us consider the galvanic cell (figure 8.8).

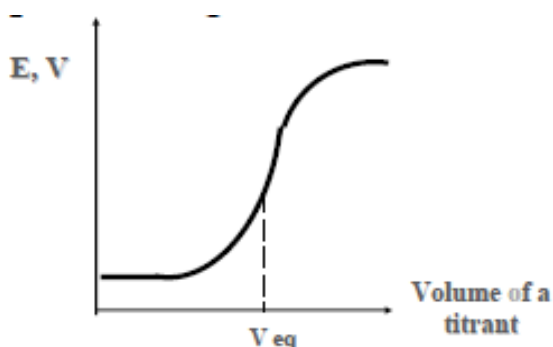


**Figure 8.8 — Galvanic cell for pH measuring**



Potentiometric pH determination is widely used in medical practice. A galvanic cell used for such an investigation is composed of a glass electrode (an indicator electrode) and a silver-silver chloride electrode (a reference electrode).

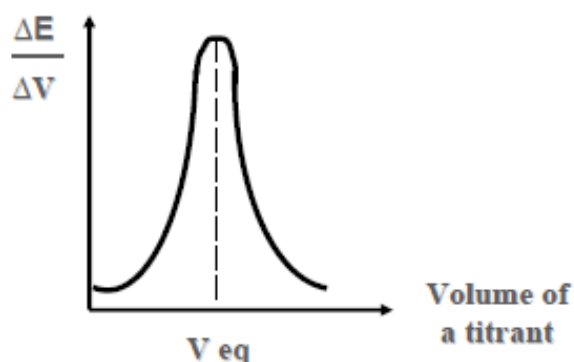
**Potentiometric titration.** Potentiometric titration is a volumetric method in which the potential between two electrodes is measured (a referent and indicator electrode) as a function of the added titrant volume. The voltage is recorded at intervals as the titrant is added. A potentiometric titration curve (figure 8.9) is a plot of potential as a function of the volume of the added titrant. The end point of the reaction is half way between the jump in voltage.



**Figure 8.9 — Integral curve of potentiometric titration**

Potentiometric titrations are preferred to manual titrations, since they are more accurate and precise. They are also more easily adapted to automation, where automated titration systems can process larger volumes of samples with minimal analyst involvement.

A differential titration curve (figure 8.10) is applied for very precise determination of the endpoint of titration. The first derivative,  $\Delta E/\Delta V$ , is the slope of the curve, and the endpoint occurs at the volume,  $V_{eq}$ , where  $\Delta E/\Delta V$  has the maximum value.



**Figure 8.10 — Differential curve of potentiometric titration**

Types of potentiometric titrations for the determination of analytes in test solutions include acid-base, redox, precipitation, and complexometric. Applications of potentiometric measurements are:

- analysis of colored and turbid solutions, pasts and gels;
- analysis of biological fluids without their destruction.

The experimental data can be received quickly and accurately (express analysis).

### ***8.5 Exercises for the self-control***

#### **Discussion questions**

1. Discuss the role of redox reactions in electrochemical processes.
2. Distinguish between galvanic and electrolytic cells.
3. Describe the basic features of a galvanic cell. Why are the two components in a galvanic cell separated from each other?
4. What is the function of a salt bridge in a galvanic cell?
5. Define the following terms: anode, cathode, electromotive force, and standard reduction potential.
6. Describe a method for the determination of the standard potential of a cell.

7. Describe a method for the determination of the pH of an aqueous solution.

8. Write the equation relating  $\Delta G^\circ$  and  $K$  to the standard emf of a cell. Define all the terms.

9. Which of the following is the strongest oxidizing agent?

(a)  $\text{H}_2\text{O}_2$  in acid

(b)  $\text{H}_2\text{O}_2$  in base

(c)  $\text{MnO}_4^-$  - in acid

(d)  $\text{MnO}_4^-$  in base

(e)  $\text{CrO}_4^{2-}$  in acid.

10. Use the overall cell potentials to predict which of the following reactions are spontaneous:

(a)  $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$   $E^\circ = 0.46 \text{ V}$

(b)  $2\text{Fe}^{3+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{Cl}_2(\text{g})$   $E^\circ = -0.59 \text{ V}$

(c)  $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$   $E^\circ = 0.24 \text{ V}$

(d)  $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O(l)} + \text{O}_2(\text{g})$   $E^\circ = 1.09 \text{ V}$

(e)  $\text{Cu(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g})$   $E^\circ = -0.34 \text{ V}$

## GLOSSARY

### A

**Acid-base indicators.** Substances that have distinctly different color in acidic and basic media.

**Activated complex.** An energetically excited state that is intermediate between reactants and products in a chemical reaction. Also called a transition state.

**Activation energy.** The minimum energy required to initiate a chemical reaction.

**Activity coefficient.** A characteristic of a quantity expressing the deviation of a solution from ideal behavior. It relates activity to concentration.

**Activity.** The activity is an effective thermodynamic concentration that takes into account deviation from ideal behavior.

**Arrhenius equation.** An equation that relates the rate constant to the preexponential factor and the activation energy:

$$k = k_0 \times e^{\frac{-E_a}{RT}}$$

**Amphoterism.** The ability to behave both as an acid and a base.

### B

**Bimolecular reaction.** An elementary step that involves two molecules.

**Bioenergetics.** The study of energy transformations in living organisms.

**Buffer capacity.** An index of a buffer solution's resistance to change in pH as a result of the addition of an acid or a base.

**Buffer solution.** A solution of (a) a weak acid or base and (b) its salts; both components must be present. The solution has the ability to resist the changes in pH upon the addition of small amounts of either acid or base.

## C

**Chain reaction.** A reaction in which an intermediate generated in one step attacks another species to produce another intermediate, and so on.

**Catalyst.** A substance that changes the rate of a reaction without itself being consumed.

**Closed system** a system that allows the exchange of energy (usually in the form of heat) but not mass with its surroundings.

**Coenzyme** a small organic molecule required in the catalytic mechanisms of certain enzymes.

**Colligative properties.** Properties of solutions that depend on the number of solute particles that are present in solution rather than on their nature.

**Conductance.** The conductance of an electrolyte solution is a measure of the ability of its ions to transport an electric current.

**Consecutive reactions** are reactions of the type  $A \rightarrow B \rightarrow C$ .

**Coupled reactions.** A process in which an endergonic reaction is made to proceed by coupling it to an exergonic reaction. Biological coupled reactions are usually mediated with the aid of enzymes.

## D

**Debye-Huckel limiting Law.** A mathematical expression for calculating the mean activity coefficient of an electrolyte solution in regions of low ionic strength.

**Dielectric constant ( $\epsilon$ ).** The dielectric constant of a solvent is a coefficient which indicates how much times a solvent reduces the attractive forces between ions in comparison with vacuum. For water  $\epsilon$  is  $\sim 81$ , for ethyl alcohol  $\epsilon \sim 24$ , for most organic solvents  $\epsilon$  is in the range 2-2.5.

**Diffusion.** The gradual migration of particles down a concentration gradient.

**Disproportionation reaction.** A reaction in which a single reactant undergoes both oxidation and reduction.

## *E*

**Electrochemical reaction** is a chemical reaction that involves the flow of electrons.

**Elementary step.** A reaction that represents the progress at the molecular level.

**Endergonic process.** A process that is accompanied by a positive change in Gibbs energy ( $\Delta G > 0$ ) and therefore is thermodynamically not favored.

**Endothermic reaction.** A reaction that absorbs heat from the surroundings.

**Energy.** The capacity to do work or to produce change.

**Enthalpy.** A thermodynamic quantity used to describe heat changes taking place in at constant pressure.

**Entropy.** A thermodynamic quantity that expresses the degree of disorder and randomness in a system.

**Enzyme.** A biological catalyst that is either the protein or an RNA molecule.

**Equivalence point (endpoint).** The point at which the acid completely reacts with or neutralized by the base.

**Exergonic process.** A process that is accompanied by a negative change in Gibbs energy ( $\Delta G < 0$ ) and there for is thermodynamically favored.

**Exothermic reaction.** A reaction that gives off heat to the surroundings.

## *F*

**First Law of thermodynamics.** The law that states that energy can be converted from one form to another but cannot be created or destroyed.

**First Raoult's Law:** the vapor pressure of nonvolatile solutions is always less than that of pure solvents; the decrease in vapor pressure is proportional to the mole fraction of a solute.

**First-order reaction.** A reaction whose rate depends on the reactant concentration raised to the first power.

**Force.** According to Newton's second law of motion, force is mass times acceleration.

## *G*

**Galvanic cell.** A galvanic cell is an electrochemical cell which uses the energy released from a spontaneous reaction to generate electricity.

**Gas constant (R)** the universal constant that appears in the ideal gas equation. It has the value  $8.314 \text{ J K}^{-1}\text{mol}^{-1}$ .

**Gibbs energy (G).** A thermodynamic quantity defined by the equation  $G = H - TS$ .

## *H*

**Half-life.** The time required for the concentration of a reactant to decrease to half of its initial concentration.

**Heat.** Transfer of energy (usually thermal energy) between two bodies that are at different temperatures.

**Henry's Law.** The law stating that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution.

**Hess's Law.** The law stating that when reactants are converted into products, the change in enthalpy is the same whether the reaction takes place in one step or a series of steps.

**Hydration number.** The number of water molecules associated with a solute molecule or an ion in aqueous solution.

**Hypertonic solution.** A concentrated solution with high osmotic pressure.

**Hypotonic solution.** A dilute solution with a low osmotic pressure.

## *I*

**Inhibitor.** A substance that is capable of stopping or retarding an enzyme-catalyzed reaction.

**Internal energy.** The internal energy of a system is the total energy of all its components.

**Ionic atmosphere.** A sphere of opposite charge surrounding each ion in an aqueous solution.

**Ionic mobility.** The ionic velocity per unit electric field.

**Ionic strength (I).** A characteristic of an electrolyte solution defined by

$$I = \frac{1}{2} \sum C_i \times Z_i^2$$

where  $C_i$  — is the molarity of the ion,  $Z_i$  is its charge.

**Irreversible inhibition.** An inhibition in which the inhibitor forms a covalent bond with the enzyme at the active site.

**Isotonic solution.** Solution with the same concentration and hence the same osmotic pressure.

### ***K***

**Kolrausch's Law of independent migration.** The law stating that molar conductance at infinite dilution is made up of independent contributions from cationic and anionic species.

### ***M***

**Maximum rate ( $V_{\max}$ )** The rate of an enzyme catalyzed reaction when all the enzymes are bound to substrate molecules.

**Mean activity coefficient.** A quantity that describes the deviation from ideality in the behavior of ions in solution.

**Membrane potential.** A voltage difference that exists across a membrane due to differences in the concentrations of ions on either side of the membrane.

**Michaelis-Menten kinetics.** A mathematical treatment that assumes the initial step in enzyme catalysis is a pre-equilibrium between the substrate and the enzyme, followed by the conversion of the enzyme-substrate complex to product.

**Microstate.** The state of a system as specified by the actual properties of each individual component (atoms or molecules).

**Molecularity.** The number of molecules reacting in an elementary step.

**Mole fraction.** The ratio of the number of moles of one component of a mixture to the total number of moles of all components in the mixture

## *N*

**Nernst equation.** An equation that reflects effects of temperature and concentration on redox properties of oxidizing and reducing agents:

$$\Phi_{\text{Ox/Red}} = \Phi^0_{\text{Ox/Red}} + \frac{R \times T}{n \times F} \times \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

**Nonvolatile.** Does not have a measurable vapor pressure.

## *O*

**Open system.** A system that can exchange mass and energy with its surroundings.

**Osmosis.** The net movement of solvent molecules through semipermeable membrane from a pure solvent or from a dilute solution to a more concentrated solution.

**Osmotic pressure.** The pressure required to stop osmosis.

**Oxidation.** Any process in which the oxidation number of an atom increases (becomes more positive).

**Oxidation number.** The charge that an atom would have if the compound in which it were found were ionic.

**Oxidizing agent (or oxidant).** The species that removes electron is the oxidation-reduction reaction.

## *P*

**pH.** A term used to describe the hydrogen ion activity in a solution;  $\text{pH} = -\log a\text{H}^+$ . In dilute solutions pH is defined as  $-\log[\text{H}^+]$ .

**Potential energy.** Energy of position or energy of interaction.

**Potential energy profile.** A plot of the potential of a system versus the coordinates of a system.

**Potentiometric titration.** Potentiometric titration is a volumetric method in which the potential between two electrodes is measured (referent and indicator electrode) as a function of the added titrant volume. The voltage is recorded at intervals as the titrant is added. A potentiometric titration curve is a plot of potential as a function of the volume of added titrant. The end point of the reaction is half way between the jump in voltage.

**Potentiometry.** A term used to describe an investigation method based on determination of emf of a specially constructed galvanic cell. Potentiometry can be of two types: direct (pH of solutions measuring) and indirect (potentiometric titration).

**Pre-exponential factor.** The factor that precedes the exponential term in the Arrhenius equation

## *R*

**Rate constant.** Constant of proportionality between the reaction rate and the concentration of reactants.

**Rate law.** An expression relating the rate of a reaction to the rate constant and the concentrations of the reactants.

**Rate-determining step.** The slowest elementary step in the sequence of steps leading to formation of products.

**Reaction mechanism.** The sequence of elementary steps that leads to product formation.

**Reaction order.** The sum of the powers to which all reactant concentrations appearing in the rate law are raised.

**Redox reaction (oxidation-reduction reaction).** A reaction in which at least one atom changes in oxidation state.

**Reducing agent (or reductant).** The species that donates electron is the oxidation-reduction reaction.

**Reversible reaction.** Reversible reaction runs spontaneously both in forward and reverse directions. An equation for a hypothetical reversible reaction can be represented by  $aA + bB \leftrightarrow cC + dD$ .

## *S*

**Salting-in effect.** The increase in solubility of an electrolyte at high ionic strength.

**Salting-out effect.** The decrease in solubility of an electrolyte at high ionic strength.

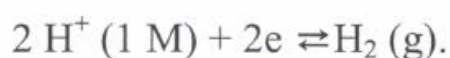
**Second Law of thermodynamics.** The entropy of the Universe increases in a spontaneous process and remains unchanged in an equilibrium process.

**Second-order reaction.** A reaction whose rate depends on the reactant concentration raised to the second power or on the concentrations of two different reactants, each raised to the first power.

**Semipermeable membrane.** A membrane that allows solvent and certain solute molecules to pass through but blocks the movement of other solute molecules.

**Spontaneous process.** A process that occurs on its own accord under a given set of conditions.

**Standard hydrogen electrode.** An electrode involving the reversible halfreaction



It is assigned a zero electrode potential when the gas is at 101.3 kPa pressure and concentration of the  $\text{H}^+$  ions is at 1 M at 298 K.

**Standard reduction potential.** The electrode potential of a substance for the reduction half-reaction  $\text{Ox} + u\text{e}^- \rightarrow \text{Red}$ , where Ox and Red are oxidized and reduced forms of the substance and  $u$  is the stoichiometric coefficient. The Ox and Red forms are in their standard states, and the measured potential is based on the standard hydrogen electrode reference scale.

**Standard solution (primary titrant).** A solution of accurately known concentration.

**Standardization.** A working solution is titrated by a standard solution.

**State function.** A property that is determined by the state of a system. The change in any state function in a process is path independent.

**Surroundings.** The rest of the universe outside the system.

**System.** A specific part of the universe that is of interest to us.

## *T*

**Termolecular reaction.** An elementary step that involves three molecules.

**Thermochemical equation.** An equation that shows both the mass and enthalpy relations.

**Thermochemistry.** The study of heat changes in chemical reactions.

**Thermodynamics.** The scientific study of the interconversion of heat and other forms of energy.

**Titration.** The gradual addition of a solution of accurately known concentration to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

**Turnover number.** The number of substrate molecules processed by an enzyme molecule per second when the enzyme is saturated with the substrate. Also referred to as  $k_2$ , the catalytic rate constant.

### *U*

**Unimolecular reaction.** An elementary step that involves one molecule.

### *V*

**Van't Hoff factor.** The ratio of the actual number of ionic particles in a solution after dissociation to the number of formula units initially dissolved in a solution.

### *W*

**Work.** In mechanics, work is force times distance. In thermodynamics, the most common forms of work are gas expansion and electrical work carried out in an electrochemical cell.

**Working solution (secondary titrant).** The working solutions of accurately unknown concentration.

### *Z*

**Zero-order reaction.** A reaction whose rate is independent of the concentrations of the reactants.

# REFERENCE BOOK

Table 1 - Periodic table of the elements

Periodic Table of the Elements

Atomic number → 1  
Symbol → H  
Atomic mass → 1.008  
Name → hydrogen

Color Code

- Metal (Yellow)
- Metalloid (Purple)
- Nonmetal (Green)
- Solid (White)
- Liquid (Blue)
- Gas (Red)

Table 2 - Molar masses of inorganic substances

|                              | OH <sup>-</sup> | O <sup>2-</sup> | Cl <sup>-</sup> | Br <sup>-</sup> | I <sup>-</sup> | S <sup>2-</sup> | SO <sub>3</sub> <sup>2-</sup> | SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> | CO <sub>3</sub> <sup>2-</sup> | SiO <sub>3</sub> <sup>2-</sup> |
|------------------------------|-----------------|-----------------|-----------------|-----------------|----------------|-----------------|-------------------------------|-------------------------------|------------------------------|-------------------------------|-------------------------------|--------------------------------|
| H <sup>+</sup>               | 18              | 18              | 36.5            | 81              | 128            | 34              | 82                            | 98                            | 63                           | 98                            | 62                            | 78                             |
| NH <sub>4</sub> <sup>+</sup> | 35              | -               | 53.5            | 98              | 145            | 68              | 116                           | 132                           | 80                           | 149                           | 96                            | 112                            |
| Na <sup>+</sup>              | 40              | 62              | 58.5            | 103             | 150            | 78              | 126                           | 142                           | 85                           | 164                           | 106                           | 122                            |
| K <sup>+</sup>               | 56              | 94              | 74.5            | 119             | 166            | 110             | 158                           | 174                           | 101                          | 212                           | 138                           | 154                            |
| Mg <sup>2+</sup>             | 58              | 40              | 95              | 184             | 278            | 56              | 104                           | 120                           | 148                          | 262                           | 84                            | 100                            |
| Ca <sup>2+</sup>             | 74              | 56              | 111             | 200             | 294            | 72              | 120                           | 136                           | 164                          | 310                           | 100                           | 116                            |
| Ba <sup>2+</sup>             | 171             | 153             | 208             | 297             | 391            | 169             | 217                           | 233                           | 261                          | 601                           | 197                           | 213                            |
| Al <sup>3+</sup>             | 78              | 102             | 133.5           | 267             | 408            | 150             | 294                           | 342                           | 213                          | 122                           | 234                           | 282                            |
| Cr <sup>3+</sup>             | 103             | 152             | 158.5           | 292             | 433            | 200             | 344                           | 392                           | 238                          | 147                           | 284                           | 332                            |
| Zn <sup>2+</sup>             | 99              | 81              | 136             | 225             | 319            | 97              | 145                           | 161                           | 189                          | 385                           | 125                           | 141                            |
| Mn <sup>2+</sup>             | 89              | 71              | 126             | 215             | 309            | 87              | 135                           | 151                           | 179                          | 355                           | 115                           | 131                            |
| Fe <sup>2+</sup>             | 90              | 72              | 127             | 216             | 310            | 88              | 136                           | 152                           | 180                          | 358                           | 116                           | 132                            |
| Fe <sup>3+</sup>             | 107             | 160             | 162.5           | 296             | 437            | 208             | 352                           | 400                           | 242                          | 151                           | 292                           | 340                            |
| Cu <sup>2+</sup>             | 98              | 80              | 135             | 224             | 318            | 96              | 144                           | 160                           | 188                          | 382                           | 124                           | 140                            |
| Ag <sup>+</sup>              | 125             | 232             | 143.5           | 188             | 235            | 248             | 294                           | 312                           | 170                          | 419                           | 276                           | 292                            |
| Pb <sup>2+</sup>             | 241             | 223             | 278             | 367             | 461            | 239             | 287                           | 303                           | 331                          | 811                           | 267                           | 283                            |

**Table 3 - Solubility of inorganic substances in water**

| Cations                              | Anions          |                |                 |                 |                |                 |                               |                               |                              |                               |                               |                                |                                  |
|--------------------------------------|-----------------|----------------|-----------------|-----------------|----------------|-----------------|-------------------------------|-------------------------------|------------------------------|-------------------------------|-------------------------------|--------------------------------|----------------------------------|
|                                      | OH <sup>-</sup> | F <sup>-</sup> | Cl <sup>-</sup> | Br <sup>-</sup> | I <sup>-</sup> | S <sup>2-</sup> | SO <sub>3</sub> <sup>2-</sup> | SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> | CO <sub>3</sub> <sup>2-</sup> | SiO <sub>3</sub> <sup>2-</sup> | CH <sub>3</sub> COO <sup>-</sup> |
| NH <sub>4</sub> <sup>+</sup>         | —               | s              | s               | s               | s              | —               | s                             | s                             | s                            | s                             | s                             | —                              | s                                |
| Na <sup>+</sup><br>K <sup>+</sup>    | s               | s              | s               | s               | s              | s               | s                             | s                             | s                            | s                             | s                             | s                              | s                                |
| Mg <sup>2+</sup>                     | L               | in             | s               | s               | s              | s               | in                            | s                             | s                            | in                            | in                            | in                             | s                                |
| Ca <sup>2+</sup>                     | L               | in             | s               | s               | s              | L               | in                            | L                             | s                            | in                            | in                            | in                             | s                                |
| Ba <sup>2+</sup>                     | s               | L              | s               | s               | s              | s               | in                            | in                            | s                            | in                            | in                            | in                             | s                                |
| Al <sup>3+</sup>                     | in              | L              | s               | s               | s              | —               | —                             | s                             | s                            | in                            | —                             | in                             | L                                |
| Cr <sup>3+</sup>                     | in              | in             | s               | s               | s              | —               | —                             | s                             | s                            | in                            | —                             | in                             | s                                |
| Zn <sup>2+</sup>                     | in              | L              | s               | s               | s              | in              | in                            | s                             | s                            | in                            | in                            | in                             | s                                |
| Mn <sup>2+</sup>                     | in              | L              | s               | s               | s              | in              | in                            | s                             | s                            | in                            | in                            | in                             | s                                |
| Co <sup>2+</sup><br>Ni <sup>2+</sup> | in              | s              | s               | s               | s              | in              | in                            | s                             | s                            | in                            | in                            | in                             | s                                |
| Fe <sup>2+</sup>                     | in              | in             | s               | s               | s              | in              | in                            | s                             | s                            | in                            | in                            | in                             | s                                |
| Fe <sup>3+</sup>                     | in              | in             | s               | s               | s              | —               | —                             | s                             | s                            | in                            | in                            | in                             | s                                |
| Cd <sup>2+</sup>                     | in              | s              | s               | s               | s              | in              | in                            | s                             | s                            | in                            | in                            | in                             | s                                |
| Hg <sup>2+</sup>                     | —               | —              | s               | L               | n              | in              | in                            | s                             | s                            | in                            | in                            | —                              | s                                |
| Cu <sup>2+</sup>                     | in              | in             | s               | s               | s              | in              | in                            | s                             | s                            | in                            | in                            | in                             | s                                |
| Ag <sup>+</sup>                      | —               | s              | in              | in              | in             | in              | in                            | L                             | s                            | in                            | in                            | in                             | s                                |
| Sn <sup>2+</sup>                     | in              | s              | sp              | s               | s              | in              | —                             | s                             | —                            | in                            | —                             | —                              | s                                |
| Pb <sup>2+</sup>                     | in              | in             | L               | L               | in             | in              | in                            | in                            | s                            | in                            | in                            | in                             | s                                |

where **s** – soluble substances; **in** – insoluble substances; **L** – substances with low solubility

**Table 4 - General physical constants**

| Constants                     | Symbol           | Value  | SI units                      |
|-------------------------------|------------------|--------|-------------------------------|
| Speed of light in vacuum      | C                | 2.9979 | $\times 10^8$ m/s             |
| Elementary charge             | e                | 1.6022 | $10^{19}$ C                   |
| Avogadro constant             | N <sub>A</sub>   | 6.0220 | $10^{23}$ mol <sup>-1</sup>   |
| Atomic mass unit              | amu <sup>a</sup> | 1.6606 | $10^{-27}$ kg                 |
| Electron rest mass            | m <sub>e</sub>   | 9.1095 | $10^{-31}$ kg                 |
| Proton rest mass              | m <sub>p</sub>   | 1.6726 | $10^{-27}$ kg                 |
| Neutron rest mass             | m <sub>n</sub>   | 1.6750 | $10^{-27}$ kg                 |
| Planck constant               | h                | 6.6262 | $10^{-34}$ J×s                |
| Rydberg constant <sup>b</sup> | R <sub>∞</sub>   | 1.0974 | $10^7$ m <sup>-1</sup>        |
| Gas constant                  | R                | 8.3144 | J/mol×K                       |
| Gas molar volume              | V <sub>m</sub>   | 2.2414 | $10^{-2}$ m <sup>3</sup> /mol |

<sup>a</sup> The symbol amu is commonly used in this country, but u is the official symbol.

<sup>b</sup> The symbol R<sub>∞</sub> refers to the Rydberg constant for infinite nuclear mass.

**Table 5 - Molar boiling-point elevation and freezing-point depression constants of several common liquids**

| Solvent     | Normal freezing point (°C) * | K <sub>f</sub> (°C/m) | Normal boiling point (°C) * | K <sub>b</sub> (°C/m) |
|-------------|------------------------------|-----------------------|-----------------------------|-----------------------|
| Water       | 0                            | 1.86                  | 100                         | 0.52                  |
| Benzene     | 5.5                          | 5.12                  | 80.1                        | 2.53                  |
| Ethanol     | - 117.3                      | 1.99                  | 78.4                        | 1.22                  |
| Acetic acid | 16.6                         | 3.90                  | 117.9                       | 2.93                  |
| Cyclohexane | 6.6                          | 20.0                  | 80.7                        | 2.79                  |

\*Measured at 1atm

**Table 6 - Distribution of major ions on opposite sides of the membrane of a typical nerve cell**

| Ion             | Concentration/ mM |               |
|-----------------|-------------------|---------------|
|                 | Intracellular     | Extracellular |
| Na <sup>+</sup> | 15                | 150           |
| K <sup>+</sup>  | 150               | 10            |
| Cl <sup>-</sup> | 10                | 110           |

**Table 7 - Some common acid-base indicators**

| Color Indicator   | In acid   | In base       | pH range * |
|-------------------|-----------|---------------|------------|
| Thymol blue       | Red       | Yellow        | 1.2 – 2.8  |
| Bromophenol blue  | Yellow    | Bluish purple | 3.0 – 4.6  |
| Methyl orange     | Orange    | Yellow        | 3.1 – 4.4  |
| Methyl red        | Red       | Yellow        | 4.2 – 6.3  |
| Chlorophenol blue | Yellow    | Red           | 4.8 – 6.4  |
| Bromothymol blue  | Yellow    | Blue          | 6.0 – 7.6  |
| Cresol red        | Yellow    | Red           | 7.2 – 8.8  |
| Phenolphthalein   | Colorless | Reddish pink  | 8.3 – 10.0 |

\*The pH range is defined as range over which the indicator changes from the acid color to the base color

**Table 8 - Density and concentration of aqueous solutions (20<sup>0</sup> C)**

| g/mL                     | Concentration |                        | g/mL   | Concentration |                        |
|--------------------------|---------------|------------------------|--------|---------------|------------------------|
|                          | w, %          | C <sub>M</sub> , mol/L |        | w, %          | C <sub>M</sub> , mol/L |
| <b>SODIUM CHLORIDE</b>   |               |                        |        |               |                        |
| 1.0053                   | 1             | 0.172                  | 1.1009 | 14            | 2.639                  |
| 1.0125                   | 2             | 0.346                  | 1.1162 | 16            | 3.057                  |
| 1.0268                   | 4             | 0.703                  | 1.1319 | 18            | 3.489                  |
| 1.0413                   | 6             | 1.069                  | 1.1478 | 20            | 3.930                  |
| 1.0559                   | 8             | 1.446                  | 1.1640 | 22            | 4.384                  |
| 1.0707                   | 10            | 1.834                  | 1.1804 | 24            | 4.849                  |
| 1.0857                   | 12            | 2.231                  | 1.1972 | 26            | 5.329                  |
| <b>HYDROCHLORIC ACID</b> |               |                        |        |               |                        |
| 1.0032                   | 1             | 0.275                  | 1.1083 | 22            | 6.684                  |
| 1.0082                   | 2             | 0.553                  | 1.1187 | 24            | 7.365                  |
| 1.0181                   | 4             | 1.117                  | 1.1290 | 26            | 8.051                  |
| 1.0279                   | 6             | 1.692                  | 1.1392 | 28            | 8.750                  |
| 1.0376                   | 8             | 2.277                  | 1.1493 | 30            | 9.454                  |
| 1.0474                   | 10            | 2.872                  | 1.1593 | 32            | 10.15                  |
| 1.0574                   | 12            | 3.481                  | 1.1691 | 34            | 10.93                  |
| 1.0675                   | 14            | 4.099                  | 1.1789 | 36            | 11.64                  |
| 1.0776                   | 16            | 4.729                  | 1.1885 | 38            | 12.39                  |
| 1.0878                   | 18            | 5.371                  | 1.1980 | 40            | 13.14                  |
| 1.0980                   | 20            | 6.023                  |        |               |                        |

**Table 9 - Ionic strength and activity coefficients of the ions**

| Ions   | Ionic strength of the solution |       |      |      |      |      |      |      |      |
|--|--------------------------------|-------|------|------|------|------|------|------|------|
|  | 0.0005                         | 0.001 | 0.01 | 0.02 | 0.1  | 0.2  | 0.3  | 0.5  | 1.0  |
| H <sup>+</sup>   | 0.98                           | 0.97  | 0.91 | 0.90 | 0.87 | 0.81 | 0.80 | 0.79 | 0.85 |
| NH <sub>4</sub> <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> | 0.98                           | 0.96  | 0.90 | 0.87 | 0.75 | 0.67 | 0.62 | 0.55 | 0.44 |
| OH <sup>-</sup> , F <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>   | 0.98                           | 0.96  | 0.90 | 0.87 | 0.76 | 0.68 | 0.63 | 0.56 | 0.46 |
| Na <sup>+</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>  | 0.98                           | 0.96  | 0.90 | 0.87 | 0.77 | 0.73 | 0.70 | 0.67 | 0.63 |
| Ca <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> , Fe <sup>2+</sup>  | 0.90                           | 0.87  | 0.68 | 0.64 | 0.41 | 0.33 | 0.28 | 0.25 | 0.21 |
| Mg <sup>2+</sup> , Be <sup>2+</sup>  | 0.91                           | 0.87  | 0.69 | 0.65 | 0.45 | 0.37 | 0.34 | 0.28 | 0.23 |
| PO <sub>4</sub> <sup>3-</sup>  | 0.80                           | 0.73  | 0.40 | -    | 0.10 | -    | -    | -    | -    |
| Al <sup>3+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup>   | 0.80                           | 0.74  | 0.45 | -    | 0.18 | -    | -    | -    | -    |

**Table 10 - K<sub>a</sub> and pK<sub>a</sub> for acids**

| Acid  | pK <sub>a</sub> | K <sub>a</sub>        |
|---|-----------------|-----------------------|
| HClO  | 7.25            | $5.6 \times 10^{-8}$  |
| HCl   | -7              | $1.0 \times 10^7$     |
| H <sub>2</sub> SO <sub>4</sub>              | -3              | $1.0 \times 10^3$     |
| H <sub>3</sub> O <sup>+</sup>               | -1.74           | 55                    |
| HNO <sub>3</sub>                            | -1.32           | 21                    |
| H <sub>2</sub> SO <sub>3</sub>              | 1.92            | 0.012                 |
| HF  | 3.13            | $7.2 \times 10^{-4}$  |
| HNO <sub>2</sub>                            | 3.15            | $7.1 \times 10^{-4}$  |
| HCOOH                                       | 3.70            | $2.2 \times 10^{-4}$  |
| CH <sub>3</sub> COOH                        | 4.75            | $1.8 \times 10^{-5}$  |
| HCN   | 9.00            | $1.0 \times 10^{-9}$  |
| H <sub>3</sub> BO <sub>3</sub>              | 9.14            | $7.3 \times 10^{-10}$ |
| NH <sub>4</sub> <sup>+</sup>                | 9.25            | $5.6 \times 10^{-10}$ |
| H <sub>2</sub> SiO <sub>4</sub>             | 9.5             | $3.2 \times 10^{-10}$ |
| H <sub>2</sub> CO <sub>3</sub>              | 6.52            | $3.0 \times 10^{-7}$  |
| HCO <sub>3</sub> <sup>-</sup>               | 10.4            | $4.0 \times 10^{-11}$ |
| H <sub>3</sub> PO <sub>4</sub>              | 1.96            | 0.011                 |
| H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> | 7.12            | $7.6 \times 10^{-8}$  |
| HPO <sub>4</sub> <sup>2-</sup>              | 12.3            | $4.8 \times 10^{-13}$ |
| H <sub>2</sub> S                            | 6.92            | $1.2 \times 10^{-7}$  |
| HS <sup>-</sup>                             | 13              | $1.0 \times 10^{-13}$ |

**Table 11 - K<sub>b</sub> and pK<sub>b</sub> for basis**

| Base        | K <sub>b</sub>        | pK <sub>b</sub> |
|-------------|-----------------------|-----------------|
| Ammonia     | $1.8 \times 10^{-5}$  | 4.75            |
| Aniline     | $3.8 \times 10^{-10}$ | 9.42            |
| Caffeine    | $4.1 \times 10^{-4}$  | 3.39            |
| Cocaine     | $2.6 \times 10^{-6}$  | 5.59            |
| Creatine    | $1.9 \times 10^{-11}$ | 10.7            |
| Methylamine | $4.4 \times 10^{-4}$  | 3.36            |
| Morphine    | $7.4 \times 10^{-7}$  | 6.13            |
| Urea        | $1.5 \times 10^{-14}$ | 13.82           |
| Novocaine   | $7 \times 10^{-6}$    | 5.16            |
| Pyridine    | $1.7 \times 10^{-9}$  | 8.77            |
| Quinine     | $1.1 \times 10^{-8}$  | 5.96            |
| Strychnine  | $1 \times 10^{-6}$    | 6.0             |
| Ethylamine  | $5.6 \times 10^{-4}$  | 3.25            |

**Table 12 -  $K_{sp}$  for inorganic substances**

| Substances     | $K_{sp}$               | Substances      | $K_{sp}$              |
|----------------|------------------------|-----------------|-----------------------|
| $Ag_3AsO_3$    | $1.0 \times 10^{-17}$  | $AgBr$          | $5.3 \times 10^{-13}$ |
| $AgNSC$        | $1.1 \times 10^{-12}$  | $CaHPO_4$       | $2.7 \times 10^{-7}$  |
| $AgCl$         | $1.78 \times 10^{-10}$ | $Ca(H_2PO_4)_2$ | $1.0 \times 10^{-3}$  |
| $Ag_2CrO_4$    | $1.1 \times 10^{-12}$  | $Ca_3(PO_4)_2$  | $2.0 \times 10^{-29}$ |
| $Ag_2Cr_2O_7$  | $1.0 \times 10^{-10}$  | $Ca(OH)_2$      | $2.0 \times 10^{-14}$ |
| $AgI$          | $8.3 \times 10^{-17}$  | $CdS$           | $1.0 \times 10^{-29}$ |
| $AgIO_3$       | $3.0 \times 10^{-8}$   | $Co(OH)_2$      | $2.0 \times 10^{-16}$ |
| $AgNO_2$       | $1.6 \times 10^{-4}$   | $CuSO_3$        | $2.5 \times 10^{-10}$ |
| $Ag_3PO_4$     | $1.3 \times 10^{-20}$  | $CuS$           | $6.3 \times 10^{-36}$ |
| $Ag_2S$        | $6.3 \times 10^{-50}$  | $Cu(OH)_2$      | $5.0 \times 10^{-20}$ |
| $Ag_2SO_4$     | $1.6 \times 10^{-5}$   | $Cr(OH)_3$      | $6.3 \times 10^{-31}$ |
| $Al(OH)_3$     | $1.0 \times 10^{-32}$  | $Fe(OH)_2$      | $1.0 \times 10^{-15}$ |
| $AlPO_4$       | $5.7 \times 10^{-19}$  | $Fe(OH)_3$      | $3.2 \times 10^{-38}$ |
| $BaCO_3$       | $5.1 \times 10^{-9}$   | $FeCO_3$        | $3.5 \times 10^{-11}$ |
| $BaC_2O_4$     | $1.1 \times 10^{-7}$   | $FePO_4$        | $1.3 \times 10^{-22}$ |
| $BaCr_2O_4$    | $1.2 \times 10^{-10}$  | $FeS$           | $5.0 \times 10^{-18}$ |
| $BaF_2$        | $1.1 \times 10^{-6}$   | $Hg_2Cl_2$      | $1.3 \times 10^{-18}$ |
| $Ba_3(PO_4)_2$ | $6.0 \times 10^{-39}$  | $HgS$           | $4.0 \times 10^{-53}$ |
| $BaSO_3$       | $8.0 \times 10^{-7}$   | $Hg_2SO_4$      | $6.8 \times 10^{-7}$  |
| $BaSO_4$       | $1.1 \times 10^{-10}$  | $Li_2CO_3$      | $3.98 \times 10^{-3}$ |
| $Ba(OH)_2$     | $5.0 \times 10^{-3}$   | $LiF$           | $3.8 \times 10^{-3}$  |
| $Ca(OH)_2$     | $5.5 \times 10^{-6}$   | $Li_3PO_4$      | $3.2 \times 10^{-9}$  |
| $CaCO_3$       | $4.8 \times 10^{-10}$  | $MgCO_3$        | $4.0 \times 10^{-5}$  |
| $CaC_2O_4$     | $2.3 \times 10^{-9}$   | $MgC_2O_4$      | $8.6 \times 10^{-5}$  |
| $CaSO_4$       | $9.1 \times 10^{-6}$   | $Mg(OH)_2$      | $6.0 \times 10^{-10}$ |
| $CaF_2$        | $4.0 \times 10^{-11}$  | $Mg_3(PO_4)_2$  | $1.0 \times 10^{-13}$ |
| $MnCO_3$       | $1.8 \times 10^{-11}$  | $PbS$           | $2.5 \times 10^{-27}$ |
| $Mn(OH)_2$     | $4.5 \times 10^{-13}$  | $PbSO_4$        | $1.6 \times 10^{-8}$  |
| $MnS$          | $2.5 \times 10^{-10}$  | $SrCO_3$        | $1.1 \times 10^{-10}$ |
| $Na[Sb(OH)_6]$ | $4.0 \times 10^{-8}$   | $SrCrO_4$       | $3.5 \times 10^{-5}$  |
| $Ni(OH)_2$     | $2.1 \times 10^{-16}$  | $SrCr_2O_4$     | $5.5 \times 10^{-8}$  |
| $PbBr_2$       | $9.1 \times 10^{-6}$   | $Sr_3(PO_4)_2$  | $1.0 \times 10^{-31}$ |
| $PbCO_3$       | $1.0 \times 10^{-13}$  | $SrSO_4$        | $3.2 \times 10^{-7}$  |
| $PbCl_2$       | $1.6 \times 10^{-5}$   | $ZnCO_3$        | $1.4 \times 10^{-11}$ |
| $PbCrO_4$      | $1.8 \times 10^{-14}$  | $ZnC_2O_4$      | $1.5 \times 10^{-9}$  |
| $PbI_2$        | $1.1 \times 10^{-9}$   | $Zn(OH)_2$      | $7.1 \times 10^{-18}$ |
| $Pb(OH)_2$     | $1.1 \times 10^{-20}$  | $ZnS$           | $1.6 \times 10^{-24}$ |

**Table 13 - Hydrolysis constants and the hydrolysis percents of salts which involves an anion of a weak acid**

| Anion (base)              | $K_b$                 | Hydrolysis percent   | pH (0.1 mol/L) |
|---------------------------|-----------------------|----------------------|----------------|
| $\text{ClO}_3^-$          | $1 \times 10^{-14}$   | $3.2 \times 10^{-5}$ | 7              |
| $\text{HSO}_3^-$          | $8.3 \times 10^{-13}$ | $2.9 \times 10^{-4}$ | 4.6            |
| $\text{SO}_4^{2-}$        | $8.3 \times 10^{-13}$ | $2.9 \times 10^{-4}$ | 7.4            |
| $\text{H}_2\text{PO}_4^-$ | $9.1 \times 10^{-13}$ | $3.1 \times 10^{-4}$ | 4.6            |
| $\text{F}^-$              | $1.4 \times 10^{-11}$ | $1.2 \times 10^{-3}$ | 8.1            |
| $\text{NO}_2^-$           | $1.4 \times 10^{-11}$ | $1.2 \times 10^{-3}$ | 8.1            |
| $\text{HCOO}^-$           | $1.4 \times 10^{-11}$ | $2.1 \times 10^{-3}$ | 8.3            |
| $\text{CH}_3\text{COO}^-$ | $5.6 \times 10^{-10}$ | $7.5 \times 10^{-3}$ | 8.9            |
| $\text{HCO}_3^-$          | $3.3 \times 10^{-8}$  | 0.06                 | 8.5            |
| $\text{HS}^-$             | $8.3 \times 10^{-8}$  | 0.1                  | 10.0           |
| $\text{HPO}_4^{2-}$       | $1.3 \times 10^{-7}$  | 0.12                 | 9.7            |
| $\text{SO}_3^{2-}$        | $1.6 \times 10^{-7}$  | 0.13                 | 10.1           |
| $\text{ClO}^-$            | $1.8 \times 10^{-7}$  | 0.14                 | 10.1           |
| $\text{CN}^-$             | $1.0 \times 10^{-5}$  | 1.0                  | 11.0           |
| $\text{CO}_3^{2-}$        | $2.5 \times 10^{-4}$  | 5.0                  | 11.7           |
| $\text{PO}_4^{3-}$        | $1.7 \times 10^{-2}$  | 33                   | 12.5           |
| $\text{S}^{2-}$           | $1.0 \times 10^{-1}$  | 60                   | 12.8           |

**Table 14 - Some common acids and their conjugated bases**

| Acid                   |                         | Conjugate base         |                    |
|------------------------|-------------------------|------------------------|--------------------|
| Name                   | Formula                 | Name                   | Formula            |
| Hydrochloric acid      | HCl                     | Chloride ion           | $\text{Cl}^-$      |
| Nitric acid            | $\text{HNO}_3$          | Nitrate ion            | $\text{NO}_3^-$    |
| Hydrocyanic acid       | HCN                     | Cyan ion               | $\text{CN}^-$      |
| Perchloric acid        | $\text{HClO}_4$         | Perchlor ion           | $\text{ClO}_4^-$   |
| Sulfuric acid          | $\text{H}_2\text{SO}_4$ | Hydrogen sulfate ion   | $\text{HSO}_4^-$   |
| Hydrogen sulfate ion   | $\text{HSO}_4^-$        | Sulfate ion            | $\text{SO}_4^{2-}$ |
| Carbonic acid          | $\text{H}_2\text{CO}_3$ | Hydrogen carbonate ion | $\text{HCO}_3^-$   |
| Hydrogen carbonate ion | $\text{HCO}_3^-$        | Carbonate ion          | $\text{CO}_3^{2-}$ |
| Ammonium ion           | $\text{NH}_4^+$         | Ammonia                | $\text{NH}_3$      |

**Table 15 - Selected thermodynamic data at 1 atm. and 25°C**

| Substances  | State    | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K $\times$ mol) |
|---|----------|-----------------------------|-----------------------------|------------------------------|
| AgCl  | s        | -127                        | -109.7                      | 96.1                         |
| AgNO <sub>3</sub>                                 | s        | -123                        | -32.2                       | 141                          |
| Ag <sub>2</sub> O                                 | s        | -30.6                       | -10.8                       | 122                          |
| Al  | s        | 0                           | 0                           | 28.4                         |
| Al <sup>3+</sup>                                  | l        | -524.7                      | -481.2                      | -313.4                       |
| Al <sub>2</sub> O <sub>3</sub>                    | s        | -1670                       | -1576                       | 51                           |
| Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O | s        | -656                        | -575                        | 107                          |
| B <sub>2</sub> O <sub>3</sub>                     | s        | -1264                       | -1184                       | 54                           |
| H <sub>3</sub> BO <sub>3</sub>                    | s        | -1088                       | -963                        | 89.6                         |
|   | solution | -1067                       | -963                        | 160                          |
| Ba <sup>2+</sup>                                  | l        | -538                        | -561                        | 12.6                         |
| BaCl <sub>2</sub>                                 | s        | -860                        | -811                        | 126                          |
| BaCl <sub>2</sub> ·2H <sub>2</sub> O              | s        | -1460                       | -1300                       | 203                          |
| BaSO <sub>4</sub>                                 | s        | -1464                       | -1353                       | 132                          |
| Br <sub>2</sub>                                   | l        | 0                           | 0                           | 152                          |
| Br <sub>2</sub> <sup>-</sup>                      | l        | -121                        | 103                         | 81                           |
| C   | s        | 0                           | 0                           | 5.7                          |
| CO  | g        | -111                        | -137                        | 198                          |
| CO <sub>2</sub>                                   | g        | -394                        | -394                        | 214                          |
|   | l        | -413                        | -386                        | 121                          |
| H <sub>2</sub> CO <sub>3</sub>                    | l        | -700                        | -623                        | 187                          |
| HCO <sub>3</sub> <sup>-</sup>                     | l        | -691                        | -587                        | 95                           |
| CO <sub>3</sub> <sup>2-</sup>                     | l        | -676                        | -528                        | -53                          |
| Ca <sup>2+</sup>                                  | l        | -543                        | -553                        | -55                          |
| CaO   | s        | -636                        | -604                        | 40                           |
| Ca(OH) <sub>2</sub>                               | s        | -987                        | -897                        | 76                           |
| CaSO <sub>4</sub>                                 | s        | -1430                       | -1320                       | 107                          |
| CaSO <sub>4</sub> ·2H <sub>2</sub> O              | s        | -2020                       | -1790                       | 194                          |
| CaCl <sub>2</sub>                                 | s        | -795                        | -750                        | 114                          |
| CaCl <sub>2</sub>                                 | l        | -877                        | -815                        | 55                           |
| CaCl <sub>2</sub> ·6H <sub>2</sub> O              | s        | -2600                       |                             |                              |
| CaCO <sub>3</sub>                                 | s        | -1207                       | -1129                       | 93                           |
| Cl <sub>2</sub>                                   | g        | 0                           | 0                           | 223                          |
| HCl   | g        | -92.3                       | -95.3                       | 187                          |
| HCl   | l        | -167                        | -131                        | 55                           |
| CrO <sub>4</sub> <sup>2-</sup>                    | l        | -863                        | -706                        | 38.5                         |
| Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>      | l        | -1461                       | -1257                       | 214                          |
| Cu <sup>2+</sup>                                  | l        | 64.4                        | 65                          | 99                           |
| CuCl  | s        | -135                        | -119                        | 92                           |
| CuCl <sub>2</sub>                                 | s        | -206                        |                             |                              |
| CuSO <sub>4</sub>                                 | s        | -770                        | -662                        | 113                          |
| CuSO <sub>4</sub> ·3H <sub>2</sub> O              | s        | -1680                       | -1400                       | 225                          |
| CuSO <sub>4</sub> ·5H <sub>2</sub> O              | s        | -2280                       | -1880                       | 306                          |

| Substances   | State    | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K $\times$ mol) |
|--|----------|-----------------------------|-----------------------------|------------------------------|
| F <sup>-</sup>   | l        | -329                        | -276                        | -10                          |
| HF   | g        | -269                        | -271                        | 174                          |
| Fe   | s        | 0                           | 0                           | 27.2                         |
| Fe <sup>2+</sup>                                       | l        | -88                         | -85                         | -113                         |
| Fe <sup>3+</sup>                                       | l        | -48                         | -11                         | -293                         |
| FeCl <sub>3</sub>                                      | s        | -405                        |                             |                              |
| FeCl <sub>3</sub> ·6H <sub>2</sub> O                   | s        | -2220                       |                             |                              |
| FeSO <sub>4</sub>                                      | s        | -923                        | -820                        | 108                          |
| FeSO <sub>4</sub> ·7H <sub>2</sub> O                   | s        | -3000                       |                             |                              |
| H <sub>2</sub>   | g        | 0                           | 0                           | 131                          |
| H <sup>+</sup>   | l        | 0                           | 0                           | 0                            |
| HO <sup>-</sup>  | l        | -230                        | -157                        | -10.5                        |
| H <sub>2</sub> O                                       | l        | -286                        | -238                        | 70                           |
| H <sub>2</sub> O                                       | g        | -242                        | -229                        | 189                          |
| H <sub>2</sub> O <sub>2</sub>                          | l        | -188                        | -118                        |                              |
| H <sub>2</sub> O <sub>2</sub>                          | solution | -191                        |                             |                              |
| Hg   | l        | 0                           | 0                           | 77                           |
| Hg   | g        | 61                          | 32                          | 175                          |
| Hg <sup>2+</sup>                                       | l        |                             | -164                        |                              |
| HgCl <sub>2</sub>                                      | s        | -230                        | -176                        |                              |
| Hg <sub>2</sub> Cl <sub>2</sub>                        | s        | -264                        | -211                        | 196                          |
| HgO  | s        | -90                         | -58.4                       | 73                           |
| K <sup>+</sup>   | l        | -251                        | -282                        | 103                          |
| KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O | s        | -6050                       | -5176                       | 688                          |
| KBr  | s        | -392                        | -380                        | 96                           |
| KBr  | l        | -372                        | -385                        | 183                          |
| KCl  | s        | -436                        | -408                        | 83                           |
| KCl  | g        | -216                        | -235                        | 240                          |
| KCl  | l        | -419                        | -414                        | 158                          |
| KClO <sub>3</sub>                                      | s        | -391                        | -290                        | 143                          |
| KI   | s        | -328                        | -322                        | 104                          |
| KI   | l        | -307                        | -334                        | 112                          |
| KNO <sub>3</sub>                                       | s        | -492                        | -393                        | 133                          |
| KNO <sub>3</sub>                                       | l        | -458                        | -393                        | 290                          |
| KMnO <sub>4</sub>                                      | s        | -814                        | -714                        | 172                          |
| Li <sup>+</sup>  | l        | -278                        | -294                        | 14                           |
| LiOH   | s        | -487                        | -444                        | 50                           |
| Li <sub>2</sub> CO <sub>3</sub>                        | s        | -1215                       | -1130                       | 90                           |
| Mg <sup>2+</sup>                                       | l        | -462                        | -456                        | -118                         |
| MgCO <sub>3</sub>                                      | s        | -1110                       | -1030                       | 66                           |
| MgCl <sub>2</sub>                                      | s        | -641                        | -592                        | 90                           |
| MgCl <sub>2</sub> ·6H <sub>2</sub> O                   | s        | -2500                       | -1280                       | 366                          |
| MgO  | s        | -601                        | -570                        | 27                           |
| Mg(OH) <sub>2</sub>                                    | s        | -925                        | -834                        | 63                           |
| MgSO <sub>4</sub>                                      | s        | -1280                       | -1170                       | 92                           |

| Substances   | State | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K $\times$ mol) |
|--|-------|-----------------------------|-----------------------------|------------------------------|
| MgSO <sub>4</sub> ·7H <sub>2</sub> O                             | s     | -3380                       |                             |                              |
| Mn <sup>2+</sup>   | l     | -219                        | -223                        | -84                          |
| Mn <sup>3+</sup>   | l     | -100                        |                             |                              |
| MnSO <sub>4</sub>  | s     | -1060                       | -956                        | 112                          |
| N <sub>2</sub>   | g     | 0                           | 0                           | 191                          |
| NH <sub>3</sub>  | g     | -46.2                       | -16.6                       | 192                          |
| NH <sub>3</sub>  | l     | -80.7                       | -26.6                       | 110                          |
| NH <sub>4</sub> <sup>+</sup>                                     | l     | -133                        | -80                         | 113                          |
| NH <sub>4</sub> Cl   | s     | -315                        | -204                        | 94.6                         |
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>                  | s     | -1180                       | -900                        | 220                          |
| N <sub>2</sub> O   | g     | 81.6                        | 104                         | 220                          |
| NO   | g     | 90                          | 87                          | 211                          |
| NO <sub>2</sub>  | g     | 34                          | 52                          | 240                          |
| N <sub>2</sub> O <sub>4</sub>                                    | g     | 10                          | 98                          | 304                          |
| HNO <sub>3</sub>   | l     | -173                        | -80                         | 156                          |
| NO <sub>3</sub> <sup>-</sup>                                     | l     | -207                        | -114                        | 146                          |
| Na   | s     | 0                           | 0                           | 51                           |
| Na <sup>+</sup>  | l     | -240                        | -262                        | 60                           |
| Na <sub>2</sub> CO <sub>3</sub>                                  | s     | -1130                       | -1060                       | 136                          |
| Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O              | s     | -4080                       | -3906                       |                              |
| NaHCO <sub>3</sub>   | s     | -948                        | -852                        | 102                          |
| NaF  | s     | -569                        | -541                        | 58                           |
| NaCl   | s     | -411                        | -384                        | 50                           |
| NaNO <sub>2</sub>  | s     | -360                        |                             |                              |
| NaNO <sub>3</sub>  | s     | -425                        | -366                        | 116                          |
| NaOH   | s     | -425                        | -380                        | 60                           |
| Na <sub>2</sub> SO <sub>3</sub>                                  | s     | -1110                       | -1000                       | 146                          |
| Na <sub>2</sub> SO <sub>4</sub>                                  | s     | -1380                       | -1270                       | 149                          |
| Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O              | s     | -4320                       | -3640                       | 592                          |
| Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O | s     | -2600                       |                             |                              |
| O <sub>2</sub>   | g     | 0                           | 0                           | 205                          |
| O <sub>3</sub>   | g     | 142                         | 163                         | 238                          |
| P <sub>4</sub> (white)   | s     | 0                           | 0                           | 44.4                         |
| P(red)   | s     | -18.4                       |                             |                              |
| PCl <sub>3</sub>   | g     | -306                        | -286                        | 312                          |
| PCl <sub>5</sub>   | g     | -398                        | -324                        | 352                          |
| HPO <sub>4</sub> <sup>2-</sup>                                   | l     | -1299                       | -1094                       | -36                          |
| PO <sub>4</sub> <sup>3-</sup>                                    | l     | -1284                       | -1026                       | -218                         |
| Pb <sup>2+</sup>   | l     | 1.6                         | 24.3                        | 21.3                         |
| PbO  | s     | -218                        | -188                        | 69                           |
| PbO <sub>2</sub>   | s     | -277                        | -219                        | 77                           |
| Pb(CH <sub>3</sub> COO) <sub>2</sub>                             | s     | -965                        |                             |                              |

| Substances  | State | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K×mol) |
|---|-------|-----------------------------|-----------------------------|---------------------|
| Pb(CH <sub>3</sub> COO) <sub>2</sub> ·3H <sub>2</sub> O | s     | -1870                       |                             |                     |
| S   | s     | 0                           | 0                           | 32                  |
| SO <sub>2</sub>   | g     | -296                        | -300                        | 249                 |
| SO <sub>3</sub>   | g     | -395                        | -370                        | 256                 |
| H <sub>2</sub> S  | g     | -20                         | -33                         | 206                 |
| H <sub>2</sub> SO <sub>4</sub>                          | l     | -907                        | -742                        | 17                  |
| HSO <sub>4</sub> <sup>-</sup>                           | l     | -886                        | -753                        | 127                 |
| SO <sub>4</sub> <sup>2-</sup>                           | l     | -907                        | -742                        | 17.2                |
| SiO <sub>2</sub>  | s     | -859                        | -805                        | 42                  |
| Zn <sup>2+</sup>  | l     | -152                        | -147                        | 106                 |
| ZnO   | s     | -348                        | -318                        | 44                  |
| ZnCl <sub>2</sub>                                       | s     | -416                        | -369                        | 108                 |
| ZnSO <sub>4</sub>                                       | s     | -979                        | -872                        | 125                 |
| ZnSO <sub>4</sub> ·7H <sub>2</sub> O                    | s     | -3080                       | -2560                       | 386                 |
| <b>Organic compounds</b>                                |       |                             |                             |                     |
| CH <sub>4</sub>   | g     | -75                         | -51                         | 186                 |
| C <sub>2</sub> H <sub>2</sub>                           | g     | 207                         | 209                         | 201                 |
| C <sub>2</sub> H <sub>4</sub>                           | g     | 52                          | 68                          | 219                 |
| C <sub>2</sub> H <sub>6</sub>                           | g     | -85                         | -33                         | 229                 |
| C <sub>6</sub> H <sub>6</sub>                           | s     | 49                          | 173                         | 125                 |
| CH <sub>3</sub> Cl                                      | g     | -82                         | -59                         | 234                 |
| CH <sub>2</sub> Cl <sub>2</sub>                         | g     | -88                         | -59                         | 270                 |
| CHCl <sub>3</sub>                                       | g     | -100                        | -67                         | 296                 |
| CCl <sub>4</sub>  | l     | -107                        | -64                         | 310                 |
| CH <sub>3</sub> Br                                      | g     | -27                         | -26                         | 246                 |
| CH <sub>2</sub> Br <sub>2</sub>                         | g     | -4.2                        | -6                          | 294                 |
| CHBr <sub>3</sub>                                       | g     | 25                          | 16                          | 331                 |
| CBr <sub>4</sub>  | g     | 50                          | 36                          | 358                 |
| CH <sub>3</sub> OH                                      | l     | -239                        | -166                        | 127                 |
| C <sub>2</sub> H <sub>5</sub> OH                        | l     | -277                        | -174                        | 161                 |
| C <sub>3</sub> H <sub>8</sub> O <sub>3</sub> (glycerol) | l     | -671                        | -479                        | 205                 |
| CH <sub>2</sub> O                                       | g     | -116                        | -110                        | 218                 |
| CH <sub>3</sub> CHO                                     | g     | -247                        | -139                        | 264                 |
| CH <sub>3</sub> COCH <sub>3</sub>                       | l     | -247                        | -154                        | 199                 |
| HCOOH   | l     | -409                        | -346                        | 129                 |
| HCOO <sup>-</sup>                                       | l     | -410                        | -335                        | 92                  |
| CH <sub>3</sub> COOH                                    | l     | -484                        | -389                        | 160                 |
| CH <sub>3</sub> COO <sup>-</sup>                        | l     | -485                        | -404                        | 205                 |
| C <sub>3</sub> H <sub>7</sub> COOH                      | l     | -535                        | -376                        | 226                 |
| C <sub>3</sub> H <sub>7</sub> COO <sup>-</sup>          | l     | -536                        | -372                        | 202                 |
| C <sub>15</sub> H <sub>32</sub> COOH                    | s     | -891                        | -315                        | 455                 |
| C <sub>15</sub> H <sub>32</sub> COO <sup>-</sup>        | l     |                             | -259                        |                     |

| Substances                | State | $\Delta H_f^\circ$ (kJ/mol) | $\Delta G_f^\circ$ (kJ/mol) | $S^\circ$ (J/K×mol) |
|---------------------------|-------|-----------------------------|-----------------------------|---------------------|
| glucose                   | s     | -1274                       | -911                        | 212                 |
|                           | l     | -1263                       | -915                        | 264                 |
| glucoso-1-phosphoric acid | l     |                             | -1790                       |                     |
| Glycine                   | s     | -537                        | -378                        | 104                 |
|                           | l     | -523                        | -380                        | 159                 |
| Cystein                   | s     | -533                        | -343                        | 170                 |

**Table 16 - Selected standard enthalpy of combustion for organic substances at 1 atm. and 25°C**

| Substances                        | State    | $\Delta_{\text{com}}H^\circ_{298}$ , kJ/mole | Substances                                    | State | $\Delta_{\text{com}}H^\circ_{298}$ , kJ/mole |
|-----------------------------------|----------|--|---|-------|--|
| CH <sub>4</sub>                   | g        | -882   | C <sub>2</sub> H <sub>4</sub>                 | g     | -1390  |
| CH <sub>3</sub> Br                | g        | -770   | C <sub>2</sub> H <sub>2</sub>                 | g     | -1304  |
| CH <sub>3</sub> Cl                | g        | -686   | C <sub>2</sub> H <sub>5</sub> OH              | s     | -1370  |
| CH <sub>3</sub> I                 | l        | -814   | NH <sub>2</sub> CH <sub>2</sub> COOH          | s     | -981   |
| CH <sub>3</sub> NH <sub>2</sub>   | solution | -1070  | CO(CH <sub>3</sub> ) <sub>2</sub>             | l     | -1780  |
| CH <sub>3</sub> OH                | l        | -715   | C <sub>6</sub> H <sub>6</sub>                 | l     | -3170  |
| CH <sub>2</sub> O                 | g        | -561   | C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> | l     | -3400  |
| HCOOH                             | l        | -262   | C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> | l     | -3080  |
| CO(NH <sub>2</sub> ) <sub>2</sub> | s        | -634   | C <sub>6</sub> H <sub>5</sub> OH              | l     | -3060  |
| CHCl <sub>3</sub>                 | l        | -346   | glucose                                       | s     | -2810  |
| CHI <sub>3</sub>                  | s        | -677   | fructose                                      | s     | -2820  |
| C <sub>2</sub> H <sub>6</sub>     | g        | -1540  | CH <sub>3</sub> COOH                          | l     | -872   |

**Table 17 - Standard reduction potentials for metals**

| Half-Reaction                                 | $\phi^\circ$ , V | Half-Reaction                                 | $\phi^\circ$ , V |
|---|------------------|---|------------------|
| $\text{Li}^+ + e^- \rightarrow \text{Li}$     | -3.045           | $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$ | -0.250           |
| $\text{K}^+ + e^- \rightarrow \text{K}$       | -2.925           | $\text{Mo}^{3+} + 3e^- \rightarrow \text{Mo}$ | -0.200           |
| $\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$ | -2.900           | $\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$ | -0.136           |
| $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$ | -2.870           | $\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$ | -0.126           |
| $\text{Na}^+ + e^- \rightarrow \text{Na}$     | -2.714           | $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$   | 0.000            |
| $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$ | -2.370           | $\text{Bi}^{3+} + 3e^- \rightarrow \text{Bi}$ | +0.215           |
| $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$ | -1.660           | $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ | +0.337           |
| $\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$ | -1.180           | $\text{Ag}^+ + e^- \rightarrow \text{Ag}$     | +0.799           |
| $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$ | -0.762           | $\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$ | +0.854           |
| $\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$ | -0.740           | $\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$ | +0.987           |
| $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$ | -0.440           | $\text{Pt}^{2+} + 2e^- \rightarrow \text{Pt}$ | +1.190           |
| $\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$ | -0.280           | $\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$ | +1.500           |

**Table 18 - Standard reduction potentials at 25°C**

| Half-Reaction  | $\phi^\circ, V$ | Half-Reaction  | $\phi^\circ, V$ |
|--|-----------------|--|-----------------|
| $[\text{Ag}(\text{NH}_3)_2]^+ + e^- \rightarrow \text{Ag} + 2\text{NH}_3$                              | +0.373          | $\text{Cu}^{2+} + \text{Cl}^- + e^- \rightarrow \text{CuCl}$   | +0.54           |
| $\text{AlO}_2^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{Al} + 4\text{OH}^-$                     | -2.35           | $\text{Cu}^{2+} + \text{I}^- + e^- \rightarrow \text{CuI}$   | +0.86           |
| $\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2e^- \rightarrow \text{HAsO}_2 + 2\text{H}_2\text{O}$          | +0.56           | $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$  | +0.77           |
| $[\text{Au}(\text{CN})_2]^- + e^- \rightarrow \text{Au} + 2\text{CN}^-$                                | -0.61           | $[\text{Fe}(\text{CN})_6]^{3-} + e^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$                      | +0.356          |
| $\text{BiO}_3^- + 6\text{H}^+ + 2e^- \rightarrow \text{Bi}^{3+} + 3\text{H}_2\text{O}$                 | +1.80           | $\text{Fe}(\text{OH})_3 + e^- \rightarrow \text{Fe}(\text{OH})_2 + \text{OH}^-$                      | -0.56           |
| $\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$  | +1.065          | $\text{Fe}(\text{OH})_2 + 2e^- \rightarrow \text{Fe} + 2\text{OH}^-$                                 | -0.877          |
| $\text{BrO}^- + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{Br}^- + 2\text{OH}^-$                     | +0.76           | $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$                          | +1.77           |
| $2\text{BrO}_3^- + 6\text{H}_2\text{O} + 10e^- \rightarrow \text{Br}_2 + 12\text{OH}^-$                | +0.50           | $\text{H}_2\text{O}_2 + 2e^- \rightarrow 2\text{OH}^-$   | +0.88           |
| $2\text{BrO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Br}^- + 6\text{OH}^-$                  | +0.61           | $\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2$                                   | +0.68           |
| $\text{BrO}_3^- + 6\text{H}^+ + 6e^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$                    | +1.45           | $\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$                                    | +1.23           |
| $2\text{BrO}_3^- + 12\text{H}^+ + 10e^- \rightarrow \text{Br}_2 + 6\text{H}_2\text{O}$                 | +1.51           | $\text{O}_3 + 2\text{H}^+ + 2e^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$                        | +2.07           |
| $\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$  | +1.359          | $2\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}_2^{2+}$  | +0.92           |
| $\text{ClO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^-$                      | +0.88           | $2\text{HgCl}_2 + 2e^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{Cl}^-$                            | 0.62            |
| $\text{ClO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Cl}^- + 6\text{OH}^-$                   | +0.63           | $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$  | +0.54           |
| $\text{ClO}_3^- + 6\text{H}^+ + 6e^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O}$                    | +1.45           | $\text{IO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{I}^- + 6\text{OH}^-$                   | +0.26           |
| $\text{Co}^{3+} + e^- \rightarrow \text{Co}^{2+}$  | +1.84           | $\text{IO}_3^- + 6\text{H}^+ + 6e^- \rightarrow \text{I}^- + 3\text{H}_2\text{O}$                    | +1.08           |
| $[\text{Co}(\text{NH}_3)_6]^{3+} + e^- \rightarrow [\text{Co}(\text{NH}_3)_6]^{2+}$                    | -0.43           | $2\text{IO}_3^- + 2\text{H}_2\text{O} + 10e^- \rightarrow \text{I}_2 + 12\text{OH}^-$                | +0.21           |
| $\text{CrO}_2^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{Cr} + 4\text{OH}^-$                     | -1.2            | $\text{MnO}_4^- + e^- \rightarrow \text{MnO}_4^{2-}$   | +0.56           |
| $\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e^- \rightarrow \text{Cr}(\text{OH})_3 + 5\text{OH}^-$     | -0.13           | $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$                | +0.60           |
| $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$   | +1.33           | $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$               | +1.51           |
| $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$   | +0.153          | $\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$                 | +1.23           |
| $\text{PbO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$                   | +1.455          | $2\text{NO}_3^- + 12\text{H}^+ + 10e^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$                 | +1.24           |
| $\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$ | +1.68           | $\text{NO}_3^- + 4\text{H}^+ + 3e^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$                     | +0.96           |
| $\text{S} + 2e^- \rightarrow \text{S}^{2-}$  | -0.48           | $\text{NO}_3^- + 3\text{H}^+ + 2e^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O}$                   | +0.94           |
| $\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{SO}_2 + 2\text{H}_2\text{O}$                  | +0.17           | $\text{HNO}_2 + \text{H}^+ + e^- \rightarrow \text{NO} + \text{H}_2\text{O}$                         | +0.99           |
| $\text{SO}_4^{2-} + 10\text{H}^+ + 8e^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$          | +0.311          | $\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$                 | + 0.01          |
| $\text{SO}_4^{2-} + \text{H}_2\text{O} + 2e^- \rightarrow \text{SO}_3^{2-} + 2\text{OH}^-$             | -0.93           | $\text{NO}_3^- + 2\text{H}^+ + e^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$                     | + 0.80          |
| $\text{S}_2\text{O}_8^{2-} + 4e^- \rightarrow 2\text{SO}_4^{2-}$                                       | +2.01           | $\text{SeO}_8^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{SeO}_4^{2-} + \text{H}_2\text{O}$          | +1.15           |
| $\text{S} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{S}$   | +0.171          | $\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+}$   | +0.15           |
| $\text{SO}_4^{2-} + 10\text{H}^+ + 8e^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$          | +0.31           | $\text{C}_6\text{H}_4\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{C}_6\text{H}_4(\text{OH})_2$  | +0.7            |
| $\text{SO}_4^{2-} + 8\text{H}^+ + 6e^- \rightarrow \text{S} + 4\text{H}_2\text{O}$                     | +0.36           | $\text{HCHO} + 2\text{H}^+ + 2e^- \rightarrow \text{CH}_3\text{OH}$                                  | +0.19           |
| $\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$  | +2.77           | $\text{CH}_3\text{CHO} + 2\text{H}^+ + 2e^- \rightarrow \text{C}_2\text{H}_5\text{OH}$               | +0.19           |
| $\text{PO}_4^{3-} + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{HPO}_3^{2-} + 3\text{OH}^-$           | -1.12           | $\text{CH}_3\text{COOH} + 2\text{H}^+ + 2e^- \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$ | -0.12           |
| $\text{TeO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{Te} + 2\text{H}_2\text{O}$                        | +0.53           | $\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH}$  | -0.20           |

\*For all half-reaction is 1M for dissolved species and the pressure is 1 atm for gases.

**Table 19 - Standard reduction potentials for some biological half-reactions at 298k (pH = 7)**

| <i>System</i>                                     | <b>Half-Cell Reactions</b>   | $\phi^\circ, V$ |
|---|--|-----------------|
| O <sub>2</sub> / H <sub>2</sub> O                 | $O_2(q) + 4H^+ + 4e^- \rightarrow 2H_2O$   | +0.816          |
| Cu <sup>2+</sup> / Cu <sup>+</sup><br>hemocyanin  | $Cu^{2+} + e^- \rightarrow Cu^+$   | +0.540          |
| Cyt f <sup>3+</sup> / Cyt f <sup>2+</sup>         | $Fe^{3+} + e^- \rightarrow Fe^{2+}$  | +0.365          |
| Cyt a <sup>3+</sup> / Cyt a <sup>2+</sup>         | $Fe^{3+} + e^- \rightarrow Fe^{2+}$  | +0.29           |
| Cyt c <sup>3+</sup> / Cyt c <sup>2+</sup>         | $Fe^{3+} + e^- \rightarrow Fe^{2+}$  | +0.254          |
| Fe <sup>3+</sup> / Fe <sup>2+</sup><br>hemoglobin | $Fe^{3+} + e^- \rightarrow Fe^{2+}$  | +0.17           |
| Fe <sup>3+</sup> / Fe <sup>2+</sup><br>myoglobin  | $Fe^{3+} + e^- \rightarrow Fe^{2+}$  | +0.046          |
| Fumarate/succinate                                | $^-\text{OOCCH=CHCOO}^- + 2H^+ + 2e^- \rightarrow ^-\text{OOCCH}_2\text{CH}_2\text{COO}^-$ | +0.031          |
| MB / MBH <sub>2</sub> <sup>b</sup>                | $MB + 2H^+ + 2e^- \rightarrow MBH_2^b$   | +0.011          |
| Pyruvate / Lactate                                | $CH_3COCOO^- + 2H^+ + 2e^- \rightarrow CH_3CHOHCOO^-$                                      | -0.185          |
| Acetaldehyde / ethanol                            | $CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_2OH$   | -0.197          |
| FAD / FADH <sub>2</sub>                           | $FAD + 2H^+ + 2e^- \rightarrow FADH_2$   | -0.219          |
| NAD <sup>+</sup> / NADH                           | $NAD^+ + H^+ + 2e^- \rightarrow NADH$  | -0.320          |
| NADP <sup>+</sup> / NADPH                         | $NADP^+ + H^+ + 2e^- \rightarrow NADPH$  | -0.324          |
| CO <sub>2</sub> / Formate                         | $CO_2 + H^+ + 2e^- \rightarrow HCOO^-$   | -0.414          |
| H <sup>+</sup> / H <sub>2</sub>                   | $2H^+ + 2e^- \rightarrow H_2$  | -0.421          |
| Fe <sup>3+</sup> / Fe <sup>2+</sup><br>ferredoxin | $Fe^{3+} + e^- \rightarrow Fe^{2+}$  | -0.432          |
| Acetic acid<br>/ acetaldehyde                     | $CH_3COOH + 2H^+ + 2e^- \rightarrow CH_3CHO + H_2O$  | -0.581          |
| Acetate / pyruvate                                | $CH_3COOH + CO_2 + 2H^+ + 2e^- \rightarrow CH_3COCOOH + H_2O$                              | -0.700          |

**Table 20 - Student's-t number**

| Student's-t Values at Common Confidence Levels |       |       |       |       |
|--|-------|-------|-------|-------|
| Degrees of Freedom                             | 50%   | 90%   | 95%   | 99%   |
| 1  | 1.000 | 6.314 | 12.71 | 63.66 |
| 2  | 0.816 | 2.920 | 4.303 | 9.925 |
| 3  | 0.765 | 2.353 | 3.182 | 5.841 |
| 4  | 0.741 | 2.132 | 2.776 | 4.604 |
| 5  | 0.727 | 2.015 | 2.571 | 4.032 |
| 6  | 0.718 | 1.943 | 2.447 | 3.707 |
| 7  | 0.711 | 1.895 | 2.365 | 3.500 |
| 8  | 0.706 | 1.860 | 2.306 | 3.355 |
| 9  | 0.703 | 1.833 | 2.262 | 3.250 |
| 10   | 0.700 | 1.812 | 2.228 | 3.169 |
| 20   | 0.687 | 1.725 | 2.086 | 2.845 |
| <i>infinite</i>                                | 0.674 | 1.645 | 1.960 | 2.576 |

**Table 21 - The instability constants**

| Complex ion           | $K_{ins}$              | Complex ion           | $K_{ins}$              |
|-----------------------|------------------------|-----------------------|------------------------|
| $[Ag(CN)_2]^-$        | $1.41 \times 10^{-20}$ | $[CdI_4]^{2-}$        | $7.9 \times 10^{-7}$   |
| $[Ag(NH_3)_2]^+$      | $5.75 \times 10^{-8}$  | $[Cd(CN)_4]^{2-}$     | $7.76 \times 10^{-18}$ |
| $[Ag(NO_2)_2]^-$      | $1.48 \times 10^{-3}$  | $[Cu(NH_3)_4]^{2+}$   | $9.33 \times 10^{-13}$ |
| $[Ag(NCS)_2]^-$       | $5.37 \times 10^{-9}$  | $[Cu(NCS)_4]^{2-}$    | $3.02 \times 10^{-7}$  |
| $[Ag(S_2O_3)_2]^{3-}$ | $3.47 \times 10^{-14}$ | $[Co(NH_3)_4]^{2+}$   | $4.07 \times 10^{-5}$  |
| $[Au(CN)_2]^-$        | $5.0 \times 10^{-39}$  | $[Co(NH_3)_6]^{2+}$   | $8.51 \times 10^{-6}$  |
| $[Bi(NCS)_6]^{3-}$    | $5.89 \times 10^{-5}$  | $[Co(CN)_6]^{4-}$     | $8.13 \times 10^{-20}$ |
| $[Cd(NH_3)_4]^{2+}$   | $2.88 \times 10^{-7}$  | $[Co(NCS)_4]^{2-}$    | $6.31 \times 10^{-3}$  |
| $[CdBr_4]^{2-}$       | $1.17 \times 10^{-3}$  | $[Co(NH_3)_6]^{3+}$   | $6.17 \times 10^{-36}$ |
| $[Co(CN)_6]^{3-}$     | $1.0 \times 10^{-64}$  | $[PbBr_4]^{2-}$       | $1.0 \times 10^{-3}$   |
| $[Cr(NCS)_6]^{3-}$    | $1.58 \times 10^{-4}$  | $[PbI_4]^{2-}$        | $6.0 \times 10^{-7}$   |
| $[Fe(CN)_6]^{4-}$     | $1.0 \times 10^{-24}$  | $[Pb(NCS)_4]^{2-}$    | 0.14                   |
| $[Fe(CN)_6]^{3-}$     | $1.0 \times 10^{-31}$  | $[Pb(S_2O_3)_4]^{6-}$ | $6.31 \times 10^{-8}$  |
| $[Fe(NCS)_6]^{3-}$    | $5.89 \times 10^{-4}$  | $[PbCl_4]^{2-}$       | 0.1                    |
| $[HgBr_4]^{2-}$       | $1.0 \times 10^{-21}$  | $[PbBr_4]^{2-}$       | $7.9 \times 10^{-14}$  |
| $[Hg(CN)_4]^{2-}$     | $3.1 \times 10^{-42}$  | $[PtCl_4]^{2-}$       | $1.0 \times 10^{-16}$  |
| $[HgCl_4]^{2-}$       | $8.5 \times 10^{-16}$  | $[PtBr_4]^{2-}$       | $3.0 \times 10^{-21}$  |
| $[Hg(NH_3)_4]^{2+}$   | $5.0 \times 10^{-20}$  | $[Zn(NH_3)_4]^{2+}$   | $2.0 \times 10^{-9}$   |
| $[HgI_4]^{2-}$        | $0.5 \times 10^{-30}$  | $[ZnCl_4]^{2-}$       | 10                     |
| $[Hg(NCS)_4]^{2-}$    | $1.7 \times 10^{-20}$  | $[ZnBr_4]^{2-}$       | 316.2                  |
| $[Mn(C_2O_4)_3]^{3-}$ | $3.8 \times 10^{-20}$  | $[Zn(CN)_4]^{2-}$     | $1.0 \times 10^{-19}$  |
| $[Ni(NH_3)_4]^{2+}$   | $3.4 \times 10^{-8}$   | $[Zn(NCS)_4]^{2-}$    | $2.0 \times 10^{-4}$   |

## LITERATURE

1. Ковальчукова О.В., Насрин Намичемази, Русул Алабада. Химия. Конспект лекций для студентов I курса медицинского факультета специальности «Стоматология» (на английском языке). М.: Изд-во РУДН, 2015. – 164 с.
2. Латушко Т.В., Ткачѐв С.В., Барковский Е.В., Казюлевич С.Р. Руководство к практическим занятиям по общей химии = General Chemistry : Practice : практикум / Т. В. Латушко [и др.]; пер. с рус. яз. С. Ч. Папук, С. В. Ткачѐв. – 2-е изд. – Минск : БГМУ, 2012. – 115 с.
3. Общая химия. Базовый уровень = General chemistry. Basic level : учеб. пособие / Г. В. Соловьѐва, О. А. Неволина, Т. С. Берсенѐва, И. А. Мустаева ; англ. перевод Т. С. Берсенѐвой. – Екатеринбург : Изд-во Урал. ун-та, 2017. – 182, [2] с.
4. Основы химии для иностранных студентов = Essential chemistry for foreign students : учеб.-метод. пособие / С. В. Ткачѐв [и др.] ; 3-е изд. – Минск : БГМУ, 2015. – 168 с.
5. Svistunov A., Fetisova A., Litvinova T. Fundamentals of terminology, reading, interpreting and solving problems in chemistry in English. General Chemistry. Advanced Level. Textbook.-М: I.M. Sechenov First MSMU, 2016.
6. Филиппова В.А. Общая химия: учеб.-метод. пособие для студентов 1 курса факультета по подготовке специалистов для зарубежных стран медицинских вузов, обучающихся на русском языке / В. А. Филиппова, А. В. Лысенкова. - Гомель: ГомГМУ, 2016. — 276 с.
7. Филиппова, В. А. Общая химия: учеб. пособие для студентов лечебного факультета, обучающихся на английском языке. = General Chemistry: Educational guidance for students medical department in English medium.— В. А. Филиппова, А. В. Лысенкова, Л. В. Чернышева. — Гомель: УО «Гомельский государственный медицинский университет», 2009. — 192 с.

8. Филиппова В.А., Лысенкова А.В., Чернышева Л.В. Reference book. General chemistry Справочник основных физико-химических величин и постоянных для лабораторно-практических занятий к курсу по общей химии для студентов лечебного факультета, обучающихся на английском языке – Гомель: УО «Гомельский государственный медицинский университет», 2010. – С.25.
9. Хрусталёв, В. В. Введение в общую химию = Introduction to the General Chemistry : учеб.-метод. пособие / В. В. Хрусталёв, Е. В. Барковский, Т. А. Хрусталёва. – Минск : БГМУ, 2014. – 64 с.
10. Хрусталёв, В.В. Введение в общую химию = Introduction to the general chemistry : практикум / В. В. Хрусталёв, Т. В. Латушко, Т. А. Хрусталёва. – Минск : БГМУ, 2017. – 144 с.

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