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«ГОМЕЛЬСКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ»

КАФЕДРА ОБЩЕЙ И БИООРГАНИЧЕСКОЙ ХИМИИ

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ОБЩАЯ ХИМИЯ

В двух частях

Часть 1

GENERAL CHEMISTRY

In two parts

Part 1

Допущено Министерством образования Республики Беларусь
в качестве учебного пособия для студентов лечебного факультета,
обучающихся на английском языке

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В учебном пособии изложены теоретические вопросы и приведены методики выполнения лабораторных работ. Для организации самостоятельной работы студентов представлены задачи и тестовые задания. В конце учебного пособия даны необходимые справочные материалы и словарь важнейших физико-химических терминов.

Учебное пособие предназначено для студентов лечебного факультета медицинского вуза, обучающихся на английском языке.

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To our Indian students who inspired us to write this book

PREFACE FOR THE STUDENT

Welcome to your study of general chemistry, the subject that underlies all chemistry and increasingly biological chemistry, biology, pharmacology and medicine. A textbook will present general chemistry so that that whatever your discipline, you can appreciate the elegance of chemistry and master its fundamental concepts. Regardless of where your interests lie, however, the important chemical properties remain the same. These chemical properties and principles are the core of our presentation.

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 chapters 5–7 take up the introduction into volumetric analysis, including acid-base, permanganatometric and iodometric titration. As a group, chapters 8–11 deal with physical properties of solutions, emphasizing acid-base and electrochemical equilibria in aqueous solutions.

At the end of each chapter, we provide material designed to engage you in active learning. The end-of-chapter exercises consist of about 100 review questions and problems. They are intended to consolidate the understanding of the material. Most chapters contain laboratory manuals that ought to help you to develop practical skills of working in chemical labs. These manuals contain over 20 chemistry experiments. In Appendix I you will find over 100 test questions with multiple choices for the self-control. Appendix II 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.

Our aim has been to write a textbook which presents the chemistry in an understandable, learnable, interesting and appealing way. We expect that knowledge in general chemistry will be useful in your later career, and want to give you a friendly advice: **Be an active learner.** Ask questions, seek help from many sources, work extra problems, and prepare chapter outlines.

We wish you well with your studies, and hope that you find this textbook rewarding.

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> Bear in mind that the wonderful things you learn
> In your schools is the work of many generations,
> produced by enthusiastic effort and infinite labor in every
> country of the world. All this is put into your hands as your
> inheritance in order that you may receive it, honor it,
> add to it, and one day faithfully hand it on to your
> children. Thus do we mortals achieve immortality in the
> permanent thongs which we create in common.
>
> Albert Einstein

CHAPTER 1
CHEMICAL THERMODYNAMICS

> *The energy of the universe is constant,*
> *the entropy increases toward a maximum*
> *Clausius*

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, thermophisiology 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:

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

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)

Table 1.1 — Different Types of Work

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

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

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:

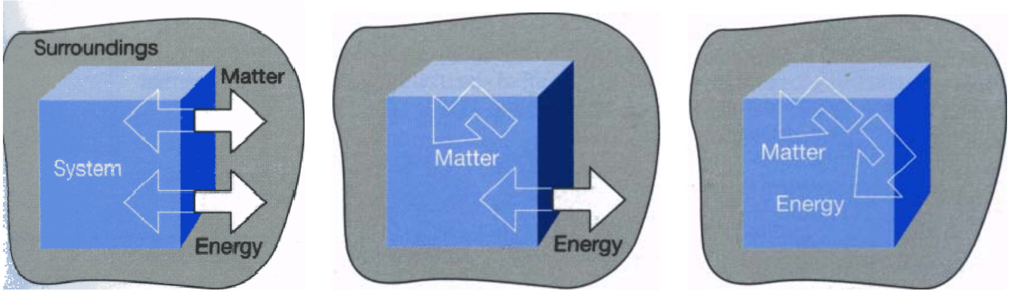
- mechanical work of muscles;
- osmotic work of kidneys;
- electrical work of nerve tissue.

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. 1.2 a);
- **closed systems** can exchange energy with the surroundings, but they cannot exchange matter, e.g. ampoule with a drug (figure 1.1, 1.2 b).

Figure 1.1 — Ampoule with a drug

- **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 (figure 1.2 (c)).



a) Isolated (b) Closed (c) Open

Figure 1.2 — Thermodynamic systems

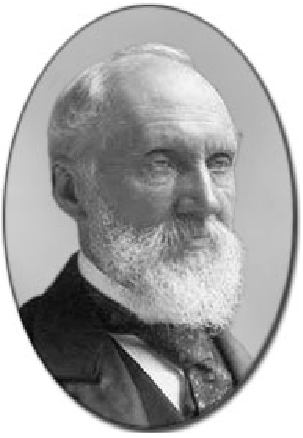
The descriptions of a system include:

- 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.



William Thompson, Lord Kelvin (1824-1907)

Scottish physicist William Thomson, better known as Lord Kelvin, was one of the most eminent scientists of the 19th century and is best known today for inventing the international system of absolute temperature that bears his name. He made contributions to electricity, magnetism, thermodynamics, hydrodynamics, geophysics and telegraphy and other fields, having published more than 650 papers during his lifetime. Thomson was also an extremely skilled engineer who patented some 70 inventions and was involved heavily in the laying of the first transatlantic telegraph cable. For that successful effort he was knighted by Queen Victoria in 1866. The Baron was raised to peerage in the 1890s, and became known as Lord Kelvin of Largs.

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 constant».**

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:

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

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

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

or

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

where Q — is the heat absorbed by a system, kJ;

A′ — is a useful work produced in a system, kJ;

pΔV — the work of gas expansion, kJ.

When a process is isobaric (p = const) and useful work is not produced (a'=0) the equation (1) may be rearranged as follows:

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

where $$\Delta H = \Delta U + P\Delta V \qquad 1.6$$

Hence Q = ΔH, thus change in the enthalpy (**ΔH) 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:

$$\mathbf{\Delta U = Q \pm \mu\Delta\nu - A,} \qquad 1.7$$

where μ — proportionality coefficient named chemical potential;

Δν — 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.**

Germain Henri Hess (1802-1850)

G. H. Hess is known primarily for his thermochemical studies, which began in 1839; his other work was of less importance. The key paper was published in 1840. The contributions of Hess to heat can be summed up in what is called the law of Hess, which is an empirical law.

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 298 K 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:

$$\mathbf{\Delta_r H = \sum \nu \Delta_f H\ (products) - \sum \nu \Delta_f H\ (reactants)}$$

where ν — is a stoichiometric coefficient.

For a hypothetical chemical reaction:

$$\mathbf{aA + bB \rightarrow cC + dD}$$

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

$$\mathbf{\Delta_r H = c \times \Delta_f H\ (C) + d \times \Delta_f H\ (D) - a \times \Delta_f H\ (A) - b \times \Delta_f H\ (B)} \qquad 1.8$$

EXAMPLE 1.1 Calculate the standard enthalpy for the following reaction, using standard enthalpy of formation:

$$\mathbf{Al_2O_3\ (s) + 3\ SO_3\ (g) \rightarrow Al_2\ (SO_4)_3\ (s)}$$

Substance	**State**	**$\Delta_f H°_{298}$, kJ/mole**
Al_2O_3	s	- 1,675.1
SO_3	g	-395.2
$Al_2(SO_4)_3$	s	-3,434

Answer:

$\mathbf{\Delta_r H = \Delta_f H^o_{298}}$ $(Al_2\ (SO_4)_3)$ – $\mathbf{\Delta_f H^o_{298}}$ (Al_2O_3) **– 3** × $\mathbf{\Delta_f H^o_{298}}$ (SO_3) **=**
= - 3,434 – (-1,675.1) – 3 × (- 395.2) = - 753.3 kJ.

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

The standard molar enthalpy of combustion of a substance ($\Delta_{com} H^0_{298}$) 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:

$$\mathbf{\Delta_r H = \sum \nu \Delta_{com} H\ (reactants) - \sum \nu \Delta_{com} H\ (products)}$$

where ν — is a stoichiometric coefficient.

For a hypothetical chemical reaction:

$$\mathbf{aA + bB \rightarrow cC + dD}$$

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

$$\mathbf{\Delta_r H^0_{298} = a \times \Delta_{com} H\ (A) + b \times \Delta_{com} H\ (B) - c \times \Delta_{com} H\ (C) - d \times \Delta_{com} H\ (D)} \qquad 1.9$$

EXAMPLE 1.2 Calculate the standard enthalpy for the following reaction using standard enthalpy of combustion:

$$\mathbf{C_6H_{12}O_6\ (s) \rightarrow 2\ C_2H_5OH\ (\ell) + 2\ CO_2 (g)}$$

Substance	**State**	**$\Delta_{com} H°_{298}$, kJ/mole**
$C_6H_{12}O_6$	s	- 2,810
C_2H_5OH	ℓ	- 1,370
CO_2	g	0

Answer:

$\Delta_r H = \Delta_{com} H^o_{298}(C_6H_{12}O_6) - 2 \times \Delta_{com} H^o_{298}(C_2H_5OH) =$

$= (-2{,}810) - 2 \times (-1{,}370) = -70$ kJ.

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) (figure 1.3)

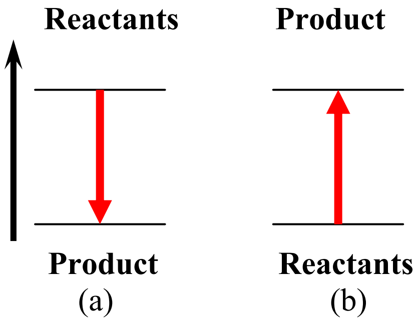


Figure 1.3 — Enthalpy changes for (a) an exothermic reaction, (b) an endothermic reaction

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.

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 1.2). 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.

Table 1.2 — Fuel values of food products

Food Product	**Content, %**				**Heat Content kJ/kg**
	proteins	**lipids**	**Carbo-hydrates**	**H_2O**	
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**

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.

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:

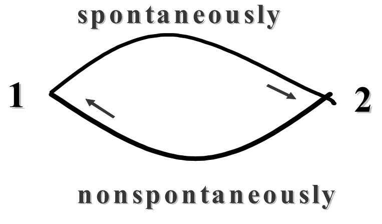
- *spontaneous processes* proceed without absorbing energy from the surroundings; they run up to the equilibrium state. They are dissolving, diffusion, osmosis, all types of explosion and many other reactions and processes.
- *nonspontaneous processes* proceed by absorbing energy from the surroundings.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

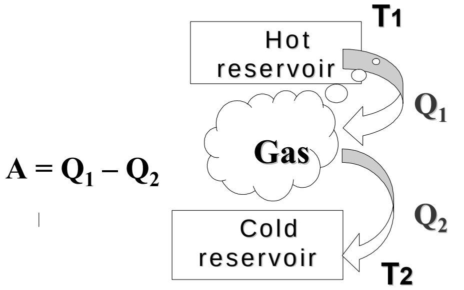


Figure 1.4 — A scheme of an ideal heat engine

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:

$$\text{Efficiency} = \frac{A}{Q_h} \le \frac{T_1 - T_2}{T_1} \qquad 1.10$$

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:

$$S = Q/T \quad 1.11$$

Rudolf Clausius (1822–1888)

Rudolf Julius Emanuel Clausius was a German physicist and mathematician and is considered one of the central founders of the science of thermodynamics. His most important paper, on the mechanical theory of heat, published in 1850, first stated the basic ideas of the second law of thermodynamics. In 1865 he introduced the concept of entropy.

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:

$$\Delta S \geq Q/T \quad 1.12$$

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 (figure 1.5).

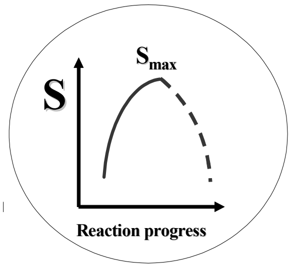


Figure 1.5 — Change in Entropy in isolated systems

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 (figure 1.6).

Figure 1.6 — (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.

Ludwig Boltzmann (1844-1906)

Ludwig eduard boltzmann was an austrian physicist famous for his profound contributions to the fields of statistical mechanics and statistical thermodynamics

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:

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

where k — the Boltzmann's coefficient ($k = 1.38 \times 10^{-23}$ 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 (figure 1.7). 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».

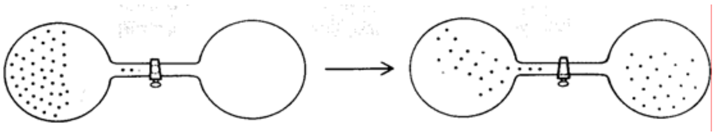


Figure 1.7 — Spontaneous processes

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 ($\Delta_r S$, J/K) may be calculated on the base of the Hess law, using *the standard molar entropy* of reactants and products (S, J /moL × K). For a hypothetical chemical reaction:

$$\mathbf{aA + bB \rightarrow cC + dD}$$

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

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

EXAMPLE 1.3 Calculate the standard entropy change for the following chemical reaction using: standard entropy values of reactants and products:

$$\mathbf{CaCO_3 (s) \rightarrow CaO (s) + CO_2(g)}$$

Substance	**State**	**$S°_{298}$, J/mole×K**
$CaCO_3$	s	92.9
CaO	s	39.8
CO_2	g	213.6

Answer:

$$\Delta_r S = S^o_{298}(CaO) + S^o_{298}(CO_2) - \Delta_{com}H^o_{298}(CaCO_3) =$$

$$= 39.8 + 213.6 - 92.9 = 160.5 \text{ J/K}.$$

Thus, when one mole of **$CaCO_3$** decomposes to form 1 mole of CaO and 1 mole of gaseous CO_2, there is an increase in entropy equal to 160.5 J/K.

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 → min); (b) a tendency for particles to separate, which increases entropy (S → 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):

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

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

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

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

$$\mathbf{\Delta H - T\Delta S = \Delta G} \qquad 1.16$$

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 ΔG 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 (figure 1.8).

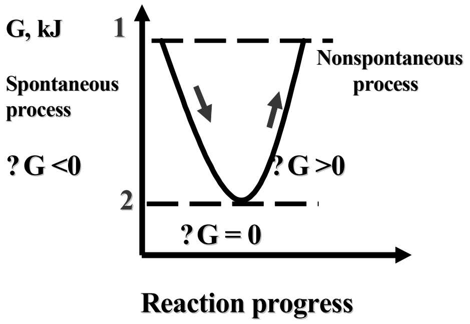


Figure 1.8 — Energy profile of spontaneous and nonspontaneous processes

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 ΔG of a Reaction

ΔH	**Δ*S***	**ΔG**
+	+	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 ΔG, 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 (Δ_rG) on the base of the Hess law, using the standard molar free energy of formation (Δ_fG, kJ/moL).

For a hypothetical chemical reaction:

$$\mathbf{aA + bB \rightarrow cC + dD}$$

the change in free energy (Δ_rG) can be calculated in the following way:

$$\Delta_rG = c \times \Delta_fG(C) + d \times \Delta_fG(D) - a \times \Delta_fG(A) - b \times \Delta_fG(B) \qquad 1.17$$

EXAMPLE 1.4 Calculate Δ_rG for a biochemical reaction under standard conditions: $\mathbf{C_6H_{12}O_6\ (aq) \rightarrow 2\ C_2H_5OH\ (\ell) + 2\ CO_2\ (g)}$

Substance	**State**	**$\Delta_fG°_{298}$, kJ/mole**
$C_6H_{12}O_6$	aq	- 917
C_2H_5OH	ℓ	- 175
CO_2	g	- 394

Answer:

$\Delta_rG = 2 \times \Delta_fG^o_{298}(C_2H_5OH) + 2 \times \Delta_fG^o_{298}(CO_2) - \Delta_fG^o_{298}(C_6H_{12}O_6) =$
$= 2 \times (-175) + 2 \times (-394) - (-917) = -221$ kJ.

This reaction runs spontaneously under standard conditions.

2. Calculating free energy change of chemical reactions (Δ_rG) on the base of the equation 1.16.

EXAMPLE 1.5 Calculate Δ_rG of a biochemical reaction under standard condition: $\mathbf{C_6H_{12}O_6\ (aq) + 6\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O\ (\ell)}$

Substance	**State**	**$\Delta_fH°_{298}$, kJ/mole**	**$S°_{298}$ J/mole×K**
$C_6H_{12}O_6$	aq	- 1,263	264
O_2	g	0	205
CO_2	g	- 394	214
H_2O	ℓ	- 286	70

Answer:

(a) $\Delta_r H = 6 \times \Delta_f H^o_{298}(CO_2) + 6 \times \Delta_f H^o_{298}(H_2O) - \Delta_f H^o_{298}(C_6H_{12}O_6) =$
$= 6 \times (-394) + 6 \times (-286) - (-1{,}263) = -2{,}817$ kJ.

(b) $\Delta_r S = 6 \times S^o_{298}(CO_2) + 6 \times S^o_{298}(H_2O) - S^o_{298}(C_6H_{12}O_6) - 6 \times S^\circ_{298}(O_2) =$
$= 6 \times 214 + 6 \times 70 - 264 - 6 \times 205 = 210$ J/K or 0.210 kJ/K.

(c) $T \times \Delta_r S = 298 \times 0.210 = 62.58$ kJ.

(d) $\Delta_r G = \Delta_r H - T \times \Delta_r S = (-2{,}817) - 62.58 = -2{,}879$ **kJ.**

This reaction runs spontaneously under standard conditions.

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:

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

where [A] и [B] — molarity of reactants, [C] и [D] – molarity of products, mol/L.

- for reactions running in gaseous phases:

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

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

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

$$\Delta_r G = \nu \times R \times T \times \ln \frac{[A]ph2}{[A]ph1} \qquad 1.20$$

where [A] *ph*2 and [A] *ph*1 are molarity of a substance in different phases.

$$[A]\,ph2 > [A]\,ph1$$

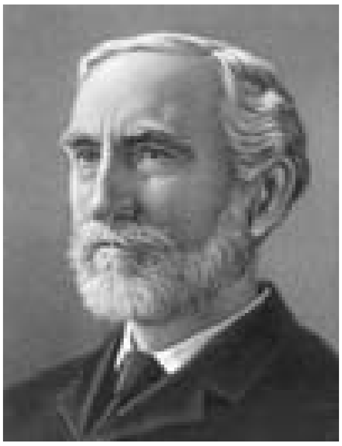
Calculating free energy change is essential for biosystems since makes it possible to understand deeply the sense of biochemical reactions. For example equation (1.20) can be applied to calculate osmotic work produced by kidneys.

EXAMPLE 1.6 Calculate osmotic work produced when kidneys excrete 0.158 moles of Cl^- in 1 L of urea at 37°C. Take into consideration that molarity of chloride ions in plasma is 0.104 mol/ℓ and in urea - 0.158 mol/L.

Answer:

$A_{osm} = -\Delta G = \nu \times R \times T \times \ln 0.158/0.104 = 0.158 \times 8.31 \times 310 \ln 1.519 = 170.2$ J

Osmotic work of kidneys is 170.2 J



J. W. Gibbs
(1839-1903)

Josiah Willard Gibbs was the American physical chemist who introduced free energy into chemical thermodynamics. A professor of mathematical physics at Yale University from 1871 until his death in 1903, Gibbs was the first to show how the laws of thermodynamics can be applied to chemical processes. Because Gibbs published his works in a not very well-known American journal at a time when most scientific work was being done in Europe, his outstanding contributions to chemical thermodynamics were not recognized until 13 years after they were first published. In the 1890s, however, his 400 pages of elegant mathematical development of this subject were translated into French and German, and European scientists quickly recognized the greatness of his work. To commemorate Gibbs, free energy is symbolized G and is sometimes called Gibbs free energy

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) $\Delta rG < 0$
- endergonic (nonspontaneous) $\Delta rG > 0$

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:

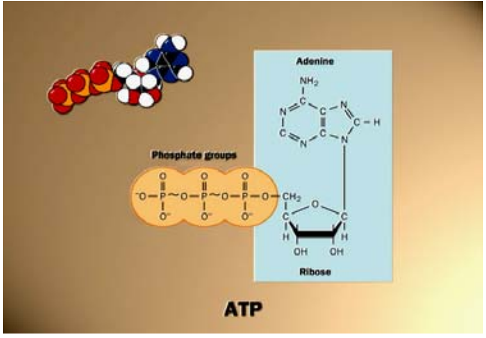
$$\mathbf{A + B \rightarrow C + D, \qquad \Delta G_1 << 0}$$
$$\mathbf{L + M \rightarrow P + Q, \qquad \Delta G_2 > 0}$$
$$\mathbf{\Delta G_{overall} = \Delta G_1 + \Delta G_2 < 0}$$

Carbohydrates and lipids metabolism involves highly spontaneous oxidation reactions:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O, \qquad \Delta G = -\ 2870\ kJ$$

$$C_{15}H_{31}COOH + 23\ O_2 \rightarrow 16\ CO_2 + 16\ H_2O, \quad \Delta G = -\ 9790\ kJ$$

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 important of these energy transport molecules 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:

$$ADP + H_3PO_4 \rightarrow ATP + H_2O,\ \Delta G = +\ 30.6\ kJ$$

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 CO_2 and water:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O,\ \ \Delta G = -\ 2870\ kJ$$

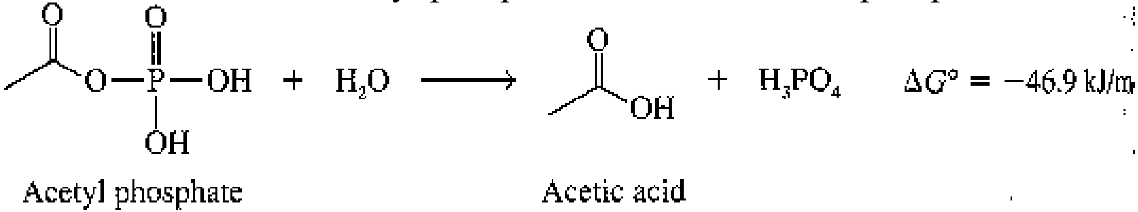
$$\underline{36\ (ADP + H_3PO_4) \rightarrow 36\ (ATP + H_2O),\ \ \Delta G = +1100\ kJ}$$

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

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.

EXAMPLE 1.7 One of the biochemical reactions that produce ATP involves the conversion of acetyl phosphate to acetic acid and phosphoric acid:



Write the overall balanced equation, and show that the coupled reaction is spontaneous.

Answer:

A coupled process links a spontaneous reaction with a nonspontaneous one. In this case the energy released in the acetyl phosphate reaction provides the energy needed to drive the conversion of ADP to ATP.

Combining the two reactions gives the overall balanced equation:

$$CH_3CO_2PO_3H_2 + H_2O \rightarrow CH_3COOH + H_3PO_4$$

$$\underline{ADP + H_3PO_4 \rightarrow ATP + H_2O\qquad\qquad}$$

$$CH_3CO_2PO_3H_2 + ADP \rightarrow CH_3COOH + ATP$$

The net energy change for the coupled process is the sum of the Δ_rG values for the individual reactions:

$$\Delta_rG = \Delta_fG^\circ_{\text{acetyl phosphate}} + \Delta_fG^\circ_{\text{ATP}} = -46.9\ \text{kJ} + 30.6\ \text{kJ} = -16.3\ \text{kJ}$$

The negative value of Δ_rG shows that the free energy released in the reaction is more than enough to drive the conversion of ADP to ATP.

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) $\Delta_rG > 0$ for any spontaneous process.

(d) $\Delta_rG = \Delta_rH + T \times \Delta_rS$.

5. A certain reaction is known to have Δ_rG 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:

(a) $N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$

(b) $2\ Mg(s) + O_2\ (g) \rightarrow 2\ MgO\ (s)$

(c) $2\ H_2O_2\ (\ell) \rightarrow 2\ H_2O\ (\ell) + O_2\ (g)$

(d) $H_2\ (g) + CO_2\ (g) \rightarrow H_2O\ (g) + CO\ (g)$

NUMERICAL EXERCISES

1. Calculate the standard enthalpy change for the following reactions:

(a) $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (\ell)$

(b) $C\ (s) + 2\ H_2\ (g) \rightarrow CH_4\ (g)$

(c) $C_2H_5OH\ (\ell) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O\ (\ell)$

(d) $Fe_2O_3\ (s) + 2\ Al\ (s) \rightarrow A1_2O_3\ (s) + 2\ Fe\ (s)$

2. Calculate the standard entropy change for the following reactions:

(a) $N_2(g) + 3H_2(g) \rightarrow 2\ NH_3(g)$

(b) $3\ O_2(g) \rightarrow 2\ O_3(g)$

(c) $PbO_2(s) + 2\ Ni(s) \rightarrow Pb(s) + 2\ NiO(s)$

(d) $C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(\ell)$

3.From the following data

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$ $\Delta_r\mathbf{H} = -393.5$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ $\Delta_r\mathbf{H} = -285.8$ kJ

$2C_2H_2(g) + 5\ O_2(g) \rightarrow 4CO_2(g) + 2H_2O(\ell)$ $\Delta_r\mathbf{H} = -2598.8$ kJ

Calculate the standard enthalpy change for the reaction:

$2\ C(\text{graphite}) + 3H_2(g) \rightarrow C_2H_2(g)$.

ANSWER: +226.6 kJ/mol

4. From the following enthalpies of combustion,

$CH_3OH(\ell) + 3/2\ O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$ $\Delta_r\mathbf{H} = -726.4$ kJ

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$ $\Delta_r\mathbf{H} = -393.5$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ $\Delta_r\mathbf{H} = -285.8$ kJ

Calculate the enthalpy of formation of methanol (CH_3OH) from its elements:

$C(\text{graphite}) + 2\ H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow CH_3OH(\ell)$

ANSWER: -238.7 kJ/mol

5. Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$ $\Delta_r\mathbf{H} = -393.5$ kJ

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta_r\mathbf{H} = -296.1$ kJ

$CS_2(\ell) + 3\ O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$ $\Delta_r\mathbf{H} = -1072$ kJ

ANSWER: +86 kJ/mol

6. Calculate $\Delta_r\mathbf{H}$, $\Delta_r\mathbf{S}$, and $\Delta_r\mathbf{G}$ for the production of NH_4NO_3 from ammonia and oxygen (t = 25°C), using the following reaction:

$$2\ NH_3(g) + 2\ O_2(g) \rightarrow NH_4NO_3(s) + H_2O(\ell).$$

(This reaction is not feasible industrially because NH_3 combustion cannot be controlled to give NH_4NO_3 product.)

ANSWER: -559 kJ; - 573 J×K^{-1}; - 388.5 kJ

7. Calculate $\Delta_r\mathbf{H}$, $\Delta_r\mathbf{S}$, and $\Delta_r\mathbf{G}$ for the production of N_2 from N_2O_4 and N_2H_4 (t = 25°C) according to the reaction:

$$N_2O_4(\ell) + 2\ N_2H_4(\ell) \rightarrow 3\ N_2(g) + 4\ H_2O(\ell).$$

ANSWER: -1254.4 kJ; + 322.7 J×K^{-1}; - 1350.6 kJ

8. Nitrogen-fixing bacteria help N_2 to interact with H_2O to produce NH_3 and O_2 using ATP as their energy source. Approximately 24 molecules at ATP are consumed per molecule of N_2 fixed. What percentage of the free energy derived from ATP is stored in NH_3?

ANSWER: **90.27%**

9. The hydrolysis of ATP to ADP has Δ_rH = -21.0 kJ/mol, where as $\Delta_rG°$ = -30.6 kJ/mol at 298 K. Calculate Δ_rS for this reaction. What happens to the spontaneity of this reaction as the temperature is increased to 37°C?

ANSWER: 32.2 J/mol×K

10. In running a mile, the average person consumes about 500 kJ of energy.

(a) How many moles of ATP does this represent?

(b) Assuming 38% conversion efficiency, how many grams of glucose must be «burned»?

ANSWER: 16.34 moles, 215 g

11. The standard enthalpy of combustion of solid phenol (C_6H_5OH) is — 3054 kJ/mol at 298 K and its standard molar entropy is 144.0 J/mol×K. Calculate the standard Gibbs energy of formation of phenol at 298 K.

ANSWER: - 211 kJ /mol

12. The standard enthalpy of combustion of solid urea $CO(NH_2)_2$ is — 632 kJ/mol at 298 K and its standard molar entropy is 104.6 J/mol×K. Calculate the standard Gibbs energy of formation of urea at 298 K.

ANSWER: - 365.2 kJ/mol

13. How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The standard entropy of reaction is + 182.4 J/mol×K.

ANSWER: 2865 kJ

14. At 298 K the standard enthalpy of combustion of sucrose is -5797 kJ/mol and the standard Gibbs energy of the reaction is -6333 kJ/mol. Estimate the additional (non-expansion) work that may be obtained by raising the temperature to blood temperature, 37°C.

ANSWER: 21.6 kJ

15. Certain bacteria in the soil obtain the necessary energy for growth by oxidizing nitrite to nitrate:

$$2\ NO_2^-(aq) + O_2\ (g) \rightarrow 2\ NO_3^-(aq)$$

The standard Gibbs energies of formation of NO_2^- to NO_3^- are -34.6 kJ/mol and -110.5 kJ/mol, respectively, calculate the amount of Gibbs energy released when 1 mole of NO_2^- is oxidized to 1 mole of NO_3^-.

ANSWER: -75.9 kJ/mol

CHAPTER 2
THE RATES OF CHEMICAL REACTIONS

> *The rate of chemical reactions*
> *is a very complicated subject.*
> *This statement is to be interpreted*
> *as a challenge to enthusiastic*
> *and vigorous chemists;*
> *it is not to be interpreted*
> *as a sad sigh of defeat.*
> *Harold S. Johnston*

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.

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 preceding in a uniform medium) is defined as the change in the concentration of reactants or products per unit time:

$$\text{Rate } (\vartheta) = \pm\frac{[A]-[A]_0}{\tau}, \qquad 2.1$$

where τ — 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 $2\ NO_2 \rightarrow 2\ NO + O_2$

the rate (ϑ) of NO_2 consumption is equal to $\vartheta = -\frac{[NO_2]-[NO_2]_0}{\tau}$

The rate of O_2 production can be calculated as $\vartheta = \frac{[O_2]-[O_2]_0}{\tau}$

In general, for the chemical reaction

$$\mathbf{aA + bB \rightarrow cC + dD}$$

the rate is given by

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

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

For *heterogeneous reactions* (reactions proceeding in non uniform 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:

$$\text{Rate } (\vartheta) = \pm\frac{\upsilon(A) - \upsilon_0(A)}{\tau \times S}, \qquad 2.3$$

where τ — time, s., min., hours

$\upsilon_0(A)$ — initial amount of a substance, mol.

$\upsilon(A)$ — final amount of a substance, mol.

S — an interface sufuse, m^2.

EXAMPLE 2.1 Write the rates for the following reactions in terms of the disappearance of reactants and appearance of products:

$3\ O_2 \rightarrow 2\ O_3$

Answer:

$$\text{Rate } (\vartheta) = -\frac{1}{3}\frac{d[O_2]}{d\tau} = \frac{1}{2}\frac{d[O_3]}{d\tau}$$

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

$$N_2O_4 \rightarrow 2\ NO,$$

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

$$H_2 + I_2 \rightarrow 2\ HI$$

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

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

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 230^0C and 300°C: $\mathbf{H_2(g) + Br_2(g) \rightarrow 2HBr(g)}$

We assume the following mechanism for a process:

1) Chain initiation (unimolecular step)

$Br\mathbf{:}\,Br \rightarrow 2Br^{\bullet}$

2) Chain propagation (involves two bimolecular steps):

(a) $Br^{\bullet} + H_2 \rightarrow HBr + H^{\bullet}$

(b) $H^{\bullet} + Br_2 \rightarrow HBr + Br^{\bullet}$

3) Chain termination (involves three bimolecular steps):

(a) $2Br^{\bullet} \rightarrow Br_2$

(b) $2H^{\bullet} \rightarrow H_2$

(c) $H^{\bullet} + Br^{\bullet} \rightarrow HBr$

Radical reactions proceed in vivo under the affect of different free radicals $OH^{\bullet}$, $HOO^{\bullet}$, $ROO^{\bullet}$, $O_2^{\bullet}$ 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 (figure 2.1).

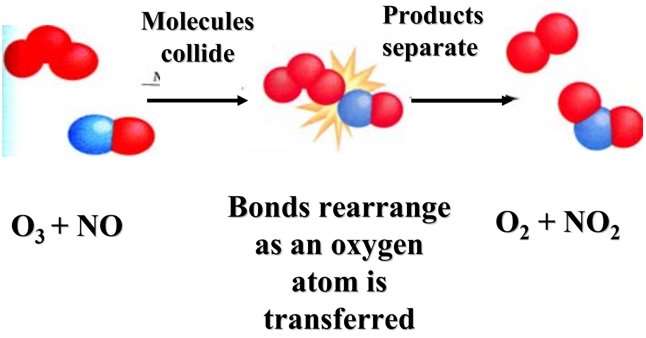


Figure 2.1 — The reaction between ozone and NO is believed to occur by a mechanism that consists of the single bimolecular step shown here in a molecular view

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

$$aA + bB \rightarrow \text{Products}$$

the rate can be expressed as

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

This equation, known as the *rate law,* tells us that the rate of a reaction is not constant; its value at any time (τ) 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

$$A \rightarrow \text{product}$$

is given by

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

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

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

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

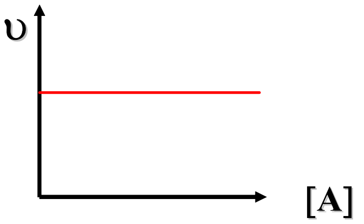


Figure 2.2 — Zero-order reaction

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:

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

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

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

A measure of considerable practical importance in kinetic studies is the *half-life* ($\tau_{½}$) 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:

$$\tau_{½} = \frac{\ln 2}{k} = \frac{0.693}{k} \qquad 2.9$$

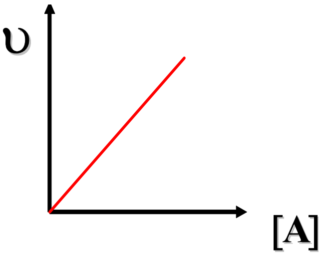


Figure 2.3 — First-order reaction

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 days
Sr^{90} = 27 years
Cs^{137} = 26.6 years

EXAMPLE 2.2. In healing some forms of cancer a medicine, containing radioisotope Ir-192 is used (its half-life is 74.08 days). Calculate how much of Ir-192 will be contained in a human body through 10 days.

Answer:

$$\tau_{½} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$k = \frac{0.693}{74.08} = 9.35\times10^{-3} \text{ day}^{-1}$$

$$\frac{[A]_0}{[A]} = e^{\boldsymbol{-0,\ 00935\times 10 days}} = 0.\ 91 \text{ or } 91\ \%$$

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

2 A → product

and that rate is

$$\text{rate } (\vartheta) = k\,[A]^2, \qquad 2.10$$

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

$$\tau_{½} = \frac{1}{k[A]_0} \qquad 2.11$$

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

A + B → products

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:

$$2\,NO_2\,(g) \rightarrow 2\,NO\,(g) + O_2\,(g)$$

$$CH_3COCl\,(aq) + H_2O\,(\ell) \rightarrow CH_3COOH\,(aq) + HCl\,(aq)$$

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 2.1 are distinguished by extremely large number of elementary steps. Other types of complex reactions are:

- reversible;
- parallel;
- consecutive.

Reversible Reactions

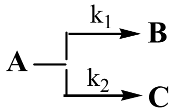
Most reactions are reversible to a certain extent, and we must consider both the forward and reverse rates. For the reversible reaction that proceeds by two elementary steps:

$$\mathbf{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{B}$$

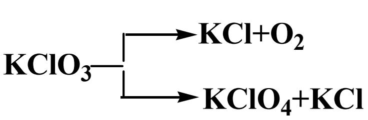
where k_1 and k_2 — are rate constants of forward and reverse reactions respectively. The rate law for a reversible reaction is $\vartheta = \mathbf{k_1\,[A] - k_2\,[B]}$

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:

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_2} \mathbf{C}\,.$$

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

$$CH_3COCH_3 \rightarrow CH_2C{=}O + CH_4$$

$$CH_2C{=}O \rightarrow CO + \tfrac{1}{2} C_2H_4$$

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.2.4). 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: $\vartheta = k_1 [B]$

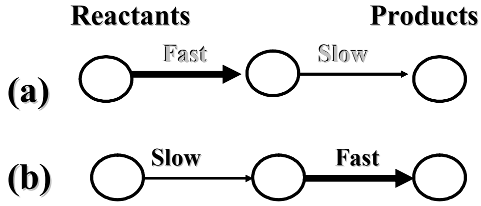


Figure 2.4 — In these diagrams of reaction schemes, heavy arrows represent fast steps and light arrows represent slow steps

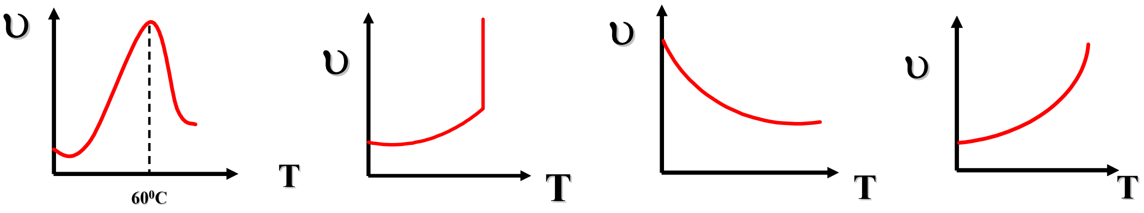
Kinetics of complex reactions is summarized in table 2.1

Table 2.1 — Kinetics of Complex Reactions

№	Type of a reaction	A Scheme	A Rate Law
1	Reversible Reactions	$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$	$\upsilon = k_1[A] - k_2[B]$
2	Parallel Reactions	$A - \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$	$\upsilon = k_1 ([A]_0 - [B]) + k_2 ([A]_0 - [C])$
3	Consecutive Reactions	$A \xrightarrow{k_1} B \xrightarrow{k_2} C$	The rate determining step governs the rate of the overall chemical reaction: $\upsilon = k_2 [B]$

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.



(a) (b) (c) (d)

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.

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

where γ — 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:

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

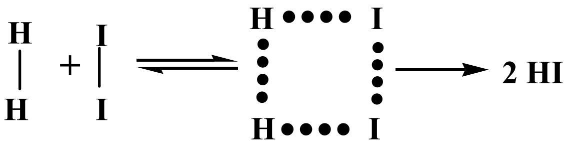
where k_0 — pre-exponential factor;

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:

$$\mathbf{A + B \rightleftarrows \underset{\text{activated complex}}{A \ldots B} \rightarrow AB}$$

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:



activated complex

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 (figure 2.6):

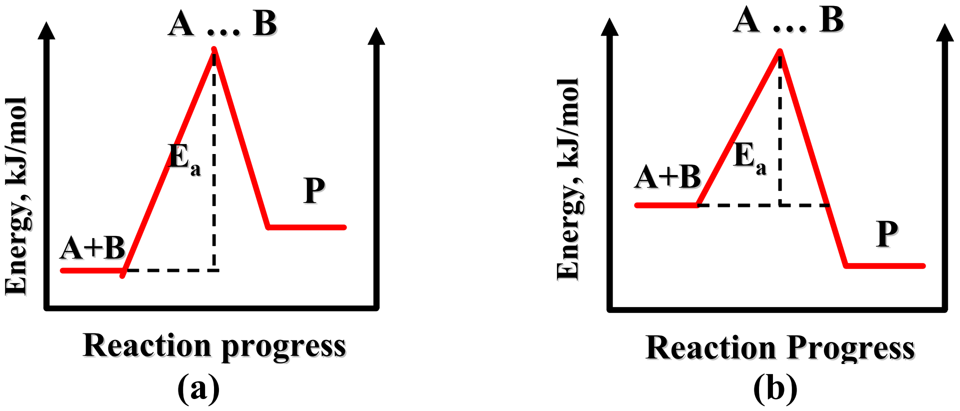


Figure 2.6 — Potential energy profiles of (a) an exothermic reaction, (b) an endothermic reaction

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:

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

EXAMPLE 3. The rate constant of a first-order reaction is $4.60\times10^{-4}\ \mathrm{s}^{-1}$ at 350°C. Its activation energy is 104 kJ/mol. Calculate the temperature at which rate constant of a reaction is $8.80\times10^{-4}\ \mathrm{s}^{-1}$.

Answer:

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

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

$$\ln 4.6\times10^{-4}-\ln 8.8\times10^{-4}=\frac{104000}{8.314}\times\left(\frac{350-T_2}{350\times T_2}\right)$$

$$\left(\frac{350-T_2}{350\times T_2}\right)=\frac{\ln\dfrac{4.6\times10^{-4}}{8.8\times10^{-4}}\times8.314}{104000}$$

$$\left(\frac{350-T_2}{350\times T_2}\right)=-\ 5.18\times10^{-5}$$

$350-T_2=-\ 0.018\times T_2$

$0.98\times T_2=350$

$T_2=356.5$ K

2.5 Laboratory Work

CHEMICAL KINETICS

2.5.1 TEST 1: EFFECT OF THE REACTANTS' CONCENTRATIONS ON THE REACTION RATE

The aim of an experiment is to determine a linkage between reactants concentrations and the rate for the following chemical reaction:

$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2S_2O_3$$

$$H_2S_2O_3 \rightarrow H_2O + SO_2 + S\downarrow$$

The end of the reaction is identified by evident appearance of sulfur precipitate. Fill 10 test tubes with solution of sodium thiosulfate, sulfuric acid and water according to the scheme, given in table 2.2.

Table 2.2

№ of a test tube	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Initial solutions 1 M **$Na_2S_2O_3$**, mℓ	**1**		**2**		**3**		**4**		**5**	
Water, mℓ	**4**		**3**		**2**		**1**		**0**	
$Na_2S_2O_3$ concentration, mol/ℓ	**0.1**		**0.2**		**0.3**		**0.4**		**0.5**	
1 M H_2SO_4, mℓ		**5**		**5**		**5**		**5**		**5**
Time after which sulfur precipitate appears, s.										

Rate of a chemical reaction: $\vartheta = \dfrac{1}{\tau}$ 2.15

Mix solutions of $Na_2S_2O_3$ and H_2SO_4, contained in test tubes1 and 2, 3 and 4, 5 and 6, 7 and 8, 9 and 10 respectively. Mark the time of solutions' mixing, and the time, when sulfur precipitate appears.

Calculate rates of a chemical reaction using formula 2.15 and represent the obtained data in a graph form (a plot of rates against $Na_2S_2O_3$ concentrations).

2.5.2 TEST 2: EFFECT OF THE TEMPERATURE ON THE REACTION RATE

In this experiment we shall use the same $Na_2S_2O_3$ and H_2SO_4 solutions as in the first experiment. Pour 5 mℓ of $Na_2S_2O_3$ solution into four test tubes, and 5 mℓ of H_2SO_4 solution into another four test tubes. Arrange these test tubes into four couples. Mark the temperature in a laboratory, and mix solutions of the first couple. Determine time of the reaction under this temperature. Immerse all other test tubes into a chemical glass with water and heat them by ten degrees. Mix solutions of the second couples of test tubes and measure a time of a reaction. Repeat the experiment when the temperature rises is ten degrees higher and so on. Write the obtained data into table 2.3.

Table 2.3

Number of a test tube	Volume of $Na_2S_2O_3$, mℓ	Volume of H_2SO_4, mℓ	Temperature °C	Time after which sulfur precipitate appears, s.	$\vartheta = \frac{1}{\tau}$
1					
2					
3					
4					

Calculate temperature coefficients of the examined reaction. Does the reaction obey the Van’t Hoff’s rule or not?

2.6 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 (b) increases with the increasing temperature.

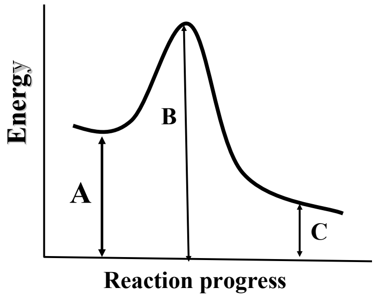
8. For the energy profile presented below, which of the following statements is true?

(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.



NUMERICAL EXERCISES

REACTION ORDER, RATE LAW

1. Write the rates for the following reactions in terms of reactant the disappearance product output:

(a) $C_2H_6 \rightarrow C_2H_4 + H_2$

(b) $ClO^- + Br^- \rightarrow BrO^- + Cl^-$

(c) $(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3COH + HCl$

(d) $2\ AsH_3 \rightarrow 2\ As + 3H_2$

2. The rate law for the reaction

$$\mathbf{NH_4^+ (aq) + NO_2^- \rightarrow N_2 (g) + 2\ H_2O\ (\ell)}$$

is given by rate - k[$\mathbf{NH_4^+}$][$\mathbf{NO_2^-}$]. At 25°C, the rate is 3.0×10^{-4} $M^{-1}s^{-1}$. Calculate the rate of the reaction at this temperature if [$\mathbf{NH_4^+}$] = 0.26M and [$\mathbf{NO_2^-}$] = 0.080 M

ANSWER: 6.2$\times 10^{-6}$ mol/ℓ×s

3. Certain of first-order reaction is 34.5 % complete in 49 min at 298 K. What is its rate constant?

ANSWER: $8.6\times 10^{-3} min^{-1}$

4. What is the half-life of a compound if 75 % of the given sample of the compound decomposes in 60 min? Assume first-order kinetics.

ANSWER: 30.1 min.

5. The half-life for the (first-order) radioactive decay of ^{14}C is 5730 years. The amount of ^{14}C present in an object can be used to determine its age. An archaeological sample contained wood that had only 10 per cent of the ^{14}C found in living trees. What is its age?

ANSWER: 19,000 years.

6. One of the hazards of nuclear explosions is the generation of ^{90}Sr and its subsequent incorporation in place of calcium in bones. This nuclide has the half-life of 28.1 years. Suppose 1.00 μg was absorbed by a newly born child. How much will remain in (a) 18 years, (b) 70 years if none is lost metabolically?

ANSWER: (a) 0.642μg; (b) 0.177 μg

7. Consider the following nuclear decay

$$\mathbf{^{64}Cu \rightarrow {}^{64}Zn + {}^{0}_{-1}\beta \quad t_{1/2} = 12.8\ hr}$$

Starting with one mole of ^{64}Cu, calculate the number of grams of ^{64}Zn formed in 25.6 hours.

ANSWER: **16.64 g.**

ACTIVATION ENERGY

8. Use the equation (2.13) to calculate the rate constant at 300 K for E_a = 0.2, and 50 kJ mol^{-1}. Assume that A = 10^{11} s^{-1} in each case.

ANSWER:$4.5\times 10^{10}s^{-1}$; $2.0\times 10^{2}s^{-1}$

9. The rate constant of some reactions double with every 10-degree rise in temperature. Assume that such a reaction takes place at 295 K and 305 K. What must its activation energy be for rate constant to double as described?

ANSWER: 51.9 kJ/mol

10. The rate constant of some reactions double with every 10-degree rise in temperature. Assume that such a reaction takes place at 295 K and 305 K. What must its activation energy be for rate constant to double as described?

ANSWER: 51.9 kJ/mol

11. The rate constant of a first-order reaction is 3.46×10^{-2} s^{-1} at 298K. What is the rate constant at 350K if the activation energy for the reaction is 50.3 kJ/mol?

ANSWER: 0.702 s^{-1}.

12. The rate constant of a first-order reaction is 4.6×10^{-4} s^{-1} at 350°C. Calculate the temperature at which its rate constant 8.80×10^{-4} s^{-1} provided that the activation energy is 104 kJ/mol.

ANSWER: 644 K.

CHAPTER 3
ENZYME KINETICS

> *In recent years there has been some controversy*
> *about how enzymes manage to catalyze chemical*
> *reactions as fast as they do. Lost sight of*
> *in these arguments, however,*
> *has been the fact that the actual chemical*
> *reaction is seldom what limits the rate of an*
> *enzymatic reaction.*
>
> *W.W. Cleland*

After reading this chapter, you should be able to:

- define catalysis and it's 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.

3.1 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 $A + B \rightleftarrows A...B \rightarrow AB$

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

Positive catalysts decrease activation energy of a reaction (figure 3.1).

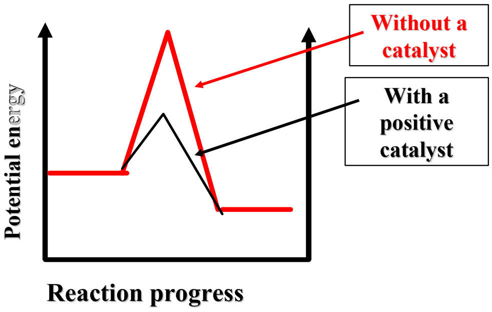


Figure 3.1 — Positive catalysts

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 (figure 3.2).

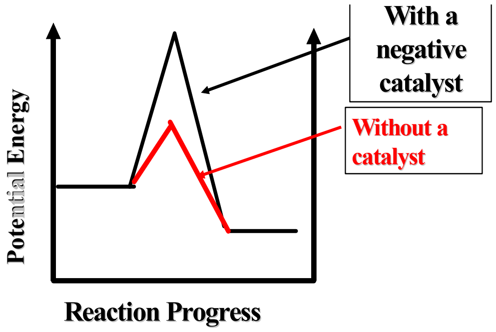


Figure 3.2 — Negative catalysts

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.

Table 3.1 — Activation energy of catalytical and noncatalytical chemical reactions

Reactions	E_a, kJ/mol		Catalyst
	Without a catalyst	With a catalyst	
$C_2H_4 + H_2 >> C_2H_6$	180	40	Pt
		8	Cu
$2H_2O_2 > 2H_2O + O_2$	750	55	I_2
		20	Catalase

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

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 \rightarrow 2\,MnSO_4 + 10\,CO_2 + K_2SO_4 + 8\,H_2O$$

Catalyst: Mn^{2+}. The kinetic curve of autocatalytic reaction is represented in figure 3.3.

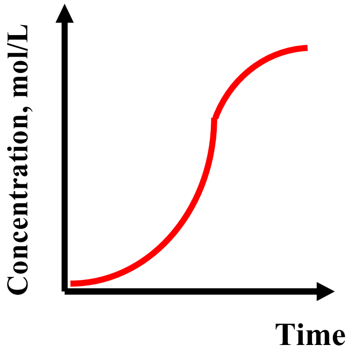
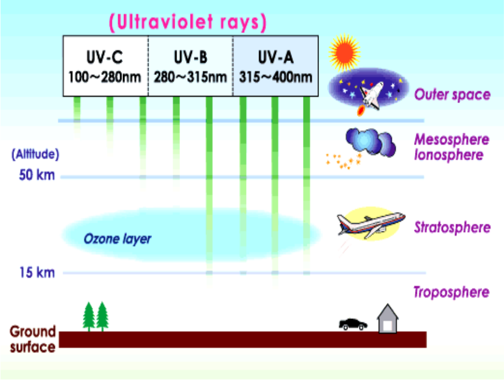


Figure 3.3 — Kinetic curve of autocatalytic reaction

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 (CF_2Cl_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: $\mathbf{CF_2Cl_2 \rightarrow CF_2Cl\bullet + Cl\bullet}$**,** where Cl• is a catalyst.

Without a catalyst a reaction proceeds as follows:

$$O_3 + O \rightarrow 2\,O_2 \qquad E_a = 17.1\ \text{kJ/mol}$$

Under the effect of a catalyst:

$$O_3 + Cl \rightarrow ClO + O_2 \qquad E_a = 2.1\ \text{kJ/mol}$$
$$\underline{ClO + O \rightarrow Cl + O_2 \qquad E_a = 0.4\ \text{kJ/mol}}$$
$$O_3 + O \rightarrow 2\,O_2$$

A catalyst decreases the activation energy of a reaction thus increasing its rate (figure 3.4).

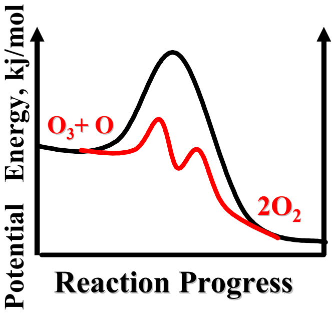


Figure 3.4 — The energy profile for the reaction between O_3 and O. The direct reaction has a much higher activation energy than the chlorine-catalyzed reaction, so Cl atoms are effective catalysts for this reaction

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

3.2 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°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°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:

$$\mathbf{S + E \rightleftarrows ES \rightarrow P + E}$$

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

The initial rate of product formation is given by

$$\vartheta = k_2\,[ES], \qquad 3.1$$

where k_2 — is a first-order rate constant, known as molar enzyme activity or *turnover number*, expressed in 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 $1\times10^4 < k_2 < 6\times10^6\ min^{-1}$

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

$$\vartheta = \frac{k_2 \times [E]_0 \times [S]}{K_M + [S]} \qquad 3.2$$

Substituting equation 3.1 with equation 3.3 yields

$$\vartheta = \frac{k_2 \times [E] \times [S]}{K_M + [S]} = \frac{\vartheta_{\max} \times [S]}{K_M + [S]}, \qquad 3.3$$

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 $k_2\times[E]_{overall}$ is constant and is defined as ϑ_{max} (maximum rate). Maximum rate corresponds to the zero-order enzymatic reaction.

Equation (3.2) 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 (3.3) becomes

$$\vartheta = \frac{\vartheta_{max}}{K_m}\times[S] \qquad 3.4$$

It is the first-order reaction in [S]. This rate law corresponds to the initial linear portion of the plot in figure 3.5.

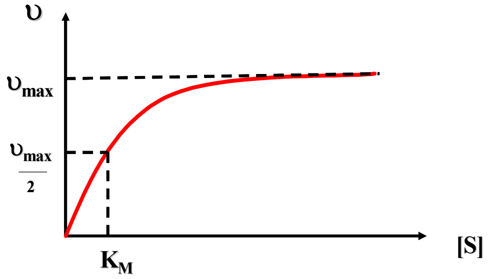


Figure 3.5 — Kinetic curve of enzymatic reaction

At high substrate concentrations ($[S] \gg K_M$), equation (3.3) can be written as

$$\vartheta = \vartheta_{max}; \qquad 3.5$$

It's a zero order in [S] and corresponds to the horizontal portion of the plot in figure 3.5. Now consider what happens when $[S] = K_M$. From equation 3.3 we find that this condition gives $\vartheta = \vartheta_{max}/2$, 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 3.5. We may use it for graphical determination of ϑ_{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 $\mathbf{A + B \rightleftarrows P + Q}$**,** 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 (figure 3.6) or nonsequential mechanism (figure 3.7).

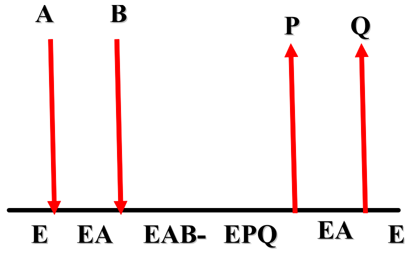


Figure 3.6 — The Sequential Mechanism. In this mechanism, one substrate must bind before a second substrate can bind

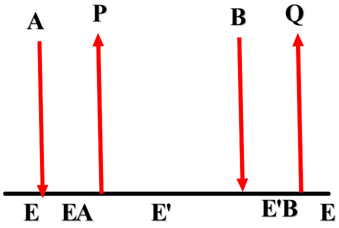


Figure 3.7 — The Nonsequential Mechanism

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 (figure 3.8). 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.

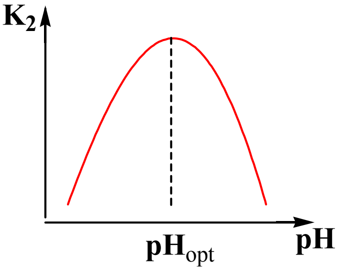
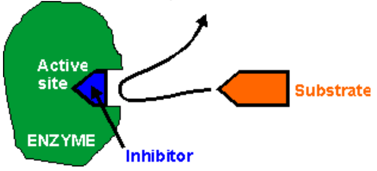


Figure 3.8 — The effect of acidity on enzymes' activity

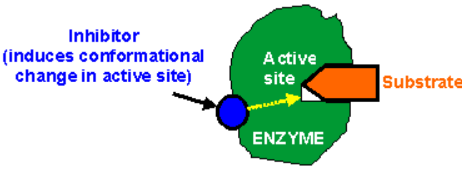
We consider two forms of inhibition (there are others):

- competitive inhibition;
- noncompetitive inhibition.

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



Original (uninhibited) ϑ_{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.

3.3 Exercises for the self control

DISCUSSION QUESTIONS

1. How does a catalyst increase the rate of a reaction?

2. What are the characteristics of a catalyst?

3. Why does a catalyst must affect the rate of the reaction in both directions

4. 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?

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

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

7. 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.

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

NUMERICAL EXERCISES

1. Activation energy of hydrogen peroxide decomposition

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

is 75.0 kJ/mol. Activation energy of the same reaction catalyzed by free iodine is 55.0 kJ/mol. Calculate how much times does a catalyst accelerate a reaction.

ANSWER: 3,205

2. The hydrolysis of acetylcholine is catalyzed by the enzyme acetyl cholinesterase, which has a turnover rate of 25,000 s^{-1}. Calculate how long it takes for the enzyme to cleave one acetylcholine molecule.

ANSWER: 4×10^{-5}s.

3. An enzyme that has a K_M value of $3.9\text{x}10^{-5}$M is studied at an initial substrate concentration of 0.035 M. In 1 min, it is found that 6.2 μM of a product has been produced. Calculate the value of $\vartheta_{\max}$ and the amount of a product formed in 4.5 min.

ANSWER:. 6.21×10^{-6} mol/ℓ×min

4. The enzyme-catalyzed conversion of a substrate at 25^0C has a Michaelis constant of 0.042 mol/ℓ. The rate of the reaction is 2.45×10^{-4} mol/ℓ×s when the substrate concentration is 0.890 mol/ℓ. What is the maximum velocity of this enzymolysis?

ANSWER: 2.56×10^{-4} mol/ℓ ×s

5. The enzyme-catalyzed conversion of a substrate at 25^0C has a Michaelis constant of 0.035 mol/ℓ. The rate of the reaction is 1.15×10^{-3} mol/ℓ×s when the substrate concentration is 0.110 mol/ℓ. What is the maximum velocity of this enzymolysis?

ANSWER: 1.52×10^{-3} mol/ℓ×s

6. The enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide: $(NH_2)_2CO + H_2O \rightarrow CO_2 + 2\ NH_3$. The uncatalyzed reaction has activation energy of 125 kJ/mol. The enzyme catalyzes a mechanism that has activation energy of 46 kJ/mol. By what factor does urease increase the rate of urea hydrolysis at 21°C? (Use the Arrhenius equation).

ANSWER: Urease increases the rate by a factor of 1.1×10^{14}

CHAPTER 4
KINETICS AND THERMODYNAMICS OF CHEMICAL EQUILIBRIUM

> *When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other factors involved in this shift, it would lead to a change of opposite sign in the parameter considered.*
>
> *Henri-Louis Le Chatelier*

After reading this chapter, 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) an base ionization equilibrium constant (K_b);
- describe salt hydrolysis and be able to calculate the hydrolysis equilibrium constants.

4.1. 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

$$\mathbf{aA + bB \rightleftarrows cC + dD}$$

For example:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

$$NH_4Cl + H_2O \rightleftarrows NH_4OH + HCl$$

$$Hb + O_2 \rightleftarrows HbO_2$$

HemoglobinOxyhemoglobin

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:

$$Na_2CO_3 + CaCl_2 \rightleftarrows CaCO_3 + 2\,NaCl$$

Claude Louis Berthollet (1748-1822)

This reaction was known to proceed to completion in the laboratory. He immediately realized that Na_2CO_3 must have been formed by the reverse of this process brought about by the very high concentration of salt in the slowly-evaporating waters. This led Berthollet to the belief that some reactions proceed both in forward and reverse directions. His famous textbook *Essai de statique chi-mique* presented discovery that an excess of the product of a reaction could drive it in the reverse direction.

Reversible reactions tend to chemical equilibrium. *Chemical Equilibrium* is a state of a reversible process characterized by equal rates of forward and reverse reactions (Figure 4.1).

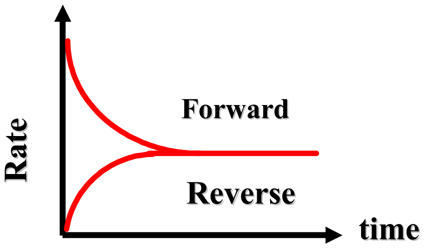


Figure 4.1 — Kinetic curves of forward and reverse reactions

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 (figure 4.2).

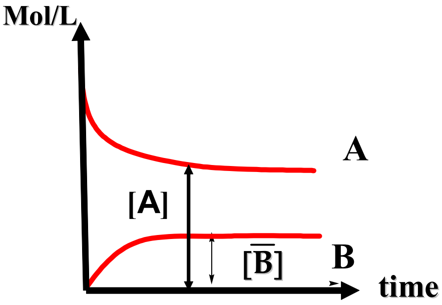


Figure 4.2 — Kinetic curves of a reversible reaction: $aA \rightleftarrows bB$

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.

Rate of forward reaction = $\mathbf{k_f[A]^a \times [B]^b}$

Rate of reverse reaction =$\mathbf{k_r[C]^c \times [D]^d}$**,**

where the proportionality coefficients k are called *rate constants,* and the quantities in square brackets represent concentrations, mol/L.

At equilibrium state

$$\vartheta_f = k_f [\overline{A}]^a \times [\overline{B}]^b \tag{4.1}$$

$$\vartheta_r = k_r [\overline{C}]^c \times [\overline{D}]^d \tag{4.2}$$

where ϑ_f and ϑ_r are the rates of forward and reverse reaction respectively.

Since $\vartheta_f = \vartheta_r$, we can rearrange equations (4.1) and (4.2) in a following way:

$$\frac{k_f}{k_r} = \frac{[\overline{C}]^c \times [\overline{D}]^d}{[\overline{A}]^a \times [\overline{B}]^b} \tag{4.3}$$

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

$$\frac{k_f}{k_r} = K \tag{4.4}$$

4.2 Ways of Expressing Equilibrium Constants

Two types of equilibrium constants can be distinguished: $\mathbf{K_c}$ and $\mathbf{K_p}$.

The notation K_c 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:

$$K_C = \frac{[\overline{C}]^c \times [\overline{D}]^d}{[\overline{A}]^a \times [\overline{B}]^b} \tag{4.5}$$

For example, for a biochemical reaction:

$\mathbf{Hb + O_2 \rightleftarrows HbO_2}$

K_c is equal to

$$K_C = \frac{[HbO_2]}{[Hb] \times [O_2]} = 1300 \tag{4.6}$$

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:

$\mathbf{CO_2\,(g) + 2\,NH_3\,(g) \rightleftarrows H_2O\,(g) + CO(NH_2)_2\,(s)}$

K_c can be calculated as:

$$K_C = \frac{[H_2O]}{[CO_2] \times [NH_3]^2} \tag{4.7}$$

EXAMPLE 4.1 The following equilibrium process has been studied at 230°C: $2\,NO\,(g) + O_2\,(g) \rightleftarrows 2\,NO_2\,(g)$. In one experiment the concentrations of the reacting species at equilibrium are found to be $[NO] = 0.0542$ M, $[O_2] = 0.127$ M, and $[NO_2] = 15.5$ M. Calculate the equilibrium constant (K_c) of the reaction at this temperature.

Answer:

The equilibrium constant is given by $K_C = \dfrac{[NO_2]^2}{[NO]^2 \times [O_2]}$

Substituting the concentrations, we find that

$$K_C = \frac{(15.5)^2}{(0.0542)^2 \times (0.127)} = 6.44 \times 10^5$$

Note that K_c is given without units.

The notation K_p is used when the amounts of materials are expressed as gas pressures.

$$K_P = \frac{\overline{P}_C^{\,C} \times \overline{P}_D^{\,d}}{\overline{P}_A^{\,a} \times \overline{P}_B^{\,b}} \tag{4.8}$$

EXAMPLE 4.2 The equilibrium constant K_p for the reaction:

$$PCl_5\,(g) \rightleftarrows PCl_3\,(g) + Cl_2\,(g)$$

is found to be 1.05 at 250°C. If the equilibrium partial pressure of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?

Answer:

First, we write K_p in terms of the partial pressures of the reacting species:

$$K_P = \frac{\overline{P}_{PCl_3} \times \overline{P}_{Cl_2}}{\overline{P}_{PCl_5}}$$

Knowing the partial pressures, we write

$$1.05 = \frac{(0.463) \times (P_{Cl_2})}{(0.875)} \qquad \text{or} \qquad P_{Cl_2} = \frac{(1.05) \times (0.875)}{(0.463)} = 1.98\,atm\,.$$

Note that we have added atm as the unit for P_{Cl_2}.

A relationship between K_c and K_p is given by the equation:

$$K_C = K_P \times (RT)^{(a+b-c-d)} \tag{4.9}$$

EXAMPLE 4.3 The equilibrium constant (K_c) for the reaction:

$$N_2O_4\,(g) \rightleftarrows 2\,NO_2\,(g)$$

is 4.63×10^{-3} at 25°C. What is the value of K_p at this temperature?

Answer:

From Equation (4.9) we write $K_p = K_c\,(0.0821\ T)^{\Delta n}$.

Since T = 298 K and $\Delta n = 2 - 1 = 1$, we have

$K_p = (4.63 \times 10^{-3})\,(0.0821 \times 298) = 0.113$

Note that K_p like K_c, is treated as a dimensionless quantity. This example shows that we can get quite a different value for the equilibrium constant for the same reaction, depending on whether we express the concentrations in moles per liter or in atmospheres.

4.3 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:

$$Q = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \qquad 4.10$$

↘

These 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, ΔG, also signals the direction of a chemical reaction. These two criteria can be compared:

Reaction goes right when	Equilibrium when	Reaction goes left when
Q < K	**Q = K**	**Q > K**
ΔG < 0	**ΔG = 0**	**ΔG > 0**

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

$$\Delta G = \Delta G^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad 4.11$$

At equilibrium state ΔG = 0, and concentrations of all reactants are equilibrium concentrations. Hence

$$\Delta G^o = - RT \times \ln K \qquad 4.12$$

We can calculate equilibrium constant applying thermodynamic data:

$$K = e^{-G^0/RT} \qquad 4.13$$

EXAMPLE 4.4 Using standard thermodynamic data, find the value of K at 298°C for the following reaction: $N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$

Answer:

Equation (4.11) provides a link between thermodynamic data and K. We must first calculate ΔG^o from tabulated standard free energies of formation:

$\Delta G^o = 2\times\ \Delta_f G^o(NH_3) - \Delta_f G^o(N_2) - 3\times\Delta_f G^o(H_2)$

Appendix 2, table 12 contains the appropriate values:

$\Delta_f G^o\ (N_2) = 0$, $\Delta_f G^o\ (H_2) = 0$, $\Delta_f G^o\ (NH_3) = -16.4$ kJ/mol

$\Delta G^o = 2\times\ (-16.4) = -\ 32.8$ kJ

To determine the equilibrium constant, equation (4.11) must be rearranged to isolate lnK:

$$\ln K = \frac{\Delta G^0}{RT} = \frac{-(32.8kJ)\times(10J/kJ)}{(8.314J/K)\times(298K)} = 13.24$$

$K = e^{13.24} = 5.6\times10^5$ atm^{-2}

The exponential gives a dimensionless number, since e^x 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.

4.4 Equilibrium Constants and Temperature

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

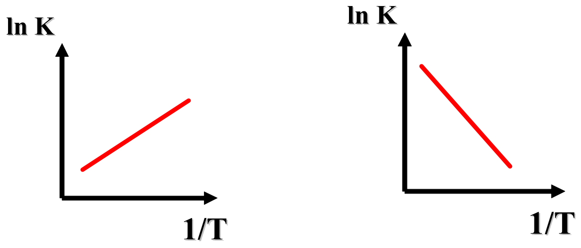
$$\begin{cases} \Delta G° = \Delta H° - T\Delta S° \\ \Delta G° = -RT \times \ln K \end{cases}$$

As the result:

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad 4.14$$

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 (figure 4.3a).

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 (figure 4.3b).



a b

Figure 4.3 — Graphs of ln K versus 1/T (a) ΔH>0, (b) ΔH<0

4.5 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}) (Figure 4.4).

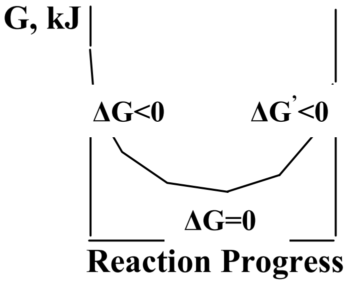


Figure 4.4 — Energy diagram of a reversible reaction

Henry A.
Le Chatelier
(1850–1936)

In 1884 French chemist and mining engineer Le Chatelier developed the principle, which was a compact summery of how several factors can affect equilibrium.

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:

$$Hb + O_2 \rightleftarrows HbO_2, \Delta_r H^0 = - 10 \text{ kJ}$$

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:

$$N_2 + O_2 \rightleftarrows 2\,NO$$

For the reaction of hemoglobin oxidation into oxyhemoglobin when blood is in lungs under high pressure of O_2 gas the equilibrium shifts to the right (blood absorbs oxygen). Venus blood is exposed under a low pressure of 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 4.5 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 ΔG^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.

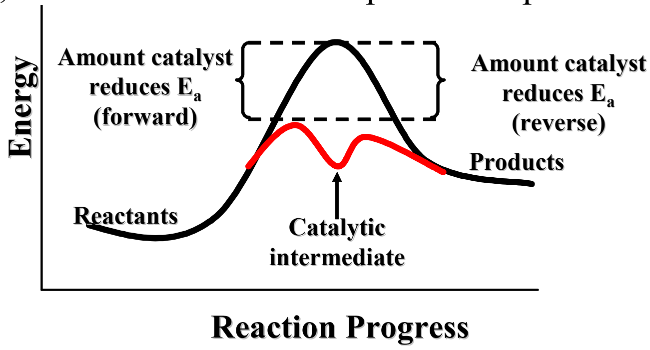


Figure 4.5 — Energy profile of a reversible catalytic reaction

EXAMPLE 4.5 Consider the following equilibrium process:

N_2F_4 (g) ⇄ 2 NF_2 (g) $\Delta H^0 = 38.5$ kJ

Predict the changes in the equilibrium if (a) the reacting mixture is heated at constant volume; (b) NF_2 gas is removed from the reacting mixture at constant temperature and volume; (c) the pressure on the reacting mixture is decreased at constant temperature; (d) an inert gas, such as helium, is added to the reacting mixture at constant volume and temperature.

Answer:

(a) Since the forward reaction is endothermic, an increase in temperature favors the formation of NF_2. The equilibrium constant:

$K_C = \frac{[NF_2]^2}{[N_2F_4]}$ will therefore increase with increasing temperature.

(b) The stress here is the removal of NF_2 gas. To offset it, more N_2F_4 will decompose to form NF_2. The equilibrium constant K_c remains unchanged, however.

(c) A decrease in pressure (which is accompanied by an increase in gas volume) favors the formation of more gas molecules, that is, the forward reaction. Thus, more NF_2 gas will be formed. The equilibrium will remain unchanged.

(d) Adding helium to the equilibrium mixture at constant volume will not shift the equilibrium.

4.6 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:

$$H_2O \rightleftarrows H^+ + OH^-$$

This reaction is sometimes called the *autoionization of water* thus it is assumed that one H_2O molecule is an acid (proton's donor) and another is a base (proton's acceptor):

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

Base Acid

Expressing the hydrated proton as H^+ rather than H_3O^+, we can write the equilibrium constant for the autoionization of water:

$$K_C = \frac{[H]\times[OH^-]}{[H_2O]} \qquad 4.15$$

Since a very small fraction of water molecules are ionized, the concentration of water, that is, $[H_2O]$, remains virtually unchanged. Therefore we rearrange the equation as

$$\mathbf{K_c\,[H_2O] = K_w = [H^+]\times[OH^-]} \qquad 4.16$$

The «new» equilibrium constant, $\mathbf{K_w}$, is called the *ion-product constant* or *water equilibrium constant.*

In pure water at 25°C, the concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0\times10^{-7}$ M and $[OH^-] = 1.0\times10^{-7}$ M. Thus, from the Equation (4.16) we can derive:

$$K_w = (1.0\times10^{-7})\times(1.0\times10^{-7}) = 10^{-14} \qquad 4.17$$

Note that whether we have pure water or a solution of dissolved species, the following relation always holds at 25°C:

$$K_w = [H^+]\times[OH^-] = 10^{-14} \qquad 4.18$$

It is important to remember that, because K_w is equilibrium constant, its value changes with temperature.

In pure water and aqueous solutions the concentrations of H^+ and OH^- can be calculated by:

$$[H^+] = \frac{K_W}{[OH^-]} \qquad 4.19$$

$$[OH^-] = \frac{K_W}{[H^+]} \qquad 4.20$$

EXAMPLE 4.6 The concentration of OH^- ions in a certain household ammonia cleaning solution is 0.0025 M. Calculate the concentration of H^+ ions.

Answer:

Applying Equation (4.19), we write

$$\left[H^+\right]=\frac{K_W}{\left[OH^-\right]}=\frac{1.0\times10^{-14}}{0.0025}=4.0\times10^{-12}M$$

Since $[H^+] < [OH^-]$, the solution is basic.

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 $\mathbf{HA + H_2O \rightleftarrows H_3O^+ + A^-}$ or $\mathbf{HA \rightleftarrows H^+ + A^-}$

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

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

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

$$K_a=\frac{\left[H^+\right]\times\left[CH_3COO^-\right]}{\left[CH_3COOH\right]} \qquad 4.21$$

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

$$\text{percent dissociation}=\frac{\left[H^+\right]_{eq}}{\left[HA\right]_0}\times100\% \qquad 4.22$$

where $[H^+]$ is the hydrogen ion concentration at equilibrium and $[HA]_o$ is the initial concentration of the acid.

EXAMPLE 4.7 Calculate the concentration of the undissociated acid, the H^+ ions, and the CN^- ions of a 0.05 M HCN solution and the percent dissociation at 25°C.

Answer:

Let x be the concentration of H^+ and CN^- at equilibrium. Thus, we have

$$\begin{array}{ccc} HCN\ (aq) \rightleftarrows & H^+\ (aq) + & CN^-\ (aq) \\ (0.05-x)\ M & x\ M & x\ M \end{array}$$

Using the value of K_a from Appendix 2, table 8, we write

$$\frac{x^2}{0.05-x}=4.9\times10^{-10}$$

Since K_a values for weak acids are generally known to an accuracy of only ±5 %, it is reasonable to require x to be less than 5% of 0.05, the number from which it is subtracted. Assuming that this approximation holds ($0.05 - x \approx 0.05$), we have $x^2 = 2.5\times 10^{-11}$ or $x = 5.0 \times 10^{-6}$ M

Therefore, at equilibrium,
$[H^+] = 5.0 \times 10^{-6}$ M
$[CN^-] = 5.0 \times 10^{-6}$ M
$[HCN] = 0.05 - 5.0 \times 10^{-6} \approx 0.05$ M
Finally, the percent dissociation is given by

$$\frac{5.0\times10^{-6}}{0.05}\times100\% = 1.0\times10^{-2}\%$$

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: $\mathbf{NH_4OH \rightleftarrows NH_4^+ + OH^-}$

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

$$K_b = \frac{[NH_4^+]\times[OH^-]}{[NH_4OH]} \qquad 4.23$$

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:

$NH_4Cl + H_2O \rightleftarrows NH_4OH + HCl$

$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+$

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

$$K_h = \frac{[NH_4OH]\times[H^+]}{[NH_4^+]} = \frac{[NH_4OH]\times K_W}{[NH_4^+]\times[OH^-]} = \frac{K_W}{K_b} \qquad 4.24$$

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:

$CH_3COONa + H_2O \rightleftarrows CH_3COOH + NaOH$

$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$

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

$$K_h = \frac{K_W}{K_a} \qquad 4.25$$

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:

$CH_3COONH_4 + H_2O \rightleftarrows NH_4OH + +CH_3COOH$

Its hydrolysis equilibrium constant is equal to

$$K_h = \frac{K_W}{K_a \times K_b} \qquad 4.26$$

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

$$\mathbf{h} = \frac{\text{Number of salt's particles, which undergo hydrolysis}}{\text{Initial number of salt's particles in a solution}} \qquad 4.27$$

Hydrolysis percent can be calculated as

$$\mathbf{h} = \sqrt{\frac{K_h}{C_M}} \qquad 4.28$$

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.

4.7 Laboratory Work

CHEMICAL EQUILIBRIUM

Chemical Equipment: 100 mℓ- and 250 mℓ-chemical glasses, test tubes, pipettes.

Reagents: $FeCl_3$ and NH_4CNS saturated solutions, 0.05M iodine solution, 0.5 percent by mass starch solution, KCl (solid).

Test 1: Effect of the reactants' concentrations on the equilibrium position

The reversible chemical reaction under study is:

$$FeCl_3 + 3\ NH_4CNS \rightleftarrows Fe(CNS)_3 + 3\ NH_4Cl$$

Before you start an experiment keep in mind that $Fe(CNS)_3$ solution is red, $FeCl_3$ solution is yellow, KCl and NH_4CNS solutions are colorless. When $Fe(CNS)_3$ concentration in a solution alters its red color can be deepened or fade which signals about shift in equilibrium.

Carry out an experiment in the following sequence of operations:

1) Pour 20 mℓ of distilled water into a chemical glass and treat it with 1–2 drops of $FeCl_3$ and NH_4CNS solutions.

2) Pour the prepared solution into four different test tubes.

3) The first test tube's solution is assumed to be standard; we shall compare its color with the colors of the solutions in the other test tubes.

4) Treat a solution of the second test tube with some drops of $FeCl_3$ saturated solution and compare its color with the color of a standard solution. Does the color deepened or fade? Write a result into table 4.1.

5) Treat a solution in the third test tube with some drops of NH_4CNS saturated solution and compare its color with the color of a standard solution. Does the color deepened or fade? Write a result into table 4.1.

6) Add some KCl crystals into the solution of the fourth test and compare its color with the color of a standard solution. Does the color deepened or fade? Write a result into table 4.1.

Table 4.1 — The influence of concentration on the chemical equilibrium

Number of a test tube	A substance added to test solutions	The observed result -change in color	Conclusion -a direction of shift in equilibrium
1	—		
2	$FeCl_3$ (soln.)		
3	NH_4CNS (soln.)		
4	KCl (solid)		

Make a conclusion whether the observed shifting in equilibrium occurs in accordance with Le Chatelier’s Principle?

TEST 2: EFFECT OF TEMPERATURE ON THE EQUILIBRIUM POSITION

The reversible chemical reaction under study is:

$$\underset{\text{yellow}}{I_2} + \underset{\text{colorless}}{\text{Starch Solution}} \rightleftarrows \underset{\text{blue}}{[I_2\cdot\text{Starch}]}$$

Carry out an experiment in the following sequence of operations:

1) Pour distilled water into 250 mℓ-chemical glass and heat water up to the boiling point.

2) Take two test tubes and pour 4–5 mℓ of starch solution and 3–4 mℓ of iodine solution into each of them. Mark a color of the prepared solution.

3) Immerse one test tube into hot water and compare the color of the solution after heating with its initial color. Does the blue color of starch-iodine complex deepened or fade after heating?

4) Immerse the same test tube into cold water and examine its color. Does the blue color of starch-iodine complex deepened or fade after cooling?

5) Use experimental data to answer the following questions:

(a) What reaction (forward or reverse) is favorable under heating and under cooling?

(b) What reaction (forward or reverse) is exothermic or endothermic?

(c) How to write the equation of the Law of mass action for the given process?

4.8 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, $NaNO_3$, NH_4NO_2, $MgSO_4$, KCN, C_6H_5COONa, RbI, Na_2CO_3, $CaCl_2$, HCOOK.

7. Predict the pH(>7, <7, or ≈ 7) of the aqueous solutions containing the following salts: (a) KBr, (b) $Al(NO_3)_3$, (c) $BaCl_2$, (d) $Bi(NO_3)_3$

8. A certain salt, MX (containing the M^+ and 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?

NUMERICAL EXERCISES

PROPERTIES OF EQUILIBRIUM CONSTANTS

1. Write the expression for the equilibrium constants K_c and K_p, if applicable, of each of the following reactions:

(a)$H_2O\ (\ell) \rightleftarrows H_2O\ (g)$

(b)$H_2O\ (g) + CO\ (g) \rightleftarrows H_2(g) + CO_2\ (g)$

(c)$2\ Mg\ (s) + O_2\ (g) \rightleftarrows 2\ MgO\ (s)$

(d)$PCl_5\ (g) \rightleftarrows PCl_5\ (g) + Cl_2\ (g)$

2. Write the expression for the equilibrium constants K_c and K_p , if applicable, for the following reactions:

(a)$2\ NO_2(g) + 7\ H_2\ (g) \rightleftarrows 2\ NH_3\ (g) + 4\ H_2O\ (\ell)$

(b)$2\ ZnS\ (s) + 3\ O_2(g) \rightleftarrows 2\ ZnO\ (s) + 2\ SO_2\ (g)$

(c)$C\ (s) + CO_2\ (g) \rightleftarrows 2\ CO\ (g)$

(d)$N_2O_5\ (g) \rightleftarrows 2\ NO_2\ (g) + \frac{1}{2}\ O_2$

(e)$C_6H_5COOH\ (aq) \rightleftarrows C_6H_5COO^-(aq) + H^+(aq)$

3. Consider the following equilibrium process at 700°C:

$$2\ H_2\ (g) + S_2\ (g) \rightleftarrows 2\ H_2S\ (g)$$

Analysis shows that there are 2.50 moles of H_2, 1.35×10^{-5} mole of S_2 and 8.70 moles of H_2S present in a 12.0 ℓ-flask. Calculate the equilibrium constant K_c for the reaction.

ANSWER: 1.08×10^{7}

4.Consider the following reaction:

$$N_2\ (g) + O_2\ (g) \rightleftarrows 2\ NO\ (g)$$

If the equilibrium partial pressure of N_2, O_2 and NO are 0.15 atm, 0.33 atm, and 0.050 atm respectively, at 2200°C, what is K_p?

ANSWER: 5.05×10^{-2}

5. Using standard thermodynamic data from Appendix 2, table 12, calculate equilibrium constants at 298 K for each of the following chemical equilibria:

(a) $2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$

(b) $2\ CO(g) + O_2(g) \rightleftarrows 2\ CO_2(g)$

(c) $BaCO_3(s) + C(s) \rightleftarrows BaO(s) + 2\ CO_2(g)$

6. Using standard thermodynamic data from Appendix 2, table 12, calculate equilibrium constants at 298 K for each of the following chemical equilibria:

(a) $CO(g) + H_2O(\ell) \rightleftarrows CO_2(g) + H_2(g)$

(b) $CH_4(g) + H_2O(\ell) \rightleftarrows CO(g) + 3\ H_2(g)$

(c) $SnO_2(s) + 2\ H_2(g) \rightleftarrows Sn(s) + 2\ H_2O(\ell)$

(d) $4\ NH_3(g) + 5\ O_2(g) \rightleftarrows 4\ NO(g) + 6\ H_2O(\ell)$

(e) $3\ Fe(s) + 4\ H_2O(g) \rightleftarrows Fe_3O_4(s) + 4\ H_2(g)$

SHIFTS IN EQUILIBRIUM

7. Photosynthesis can be represented by

$$6\ CO_2(g) + 6\ H_2O(\ell) \rightleftarrows C_6H_{12}O_6(s) + 6\ O_2 \qquad \Delta H^0 = 2801\ kJ$$

Explain how the equilibrium would be effected by the following changes: (a) the partial pressure of CO_2 is increased, (b) O_2 is removed from the mixture, (c) $C_6H_{12}O_6$ (glucose) is removed from the mixture, (d) more water is added, (e) a catalyst is added, (f) the temperature is decreased, and (g) more sunlight shines on the plants.

8. Consider the following equilibrium system:

$$SO_2(g) + Cl_2(g) \rightleftarrows SO_2Cl_2(g)$$

Predict how the equilibrium position would change if (a) Cl_2 gas were added to the system; (b) SO_2Cl_2 were removed from the system; (c) SO_2 were removed from the system. The temperature remains constant.

9. Consider the following equilibrium:

$$3\ O_2(g) \rightleftarrows 2\ O_3(g) \qquad \Delta H^0 = 284\ kJ$$

What is the effect on the position of equilibrium of (a) increasing the total pressure on the system by decreasing its volume; (b) adding O_2 to the reaction mixture; (c) decreasing the temperature?

10. Consider the following equilibrium process:

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g) \qquad \Delta H^0 = 92.5\ kJ$$

Predict the direction of the shift in equilibrium when (a) the temperature is raised; (b) more chlorine gas is added to the reaction mixture; (c) some PCl_5 is removed from the mixture; (d) the pressure on the gases is increased; (e) a catalyst is added to the reaction mixture.

11. Consider the following reaction at equilibrium in a closed container:

$$CaCO_3\,(s) \rightleftarrows CaO\,(s) + CO_2\,(g)$$

What would happen if (a) the volume were increased; (b) some CaO were added to the mixture; (c) some $CaCO_3$ were removed; (d) some CO_2 were added to the mixture; (e) a few drops of a NaOH solution were added to the mixture; (f) a few drops of a HCl solution were added to the mixture (ignore the reaction between CO_2 and water); (g) the temperature were increased?

12. Consider the following reaction at equilibrium in water:

$$PbCl_2\,(s) \rightleftarrows Pb^{2+}\,(aq) + 2\,Cl^{-}(aq)$$

Will $PbCl_2$ dissolve or precipitate, or will nothing occur after each of the following changes?

(a) More $PbCl_2$ (s) is added.
(b) More $PbCl_2$ (s) is added.
(c) Solid NaCl is added.
(d) Solid KNO_3 is added.

EQUILIBRIA IN AQUEOUS SOLUTIONS

13. Calculate the percent dissociation of hydrofluoric acid at the following concentrations: (a) 1.00 M, (b) 0.60 M, (c) 0.080 M, (d) 0.0046 M. Comment on the trends.

ANSWER: 2.68%; 3.46 %; 9.50 %; 39.6 %

14. A 0.040 M solution of a monoprotic acid in water is 14 percent ionized. Calculate the ionization constant of the acid.

ANSWER: 7.84×10^{-4}

15. In a 0.08 M NH_3 solution, what percent of the NH_3 is present as NH_4^+?

ANSWER: 1.5×10^{-3} %

CHAPTER 5
INTRODUCTION TO VOLUMETRIC ANALYSIS

And it's hard, and it's hard, aim's it hard, good Lord
Woody Guthrie

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.

5.1. 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:

$$M_e = f_e \times M, \qquad 5.1$$

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:

$$\text{For acids: } f_e = \frac{1}{a\ number\ of\ hydrogen\ atoms\ substituted\ in\ amolecule} \qquad 5.2$$

For monoprotic acids (HCl, HNO_3 and others) the equivalent factor is equal to one ($f_e = 1$); for diprotic acids (H_2SO_4, H_2CO_3 and others) the equivalent factor takes the values 1 and ½ (f_e = 1 and ½); for triprotic acids (H_3PO_4) the equivalent factor takes the values 1, ½ and 1/3 (f_e = 1, ½ and 1/3)

$$\text{For bases: } f_e = \frac{1}{a\ number\ of\ OH-groups\ substituted\ \ in\ a\ molecule} \qquad 5.3$$

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 ($Ca(OH)_2$, $Ba(OH)_2$ and others) the equivalent factor takes the values 1 and ½ (f_e = 1 and ½); for the bases with three hydroxyl groups ($Al(OH)_3$ and others) the equivalent factor takes the values 1, ½ and 1/3 (f_e = 1, ½ and 1/3).

$$\text{For salts: } f_e = \frac{1}{a\ number\ of\ metall\ atoms \times oxidation\ number} \qquad 5.4$$

For example: f_e (NaCl) = 1,
f_e (Na_2SO_4) = ½,
f_e ($Ca_3(PO_4)_2$) = 1/6.

$$\text{For elements: } f_e = \frac{1}{oxidation\ \ number} \qquad 5.5$$

For example: the equivalent factor of nitrogen in nitrogen (I) oxide N_2O is equal to ½ (f_e = ½)

REMEMBER!!!

M_e (H) = 1 g/mol

M_e (O) = 8 g/mol

M_e (H_2O) = 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 **a A + b B = c C + d D**

the amounts of equivalents for reactants and products are identical:

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

where υ_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:

$$\upsilon_e = \frac{m}{M_e}, \qquad 5.6$$

where m — is the mass of a substance, g.

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

5.2. 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 (ω). The percent by mass (also called the percent by weight or the weight percent) is defined as

$$percent\ by\ mass\ of\ solution = (\omega) = \frac{mass\ of\ solute}{mass\ of\ solute + mass\ of\ solvent} \times 100\% \qquad 5.7$$

or

$$percent\ by\ mass\ of\ solution = (\omega) = \frac{mass\ of\ solute}{mass\ of\ solution} \times 100\,\% \qquad 5.8$$

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

Mole Fraction (χ). The mole fraction of a component in a solution, say, component A, is written χ_A and is defined as

$$mole\ fraction\ of\ component\ A = \chi(A) = \frac{moles\ of\ A}{sum\ of\ moles\ of\ all\ components} \qquad 5.9$$

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

Molality (C

Molality (C_m). Molality is a number of moles of a solute dissolved in 1 kg (1000 g) of solvent—that is,

$$molality = C_m = \frac{moles\ of\ solute}{mass\ of\ solvent\ (kg)} \qquad 5.10$$

For example, to prepare a 1 mol/kg sodium sulfate (Na_2SO_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,

$$molarity = C_M = \frac{moles\ of\ solute}{liters\ of\ solution} \qquad 5.11$$

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,

$$normality = C_N = \frac{equivalent\ moles\ of\ solute}{liters\ of\ solution} \qquad 5.12$$

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,

$$titer = T = \frac{mass\ of\ solute}{milliliters\ of\ solution} \qquad 5.13$$

Thus, titer has the units of g/mℓ.

Concentration units are interconvertible

$$molarity = \frac{1000 \times T}{molar\ mass\ of\ solute} \qquad 5.14$$

$$molarity = \frac{10 \times density\ of\ solution \times percent\ by\ mass(\%)}{molar\ mass\ of\ solute} \qquad 5.15$$

$$percent\ by\ mass\ of\ solute\ (\%) = \frac{molarity \times molar\ mass\ of\ solute}{10 \times density\ of\ solution} \qquad 5.16$$

$$molarity = C_N \times f_e \qquad 5.17$$

$$normality = \frac{C_M}{f_e} \qquad 5.18$$

$$normality = \frac{1000 \times T}{equivalent\ molar\ mass\ of\ solute} \qquad 5.19$$

5.3. Laboratory Work

PREPARING OF DILUTE SOLUTIONS FROM CONCENTRATED SOLUTIONS

We frequently find it convenient to prepare a less concentrated solution from a more concentrated one. The procedure for this preparation is called dilution.

In carrying out a dilution process, it is useful to remember that adding more solvent to a given amount of the stock solution changes (decreases) the concentration of the solution without changing the number of moles of a solute present in it; that is,

Moles of solute before dilution = moles of solute after dilution

Since the whole amount of a solute comes from the original stock solution, we can conclude that

$$\underbrace{C_{M\ \text{initial}} V_{\text{initial}}}_{\substack{\text{moles of solute}\\ \text{before dilution}}} = \underbrace{C_{M\ \text{final}} V_{\text{final}}}_{\substack{\text{moles of solute}\\ \text{after dilution}}}$$

EXAMPLE: Suppose that we want to prepare 1 liter of a 0.400 M $KMnO_4$ solution from a solution of 1.00 M $KMnO_4$. This requires the use of 0.400 mole of $KMnO_4$ from a 1.00 M $KMnO_4$ solution. Since there is 1.00 mole of $KMnO_4$ in 1 liter, or 1000 mℓ, of a 1.00 M $KMnO_4$ solution, there is 0.400 mole of $KMnO_4$ in 0.400 X 1000 mℓ, or 400 mℓ, of the same solution:

$$\frac{1.00\ \text{mol}}{1000\ \text{m}\ell\ \text{solution}} = \frac{0.400\ \text{mol}}{400\ \text{m}\ell\ \text{solution}}$$

Therefore, we must withdraw 400 mℓ from the 1.00 M $KMnO_4$ solution and dilute it to 1000 mℓ by adding water (in a 1-liter volumetric flask). This method gives us 1 liter of the desired solution of 0.400 M $KMnO_4$. Such concentrated solutions (that is, the 1 M $KMnO_4$ solution) are often stored and used repeatedly over a prolonged period of time. They are stored as the «stock» of a chemical stockroom. For this reason, they are called stock solutions.

***TASK*:** you ought to prepare 100 mℓ of 6 % by mass hydrochloric acid solution using more concentrated stock solution.

Carry out an experiment in the following sequence of operations:

1) Determine a density of a concentrated solution using a set of areometers (densimeters).

2) Find its percent by mass concentration using a reference book.

3) Calculate a volume of a concentrated solution required for a dilute solution's preparing.

4) Prepare a dilute solution and determine its density.

5) Calculate an absolute (D) and a relative (D_o) errors of an experiment:

$$D = \rho\ (exp) - \rho\ (table) \qquad 5.20$$

$$D_o = \frac{|D|}{\rho(table)} \times 100\% \qquad 5.21$$

5.4. Problems

PROBLEM 5.1 The equal volumes of hydrogen gas were released from an acid as a result of it's interaction with 0.69 g of Ca and 1.13 g of Zn. Calculate M_e of zinc when M_e of calcium is 20 g/mol.

Answer:

Write the Equivalent Law for a given chemical reaction:

$$\upsilon_e(Ca) = \upsilon_e(Zn)$$

$$\frac{m(Ca)}{M_e(Ca)} = \frac{m(Zn)}{M_e(Zn)}$$

From this equation we can derive that:

$$M_e\ (Zn) = \frac{m(Zn) \times M_e(Ca)}{m(Ca)} = \frac{1.13 \times 20}{0.69} = 32.7 \text{ g/mol}$$

PROBLEM 5.2 An acid with mass of 9 g was neutralized by 8 g of sodium hydroxide NaOH. Calculate the equivalent molar mass of an acid.

Answer:

Write the Equivalent Law for a given chemical reaction:

$$\upsilon_e(acid) = \upsilon_e(NaOH)$$

$$\frac{m(acid)}{M_e(acid)} = \frac{m(NaOH)}{M_e(NaOH)},$$

From this equation we can derive that:

where $M_e\ (NaOH) = M\ (NaOH) \times f_e = 40$ g/mol

$$M_e\ (acid) = \frac{m(acid) \times M_e(NaOH)}{m(NaOH)} = \frac{9 \times 40}{8} = 45 \text{ g /mol}$$

PROBLEM 5.3 A sample of potassium chloride (KC1) of 0.892 g is dissolved in 54.6 g of water. What is the percent by mass of KC1 in a prepared solution?

ANSWER:

$$percent\ by\ mass\ of\ KCl = \frac{mass\ of\ solute}{mass\ of\ solution} \times 100\%$$

$$percent\ by\ mass\ of\ KCl = \frac{0.892g}{0.892g + 54.6g} \times 100\% = 1.61\%$$

PROBLEM 5.4 A chemist prepared a solution by adding 200.4 g of pure ethanol (C_2H_5OH) to 143.9 g of water. Calculate the mole fractions of these two components. The molar masses of ethanol and water are 46.02 g and 18.02 g, respectively.

ANSWER:

The number of moles of C_2H_5OH and H_2O present are

$$\text{moles of } C_2H_5OH = 200.4\text{ g} \times \frac{1\text{ mol } C_2H_5OH}{46.02\text{ g}} = 4.355\text{ mol } C_2H_5OH$$

$$\text{moles of } H_2O = 143.9\text{ g} \times \frac{1\text{ mol } H_2O}{18.02\text{ g}} = 7.986\text{ mol } H_2O$$

In a two-component system made up of A and B molecules, the mole fraction of A is given by

$$\textit{mole fraction of component } A = \chi(A) = \frac{\textit{moles of } A}{\textit{sum of moles of all components}}$$

Using this equation we can write the mole fractions of ethanol and water as

$$\chi(C_2H_5OH) = \frac{4.533\ \text{mol}}{(4.355 + 7.986)\ \text{mol}} = 0.3529$$

$$\chi(H_2O) = \frac{7.986\ \text{mol}}{(4.355 + 7.986)\ \text{mol}} = 0.6471$$

By definition, the sum of the mole fractions of all components in a solution must be 1.

Thus; $\chi(H_2O) + \chi(C_2H_5OH) = 0.3529 + 0.6471 = 1.0000$

PROBLEM 5.5 Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water. The molar mass of sulfuric acid is 98.08 g/mol

ANSWER

From the known molar mass of sulfuric acid, we can calculate the molality in two steps. First we need to find the number of grams of sulfuric acid dissolved in 1000 g (1 kg) of water. Next we must convert the number of grams into the number of moles. Combining these two steps we write

$$\textit{molality} = C_m = \frac{\textit{moles of solute}}{\textit{mass of solvent } (kg)}$$

$$C_m = \frac{24.4\text{ g } H_2SO_4}{198\text{ g } H_2O} \times \frac{1000\text{ g } H_2O}{1\text{ kg } H_2O} \times \frac{1\text{ mol } H_2SO_4}{98.08\text{ g } H_2SO_4} = 1.26\ \text{mol/kg}$$

5.5. Exercises for the self – control

NUMERICAL EXERCISES

1. Calculate f_e and M_e for H_3PO_4 in the following reactions:

$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$

$H_3PO_4 + 2\ NaOH = Na_2HPO_4 + 2\ H_2O$

$H_3PO_4 + 3\ NaOH = Na_3PO_4 + 3\ H_2O$

2. Calculate f_e and M_e for $Fe(OH)_3$ in the following reactions:
$Fe(OH)_3 + HCl = Fe(OH)_2Cl + H_2O$
$Fe(OH)_3 + 2\ HCl = FeOHCl_2 + 2\ H_2O$
$Fe(OH)_3 + 3\ HCl = FeCl_3 + 3\ H_2O$

3. Calculate zink equivalent molar mass if 1.168 g of its displace 438×10^{-6} ℓ under 17°C and 98.64 kPa.

ANSWER: 32.62 g/mol.

4. The oxygen content in a metal oxide is 28.57 % by mass. The fluorine content in its fluoride is 48.72 % by mass. Compute an equivalent molar mass of the fluorine.

ANSWER: 19 g/mol.

5. Interaction of 5.95 g of a substance and 2.75 g of hydrochloric acid gives 4.45 g of salt. Calculate the equivalent molar mass of the given substance and the obtained salt.

ANSWER: 36.5 g/mol, 79 g/mol, 59 g/mol.

6. The reduction of 2.32 g of a tungsten oxide runs with 0.54 g of water elimination. Calculate the equivalent molar mass of the given oxide.

ANSWER: 38.7 g/mol.

7. 0.15 g of metal displaces 0.367 g of nickel from a nickel salt or 140 mℓ of hydrogen gas (normal conditions) from an acid solution. Calculate the equivalent molar masses of a metal and nickel.

ANSWER: 12 g/mol, 29.4 g/mol.

8. Calculate the percent by mass of the solute in each of the following aqueous solutions:
a) 5.5 g of NaBr in 78.2 g of solution;
b) 31 g of KCl in 152 g of water.

ANSWER: a) 7%; b) 17%.

9. A solution is prepared by mixing 62.6 mℓ of benzene (C_6H_6) with 80.3 mℓ of toluene (C_7H_8). Calculate the mole fractions of these two components. The densities are: benzene, 0.879 g/cm^3; and toluene, 0.867 g/cm^3.

ANSWER: 48%; 52%.

10. Calculate the molality of each of the following solutions:
a) 14.3 g of sucrose ($C_{12}H_{22}O_{11}$) in 676 g of water;
b) 7.2 mole of ethylene glycol ($C_2H_6O_2$) in 3546 g of water.

ANSWER: a) 0.08 mol/kg; b) 0.03 mol/kg

11. Calculate the molalities of each of the following aqueous solutions:
a) 1.22 M NaCl solution (density of solution = 1.12 g/mℓ);
b) 0.87 M NaOH solution (density of solution = 1.19 g/mℓ);
c) 5.24 M $NaHCO_3$ solution (density of solution = 1.19 g/mℓ).

ANSWER: a) 1.5M; b) 1.1M; c) 13.1M.

12. The concentrated sulfuric acid we use in the laboratory is 98 percent H_2SO_4 by mass. Calculate the molality and molarity of the acid solution. The density of the solution is 0.982 g/mℓ.

ANSWER: 5.0×10^2 mol/kg; 18.3 M.

13. Calculate the mole fractions, molality and molarity of NH_3 for the solution of 30 g of NH_3 in 70 g of water. His density of the solution is 0.982 g/mℓ.

ANSWER: 25.2 mol/kg; 17.5M; 31.2%.

14. The density of an aqueous solution containing 10 percent of ethanol (C_2H_5OH) by mass is 0.984 g/mℓ.

a) Calculate the molality of this solution.
b) Calculate the molarity of this solution.
c) What volume of the solution would contain 0.125 mole of ethanol?

ANSWER: a) 2.41 mol/kg; b) 2.13M; c) 0.059ℓ.

15. It is estimated that 1 mℓ of seawater contains about 4×10^{-12} g of gold. The total volume of ocean water is 1.5×10^{21} ℓ. Calculate the total amount of gold present in seawater. With so much gold out there, why hasn't someone become rich by mining gold from the ocean?

ANSWER: 6.0$\times10^9$ kg

CHAPTER 6

6.1. FUNDAMENTALS OF VOLUMETRIC ANALYSIS

After studying this section, you will

- understand the principles of volumetric analysis;
- understand the classification of titration methods and types of solutions applied for titration;
- be able to perform static treatment of experimental data;
- be able to perform typical calculations involving the rules of significant figures.

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 administrated 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-hydroscopic 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 to be:

- practically irreversible ($K > 10^8$);
- fast (equivalent oint ought to be reached within several minutes);
- no by products ou ght 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.

6.2. Static treatment of experimental data

Introduction: Two important, though often neglected, parts of analysis are error analysis and correct results reporting. Results should always be reported along with some estimation of the errors involved. The best way to do this is to report the most likely value along with a **confidence interval**. A confidence interval gives the range of values thought to contain the «true» value. The statistical treatment of data involves basing the error estimation on firm theoretical principles. This laboratory exercise on treatment of data should help you understand and apply these principles.

Classification of errors

Two basic classes of errors occur in measurements; systematic and random. Systematic errors have a determinate origin. Determinate means that there is a cause for an error, and that an error itself can be identifid by performing an auxiliary measurement. Though possible, it is more often the case that determinate errors are not recognized until it is too late to make an auxiliary measurement. Systematic errors produce measurements that are either consistently high or low, relative to the «true» value. These errors are always in the same direction and are often of the same magnitude. An example of this is a contaminant on a balance pan that always causes measured weights to be too high. Random errors are indeterminate in origin and cause a measured quantity to fluctuate around the central value. Indeterminate means that one is not able to identify an error by an auxiliary measurement, just as one cannot know the outcome of flipping a (unbiased) coin prior to the actual event. Random errors vary in direction and magnitude from measurement to measurement.

The size of an error is often independent of measurement magnitude. These types of errors are called constant errors. With constant errors, there is no relationship between, or correlation, measurement and error magnitude. A constant error becomes less significant as the magnitude of measurement increases. On the other hand, an error may increase with the magnitude of measurement. In this case errors are called proportional errors. In this case increasing the sample size does not diminish the significance of an error.

Central tendency. When reporting central tendency for a series of measurements, we often use the mean or average value. The symbol for the mean is a variable with a line over the top. The formula for the mean, for example of x, is

$$\bar{x} = \frac{1}{N}\sum_{i-1}^{N} x_i \qquad 6.1$$

For example, the average value of KOH mass is:

$$\overline{m}(KOH) = \frac{m_1 + m_2 + m_3}{3} \qquad 6.2$$

Measurement variance

The formula for measurement variance, s^2, is

$$S^2 = \frac{d_1^2 + d_2^2 + d_3^2}{n \times (n-1)}, \qquad 6.3$$

where d — is a deviation from the average value. In our experiment:

$$\mathrm{d}_1 = \mathrm{m}_1 - \overline{m}(KOH)$$

$$\mathrm{d}_2 = \mathrm{m}_2 - \overline{m}(KOH)$$

$$\mathrm{d}_3 = \mathrm{m}_3 - \overline{m}(KOH),$$

where n — a number of parallel experiments.

Measurement standard deviation

A measurement standard deviation is more often used to indicate precision or probable error. The greater the standard deviation is, the less precise the data are. A measurement standard deviation is simply related to the measurement variance through

$$S = \sqrt{S^2} \qquad 6.4$$

where s^2 — is the measurement variance.

Confidence intervals

Clearly, the greater the «true» standard deviation is, the greater the range over which 95 % of measurements will be. For example, if the «true» mean is 25.000 g, and the «true» standard deviation is 0.5102 g, then 95 % of measurements should be within 25±1 g. To put it in another way, one is 95% sure that a single measurement will be within the 25±1 g range. For this case, ±1 g is a confidence interval, or range, at a 95 % confidence level. If, on the other hand, the «true» standard deviation was 0.5102 g, then the one would state that they were 95 % sure that a single measurement would be in the range of 25.0±0.1 g. The smaller standard deviation results in a smaller confidence interval. In general, the fewer measurements are, the less the confidence level that can be assigned to a particular interval is. Similarly, fewer measurements also mean larger confidence intervals for a given confidence level.

The formula for the confidence interval of a definite number is:

$$\varepsilon_\alpha = t \times s, \qquad 6.5$$

where t — is a Student's-*t* number which indicates probabilities that the mean found with the help of a finite number of measurements will differ from the «true» mean by a given amount. (where *t* is the Student's-*t* number).

One can look up *t* in a table 6.1 for a given confidence and a number of degrees-of-freedom (n-1).

Table 6.1 — 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
infinite	0.674	1.645	1.960	2.576

The result of the experimental work must be given in the following way:

$$x = \overline{X} \pm \varepsilon_{\alpha} \qquad 6.6$$

In the experiment for KOH mass determination the answer ought to be represented as follows:

$$m\,(KOH) = \overline{m}(KOH) \pm \varepsilon_{\alpha} \qquad 6.7$$

6.3. The Rules of Significant figures

In one number there may be significant and insignificant figures. All figures from 1 to 9 are significant. So in number **517** there are **3** significant figures.

Zeroes before these figures are insignificant figures.

In number **0.00517** there are 3 significant figures.

Zeroes between and after these figures are also significant:

In number **0.5070** there are **4** significant figures.

In multiplication and division a number of significant figures in the result is determined by the original number that has the smallest quantity of significant figures.

6.4. 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 direct, back and displacement titration methods.

CHAPTER 7
ACID – BASE TITRATION

After studying this section, you will
- 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.

7.1. The theoretical bases for acid-base titration

Acid-base titration is one of the titration methods based on a neutralization reaction: $\mathbf{H^+ + OH^- \rightarrow H_2O}$.

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.

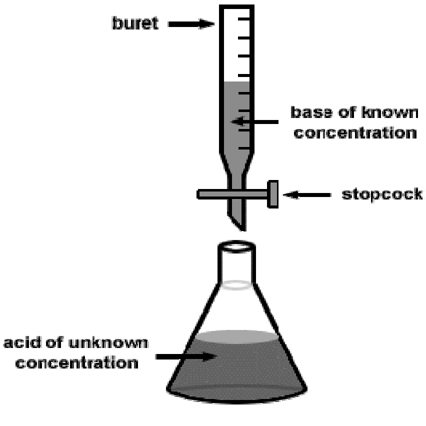


Figure 7.1 — A titration setup

Primary standards applied in acid-base titration are the solutions of sodium tetraborate (borax) ($Na_2B_4O_7 \times 10\ H_2O$), oxalic acid ($H_2C_2O_4 \times 2\ H_2O$) and succinic acid ($H_2C_4H_4O_4$). **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:

$$\underset{\text{colourless}}{\text{phenolphthalein-H}} + H_2O \rightleftharpoons \underset{\text{red}}{\text{phenolphthalein}^-} + H_3O^+$$

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

Table 7.1 — Some common acid-base indicators

Color Indicator	**In acid**	**In base**	**pH rage***	**pK_{in}**
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
Bromothymol 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 (Figure 7.2).

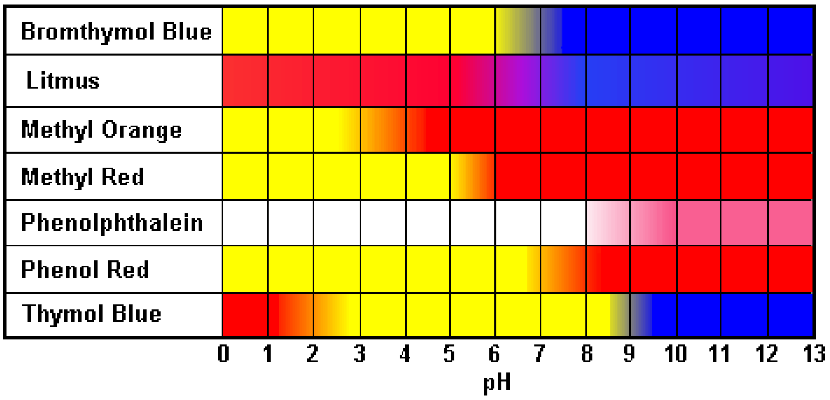


Figure 7.2 — The change of the color in the deferent media

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:

$$\mathbf{pH = pK_{in} \pm 1} \qquad 7.1$$

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

EXAMPLE 7.1 The pKin value for phenolphthalein is 9.4. Can it be used to monitor the titration of CH_3COOH versus NaOH?

Answer. From the equation (7.1), we have pH = 9.4 ± 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 (figure 7.3).

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.

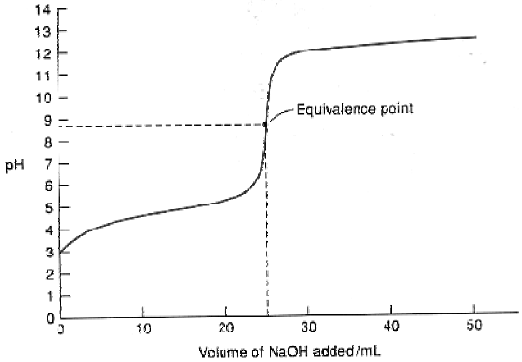


Figure 7.3 — The pH profile of a weak acid-strong base titration

EXAMPLE 7.2 The titration of a strong acid with a strong base produces the following pH profile (fig. 7.4). 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.

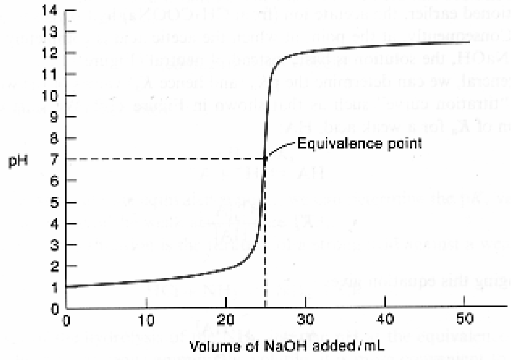


Figure 7.4 — The pH profile of a strong acid-strong base titration

EXAMPLE 7.3 The pH profile of a weak base-strong acid titration is given in figure 7.5. 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. (figure 7.5).

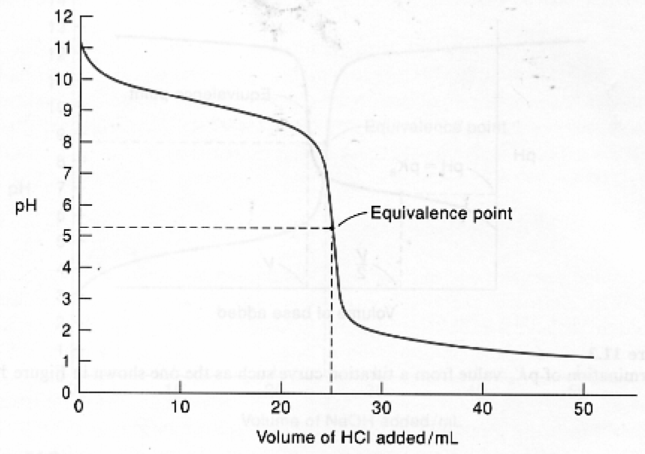


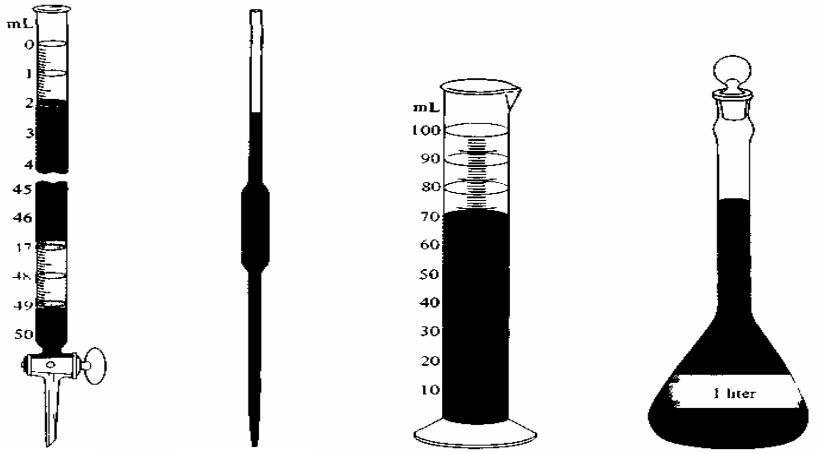
Figure 7.5 — The pH profile of a weak base -strong acid titration

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 end-point of titration.

7.2. Laboratory work

Acid-Base Titration

You will use the following chemical instruments: burettes, pipettes, finals, volumetric flasks, flasks for titration (Figure 7.6).



Buret **Pipette** **Graduated cylinder** **Volumetric flask**

Figure 7.6 — Some common measuring devices found in a chemistry laboratory

7.2.1. Test 1: Standardization of hydrochloric solution against borax primary standard

Reagents: sodium tetraborate (borax) standard solution, working solutions of hydrochloric acid and potassium hydroxide, methyl orange and phenolphthalem solutions, distilled water.

Standardization of hydrochloric solution is fulfilled by means its titration against borax standard solution. This procedure is based on the following chemical reaction: $Na_2B_4O_7 + 2\ HCl + 5\ H_2O \rightarrow 2\ NaCl + 4\ H_3BO_3$

At the end point of the titration the medium is a weak acid because a weak boric acid is prepared as a result of a given reaction. **Methyl orange** is a valid indicator to fix the endpoint of a particular titration since it changes its colour in the acid medium (pH range is 3.1 – 4.4)

Carry out the experiment in the following sequence of operations:

1) Take an analytical pipette and pour 10 mℓ of borax solution into every flask for titration.

2) Add two drops of methyl orange into each flask.

3) Pour hydrochloric solution into the buret up to the zero mark.

4) Titrate borax solution against hydrochloric acid up to the endpoint when yellow color of an initial solution turns red after adding one drop of hydrochloric acid.

5) Repeat such titration three times; the obtained results must not differ greatly from each other.

6) Fill in the table 7.2 given below with the obtained data.

Table 7.2 — The results of borax solution titration against hydrochloric acid

№	Volume of $Na_2B_4O_7$, mℓ	Volume of HCl, mℓ	C_N (HCl), mol/ℓ	T (HCl), g/mℓ
1	10.0			
2	10.0			
3	10.0			

7) Calculate the average volume of HCl solutions:

$$V_{av}(HCl) = \frac{V_1 + V_2 + V_3}{3} \qquad 7.2$$

8) Calculate normality (C_N) and titer (T) of the HCl working solution:

$$C_N(HCl) \times V(HCl) = C_N(Na_2B_4O_7) \times V(Na_2B_4O_7)$$

$$C_N(HCl) = \frac{C_N(Na_2B_4O_7) \times V(Na_2B_4O_7)}{V_{av}(HCl)} \qquad 7.3$$

$$T(HCl) = \frac{C_N(HCl) \times M_e(HCl)}{1000} \qquad 7.4$$

9) Fill in the table with the results of the experiment (table 7.2).

7.2.2. TEST 2: DETERMINATION OF POTASSIUM HYDROXIDE (KOH) MASS IN A TEST SOLUTION

Calculate the mass of KOH in a test solution by its titration against a working hydrogen chloride (HCl) solution. This procedure is based on the following chemical reaction: $KOH + HCl \rightarrow KCl + H_2O$

The acid-base indicator is phenolphthalein.

Carry out Do an experiment in the following sequence of operations:

1) Take a volumetric flask with a KOH solution of the unknown concentration.

2) Take a pipette and pour 10 mℓ of a KOH solution into every flask for titration.

3) Add two drops of phenolphthalein into each flask.

4) Pour hydrochloric acid solution into a buret up to the zero mark.

5) Titrate KOH solution against hydrochloric acid up to the endpoint when reddish pink color of an initial solution turns colorless after adding one drop of hydrochloric acid.

6) Repeat such titration three times; the results must not differ greatly from each other.

7) Fill in the table below with the obtained data (table 7.3).

Table 7.3 — The results of KOH solution titration against hydrochloric acid

№	Volume of KOH, mℓ	Volume of HCl, mℓ	C_N KOH, mol/ℓ	T (KOH), g/mℓ	m (KOH), g
1	10.0				
2	10.0				
3	10.0				

8) Calculate Normality (C_N) and titre (T) of the KOH solution according to the equations:

$$C_N(HCl)\times V(HCl)=C_N(KOH)\times V(KOH)$$

$$C_N(KOH)=\frac{C_N(HCl)\times V(HCl)}{V(KOH)} \qquad 7.5$$

$$T(KOH)=\frac{C_N(KOH)\times M_e(KOH)}{1000} \qquad 7.6$$

9) Calculate the mass of KOH, using the following formula:

$$m\ (KOH) = T\ (KOH)\times V\ (KOH), \qquad 7.7$$

where V (KOH) = 50 mℓ

10) Make a statistic treatment of the experimental data.

7.3. Problems

PROBLEM 7.1 How many milliliters (mℓ) of a 0.610 M NaOH solution are needed to completely neutralize 20.0 mℓ of a 0.245 M H_2SO_4 solution?

Answer:

2 NaOH (aq) + H_2SO_4 (aq) = Na_2SO_4 (aq) + 2 H_2O (ℓ)

Write the Equivalent Law:

$\upsilon_e(NaOH) = \upsilon_e(H_2SO_4)$

$$molality = C_m = \frac{moles\ of\ solute}{mass\ of\ solvent\ (kg)}$$

Since $C_N\ (NaOH)\times V\ (NaOH) = C_N\ (H_2SO_4)\times V\ (H_2SO_4)$

$$V(NaOH)=\frac{V(H_2SO_4)\times C_N(H_2SO_4)}{C_N(NaOH)}$$

$$C_N(H_2SO_4)=\frac{C_M(H_2SO_4)}{f_e(H_2SO_4)}$$

$$C_N(H_2SO_4)=0.49\ \text{N}$$

$$V(NaOH)=\frac{20.0\times 0.49}{0.610}=16.07\ \text{mℓ}$$

PROBLEM 7.2 A 12.5 mℓ volume of 0.5000 M H_2SO_4 neutralizes 50.0 mℓ of KOH. What is the normality of a KOH solution?

Answer:

2 KOH (aq) + H_2SO_4 (aq) = K_2SO_4 (aq) + 2 H_2O (ℓ)

Write the Equivalent Law:

$\upsilon_e(KOH) = \upsilon_e(H_2SO_4)$

$$molality = C_m = \frac{moles\ of\ solute}{mass\ of\ solvent\ (kg)}$$

Since $C_N\ (KOH) \times V\ (KOH) = C_N\ (H_2SO_4) \times V\ (H_2SO_4)$

$$V(KOH) = \frac{V(H_2SO_4) \times C_N(H_2SO_4)}{C_N(KOH)}$$

$$C_N(H_2SO_4) = \frac{C_M(H_2SO_4)}{f_e(H_2SO_4)}$$

$$C_N(H_2SO_4) = 1.000\ \mathrm{N}$$

$$C_N(KOH) = \frac{12.5 \times 1.000}{50.0} = 0.250\ \mathrm{N}$$

7.4. Exercises for the self control

DISCUSSION QUESTIONS

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

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

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

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

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

6. Referring to Table 7.1, specify which indicator or indicators you would use for the following titrations: (a) HCOOH versus NaOH, (b) HCl versus KOH, (c) HNO_3 versus NH_3.

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

(a) NaClO (aq) titrated with HCl (aq);

(b) HNO_3 (aq) titrated with KOH (aq);

(c) $NaNO_2$ (aq) titrated with HClO (aq);

(d) NH_4Cl (aq) titrated with NaOH (aq).

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

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

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

NUMERICAL EXERCISES

1. Calculate the volume in mℓ of a 1.420 M NaOH solution required to titrate the following solution:

a) 25.00 mℓ of a 2.430 M HC1 solution;

b) 25.00 mℓ of a. 4.500 M H_2SO_4 solution;

c) 25.00 mℓ of a 1.500 M H_3PO_4 solution.

ANSWER: a) 42.78mℓ; b) 158.45 mℓ; c) 79.22mℓ.

2. Acetic acid (CH_3COOH) is an important ingredient of vinegar. A sample of 50.0 mℓ of commercial vinegar is titrated against a 1.00 M NaOH solution. What is the concentration (in C_M) of acetic acid present in the vinegar if 5.75 mℓ of the base were required for the titration?

ANSWER: 0.115M

3. What volume of a 0.50 M KOH solution is needed to completely neutralize each of the following?

a) 10.0 mℓ of a 0.30 M HC1 solution;

b) 10.0 mℓ of a 0.20 M H_2SO_4 solution;

c) 15.0 mℓ of a 0.25 M H_3PO_4 solution.

ANSWER: a) 6 mℓ; b) 8 mℓ; c) 22.5 mℓ.

4. Calculate the mass of H_3PO_4 if its solution was neutralized by 25.00 mℓ of a 0.2 N KOH solution.

ANSWER: 0.163 g

5. A 12.5 mℓ volume of 0.500 M H_2SO_4 neutralizes 50.0 mℓ of NaOH. What is the concentration of the NaOH solution?

ANSWER: 0.25 M

6. A 0.2688 g sample of monoprotic acid neutralizes 16.4 mℓ of a 0.08133 M KOH solution. Calculate the molar mass of the acid.

ANSWER: 201.5 g/mol

7. A 5.00 g of diprotic acid is dissolved in water and made up to exactly 250 mℓ. Calculate the molar mass of the acid if 25.0 mℓ of this solution required to neutralize 11.1 mℓ of 1.00 M KOH. Assume that both protons of the acid are titrated.

ANSWER: 89 g/mol

8. A quantity of 0.560 g of KOH is added to 25.0 mℓ of 1.00 M HCl. Excess Na_2CO_3 is then added to the solution. What mass (in grams) of $CO_2$is formed?

ANSWER: 0.330 g

9. Calculate y, a number of molecules of water in oxalic acid hydrate $H_2C_2O_4 \times yH_2O$, using the following data: 5.00 g of the compound is made up to exactly 250 mℓ solution and 25.0 mℓ of this solution is required for neutralization 15.9 mℓ of a 0.500 M sodium hydroxide solution.

ANSWER: $H_2C_2O_4 \times 2\ H_2O$

CHAPTER 8

REDOX TITRATIONS

After studying this section, you will

- understand the general concepts of oxidation-reduction processes;
- understand the principles of Redox titration;
- be able to perform typical calculations involving oxidation-reduction titrations.

8.1. 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.**

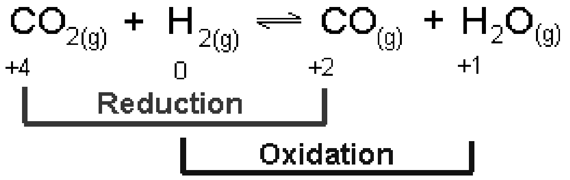
Oxidation-reduction reactions are very much a part of the world around us. They range from combustion of fossil fuels to the action of household bleaching agents. Most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction. Most biochemical processes are 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 %.

This section will deal with some basic definitions, types of oxidation-reduction reactions, and a method for balancing the equations representing these reactions.

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.



$$\underset{+4}{CO_{2(g)}} + \underset{0}{H_{2(g)}} \rightleftharpoons \underset{+2}{CO_{(g)}} + \underset{+1}{H_2O_{(g)}}$$

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 H_2, Br_2, Na, Be, K, O_2, P_4, and 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 Li^+ has an oxidation number of +1; Ba^{2+} ion, +2; 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, MgO and H_2O) is -2, but in hydrogen peroxide (H_2O_2) and peroxide ions (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 LiH, NaH, and 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, 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.

8.1.1. 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_2, C);
- some oxides (CO, NO, N_2O, SO_2);
- some acids (H_2S, H_2SO_3, HCl, HBr, HI);
- salts of these acids;
- most organic compounds.

The most important oxidizing agents are:

- some nonmetals: O_2, O_3, F_2, Cl_2, Br_2, I_2;
- H_2SO_4 (concentrated), HNO_3;
- some salts ($KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, $FeCl_3$, $CuCl_2$).

8.1.2. The Types of Redox Reactions

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

$$\mathbf{2Ca(s) + O_2(g) \rightarrow 2CaO(s)}$$

Red Ox

- **Intramolecular reactions:** oxidizing and reducing agents are atoms in a molecule of one substance. For example: **$2KNO_3$ (s) → $2KNO_2$ (s) + O_2(g).**
- **Disproportionation reactions:** an element is both oxidized and reduced in a process. For example: **2 H_2O_2 (aq) → 2 H_2O (ℓ) + O_2 (g).**

8.1.3. 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:

$$Mn^{+4}O_2^{-2} + 4\ H^{+1}Cl^{-1}(\text{conc.}) \rightarrow Mn^{+2}Cl^{-1}_2 + Cl^0_2 + 2\ H^{+1}_2O^{-2}$$

$$\begin{array}{l|l} Mn^{+4} + 2e^- \rightarrow Mn^{+2} & 1 \\ 2\ Cl^{-1} - 2e^- \rightarrow Cl_2^0 & 1 \end{array}$$

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

$$\mathbf{f_e = 1/z}, \qquad 8.1$$

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:

$$Fe^{2+} + Cr_2O_7^{2-} \rightarrow Fe^{3+} + Cr^{3+}$$

The equations for the two half-reactions are

Oxidation: $Fe^{2+} \rightarrow Fe^{3+}$

Reduction:$Cr_2O_7^{2-} \rightarrow Cr^{3+}$

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 Cr^{3+} by 2 to balance the Cr atoms. Since the reaction takes place in an acidic medium, we add seven H_2O molecules to the right-hand side of the equation to balance the O atoms:

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7\ H_2O$

To balance the H atoms, we add fourteen H^+ ions on the left side:

$14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$

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:

$Fe^{2+} - e^- \rightarrow Fe^{3+}$.

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.

$14\ H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$

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

$6\ Fe^{2+} + 6e^- \rightarrow 6\ Fe^{3+}$

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

$14\ H^+ + Cr_2O_7^{2-} + 6\ Fe^{2+} \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$

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.

PROBLEM 1. Write a balanced ionic equation to represent the oxidation of iodide ion (I^-) by permanganate ion (MnO_4) in basic solution to yield molecular iodine (I_2) and manganese (IV) oxide (MnO_2).

Answer:

Step 1: The basic equation is

$MnO_4^- + I^- \rightarrow MnO_2 + I_2$

The two half-reactions are

Oxidation: $2\ I^- \rightarrow I_2$

Reduction: $MnO_4^- \rightarrow MnO_2$

Step 2: To balance the I atoms in the oxidation half-reaction, we write

$2\ I^- \rightarrow I_2$

In the reduction half-reaction, to balance the O atoms we add four OH^- ions to the right-side and two H_2O molecules on the left-side:

$MnO_4^- + 2\ H_2O \rightarrow MnO_2 + 4\ OH^-$

Step 3. Next, we balance the charges of the two half-reactions as follows:

$2\ I^- - 2e^- \rightarrow I_2$

$MnO_4^- + 2\ H_2O + 3e^- \rightarrow MnO_2 + 4\ OH^-$

To equalize the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2:

$6\ I^- - 6e^- \rightarrow 3\ I_2$

$2\ MnO_4^- + 4\ H_2O + 6e^- \rightarrow 2\ MnO_2 + 8\ OH^-$

Step 4. The two half-reactions are added together to give

$6\ I^- + 2\ MnO_4^- + 4\ H_2O \rightarrow 3\ I_2 + 2\ MnO_2 + 8\ OH^-$

Step 5. A final check shows that the equation is balanced in terms of both atoms and charges.

8.1.4. 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 $KMnO_4$ solution is applied as a titrant;
- **iodometric titration**: solutions of iodine I_2 and sodium thiosulfate $Na_2S_2O_3 \times 5\ H_2O$ are used as titrants;
- **bromatometric titration**: potassium bromate $KBrO_3$ solution is used as a titrant.

8.2. Permanganatometric Titration

Permanganatometric titration is a method of redox titration based on permanganate anion reduction in acid medium according to the following half-reaction: $\mathbf{MnO_4^- + 8\ H^+ + 5e^- \rightarrow Mn^{2+} + 4\ H_2O}$**.**

The reddish violet $KMnO_4$ solution turns colored at the endpoint of titration thus no indicator is required for analyses.

Potassium permanganate exhibits its oxidizing properties in all media: acid, base and neutral as well. The reduction products depend upon a medium:

$$
MnO_4^- \begin{cases} \nearrow + 8\,H^+ + 5e^- \rightarrow Mn^{2+} + 4\,H_2O & \text{acid medium} f_e = 1/5 \\ \rightarrow + e^- \rightarrow MnO_4^{2-} & \text{base medium} f_e = 1/1 \\ \searrow + 2\,H_2O + 3e^- \rightarrow MnO_2 + 4\,OH^- & \text{neutral medium} f_e = 1/3 \end{cases}
$$

In acid medium its oxidizing properties appeared to be the strongest.

In the permanganatometric method aqueous solutions of oxalic acid ($H_2C_2O_4 \times 2H_2O$) or its salts ($Na_2C_2O_4$) are used as primary standards, and $KMnO_4$ solution – as a secondary standard. Dilute sulfuric acid is employed to make acid medium in test solutions.

Permanganatometric titration is widely used for medical and biological investigations. Determination of essential metals, some vitamins, hydrogen peroxide H_2O_2 and metal peroxides are illustrative examples of this type of volumetric analysis.

8.2.1. Laboratory Work

PERMANGANATOMETRIC TITRATION

You will use the following chemical equipments: burets, pipettes, finals, volumetric flasks, flasks for titration.

Test 1: Standardization of $KMnO_4$ solution against a primary standard $H_2C_2O_4 \times 2\,H_2O$

Reagents: oxalic acid standard solutions, $KMnO_4$ working solutions, 1M H_2SO_4 solutions, test solutions of $FeSO_4$.

In order to standardize $KMnO_4$ solution it is titrated against a standard solution of oxalic acid in a sulfuric acid medium:

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 \rightarrow 2\,MnSO_4 + K_2SO_4 + 10\,CO_2 + 8\,H_2O$$

$$
\begin{array}{l|ll}
MnO_4^- + 8\,H^+ + 5e^- \rightarrow Mn^{2+} + 4\,H_2O & 2 & f_e = 1/5 \\
H_2C_2O_4\ - 2e^- \rightarrow 2\,CO_2 + 2\,H^+ & 5 & f_e = 1/2 \\
\hline
\end{array}
$$

$$2\,MnO_4^- + 6\,H^+ + 5\,H_2C_2O_4 \rightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

This redox reaction is catalyzed by Mn^{2+} cations, which are produced in its process. Since Mn^{2+} cations' initial concentration is negligibly small, the rate of a reaction is rather low. In order to accelerate a process titration is fulfilled in hot solutions. For this purpose the solutions containing a mixture of oxalic and sulfuric acids ought to be heated up to the boiling point but never boil in order to avoid oxalic acid decomposition. Addition of a new portion of a titrant ought to be done only after the previous one becomes coloures.

Carry out an experiment in the following sequence of operations:

1) Take a pipette and pour 10 mℓ of oxalic acid solution into each flask for titration.
2) Add approximately 10 mℓ of sulfuric acid into them using a graduated cylinder.

3) Heat a prepared mixture up to the boiling point.

4) Pour $KMnO_4$ solution into the buret up to the zero mark.

5) Titrate oxalic acid against potassium permanganate solution up to the end point when a colorless solution turns reddish violet after one drop of a titrant addition.

6) Repeat a titration for three times; their results must not differ greatly from one another.

7) Fill in the table below with the obtained data (table 8.1).

Table 8.1 — The results of oxalic acid titration against $KMnO_4$ solution

№	Volume of $H_2C_4O_2$, mℓ	Volume of $KMnO_4$, mℓ	C_N $KMnO_4$, mol/ℓ	T ($KMnO_4$), g/mℓ
1	10.0			
2	10.0			
3	10.0			

Test 2: Determination of iron mass in a test solution

Iron (Fe^{2+}) determination is based on the following redox reaction:

$$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 \rightarrow 5\ Fe_2(SO_4)_3 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O$$

$$\begin{array}{l|l} MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O & 2 \\ 2\ Fe^{2+} - 2\ e^- \rightarrow 2\ Fe^{3+} & 5 \\ \hline \end{array}$$

$$2\ MnO_4^- + 10\ Fe^{2+} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ Fe^{3+} + 8\ H_2O$$

Carry out an experiment in the following sequence of operations:

1) Take a volumetric flask with $FeSO_4$ solution of an unknown concentration.

2) Add distilled water into a volumetric flask up to the round mark.

3) Take an analytical pipette and pour 10 mℓ of $FeSO_4$ solution into each flask for titration; treat the solutions with approximately 10 mℓ of sulfuric acid.

4) Pour potassium permanganate solution into the buret up to the zero mark.

5) Titrate $FeSO_4$ solution against $KMnO_4$ up to the endpoint when colourless $FeSO_4$ solution turns reddish violet after one drop of a titrant addition.

6) Repeat titration for three times; their results must not differ greatly from one or another.

7) Fill in the table below with the obtained data (table 8.2).

Table 8.2 — Iron (Fe^{2+}) mass determination in a test solution

№	V (Fe^{2+}), mℓ	V ($KMnO_4$), mℓ	C_N (Fe^{2+}), mol /ℓ	T (Fe^{2+}), g/mℓ	m (Fe^{2+}), g
1	10.0				
2	10.0				
3	10.0				

8) Calculate normality and a titer of the given solution and a mass of iron contained in it.

9) Fulfill the statistical treatment of the experimental data.

8.3 Iodometric titration

Iodometric titration is a method of redox titration based on a reversible reaction: $\mathbf{I_2 + 2\,e^- \rightleftarrows 2\,I^-}$

Ox   Red

It can be performed to determine the concentrations of a wide variety of redox-capable solutes, with only a few limitations. This method permits to analyze oxidizing and reducing agents' solutions, containing organic and inorganic substances as well.

Starch is applied as an indicator in iodometric titration. The starch forms a blue-black complex with iodine, which is rendered colorless when all the iodine has been removed.

The scheme of iodometric analysis of oxidizing agents' solutions (displacement titration)

When the excess of KI is added to the test solution of an oxidizing agent it gives rise for the following reaction: $\mathbf{Ox + 2\,I^- \leftrightarrow Red + I_2}$.

The released I_2 is titrated against $Na_2S_2O_3 \times 5H_2O$ up to the endpoint, which is determined with the help of starch:

$$I_2 + 2\,Na_2S_2O_3 \rightarrow 2\,NaI + Na_2S_4O_6$$

In the endpoint the blue color of the iodine-starch complex turns colourless after one drop of sodium thiosulfate added from a buret. In order not to lose free iodine, starch ought to be added to a flask when a solution's color becomes straw yellow.

$Na_2S_2O_3 \times 5H_2O$ solution is a secondary standard, thus it ought to be standardized by titration against $K_2Cr_2O_7$ solution, which is a primary standard in this method.

The scheme of iodometric analysis of reducing agents' solutions (direct titration)

A solution of a reducing agent is titrated against a standard solution of free iodine: $\mathbf{Red + I_2 \leftrightarrow Ox + 2\,I^-}$.

The endpoint is detected by starch: colourless solution turns blue due to starch-iodine complex formation.

8.3.1. Laboratory Work

IODOMETRIC TITRATION

Test 1: Standardization of $Na_2S_2O_3 \times 5H_2O$ solution against primary standard $K_2Cr_2O_7$

Standardization of $Na_2S_2O_3 \times 5H_2O$ solution against the primary titrant $K_2Cr_2O_7$ is based on the following reactions:

$$\begin{array}{l|l} K_2Cr_2O_7 + 6\ KI + 7\ H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3\ I_2 + 7\ H_2O & \\ \qquad Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O & 1 \\ \qquad 2\ I^- - 2\ e^- \rightarrow I_2 & 3 \\ \hline \end{array}$$

$Cr_2O_7^{2-} + 6\ I^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 3\ I_2 + 7\ H_2O$

The released iodine is titrated against the secondary standard $Na_2S_2O_3 \times H_2O$:

$$\begin{array}{l|l} I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6 & \\ \qquad I_2 + 2\ e^- \rightarrow 2\ I^- & 1 \\ \qquad 2\ S_2O_3^{2-} - 2\ e^- \rightarrow S_4O_6^{2-} & 1 \\ \hline \end{array}$$

$I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

Carry out an experiment in the following sequence of operations:

1) Take a pipette and pour 10 mℓ of $K_2Cr_2O_7$ standard solution into each flask for titration; then add approximately 10 mℓ of sulfuric acid into them, using a graduated cylinder.

2) Add an excess of potassium iodide crystals into each flask and close them with slides. Wait 3-5 minutes until the reaction is over.

3) Pour $Na_2S_2O_3 \times 5H_2O$ solution into a buret up to the zero mark.

4) Titrate the released iodine against $Na_2S_2O_3 \times 5H_2O$ solution. In order not to lose free iodine, starch must be added to a flask when a solution's color becomes straw yellow. In the endpoint blue color of the iodine-starch complex turns colorless after one drop of sodium thiosulfate added from a buret.

5) Repeat a titration for three times; their results must not differ greatly from each other.

6) Fill in the table below with the obtained data (table 8.3).

Table 8.3 — The results of iodine titration against $Na_2S_2O_3 \cdot 5H_2O$ solution

№	V ($K_2Cr_2O_7$), mℓ	V ($Na_2S_2O_3$), mℓ	V average ($Na_2S_2O_3$), mℓ	C_N ($Na_2S_2O_3$), mol/ℓ	T($Na_2S_2O_3$), g/mol
1	10.0				
2	10.0				
3	10.0				

Test 2: Determination of copper mass in a test solution

Determination of copper mass in a test solution is based on the following reactions:

$$\begin{array}{l|l} 2\ CuSO_4 + 4\ KI \rightarrow Cu_2I_2\downarrow + I_2 + 2\ K_2SO_4 & \\ \qquad 2\ I^- - 2\ e^- \rightarrow I_2 & 1 \\ \qquad 2\ Cu^{2+} + 2\ I^- + 2\ e^- \rightarrow Cu_2I_2 & 1 \\ \hline \end{array}$$

$$2\ Cu^{2+} + 4\ I^- \rightarrow Cu_2I_2 + I_2$$

The released iodine is titrated against secondary standard $Na_2S_2O_3 \times 5H_2O$:

$$I_2 + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + Na_2S_4O_6$$

Carry out an experiment in the following sequence of operations:

1) Take a volumetric flask with $CuSO_4$ solution of unknown concentration.

2) Add distilled water into a flask up to the round mark.

3) Take a pipette and pour 10 mℓ of $CuSO_4$ solution into every flask for titration and treat them with approximately 10 mℓ of sulfuric acid.

4) Add an excess of potassium iodide crystals into each flask and close them with slides. Wait 3–5 minutes until the reaction is over.

5) Pour $Na_2S_2O_3 \times 5H_2O$ solution into a buret up to the zero mark.

6) Titrate the released iodine against $Na_2S_2O_3 \times 5H_2O$ solution. In order not to lose free iodine, starch must be added to a flask when a solution colour becomes straw yellow. In the endpoint a suspension in the flask will have an ivory colour.

7) Repeat such a titration for three times; the results must not differ greatly from each other.

8) Fill in the table below with the obtained data (table 8.4).

Table 8.4 — Copper (Cu^{2+}) mass determination in a test solution

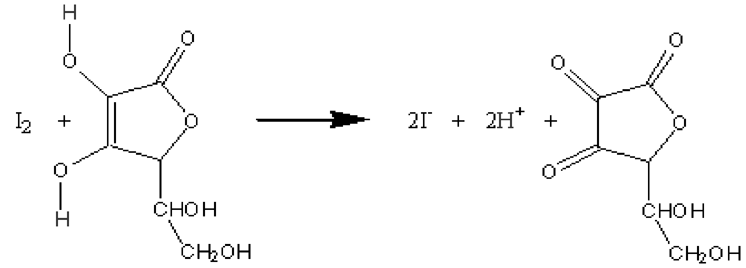
№	V ($CuSO_4$), mℓ	V($Na_2S_2O_3$) mℓ	C_N ($CuSO_4$), mol/ℓ	T (Cu^{2+}), g/mℓ	m (Cu^{2+}), g
1	10.0				
2	10.0				
3	10.0				

9) Calculate normality and a titer of the given solution and a copper mass in it.

10) Do the statistical treatment of experimental data.

Test 3 Determination of normality and titer in ascorbic acid's solution

Ascorbic acid (vitamin C) determination is based on its oxidation by free iodine:



In a simplified way a reaction may be represented as $C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2\ HI$

Vitamin C is the organic reducing agent thus iodine is reduced while vitamin C is oxidized. Again, the endpoint is reached when all of the vitamin C has been oxidized, making this reaction suitable for determining the concentration of vitamin C in a solution

Carry out an experiment in the following sequence of operations:

1) Take a pipette and pour 10 mℓ of ascorbic acid solution into every flask for titration; treat them with 2–3 drops of starch.

2) Pour the standard free iodine solution into the burette up to the zero mark.

3) Titrate the ascorbic acid solution against I_2 solution up to the endpoint when colourless solution in a flask turns blue due to the iodine-starch complex formation.

4) Repeat such a titration for three times; their results must not differ greatly from each other. Write out the obtained data into table 8.5.

Table 8.5 — Determination of normality and titer of ascorbic acid solution

№	V(ascorbic acid), mℓ	V (I_2), mℓ	C_N (ascorbic acid), mℓ	T (ascorbic acid), g/mℓ	m (ascorbic acid), g
1	10.0				
2	10.0				
3	10.0				

5) Calculate normality and a titer in the given solution and an ascorbic acid mass in it.

8.4 Exercises for the self-control

DISCUSSION QUESTIONS

1. Define the following terms: half-reaction, oxidizing agent, reducing agent, redox reaction.

2. Is it possible to have a reaction in which oxidation occurs and reduction does not? Explain.

3. Define an oxidation number. Explain why, except for ionic compounds, oxidation number does not have any physical significance.

4. Arrange the following species in order of increasing oxidation number of the sulfur atom: (a) H_2S, (b) S_8, (c) H_2SO_4, (d) HS^-, (e) SO_2.

5. On the basis of oxidation number considerations, one of the following species would not react with molecular oxygen: NO, N_2O, SO_2, SO_3, P_4O_6. Which one is it? Why?

6. What is a disproportionation reaction? What is the criterion for a substance to be able to undergo a disproportionation reaction?

7. Which of the following are redox reactions?

(a) $NH_3 + HCl \rightarrow NH_4Cl$
(b) $2\ Fe^{2+} + H_2O_2 \rightarrow 2\ Fe^{3+} + OH^-$
(c) $Fe^{2+} + 2\ OH^- \rightarrow Fe\ (OH)_2$
(d) $3\ O_2 \rightarrow 2\ O_3$

8. Complete the following redox reactions and balance them using the half-reaction method:

a) $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow$
b) $K_2SO_3 + KMnO_4 + KOH \rightarrow$
c) $KMnO_4 + KNO_2 + H_2SO_4 \rightarrow$
d) $KMnO_4 + KNO_2 + H_2O \rightarrow$
e) $KMnO_4 + KNO_2 + KOH \rightarrow$
f) H2O2 + KMnO4 + H2SO4 →
g) KMnO4 + H2S + H2SO4 →

NUMERICAL EXERCISES

1. Calculate $KMnO_4$ mass, which is required to prepare 1 ℓ of 0.1 N solution.

Answer: 3.16 g

2. 2.5 g of hydrogen peroxide H_2O_2 sample was diluted by water up to 200 mℓ in a volumetric flask. 5.0 mℓ of a prepared solution was titrated against 20 mℓ of 0.05 N $KMnO_4$ solution in acid medium. Calculate H_2O_2 percent by mass content in its initial sample.

Answer: 27.2%

3. 10.2 mℓ of $NaNO_2$ was titrated against 25.0 mℓ of $KMnO_4$ solution (0.05 N) in an acidic medium. Calculate a mass of $NaNO_2$ in 100 mℓ of a solution.

Answer: 0.423 g

4. 19.5 mℓ of $KMnO_4$ solution was titrated against a solution which contained 0.0244 g of oxalic acid ($H_2C_2O_4 \times 2H_2O$). Calculate normality and a titer of $KMnO_4$ solution.

Answer: 0.01986 N, 0.0627 g/mℓ

5. 0.098 g pure for analyses $K_2Cr_2O_7$ were treated by the excess of KI solution in an acidic medium. The obtained solution was titrated against 25.5 mℓ $Na_2S_2O_3 \times 5H_2O$ solution. Calculate normality and titer of $Na_2S_2O_3 \times 5H_2O$ solution.

Answer: 0.0784 N, 0.01945 g/mℓ

6. Analyses of $Na_2S_2O_3 \times 5H_2O$ solution is based on the following reactions:

$$2\,Cu^{2+} + 4\,I^- = 2\,CuI + I_2$$

$$I_2 + 2\,S_2O_3^{2-} = 2\,I^- + S_4O_6^{2-}$$

0.153 g Cu^{2+} containing sample was titrated against 24.18 mℓ of $Na_2S_2O_3 \times 5H_2O$ solution. Calculate normality of $Na_2S_2O_3 \times 5H_2O$ solution.

Answer: 0.09887 N.

7. 20.0 mℓ of 0.0195 N $Na_2S_2O_3 \times 5H_2O$ solution was titrated against an iodine solution. 20.1 mℓ of the iodine solution was used. Calculate normality and titer of an iodine solution.

Answer: 0.0194 N, 0.00246 g/mℓ

8. 81.5 mℓ of 0.100 N iodine solution was used to titrate 2.5 g of a technique sample of $Na_2S_2O_3 \times 5H_2O$. Calculate the percent by mass content of thiosulfate in a given sample.

Answer: 80.88%

CHAPTER 9
PHYSICAL PROPERTIES OF SOLUTIONS

> *If a solution of iodine in benzene is cooled,*
> *the red color deepens, while if it is warmed,*
> *the color approaches the violet of iodine vapor,*
> *indicating that the solvation decreases*
> *with rising temperature,*
> *as would be expected.*
> *J.H.Hildebrand and C.A. Jenks*

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.

9.1 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, H_2O, concentrated H_2SO_4, N_2H_4) and *nonpolar* (for example, benzene, toluene, hexane).

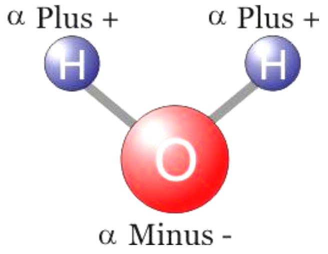
Water is the most important solvent in nature and the most abundant substance in the world. In biosphere the overall volume of water is 1.5×10^9 km^3. Living beings contain 2.3×10^3 km^3 of water. Most of the human body is made up of water (2/3 of the body mass). Different organs and tissues contain 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 ~ 2 ℓ.

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.

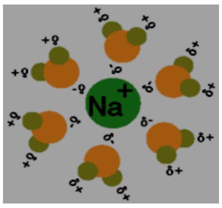
(b) According to the degree of dispersity solutions are:

- 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 ($\Delta_{soln}H$) is an integral magnitude which is calculated as $\Delta_{soln} H = \Delta H_1 + \Delta H_2 + \Delta H_3$.

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 ($\Delta_{soln}H>0$) 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 ($\Delta_{soln}H< 0$) 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 ($\Delta_{soln}H \approx 0$), 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 (figure 9.1).

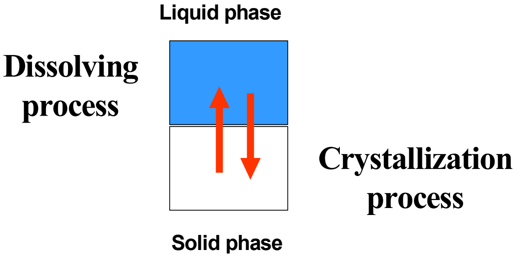


Figure 9.1 — Saturated solutions exist at equilibrium state with the excess of a solute

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.

Solubility. 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_2 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: $A(g) + H_2O(\ell) \rightleftarrows A(aq)$, $\Delta_{soln}H < O$

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 9.1 — Solubility of gases ($\ell/1\ell$ H_2O) at 1 atm

Gas	**Temperature, °C**		
	0	**20**	**100**
N_2	0.0235	0.0154	0.0095
O_2	0.0489	0.0310	0.0172
NH_3	1150	690	95

In accordance with Le Chatelier's Principle increase in pressure shifts equilibrium to the right, thus increasing solubility, while decrease in pressure reduces 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:

$$S = k \times p, \qquad 9.1$$

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_2 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:

$$S = S_o \times e^{-kc}, \qquad 9.2$$

where S — gas solubility in a solution;

S_o — 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 9.2 — Solubility of gases in water and blood plasma at 38°C

Gas	**Solubility, per cent by volume**	
	In water	**In blood plasma**
O_2	0.0263	0.0255
N_2	0.0137	0.0135
CO_2	0.387	0.381

Solubility of liquids in other liquids. Liquids dissolution in water may be represented by the following scheme: $A(\ell) + H_2O \rightleftarrows A(aq)$

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_2SO_4/H_2O, C_2H_5OH/H_2O;

b) partially soluble in each other: for example C_6H_6/H_2O;

c) insoluble in each other (immiscible) for example: Hg/H_2O.

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.** (figure 9.2).

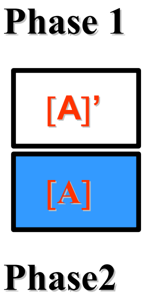


Figure 9.2 — A scheme of two-phase system composed of immiscible liquids, where [A]′ and [A] are concentrations of the third component in both phases

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

$$\frac{[A]'}{[A]} = K \qquad 9.3$$

where K — is distributional Equilibrium constant.

The Nernst-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: $\mathbf{A\,(s) + H_2O \rightleftarrows A\,(aq), \Delta_{sol} H > 0}$

According to Le Chatelier's principle temperature rice 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

$$\mathbf{A_nB_m\,(s) \rightleftarrows nA^{m+}(aq) + mB^{n-}\,(aq).}$$

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}:**

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

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

$$S = \sqrt[n+m]{\frac{K_{sp}}{n^n \times m^m}}, \qquad 9.4$$

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

$$S = \sqrt{K_{sp}} \qquad 9.5$$

For example: $BaSO_4\ (s) \rightleftarrows Ba^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp} = [Ba^{2+}]\times[SO_4^{2-}] = 1.1\times10^{-10}$,

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

$\sqrt{K_{sp}} = \sqrt{1.1\times10^{-10}} = 1.05\times10^{-5}$ M

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 $[A^+] \times [B^-] > K_{sp}$

EXAMPLE 9.1 0.0005 M $AgNO_3$ solution is treated with equal volume of 0.0001 M KBr solution. Does AgBr precipitate from this solution?

K_{sp} (AgBr) = 5.3×10^{-13}.

Answer:

$AgNO_3 + KBr \rightarrow AgBr\downarrow + KNO_3$

If $[Ag^+] \times [Br^-] \geq K_{sp}$ then AgBr precipitate from this solution. Let's calculate the concentration of each ion in a given solution:

$[Ag^+] = 0.0005 / 2 = 0.00025$ M

$[Br^-] = 0.0001 / 2 = 0.00005$ M

$[Ag^+] \times [Br^-] = 0.00025 \times 0.00005 = 1.25\times10^{-8}$

1.25×10^{-8} M $\geq 5.3\times10^{-13}$. Hence AgBr precipitates from this solution.

EXAMPLE 9.2 What is the concentration of Ca^{2+} in a saturated $CaHPO_4$ solution (mol/ℓ and g/ℓ)?

Answer:

K_{sp} ($CaHPO_4$) = 2.7×10^{-7}.

$K_{sp}(CaHPO_4) = [Ca^{2+}] \times [HPO_4^{2-}]$

$[Ca^{2+}] = \sqrt{K_{sp}}$

$[Ca^{2+}] = 5.19\times10^{-4}$ mol/ℓ or $5.19 \times 10^{-4}\times40 = 2.08\times10^{-2}$ g/ℓ.

EXAMPLE 9.3 What is the concentration of Pb^{2+} in a saturated $PbCl_2$ solution?

Answer:

$$C_M(Pb^{2+}) = \sqrt[1+2]{\frac{K_{sp}}{\left[Pb^{2+}\right]\times\left[Cl^{-}\right]^{2}}}$$

$$C_M(Pb^{2+}) = \sqrt[3]{\frac{1.6\times10^{-5}}{1\times2^{2}}} = \sqrt[3]{\frac{1.6\times10^{-5}}{4}} = 0.158\ \text{M}$$

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 $Ca_5(PO_4)_3OH$ is the mineral component of bones (figure 9.3).

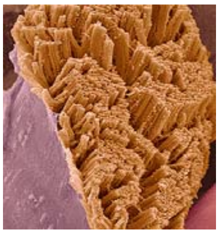


Figure 9.3 — Hydroxy apatite $Ca_5(PO_4)_3OH$ is the mineral component of bones

In blood at pH 7.4 calcium cations Ca^{2+} and anions of phosphoric acid HPO_4^{2-} and $H_2PO_4^{-}$ are present. The amounts of both anions are approximately equal but $CaHPO_4$ ($K_{sp}=2.7\times10^{-7}$) is less soluble than $Ca(H_2PO_4)_2$.($K_{sp}=1\times10^{-3}$) thus formation of $CaHPO_4$ is proved to be the first step in bone tissue generation:

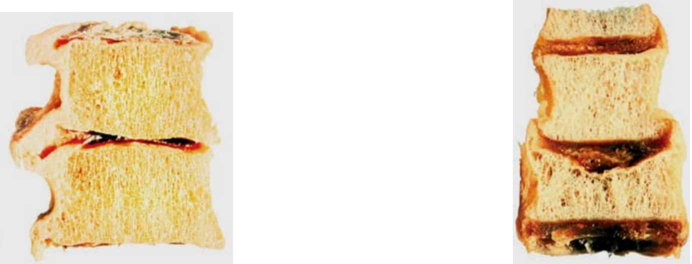
$$Ca^{2+} + HPO_4^{2-} \rightleftarrows CaHPO_4$$

In the next steps the following salts are produced

$$3CaHPO_4 + Ca^{2+} + 2OH^{-} \rightleftarrows Ca_4H(PO_4)_3 + 2H_2O$$

$$Ca_4H(PO_4)_3 + Ca^{2+} + 2OH^{-} \rightleftarrows Ca_5(PO_4)_3OH + H_2O$$

Solubility of hydroxy apatite is very low ($K_{sp} = 1.0\times10^{-58}$) thus bones are extremely stable. The excess of Ca^{2+} shifts equilibrium to the right, which results in bones calcification. Ca^{2+} deficiency shifts equilibrium to the left which results in destruction of bones. Children suffer from rachitis, in adults osteoporosis develops (figure 9.4).



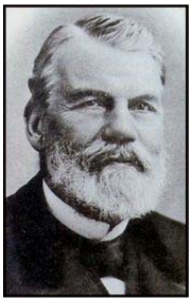
(a) **(b)**

Figure 9.4 — 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.

9.2 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.



Francois-Marie Raoult (1830-1901)

The French chemist Francois-Marie Raoult, a professor of Grenoble University, developed the laws, which describe colligative properties of dilute solutions. His earliest researches were concerned with the phenomena of the voltaic cell, but his name is best known in connection with the work on solutions, to which he devoted the last two decades of his life

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 (figure 9.5) 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.

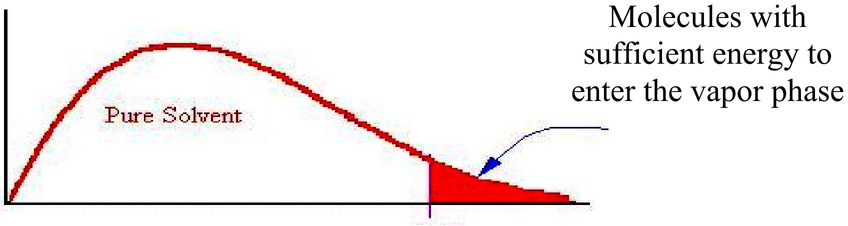


Figure 9.5 — The Boltzman's curve illustrates an energy distribution of molecules in a pure solvent. The area under the curve represents the total number of molecules

Nonvolatile solutes bind solvent molecules thus decreasing a fraction of solvent molecules with energies enough to enter the vapor phase (fig. 9.6). Because of this a solution has a lower vapor pressure than a pure solvent.

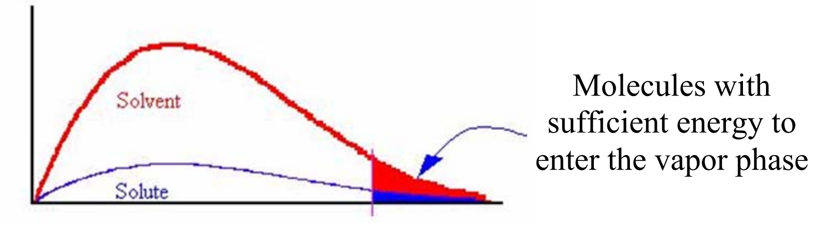


Figure 9.6 — The Boltzman's curve illustrates an energy distribution of molecules in a solution of a nonvolatile solute

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

$$\frac{P_0 - P}{P_0} = \chi\,(A) \qquad 9.6$$

where χ (A) — is a mole fraction of a solute.

For a two-component solution:

$$\frac{P_0 - P}{P_0} = \frac{\vartheta(solute)}{\vartheta(solute) + \vartheta(solvent)}, \qquad 9.7$$

where P_0 — the vapor pressure of a pure solvent.

P — the vapor pressure of a solution.

To make the equation (9.6) available for electrolyte solutions Van't Hoff's factor (i) must be added:

$$\frac{P_0 - P}{P_0} = \frac{i \times \vartheta(solute)}{i \times \vartheta(solute) + \vartheta(solvent)} \qquad 9.8$$

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

$$\alpha = \frac{i - 1}{n - 1} \qquad 9.9$$

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.

$$\mathbf{\Delta T_b = K_b \times C_m}\text{,(for nonelectrolytes),} \qquad 9.10$$

$$\mathbf{\Delta T_b = i \times K_b \times C_m}\text{,(for electrolytes}\mathbf{)} \qquad 9.11$$

where ΔT_b — is boiling-point elevation, which is equal to:

$$\Delta T_b = T_2 - T_1, \qquad 9.12$$

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 non-volatile 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.

$$\Delta \mathbf{T_f} = \boldsymbol{K_f} \times \mathbf{C_m}, \text{(for nonelectrolytes)}, \qquad 9.13$$

$$\Delta \mathbf{T_f} = \mathbf{i} \times \boldsymbol{K_f} \times \mathbf{C_m}, \text{(for electrolytes)}, \qquad 9.14$$

where ΔT_f — is freezing point depression , which is equal to: $\Delta T_f = T_1 - T_2$;

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 ΔT_f equals to 0.56°, for blood plasma of mammals ΔT_f is a bit higher (0.58°).

J.H.Van't Hoff (1852-1911)

J.H. Van't Hoff is a founder of physical chemistry. His most distinguished works were devoted to thermodynamics of chemical processes

EXAMPLE 9.4 Calculate the boiling and freezing points of a solution containing 1.49 g of KCl in 360 mℓ of water.

Answer:

$\Delta \mathbf{T_f} = \mathbf{i} \times \boldsymbol{K_f} \times \mathbf{C_m}$

$\Delta \mathbf{T_b} = \mathbf{i} \times \mathbf{K_b} \times \mathbf{C_m}$

$$C_m(KCl) = \frac{moles\ of\ solute - \nu\,(KCl)}{mass\ of\ solvent\,(kg) - m\,(H_2O)}$$

ν (KCl) = 1.49 / 74.5 = 0.02 mol

$m(H_2O) = 0.360$ kg

$$\mathbf{C_m\ (KCl)} = \frac{0.02}{0.360} = 0.055 \text{ mol/kg}$$

KCl is a strong electrolyte hence α (KCl) = 100% or 1.

$\alpha = \frac{i-1}{n-1}$ (where n — a number ions contained in a molecule), hence

$i = 1\times(2-1) + 1 = 2$.

$\Delta \mathbf{T_f} = 1.86\times2\times0.055 = 0.2046°$.

$\Delta \mathbf{T_b} = 0.52\times2\times0.055 = 0.0570°$.

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 (figure 9.7).

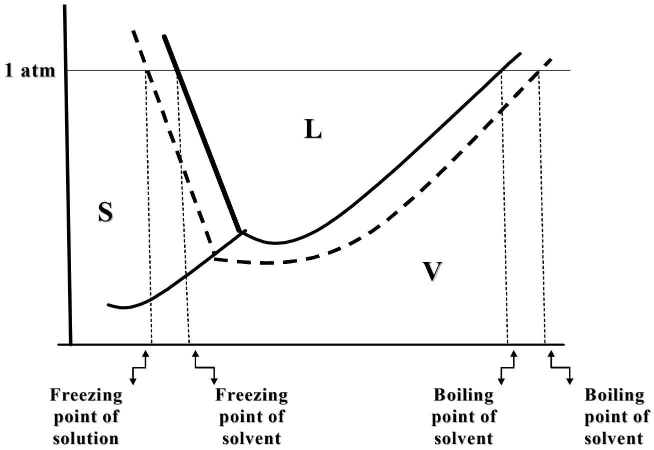


Figure 9.7 — Phase diagrams of pure water (solid lines) and of water in an aqueous solution containing a nonvolatile solute (dashed lines)

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 ΔT_f and ΔT_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 (figure 9.8).

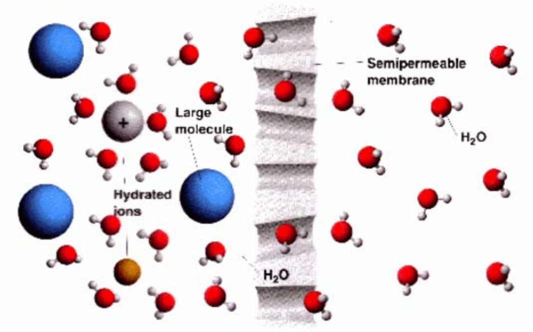


Figure 9.8 — Scheme of the osmosis

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

$$\pi = R \times T \times C_M \text{(for nonelectrolytes)}, \qquad 9.15$$

$$\pi = i \times R \times T \times C_M \text{ (for electrolytes)} \qquad 9.16$$

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 ~ 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 $MgSO_4$ solution is applied to treat hypertonic crises.

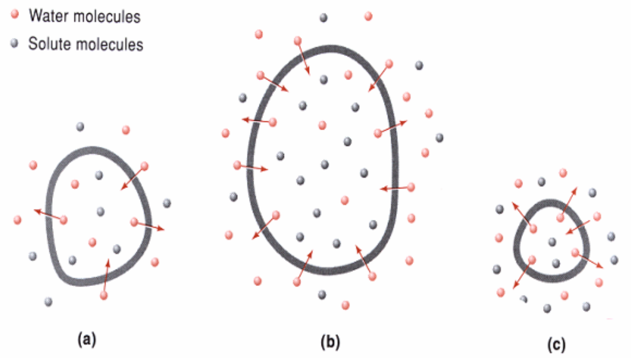


Figure 9.9 — A cell in (a) a isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c)

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

EXAMPLE 9.5 0.63 M solution of HNO_3 is used in laboratory as an oxidizing agent. What is its osmotic pressure under t = 20°C?

Answer:

$\pi = i \times R \times T \times C_M$ hence calculate I and C_M.

HNO_3 — a strong electrolyte hence α (HNO_3) = 100% or 1.

$\alpha = \frac{i - 1}{n - 1}$ (where n — a number of ions is contained molecule),

$i = 1 \times (2-1) + 1 = 2$

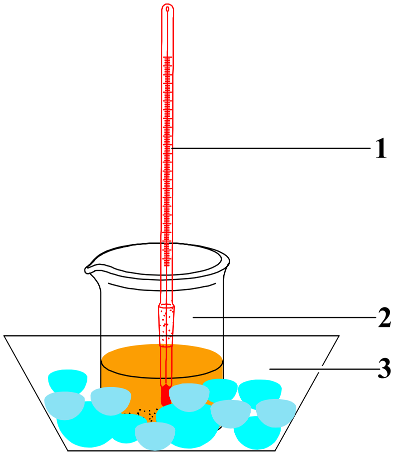
Hence $\pi = 2 \times 8.31 \times (273+20) \times 0.63 = 3067.8$ kPa

9.3 LABORATORY WORK

CRYOSCOPY

Test 1. Cryoscopic method of a glucose molar mass determination

Scheme a simplified cryoscope you can see in figure 9.10.



1 – A thermometer
2 – A chemical glass
3 – A crystallizer

Figure 9.10 — Cryoscope

Prepare a cooling mixture composed of small pieces of ice and some amount of table salt crystals and put it into a crystallizer. The temperature of a cooling mixture must be approximately -6°C.

Pour 25 mℓ of a glucose solution into a chemical glass and put a glass into a cooling mixture. Dip a thermometer into the solution and look after a temperature decreasing. Don't forget to mix the solution to avoid its local overcooling. Mark a temperature when the first ice crystals appear in a glass.

Writing of experimental data

Mass of a glucose solution	25 g.
Mass of glucose	m_1
Mass of water	m_2
Freezing-point of water °C	t_1 ($t_1 = 0^oC$)
Freezing-point of a solution °C	t_2
Freezing-point depression	$\Delta t = t_1 - t_2$.

Using Cryoscopic Raoult's Law calculate glucose molar mass:

$$\Delta t = K_f \times \frac{m(C_6H_{12}O_6) \times 1000}{M(C_6H_{12}O_6) \times m(H_2O)} \qquad 9.17$$

The molar freezing-point depression constant of water is 1.86.

Calculate absolute and relative errors of an experiment, taking into consideration that true molar mass of glucose is 180.1 g/moL.

Test 2. Cryoscopic method of Van't Hoff's factor and ionization degree of sodium chloride determination

Prepare a cryoscope as described in experiment № 1. Pour 25 mℓ of a NaCl solution into a chemical glass and put a glass into a cooling mixture. Dip a thermometer into the solution and look after a temperature decreasing. Mark a temperature when the first ice crystals appear in a glass.

Writing of experimental data

Mass of a NaCl solution	25 g
Mass of NaCl	m_1
Mass of water	m_2
Freezing-point of water °C	t_1 ($t_1 = 0^oC$)
Freezing-point of a solution °C	t_2
Freezing-point depression	$\Delta t = t_1 - t_2$

Calculate van't hoff factor using the following equation:

$$i = \frac{\Delta t(\exp)}{\Delta t(theory)} \tag{9.18}$$

Calculate Δt (theory) according to the formula:

$$\Delta t(theory) = 1.86 \times \frac{\mathrm{m\,(NaCl)} \times 1000}{\mathrm{M\,(NaCl)} \times \mathrm{m\,(H_2O)}} \tag{9.19}$$

Calculate ionization degree of NaCl according to the equation:

$$\alpha(\exp) = \frac{i-1}{n-1} \tag{9.20}$$

where *n* — a number of ions formed when one electrolyte molecule dissociates in an aqueous solution (for NaCl n = 2).

9.4 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.

NUMERICAL EXERCISES

Solubility

1. What is the concentration of metal ions in the following saturated solutions (mol/ℓ and g/ℓ) at 298 K ?

(a) AgNCS, $K_{sp} = 1.1\times10^{-12}$
(b) AgI, $K_{sp} = 8.3\times10^{-17}$
(c) $Cu(OH)_2$, $K_{sp} = 5.0\times10^{-20}$
(d) $Pb(OH)_2$, $K_{sp} = 1.1\times10^{-20}$

ANSWER: (a) 1.05×10^{-6} M, 1.13×10^{-4} g/ℓ; (b) 9.11×10^{-9} M, 9.84×10^{-7} g/ℓ; (c) 2.32×10^{-7} M, 1.49×10^{-5} g/ℓ; (d) 1.40×10^{-2} M, 2.90×10^{-5} g/ℓ

2. 0.005 M $AgNO_3$ solution is treated with equal volume of 0.001 M KNO_2. Does $AgNO_2$ precipitate from this solution? K_{sp} ($AgNO_2$) = 1.6×10^{-4}.

ANSWER: precipitation occurs

3. Calculate the solubility of $BaSO_4$ (in g/ℓ) in water. The solubility product constant of $BaSO_4$ is 1.1×10^{-10}. Compare its solubility in water and in Na_2SO_4 solution.

ANSWER: 2.44×10^{-3} g/ℓ

4. The apparent solubility products constants of CdS and CaF_2 at 25°C are 3.8×10^{-29} and 4.0×10^{-11}, respectively. Calculate the solubility (mol/ℓ) of these compounds.

ANSWER: 6.16×10^{-15} M; 2.15×10^{-4} M

5. Oxalic acid $(COOH)_2$, is a poisonous compound present in many plants and vegetables, including spinach. Calcium oxalate is only slightly soluble in water (Ksp = 3.0×10^{-9} at 25°C) and its ingestion can result in kidney stones. Calculate:

a.solubility of calcium oxalate in water,
b.the concentration of calcium and oxalate ions in water.

ANSWER: 7.00×10^{-5} g/ℓ; 5.48×10^{-7} M

6. 0.01 M $Mg(NO_3)_2$ solution is treated with 0.01 M K_2CO_3 solution. Does $MgCO_3$ precipitate from this solution? K_{sp} ($MgCO_3$) = 4.0×10^{-5}.

ANSWER: precipitation occurs

HENRY'S LAW

7. The Henry's law constant of oxygen in water at 25°C is 773 atm $mol^{-1}\times kg$ of water. Calculate the molality of oxygen in water under the partial pressure of 0.20 atm. Assuming that the solubility of oxygen in blood at 37°C is roughly the same as that in water at 25°C, comment on the prospect for our survival without hemoglobin molecules. (The total volume of blood in the human body is about 5ℓ).

ANSWER: 2.6×10^{-4} mol/kg

8. Calculate the molal solubility of carbon dioxide in water at 298 K and a CO_2 pressure of 3.3×10^{-4} atm, which corresponds to the partial pressure of CO_2 in air.

ANSWER: 1.12×10^{-5} mol/ kg

COLLIGATIVE PROPERTIES

9. The osmotic pressure of an aqueous solution containing 1.00 g of the sugar in 100 mℓ of water is 1.36 atm at 25°C. What is the molar mass of this sugar?

ANSWER: 180 g/mol

10. The osmotic pressure of H_3PO_4 solution is 3.03 atm at 300K. Calculate molality of the given solution.

ANSWER: 0.065 mol/kg

11. Calculate the molar mass of vitamin C if a solution containing 22.0 g of a vitamin in 100 g of water freezes at –2.33°C.

Answer: 175.6 g/mol

12. Brackish water, with a salt content around 0.5% by mass, is found in semiarid regions such as the American South west. Assuming that brackish water contains only sodium chloride, estimate the osmotic pressure of brackish water.

ANSWER: 423.5 kPa

13. Fish have blood that is isotonic with seawater freezing at – 2.30°C. What is the osmotic pressure of fish blood at 15°C?

ANSWER: 29.44 kPa

14. Calculate the osmotic pressure 1.5% by mass of NaCl solution. Can it be used in medicine for intravenous injections?

ANSWER: 1327.55 kPa

15. Lysozyme extracted from chicken egg white has a molar mass of 13.93 g/mol. Exactly 0.1 g of this protein is dissolved in 50 g of water at 298 K. Calculate the vapor pressure lowering, the depression in freezing point, the elevation of boiling point, and the osmotic of this solution. The vapor pressure of pure water at 298 K is 23.76 mmHg.

ANSWER: 0.061 mmHg; 0.075^{0}; 0.27^{0}

16. The osmotic pressure of blood plasma is approximately 7.5 atm at 37°C. Estimate the total concentration of dissolved species and the freezing point of blood plasma.

ANSWER: 0.295 M; -0.56 ^{0}C

CHAPTER 10
ELECTROLYTE SOLUTIONS

> *And when the rain has wet the kite and twine,*
> *so that it can conduct the electric fire freely,*
> *you will find it stream out plentifully from*
> *the key on the approach of your knuckle.*

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.

10.1 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.

Svante Arrhenius (1859-1927)

The first theory of Electrolytic dissociation was developed in 1884-1887 by Swedish chemist Svante Arrhenius. The basic idea of his theory is that certain substances remain ionized in solution all the time. Today, everyone accepts this as it is, but it was the subject of much dissention and disagreement in 1884, when a twenty-five year old Arrhenius presented and defended his dissertation. He was bitterly disappointed when the dissertation was awarded a fourth class (*non since laude approbatur* — approved without praise) and his defense a third class (*cum laude approbatur* — approved with praise). Essentially, he got a grade D for the dissertation and a C for his defence. However, he received the Nobel Prize in 1903 Chemistry for his electrolytic dissociation theory and that effectively put an end to public criticism

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)* (α) can be calculated by the simple relation:

$$\alpha = \frac{\text{a number of ionized molecules}}{\text{a total number of dissolved molecules}} \qquad 10.1$$

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:

$$\alpha = \frac{i-1}{n-1} \qquad 10.2$$

where i — is the van't Hoff's factor. In dilute solutions α 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 Na_2SO_4 - 3 and for Na_3PO_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 (figure 10.1).

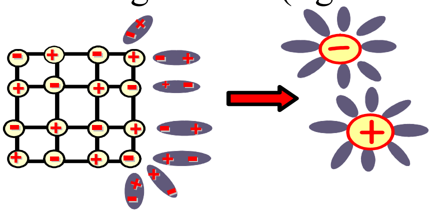


Figure 10.1 — Ionic compound dissociation in water

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:

H^+	Li^+	Na^+	NH_4^+	K^+	Rb^+	Cs^+
1	120	66	17	16	14	13

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

$$F = \frac{q_1 \times q_2}{\varepsilon \times r^2} \qquad 10.3$$

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;

ε — 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 ε is ~ 81, for ethyl alcohol $\varepsilon \sim 24$, for most organic solvents ε 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.

10.2 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 $Fe(CNS)_3$;

(d) water.

In the solutions of weak electrolytes equilibrium is maintained between ions and molecules of a substance: $CatAn \rightleftarrows Cat^+ + An^-$. Their ionization percent is always much less than one ($\alpha << 1$). 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:

$$K_{ins} = \frac{[Cat] \times [An]}{[CatAn]} \qquad 10.4$$

The examples of ionization equilibrium constants are:

- the acid ionization constant K_a;
- the base ionization constant K_b;
- the instability constant K_{ins}, and formation constant K_f that characterize ionization of complex compounds.

Weak electrolytes obey *Ostwald's dilution Law*.

Friedrich Wilhelm Ostwald (1853-1932)

Friedrich Wilhelm Ostwald was a German chemist. He received the Nobel Prize in Chemistry in 1909 for his work on catalysis, chemical equilibrium and reaction velocities

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

$$\mathbf{HA \rightleftarrows H^+ + A^-}$$

$$\mathbf{c(1\text{-}\alpha)\quad c\alpha\quad c\alpha}$$

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

$$K_a = \frac{[H^+]\times[A^-]}{[HA]} = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \qquad 10.5$$

For weak electrolytes α << 1 thus equation (10.5) can be rearranged as:

$$K_a = c\alpha^2 \qquad 10.6$$

or

$$\alpha = \sqrt{\frac{K_a}{c}} \qquad 10.7$$

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.

EXAMPLE 10.1 Calculate the concentration of the undissociated acid, H^+ ions, and the CN^- ions of a 0.050 M HCN solution and the percent dissociation at 25°C.

Answer:

Let x be the concentration of H^+ and CN^- at equilibrium. Thus, we have

$$HCN(aq) \rightleftarrows H^+(aq) + CN^-(aq)$$

$$(0.050\text{-}x)\ M \quad xM \qquad xM$$

Using the value of K_a from Appendix 2, table 10, we write

$$\frac{x^2}{0.050 - x} = 4.9\times10^{-10}$$

Because K_a values for weak acids are generally known to the accuracy of only ±5%, it is reasonable to require x to be less than 5% of 0.050, the number from which it is subtracted. Assuming that this approximation holds ($0.050 - x \approx 0.050$), we have

$$x^2 = 2.5\times10^{-11}$$

or

$$x = 5.0\times10^{-6}\ M$$

Therefore, at equilibrium, $[H^+] = 5.0\times10^{-6}$ M $[CN^-] = 5.0\times10^{-6}$ M

$[HCN] = 0.050\ M - 5.0\times10^{-6}\ M \approx 0.050\ M$

Finally, the percent dissociation is given by $\frac{5.0\times10^{-2}}{0.050}\times100\% = 1.0\times10^{-2}\%$

10.3 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, $HClO_4$, HNO_3, H_2SO_4 and others;
- hydroxides of Alkali and Alkaline Earth metals such as NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$ and others;
- most salts.

Strong electrolytes' ionization can be represented by a scheme:

$$\mathbf{CatAn \rightarrow Cat^{+} + An^{-}}$$

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:

$$\mathbf{I} = \frac{1}{2}\Sigma C_i \times Z_i^2 \qquad 10.8$$

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* (figure 10.2):

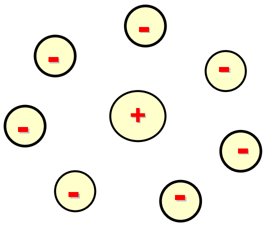


Figure 10.2 — A model of ionic atmosphere

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.

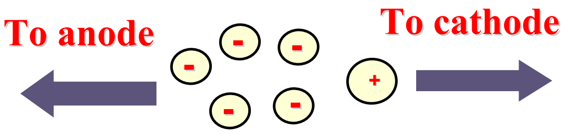


Figure 10.3 — In a conductance measurement, the movement of a cation toward the cathode is retarded by the electric field exerted by the ionic atmosphere left behind

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* (a). The activity is defined by the formula:

$$\mathbf{a} = \boldsymbol{\gamma}\ C_M \qquad 10.9$$

where γ — 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 (Appendix 2, Table 11). They depend upon the ionic strength of a solution and their charge numbers.

EXAMPLE 10.2 Calculate the ionic strength, the activity coefficient and the activity of proton in 0.1 M HNO_3 solution.

Answer:

HNO_3 is strong acids, which ionization is irreversible:

$HNO_3 \rightarrow H^+ + NO_3^-$

The ionic strength of the given solution may be calculated as:

$$I = \frac{1}{2}\Sigma C_i \times Z_i^2,$$

$$I\ (HNO_3) = \frac{1}{2} \times \left[0.1 \times (+1)^2 + 0.1 \times (-1)^2\right] = 0.1\ M$$

We find the activity coefficient for H^+ in accordance with the ionic strength of the given solution (Appendix 6); when I = 0.1 M, then $\gamma\ (H^+) = 0.87$.

$a\ (H^+) = \gamma \times C_M(H^+) = 0.87 \times 0.1 = 0.087$, where $a\ (H^+)$ – activity of a proton.

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**

$$\log \gamma_{\pm} = -\left| z_+ z_- \right| A\, I^{1/2} \qquad 10.10$$

where A = 0.509 for an aqueous solution at 25^0C,

$\gamma_{\pm}$ is the *mean activity coefficient*, which is the geometric mean of the individual coefficients for cation and anion

$$\gamma_{\pm} = (\gamma_+ \gamma_-)^{1/2} \qquad 10.11$$

EXAMPLE 10.3 Calculate the mean activity coefficient ($\gamma_{\pm}$) of a 0.010 mol/kg aqueous solution of $CuSO_4$ at 298 K.

Answer:

The ionic strength of the solution is given by

$$I = ½\ [(0.010) \times 2^2 + (0.010 \times (-2)^2] = 0.040$$

From equation (10.10)

$$\log \gamma_{\pm} = -0.509\ (2 \times 2)\ \sqrt{0.040} = -0.407$$

or

$$\gamma_{\pm} = 0.392$$

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.

10.4 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:

$$C = \frac{1}{R} = \frac{1A}{\rho \times l} = æ\frac{A}{l} \qquad 10.12$$

where R — is the resistance across a particular medium, which is directly proportional to the length (l) and inversely proportional to the across section area (A) of the medium;

ρ — is the specific resistance or resistivity;

æ — is the *specific conductance* or conductivity equal to 1/ρ.

Specific conductivity is also defined as the conductivity of 1m^3 of a solution when a distance between electrodes is 1 m.

Resistance is measured in ohms (Ω), so conductance is measured in Ω^{-1} or Siemens (S). Conductivity has the units Ω^{-1} cm^{-1}, or Ω^{-1} 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 (figure 10.4). The resistance that the solution adds to the circuit is converted into conductivity by a computer chip, and is displayed on a meter.

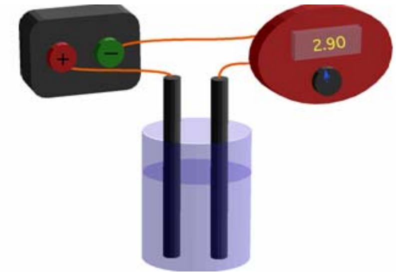


Figure 10.4 — A conductance cell

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=ν/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 (H$^+$)

impart greater conductivity to solutions than bulky ions do, like bromide ion (Br^-), or heavily hydrated ions do, like sulfate ion (SO_4^{2-}).

Table 10.1 — Ionic Mobility of some common ions at 298 K, 10^{-8} $m^2 \cdot s^{-1}$ V^{-1}

Ion	$\mathbf{u_\infty}$	**Ion**	$\mathbf{u_\infty}$
H^+	36.3	OH^-	20.50
Na^+	5.19	Cl^-	7.91
K^+	7.62	SO_4^{2-}	8.29

All the factors that effect specific conductance of solutions at a particular temperature are reflected in equation 10.13:

$$\textbf{æ} = \alpha \times C_M \times F \times (u_+ + u_-) \times 10^3 \qquad 10.13$$

We can use this equation to explain the relationship between conductivity and molarity in dilute and concentrated solutions of strong and weak electrolytes (figure 10.5).

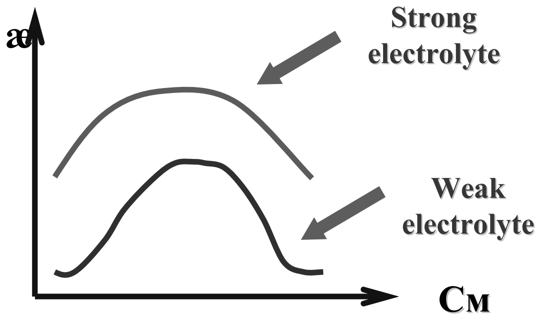


Figure 10.5 — Specific conductivity of solutions and their concentration

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).

EXAMPLE 10.4 Calculate specific conductivity of a 0.01 mol/m^3 HCl solution, using H^+ and Cl^- ionic mobility. Compare its conductance with the conductivity of a KCl solution with the same molarity. (Use data of Table 10.1)

Answer:

According to Equation (10.13)

$$æ_{HCl} = \alpha \times C_M \times F \times (U_{H+} + U_{Cl-}) \times 10^3$$

Since HCl is a strong electrolyte ($\alpha = 1$), the equation 10.13 can be rearranged as

$$æ_{HCl} = 0.01 \times 96500 \times (36.3 + 7.91) \times 10^{-8} \times 10^{3} = 42.7 \times 10^{-2}\ \Omega^{-1}\ m^{-1}$$

Specific conductance of KCl solution is given by

$$æ_{KCl} = 0.01 \times 96500 \times (7.62 + 7.91) \times 10^{-8} \times 10^{3} = 15.0 \times 10^{-2}\ \Omega^{-1}\ m^{-1}$$

So $æ_{HCl} > æ_{KCl}$ because $U_{H+} > U_{K+}$

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 10.2 — Specific conductivity of bio substrates at 37°C

Bio substrate	**æ, $\Omega^{-1}m^{-1}$**	**Bio substrate**	**æ, $\Omega^{-1}m^{-1}$**
Blood plasma	1.47–1.60	Muscles	0.66
Gastric juice	1.0–1.25	Nerve tissue	4×10^{-2}
Urea	1.6–2.3	Bone tissue	5×10^{-7}

For example, when a person suffers from kidneys' insufficiency the specific conductivity of urea decreases down to 0.9–1.4 $\Omega^{-1}m^{-1}$ 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* (λ), which can be defined as the value of specific conductance contributed by one mole of ions contained in 1000 cm^3 (1 ℓ) of a solvent. It is defined as:

$$\lambda = \frac{æ}{C_M} \times 10^{-3} \qquad 10.14$$

On the other hand we can write that

$$\lambda = \alpha \times F \times (u_+ + u_-) \qquad 10.15$$

Let's assume that the multiplication $F \times u_+ = \lambda_+$ and $F \times u_- = \lambda_-$, where λ_+ and λ_- are the molar ionic conductance of cation and anion respectively.

Thus we have

$$\lambda = \alpha \times (\lambda_+ + \lambda_-) \qquad 10.16$$

In infinite diluted solutions (c ⟶ 0) α tends to 1, therefore

$$\lambda_\infty = \lambda_{\infty+} + \lambda_{\infty-} \qquad 10.17$$

where λ_∞ — is molar conductance at infinity dilution;

$\lambda_{\infty+}$ and $\lambda_{\infty-}$ are the ionic conductances at infinite dilution.

Equation 10.17 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 (α) and solubility of electrolytes (S) can be calculated according to electric conductivity data:

$$\alpha = \frac{\lambda}{\lambda_{\infty}} \qquad 10.18$$

$$S = \frac{\text{æ} - \text{æ}(H_2O)}{\lambda_{\infty}} \qquad 10.19$$

Molar ionic conductances of some common ions at 298 K are given in table 10.3.

Table 10.3 — Molar ionic conductances of some common ions at 298 K, Ω^{-1} mol^{-1} cm^2

Ion	λ_{∞}	Ion	λ_{∞}
H^+	350	OH^-	198
Na^+	50	Cl^-	76
K^+	74	CH_3COO^-	41

EXAMPLE 10.4 The molar conductance of an aqueous acetic acid solution, concentration 0.10 M, is 5.2 Ω^{-1} mol^{-1} cm^2 at 298 K. Calculate the dissociation constant of acetic acid.

Answer:

According to Kolrausch's law of independent migration and using the data of Table 10.3.

$\lambda_{\infty}(CH_3COOH) = \lambda_{\infty+}(H^+) + \lambda_{\infty-}(CH_3COOH) = 350 + 41 = 391\ \Omega^{-1}\ mol^{-1}\ cm^2$

Using equation 10.18 we can write

$$\alpha = \lambda / \lambda_{\infty} = 5.2/391 = 0.013$$

According to Ostwald's dilution law $K_a = c\alpha^2 = 0.10 \times (0.013)^2 = 1.8 \times 10^{-5}$

10.5 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^+, K^+, Ca^{2+}, Mg^{2+}. The content of anions in blood is also ~154 mmol/ℓ. The most important for living beings are Cl^-, HCO_3^-, SO_4^{2-}, $H_2PO_4^-$, HPO_4^{2-}, 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:

a) hold water in tissues as hydrates. For example, 2 grams of NaCl hold 2 ℓ of water;

b) maintain osmotic pressure of biological fluids. The gradients in osmotic pressure are responsible for active transport of water in living systems;

c) 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.

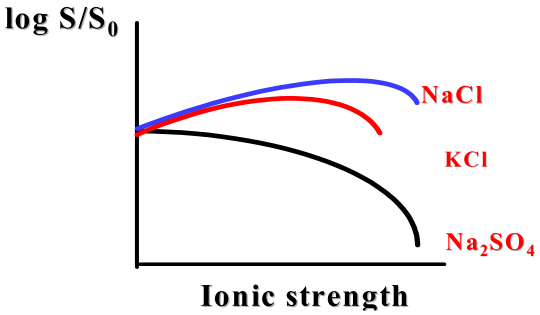


Figure 10.6 — Plots of log (S/S^0) versus ionic strength for horse hemoglobin in the presence of various inorganic salts

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 10.7 shows the range of the salting out phenomenon for several proteins in the presence of ammonium sulfate.

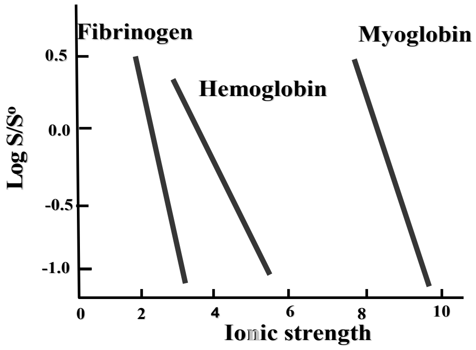


Figure 10.7 — Plots of log (S/S^0) versus ionic strength for several proteins in aqueous ammonium sulfate, demonstrating the salting-out effect

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.

10.6 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) H_2O, (b) KCl, (c) HNO_3, (d) CH_3COOH, (e) $C_{12}H_{22}O_{11}$, (f) $Ba(NO_3)_2$, (g) NaOH.

4. Classify each of the following species as a weak or strong base: (a) LiOH, (b) H_2O, (c) NaOH, (d) NH_4OH, (e) $Ba(OH)_2$, (f) $Fe(OH)_3$, (g) $Cu(OH)_2$.

5. Classify each of the following species as a weak or strong acid: (a) HNO_3, (b) HF, (c) H_2SO_4, (d) H_2CO_3, (e) HCl, (f) HNO_2, (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 Kolrausch's law of independent migration.

NUMERICAL EXERCISES

WEAK ELECTROLYTES SOLUTIONS

1. A 0.040 M solution of monoprotic acid is 13.5% dissociated. What is the dissociation constant of the acid?

Answer: 7.29×10^{-4}

2. Calculate the concentration of H^+, HCO_3^-, and CO_3^{2-} in a 0.025 M H_2CO_3 solution.

Answer: 1.025×10^{-4} mol/ℓ; 1.09×10^{-6} mol/ℓ

3. The dissociation constant of monoprotic acid at 25°C is 1.47×10^{-3}. Calculate the degree of dissociation, if concentration of the acid is 0.010 M.

Answer: 38.3%

4. Calculate the percent dissociation of HF at the following concentration: (a) 0.05 M, (b) 0.050 M. Comment on your results.

Answer: 12%; 38%

5. A 0.400 M formic acid (HCOOH) solution freezes at -0.758^0C. Calculate the value of K_a at that temperature (assume that molarity is equal to molality).

Answer: 1.6×10^{-4}

STRONG ELECTROLYTES SOLUTIONS

6. Calculate the ionic strength of a solution that is 0.01 mol/kg in KCl (aq) and 0.20 mol/kg in $CuSO_4$ (aq).

Answer: 0.01 mol/kg; 0.8 mol/kg

7. Calculate ionic strength, activity coefficients of metal cations in following solutions:

(a) 0.3 N solution of $Ca(OH)_2$

(b) 0.2 N solution of K_2SO_4.

Answer: 0.0375mol/ℓ; 0.124 mol/ℓ.

8. Calculate the ionic strength and the mean activity coefficient for the following solutions at 298 K: (a) 0.10 mol/kg NaCl, (b) 0.010 mol/kg $MgCl_2$ and (c) 0.10 mol/kg $K_4[Fe(CN)_6]$.

Answer:(a) 0.10 M; 0.69;
(b)0.030 M; **0.67;**
(c) 1.0 M; 9.1×10^{-3}

9. A 0.20 mol/kg $Mg(NO_3)_2$ solution has the mean ionic activity coefficient of 0.13 at 25°C. Calculate the mean molality, the mean activity, and the activity of the compound.

Answer: 0.32 M; 0.041; 7.0×10^{-5}

10. What molality of $CuSO_4$ has the same ionic strength as 1.00 mol/kg KCl (aq)?

Answer: 0.125 mol/kg

CHAPTER 11

ACID-BASE EQUILIBRIUM

> *Lemon tree is very pretty and the lemon flower is sweet,*
> *but the fruit of the poor lemon is impossible to eat.*
> *William Holt*

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.

11.1 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 (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 (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:

$$HCl \rightarrow H^+ + Cl^-$$
$$NaOH \rightarrow Na^+ + OH^-$$

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 H_3O^+, so a better representation for the HCl ionization is: $H_2O + HCl \rightarrow H_3O^+ + Cl^-$, 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 catalystic 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:

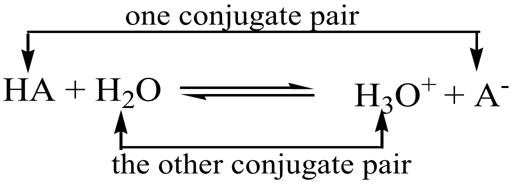
- an acid is a proton (hydrogen ion) donor;
- a base is a proton (hydrogen ion) acceptor.

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:

acid + base → conjugate acid + conjugate base

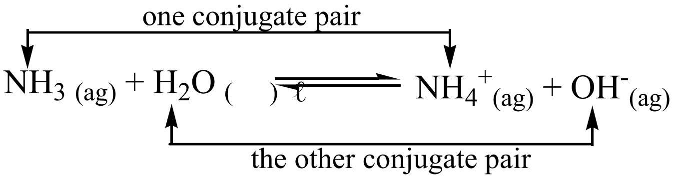
A *conjugate base* of an acid is the remainder of the acid after it has released a proton. A *conjugate acid* of a base is formed when the base acquires a proton from the acid.

For example, interaction of an acid with water can be represented by:



$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The reaction between ammonia and water also involves two conjugate pairs:



$$NH_{3\,(ag)} + H_2O_{(\;)\ell} \rightleftharpoons NH_4^+{}_{(ag)} + OH^-{}_{(ag)}$$

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:

$$H_3O^- \xleftarrow[\text{and is acting as a base}]{\text{water accepts a proton,}} H_2O \xrightarrow[\text{and is acting as a acid}]{\text{water loses a proton,}} OH^-$$

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: $H_3N + BF_3 \rightarrow H_3N{:}BF_{3.}$

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 OH- ion when placed in water. The Bronsted-Lowry theory classifies ammonia as a base because it accepts a proton from H_2O. The Lewis theory classifies 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.*

11.2 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 (H^+ or H_3O^+) and hydroxyl ions (OH^-) concentrations and expressed in pH or pOH units.

$$\mathbf{pH = -\log a\,(H^+)} \tag{11.1}$$

where $a(H^+)$ — is the activity of the H^+ ions in a solution, given by $\gamma[H^+]$.

Generally, for relatively dilute solutions at the low ionic strength γ tends to 1, so we can use the following approximate equation

$$\mathbf{pH = -\log [H^+]} \tag{11.2}$$

where $[H^+]$ is — the concentration of protons, mol/ℓ.

We can also define a pOH scale as follows

$$\mathbf{pOH = -\log a(OH^-)} \tag{11.3}$$

where $a(OH^-)$ — is the activity of the OH^- ions in a solution, given by $\gamma[OH^-]$.

Respectively for dilute solutions at low ionic strength

$$\mathbf{pOH = -log\,[OH^-]} \qquad 11.4$$

where $[OH^-]$ — is the hydroxyl ion concentration, mol/ℓ.

Taking negative logarithm of equation for the water ionization constant (Chapter 10)

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

we get

$$-\log K_w = -\log [H^+] - \log[OH^-]$$

$$\mathbf{pK_w = pH + pOH} \qquad 11.5$$

where pK_w = - - log K_w. At 25^{0}C, Equation (11.5) becomes:

$$pH + pOH = 14 \qquad 11.6$$

In terns of concentrations, we can express the acidity of a solution as follows:

In neutral medium $[H^+] = [OH^-] = 10^{-7}$ M, pH = - log $[H^+]$ = - log 10^{-7} = 7.

In acidic medium $[H^+] > [OH^-]$, hence pH < 7.

In basic medium $[H^+] < [OH^-]$, hence pH > 7.

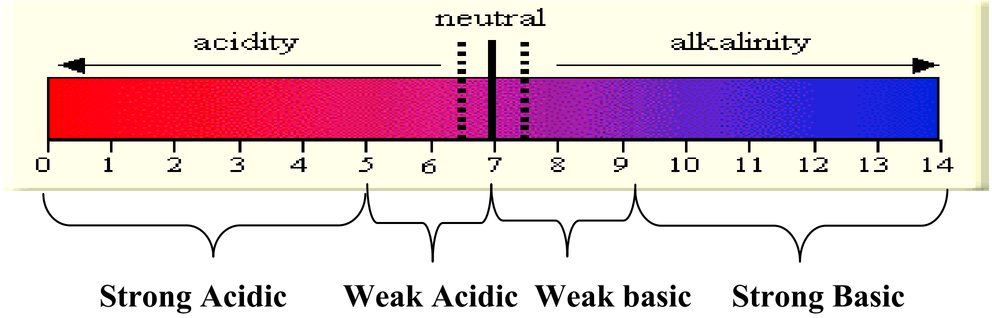


Figure 11.1 — pH Scale

pH of aqueous solutions may be determined experimentally or calculated theoretically.

11.3 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:

$$HA + H_2O \rightleftarrows H_3O^+ + A^-$$

or in a simplified form

$$HA \rightleftarrows H^+ + A^-$$

According to the law of mass action

$$K_a = \frac{[H^+]\cdot[A^-]}{[HA]} \qquad 11.7$$

where K_a — is the acid ionization constant.

Weak acids obey the Ostwald dilution Law, according to which their dissociation percent is:

$$\alpha \text{ (acids)} = \sqrt{\frac{K_a}{C_M}} \qquad 11.8$$

PROBLEM 11.1 Calculate pH and ionization degree (α) in 0.1 M nitrous acid solution.

Answer:

HNO_2 is a weak monoprotic acid, the ionization of which in water is represented by

$$HNO_2\text{ (aq)} + H_2O\ (\ell) \rightleftarrows H_3O^+\text{(aq)} + NO_2^-\text{(aq)}$$

or simply $HNO_2\text{ (aq)} \rightleftarrows H^+\text{(aq)} + NO_2^-\text{(aq)}$

According to the Ostvald dilution Law

$$\boldsymbol{\alpha}\ \mathbf{(HNO_2)} = \sqrt{\frac{K_a}{C_M}} = \sqrt{\frac{7.1\times10^{-4}}{0.1}} = 0.084$$

$[H^+] = \sqrt{K_a \times C_M} = \sqrt{7.1\times10^{-4}\times0.1} = 0.0084$ M,

where K_a — is the acid ionization constant.

$$pH = -\log[H^+] = -\log 0.0084 = 2.08$$

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 H_2SO_3 involves two steps:

$\mathbf{H_2SO_3 \rightleftarrows H^+ + HSO_3^-}$, $\quad Ka_1 = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} = 2.0\times10^{-2}$

Acid Conjugate Base

$\mathbf{HSO_3^- \rightleftarrows H^+ + SO_3^{2-}}$, $\quad Ka_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 6.0\times10^{-8}$

Acid Conjugate Base

Thus the conjugate base for the first dissociation $\mathbf{HSO_3^-}$ 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 H_2SO_3 is much greater than that of HSO_3^-.

PROBLEM 11.2 Calculate the concentrations of all the species in a 1.0×10^{-5}M carbonic acid solution at 298 K.

Answer: In this solution there are three equilibria to consider:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$$
$$H_2O \rightleftarrows H^+ + OH^-$$

There are altogether five unknowns: **$[H_2CO_3][HCO_3^-][CO_3^{2-}][H^+][OH^-]$**.

These five unknowns can be identified using five independent equations. Certain assumption will simplify the procedure. Because $K_{a1} >> K_{a2}$ and K_{a2} itself is a small number, we have **$[H_2CO_3]>>[HCO_3^-]>>[CO_3^{2-}]$**.

In the first equation dissociation is given by:

$$\begin{array}{cccc} \mathbf{H_2CO_3} & \rightleftarrows & \mathbf{H^+} + & \mathbf{HCO_3^-} \\ 1.0\times10^{-5}M & & x\,M & x\,M \end{array}$$

we write $4.2\times10^{-7} = \dfrac{x^2}{1.0\times10^{-5}}$

Solving the equation gives

$$x = 2.0\times10^{-6}\ M = [H^+] = [HCO_3^-]$$

In the second equation dissociation is given by:

$$\begin{array}{ccccc} \mathbf{HCO_3^-} & \rightleftarrows & \mathbf{H^+} & + & \mathbf{CO_3^{2-}}, \\ 2.0\times10^{-6}\ M & & (2.0\times10^{-6}+y)\ M & & y\ M \end{array}$$

Here, we have $4.8\times10^{-11} = \dfrac{(2.0\times10^{-6}+y)y}{2.0\times10^{-6}}$

Because 2.0×10^{-6} >>y, the above equation becomes

$$y = 4.8\times10^{-11}\ M$$

Finally, $\left[OH^-\right] = \dfrac{1.0\times10^{-14}}{2.0\times10^{-6}} = 5.0\times10^{-9}M$

At equilibrium the concentrations are

$$[H^+] = 2.0\times10^{-6}\ M$$
$$[OH^-] = 5.0\times10^{-9}\ M$$
$$[H_2CO_3] = 1.0\times10^{-5}\ M$$
$$[HCO_3^-] = 2.0\times10^{-6}\ M$$
$$[CO_3^{2-}] = 4.8\times10^{-9}\ M$$

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:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

By analogy with the acid ionization constant, we can write the base ionization constant K_b, as

$$K_b = \frac{\left[NH_4^+\right]\cdot\left[OH^-\right]}{\left[NH_4OH\right]} \qquad 11.9$$

Weak bases obey the Ostwald dilution Law, according to which

$$\alpha\ (\text{bases}) = \sqrt{\frac{K_b}{C_M}} \qquad 11.10$$

where α — is the ionization degree of weak bases in aqueous solutions.

PROBLEM 11.3 Calculate pH and the ionization degree (α) in a 0.1 M NH_4OH solution.

Answer:

NH_4OH is a weak base, the ionization of which in water is represented by:

$$NH_4OH(aq) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

According to the Ostwald dilution Low

$$\boldsymbol{\alpha}\ \mathbf{(NH_4OH)} = \sqrt{\frac{K_b}{C_M}} = \sqrt{\frac{1.8\times10^{-5}}{0.1}} = \mathbf{0.013}$$

$$[OH^-] = \sqrt{K_b \times C_M} = \sqrt{1.8\times10^{-5}\times0.1} = 0.0013 \text{ M}$$

where K_b — is the basic ionization constant.

$$pOH = -\log [OH^-] = -\log 0.0013 = 2.89$$

$$pH = 14 - pOH = 14 - 2.89 = 11.11$$

11.4 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

$$I = \frac{1}{2}\Sigma C_i \times Z_i^2 \qquad 11.11$$

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 (a). The activity is an effective thermodynamic concentration that takes into account a deviation from ideal behavior. Activity is defined by a formula

$$a = \gamma\times C_M \qquad 11.12$$

where γ — is the activity coefficient, a characteristic which expresses the deviation of a solution from the ideal behavior. It relates activity to concentration.

PROBLEM 11.4 Calculate the ionic strength, activity coefficient and the activity of proton in a 0.1 M solution of HNO_3.

Answer:

HNO_3 is a strong acid, the ionization of which is irreversible:

$$HNO_3 \rightarrow H^+ + NO_3^-$$

The ionic strength of the given solution may be calculated as:

$$I = \frac{1}{2}\Sigma C_i \times Z_i^2,$$

$$I\,(HNO_3) = \frac{1}{2} \times \left[0.1 \times (+1)^2 + 0.1 \times (-1)^2\right] = 0.1M$$

We find the activity coefficient for H^+ in accordance with the ionic strength of the given solution (Appendix 6); if I = 0.1 M, then $\gamma\,(H^+) = 0.87$.

$a\,(H^+) = \gamma \times C_M(H^+) = 0.87 \times 0.1 = 0.087$,

where $a\,(H^+)$ – is the activity of a proton;

$pH = -\log a\,(H^+) = -\log 0.087 = 1.06$

PROBLEM 11.5 Calculate the ionic strength, the activity coefficient, the activity of hydroxide ions and the pH in a 0.1 M KOH solution.

Answer:

KOH is a strong base, the ionization of which is irreversible:

$$KOH \rightarrow K^+ + OH^-$$

The ionic strength of the given solution may be calculated as: $I = \frac{1}{2} \Sigma C_i \times Z_i^2$

$$I\,(KOH) = \frac{1}{2} \times \left[0.1 \times (+1)^2 + 0.1 \times (-1)^2\right] = 0.1M$$

We find the activity coefficient for OH^- in accordance with the ionic strength of the given solution (Appendix 2, table 11); if I = 0.1 M, then $\gamma(OH^-) = 0.76$

$a\,(OH^-) = \gamma \times C_M(OH^-) = 0.76 \times 0.1 = 0.076$,

where $a\,(OH^-)$ –is the activity of hydroxide ions.

$pOH = -\log a\,(OH^-) = -\log 0.076 = 1.2$

$pH = 14 - pOH = 14 - 1.2 = 12.8$

11.5 Acid-base status of a human body

All biological fluids are characterized by constant pH values (Table 11.1). 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:

Respiratory, caused by hypoventilation of lungs and accumulation of carbonic acid in blood $\mathbf{CO_2 + H_2O \rightleftarrows H_2CO_3}$.

(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 11.1 — 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 % $NaHCO_3$ solution:

$$HCO_3^- + H^+ \rightleftarrows H_2CO_3$$

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

$$Ca_5(PO_4)_3F(s) \rightleftarrows 5\ Ca^{2+} + 3\ PO_4^{3-} + F^-$$

Addition of acids shifts equilibrium to the right due to decrease in F- anions: $H^+ + F^- \rightleftarrows HF$.

11.6 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 Brønsted-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:

$$pH = pK_a - \log \frac{[\text{acid}]}{[\text{conjugate base}]} \qquad 11.13$$

where $pK_a = -\log K_a$ (Ka – 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:

$$HCl + CH_3COONa \rightleftarrows CH_3COOH + NaCl$$

Neutralization of an added acid

$$NaOH + CH_3COOH \rightleftarrows CH_3COONa + H_2O$$

Neutralization of an added base

2. *Weak base and its salt.* For example, ammonia buffer system: NH_3/NH_4Cl

Mechanism of buffer activity

$$HCl + NH_3 \rightleftarrows NH_4Cl$$

Neutralization of an added acid

$$NaOH + NH_4Cl \rightleftarrows NH_3 + NaCl + H_2O$$

Neutralization of an added base

3. *Two acid salts.* For example, Hydro phosphate buffer system: NaH_2PO_4/Na_2HPO_4

Mechanism of buffer activity

$$HCl + Na_2HPO_4 \rightleftarrows NaH_2PO_4 + NaCl$$

Neutralization of an added acid

$$NaOH + NaH_2PO_4 \rightleftarrows Na_2HPO_4 + H_2O$$

Neutralization of an added base

4. *Acid salt and neutral salt.* For example, carbonate buffer system: $NaHCO_3/Na_2CO_3$

Mechanism of buffer activity

$$HCl + Na_2CO_3 \rightleftarrows NaHCO_3 + NaCl$$

Neutralization of an added acid

$$NaOH + NaHCO_3 \rightleftarrows Na_2CO_3 + H_2O$$

Neutralization of an added base

PROBLEM 11.5 Calculate the pH of a buffer solution that contains 1 mol of CH_3COOH and 1 mol of CH_3COOK in 1 ℓ of it. Calculate the pH change followed by the addition of 0.005 mol of KOH to this buffer.

Answer:

According to the Henderson-Hasselbach equation:

$$pH_1 = pK_a - \log \frac{[\text{acid}]}{[\text{conjugate base}]} = 4.75 - \log \frac{1}{1} = 4.75$$

$$CH_3COOH + KOH \rightleftarrows CH_3COOK + H_2O$$

$$C_M' (CH_3COOH) = 1 - 0.005 = 0.995 \text{ mol}$$

$$C_M' (CH_3COOK) = 1 + 0.005 = 1.005 \text{ mol}$$

$$pH_2 = pK_a - \log \frac{[\text{acid}]}{[\text{conjugate base}]} = 4.75 - \log \frac{0.995}{1.005} = 4.7543$$

$$\Delta pH = pH_2 - pH_1 = 4.7543 - 4.75 = 0.0043$$

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.

$$\mathbf{B} = \frac{C_N \times V}{\Delta pH \times V_{BS}} \tag{1.14}$$

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;
ΔpH — 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

$$\mathbf{B}_{\mathbf{max}} \text{ when } \frac{[\text{component } 1]}{[\text{component } 2]} = 1$$

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 ℓ of concentrated HCl.

11.7 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 HCO_3^-/H_2CO_3. In the erythrocyte, where the pH is 7.25, the principal buffer systems are HCO_3^-/H_2CO_3 and hemoglobin (figure 11.2).

Let's start the review of buffer systems in blood beginning from the buffers, which are present both on blood plasma and erythrocytes.

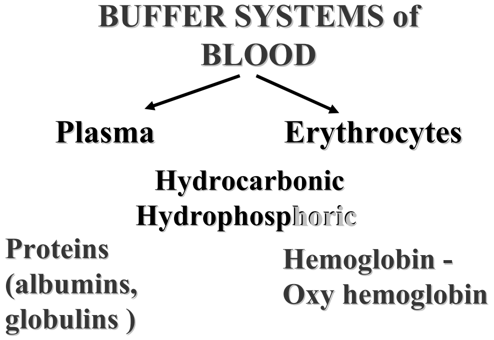


Figure 11.2 — Classification of buffer systems in blood

1. *Hydrocarbonic buffer system***.** This buffer system involves weak carbonic acid and bicarbonate anion: H_2CO_3/HCO_3^-. The formation of a buffer in biological fluids is represented by:

$$CO_2 + H_2O \overset{\text{Carbonic anhydrase}}{\rightleftarrows} H_2CO_3 \rightleftarrows HCO_3^- + H^+$$

The mechanism of buffer activity:

(a) Neutralization of acids: $H^+ + HCO_3^- \rightleftarrows H_2CO_3$

(b) Neutralization of bases: $OH^- + H_2CO_3 \rightleftarrows HCO_3^- + H_2O$

In blood plasma the ratio of H_2CO_3 and HCO_3^- concentrations is $\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{40}{1}$

Thus the excess of bicarbonate anion maintaines the *base reservoir of blood.*

Its buffer capacity of acids is much greater than buffer capacity of bases:

$$B_A = 40 \text{ mmol/ℓ}; \quad B_B = 1\text{–}2 \text{ mmol/ℓ}.$$

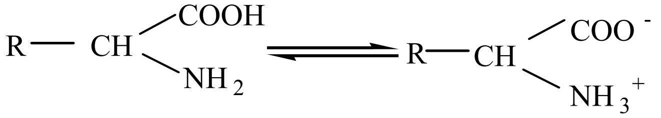
Hydrocarbonic buffer system is contained in all biological fluids of a human body. It acts together with other biological buffers. All alterations which proceed in a body effect the concentration of a carbonic system's components. HCO_3^- analysis in blood is an important diagnostical test which signals about respiratory and metabolic diseases.

2. *Hydro phosphoric buffer system***.** It is composed of anions of phosphoric acid ($H_2PO_4^-/HPO_4^{2-}$). 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 = 1–2 mmol/ℓ and B_B = 0.5 mmol/ℓ. But hydro phosphoric buffer system is crucial in urea, intracellular fluids and other biological liquids.

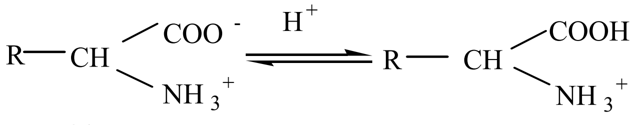
3. *Protein buffer system (albumins, globulins)* is a strong buffer which is present in blood plasma but not in erythrocytes.

Proteins are amphiprotic polyelectrolytes that exist as bipolar ions:

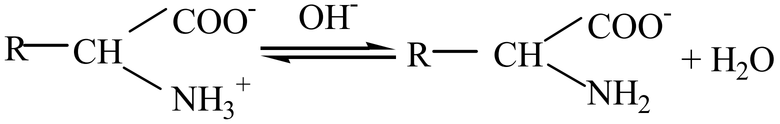


The mechanism of buffer activity is:

(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 ($HHbO_2$), formed by the combination of oxygen and hemoglobin in the lungs according to the reaction $HHb + O_2 \rightleftarrows HHbO_2$, are weak acids although the latter is considerably stronger than the former:

$$\underset{\text{Acid}}{HHb} \rightleftarrows H^+ + \underset{\text{Conjugate Base}}{Hb^-} \qquad K_a = 6.37\times10^{-9}$$

$$\underset{\text{Acid}}{HHbO_2} \rightleftarrows H^+ + \underset{\text{Conjugate Base}}{HbO_2^-} \qquad K_a = 1.17\times10^{-7}$$

The mechanism of their buffer activity can be represented as follows:

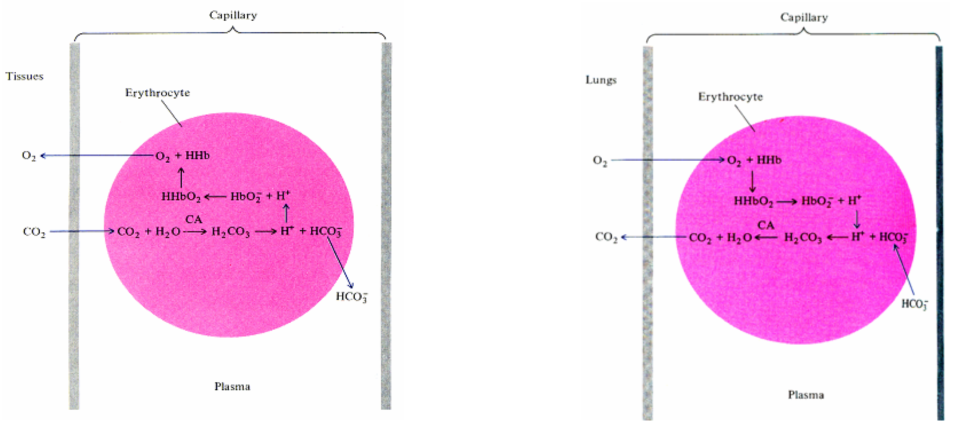
(a) Neutralization of acids: $H^+ + Hb^- \rightleftarrows HHb$

$$H^+ + HbO_2^- \rightleftarrows HHbO_2$$

(b) Neutralization of bases: $OH^- + HHb \rightleftarrows Hb^- + H_2O$

$$OH^- + HHbO_2 \rightleftarrows HbO_2^- + H_2O$$

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 (figure 11.3).



(a) **(b)**

Figure 11.3 — Oxygen-carbon dioxide is transported and released by blood. (a) In metabolizing tissues, the partial pressure of CO_2 is higher in the intestinal fluid (fluid in the tissues) than in plasma. Thus, 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 $HHbO_2$, which eventually dissociates into HHb and O_2. Because the partial pressure of 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 CO_2 binds to hemoglobin to form carbaminohemoglobin; (b) In the lungs, the processes are reversed

Biological buffer systems maintain acid-base statues of a human body.

11.8 Laboratory Work

ACID-BASE EQUILIBRIUM

Test 1: Determination of the pH in aqueous solutions by potentiometric method

Goal. Determine the pH of prepared solutions (a) using a universal indicator paper, (b) using potentiometric method of analyses.

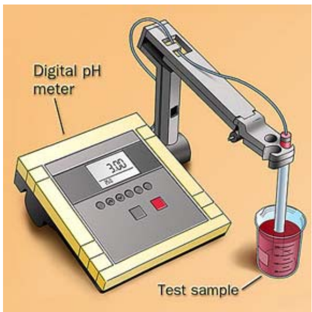


Figure 11.4 — Scheme of the pH-meter

Calculate the molar concentration of protons according to the formula:

$$[H^+] = 10^{-pH}$$

Fill in table 11.2 with the obtained data.

Table 11.2 — Experimental data and calculations

Test solution	**Tap water**	**Acidic solution**	**Basic solution**	**Buffer solution**
№ of a solution	**1**	**2**	**3**	**4**
pH,determined by indicator paper				
pH, determined by Potentiometric method				
Molar concentration of protons, Mol/ℓ				

Test 2: Preparation of buffer solutions

Goal. Prepare acetic buffer solutions using a scheme given in the table 11.3.

Table 11.3 — Experimental data

A number of a buffer solution	**1**	**2**	**3**
Volume of 0.1 M CH_3COOH, mℓ Volume of0.1 M CH_3COONa, mℓ	9.9 0.1	5 5	0.1 9.9
pH (experiment)			
pH (calculated)			

Determine the pH of each prepared buffer solution and compare them with the theoretically calculated data. Calculate absolute and relative errors of the experiments.

11.9 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 HCOOH, (b) 0.40 M $HClO_4$, (c) 0.40 M CH_3COOH.

3. Identify the strong and weak acids among the following: (a) HNO_3, (b) HOCl, (c) HOH, (d) CH_3OH.

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 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.

NUMERICAL EXERCISES

Weak Acids and Bases

1.Convert each of the following hydronium ion concentrations into the pH: (a) 0.4 M, (b) 3.75×10^{-6} M, (c) 0.0048 M, (d) 7.45×10^{-12} M.

ANSWER: (a) 0.4; (b) 5.4; (c) 2.3; (d) 11.1

2. Convert each of the following pH values into a Hydronium ion concentration: (a) 0.66, (b) 7.85, (c) 3.68.

ANSWER: (a) 0.22 M ;
(b)1.4×10^{-8} M; (c) 2.1×10^{-4} M

3. The K_a for benzoic acid is 6.5×10^{-5}. Calculate the concentrations of all species (C_6H_5COOH, $C_6H_5COO^-$, H^+ and OH^-) in a 0.10 M benzoic acid solution.

ANSWER: $[H^+] = 2.55\times10^{-3}$ M;
$[CH_3COOH] = 9.75\times10^{-2}$ M

4. The pH of a 0.060 M weak monoprotic acid is 3.44. Calculate the K_a of the acid.

ANSWER: 2.20×10^{-6}

5. Calculate the pH and the ionization degree (α) for each of the following solutions: (a) 0.010 M HNO_2, (b) 0.375 M HCN, (c) 0.200 M NH_3, (d) 0.100 M HF.

ANSWER: (a) 2.67, 21.2%; (b) 4.87, 3.6×10^{-3}%;
(c) 11.28, 0.95%; (d) 2.10, 0.79%

6. Calculate **(a)** the ionization degree of a 0.20 M solution of the monoprotic acetylsalicylic acid (aspirin, $C_9H_8O_4$), for which $K_a = 3.0\times10^{-4}$. **(b)** The pH of gastric juice in the stomach of a certain individual is 1.00. After a few aspirin tablets have been swallowed, the concentration of acetylsalicylic acid in the stomach is 0.20 M. Calculate the ionization degree of the acid under these conditions. What effect does nonionized acid have on the membranes lining the stomach?

ANSWER: (a) 3.87%; (b) 3×10^{-3}

7. What is the original molarity of a solution of formic acid (HCOOH) the pH of which is 3.26 at equilibrium?

ANSWER: 1.7×10^{-3} M

8. For a 0.010 M aqueous solution of oxalic acid ($H_2C_2O_4$):

(a) Identify the major and minor species.
(b) Calculate concentrations of all species present.
(c) Find the pH.

ANSWER: $[H^+] = 0.024$ M; $[HC_2O_4^-] = 0.024$ M;
$[C_2O_4^{2-}] = 1.25\times10^{-3}$ M; pH = 1.60

STRONG ACIDS AND BASES

9. Calculate the ionic strength, the activity coefficient, the activity of hydronium ion and the pH for each of the following solutions:(a) 0.010 M HNO_3, (b) 0.300 N HCl, (c) 0.100 M HI.

ANSWER: (a) 0.01 M, 0.91, 0.0091 mol/ℓ, 2.05;
(b) 0.30 M, 0.80, 0.24 mol/ℓ, 0.62;
(c) 0.10 M, 0.87, 0.087 mol/ℓ, 1.06

10. Calculate the ionic strength, the activity coefficient, the activity of hydroxide ions and the pH for each of the following solutions: (a) 0.010 M NaOH, (b) 0.300 M KOH, (c) 0.100 LiOH.

ANSWER: (a) 0.01 M, 0.90, 0.009 mol/ℓ, 11.95;
(b) 0.30 M, 0.63, 0.189 mol/ℓ, 13.30;
(c) 0.10 M, 0.76, 0.076 mol/ℓ, 12.90

BUFFER SOLUTIONS

11. Which of the following solutions will show buffer properties?

(a)100 mℓ of 0.25 M CH_3COONa + 150 mℓ of 0.25 M HCl,
(b)100 mℓ of 0.25 M CH_3COONa + 50 mℓ of 0.25 M HCl,
(c)100 mℓ of 0.25 M CH_3COONa + 150 mℓ of 0.25 M NaOH,
(d)100 mℓ of 0.25 M CH_3COONa + 50 mℓ of 0.25 M NaOH,

12. Calculate the pH of a buffer solution that contains 0.01 mol of CH_3COOH and 0.01 mol of CH_3COONa in 1 ℓ. Calculate the change in the pH resulting from the addition of 0.0005 mol of a NaOH solution to this buffer solution.

ANSWER: 4.75; ≈ 0.04.

13. Calculate the pH of a buffer solution that contains 1 mol of HCOOH and 1 mol of HCOOK in 1 ℓ. Calculate the change in the pH resulting from the addition of 0.05 mol of HCl solution to this buffer solution.

ANSWER: 3.70; ≈ 0.04

14. Calculate the pH of the 0.20 M NH_3/0.20 M NH_4Cl buffer. What is the pH of the buffer after the addition of 10.0 mℓ of 0.10 M HCl to 65.0 mℓ of the buffer?

ANSWER: 9.25; 9.18

15. The pH of blood plasma is 7.40. Assuming the principal buffer system to be HCO_3^-/H_2CO_3, calculate the ratio $[HCO_3^-]/[H_2CO_3]$. Is this buffer more effective against an added acid or an added base?

ANSWER:14.1

16. What is the pH of the buffer 0.10 M Na_2HPO_4 / 0.15 M NaH_2PO_4? Calculate the concentration of all the species in solution.

ANSWER: 6.94

17. Calculate the pH of a buffer solution that contains 0.50 M Na_2HPO_4 and 0.02 M NaH_2PO_4. Calculate the change in pH if 0.040 g of solid NaOH is added to 150 mℓ of a buffer.

ANSWER: 8.52; ≈ 0.18

18. A quantity of 26.4 mℓ of a 0.45 M acetic acid solution is added to 31.9 mℓ of a 0.37 M sodium hydroxide solution. What is the pH of the final solution?

ANSWER: 6.75

19. If you have 250 mℓ of a 0.200 M $NaHCO_3$ solution, which of the following solutions, and what volume, should be added to make a buffer solution at pH=10.60: 1.0 M NaOH, 1.0 M NaCl, H_2O, or 1.0 M CH_3COOH?

ANSWER: 30.7 mℓ

20. A buffer solution is prepared by mixing 0.360 ℓ of 0.300 M NH_3, and 0.640 ℓ of 0.300 M NH_4Cl (pK_a of $NH_4^+ = 9.25$).

(a) Calculate the pH of the buffer solution.

(b) Write a balanced chemical equation that shows what happens when 1.00 M HNO_3 is added to a buffer solution. What is the pH of the solution after 5.00 mℓ of 1.00 M HNO_3 is added to a buffer?

ANSWER: 9.0; 8.97

CHAPTER 12

ELECTROCHEMISTRY

Prometheus, they say,
brought fire to the service of mankind;
electricity we owe to Faraday.
Sir William Bragg

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 Nernst equation;
- discuss the structure and operation of galvanic cells, identify their types;
- discuss the application of Potentiometric investigations for analysis of biological systems.

12.1 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.

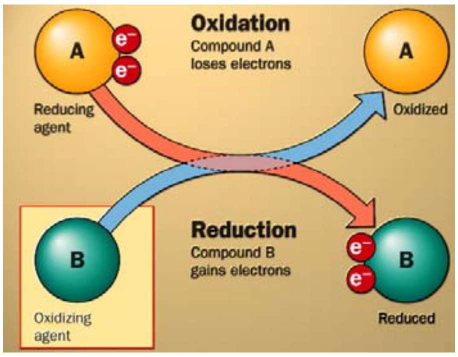


Figure 12.1 — The electrons' exchange in a Redox reaction

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:

$$Pb(CH_3COOH)_2 + Na_2S_2O_3 + H_2O \rightarrow PbS\downarrow + Na_2SO_4 + 2CH_3COOH$$

$$Cl_2 + Na_2S_2O_3 + H_2O \rightarrow 2\,HCl + S + Na_2SO_4$$

12.2 Thermodynamics of Electrochemical cells

An equation for an intermolecular Redox reaction may be represented as follows:

$$\mathbf{Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2},$$

where Ox_1 / Red_1 and Ox_2 / Red_2 are conjugate pairs of oxidizing and reducing agents.

Thus, for the reaction $\mathbf{MnO_2 + 4\,HCl \rightleftarrows Cl_2 + MnCl_2 + 2\,H_2O}$, the conjugate pairs are: $\mathbf{MnO_2 / Mn^{2+,}}$ and $\mathbf{Cl_2 / 2\,Cl^-}$**.**

To express the strength of oxidizing and reducing agents in aqueous solutions, *reduction potentials* are used ($\varphi_{Ox/Red}$, V). Standard reduction potentials are denoted as $\varphi^o_{Ox/Red}$ their values are in the range from -3 V up to +3 V (Appendix 2, table 9).

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 Li^+ /Li exhibits the minimum standard potential ($\varphi^0_{Li+/Li} = -3.045$ V), so we come to belief that Li is the strongest reducing agent and 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 F_2 / $2F^-$ exhibits the maximum standard potential (+ 2.87 V), thus F_2 is the strongest oxidizing agent and F^- is the weakest reducing agent in an aqueous solution. We can compare activity of reducing or oxidizing agents according to their reduction potentials:

PROBLEM 12.1 Which of the following is the strongest oxidizing agent:

(a) MnO_4^- in an acidic,

(b) MnO_4^- in a basic, and

(c) MnO_4^- in a neutral medium?

Answer:

We shall compare the oxidizing strength of the MnO_4^- in different media according to the rule: the greater a reduction potential of a conjugate pair is, the stronger an oxidizing agent is. Standard reduction potentials are given in Appendix 2, table 14.

In acidic medium $\varphi^o{}_{MnO_4^-/Mn^{2+}} = +1.51$ V,

In neutral medium $\varphi^o{}_{MnO_4^-/MnO_2} = +0.60$ V,

In basic medium $\varphi^o{}_{MnO_4^-/MnO_4^{2-}} = +0.56$ V

Since a reduction potential for permanganate anion takes the highest value in acidic medium, thus MnO_4^- is the strongest oxidizing agent in solutions with $pH<7$.

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:

$$\varphi_{\mathbf{Ox/Red}} = \varphi^{\mathbf{0}}{}_{\mathbf{Ox/Red}} + \frac{R \times T}{n \times F} \times \ln\frac{[Ox]}{[\mathrm{Re}d]} \qquad 12.1$$

where R — a gas constant (8.31 J/mol K);

n — a number of gained or lost electrons;

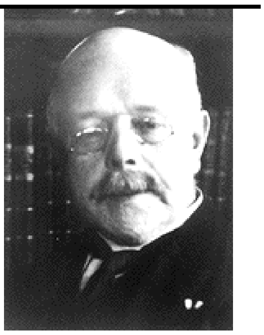
F — the Faraday constant (96500 C/mol).

When T = 298 K, $$\mathbf{2.3 \times \frac{RT}{F} = 0.0592}$$

Thus at standard temperature (298 K) the Nernst Equation may be rearranged in the following way:

$$\varphi_{\mathbf{Ox/Red}} = \varphi^{\mathbf{0}}{}_{\mathbf{Ox/Red}} + \frac{0.0592}{n} \times \lg\frac{[Ox]}{[\mathrm{Re}d]} \qquad 12.2$$

The German chemist Walter Hermann Nernst, a professor in the Berlin University, the Nobel Prize winner in 1920 fulfilled his fundamental research works in the branch of chemical kinetics and solutions. He developed a theory of Galvanic cells and postulated the third Law of Thermodynamics.



Walter Hermann Nernst (1864-1941)

Let us review the effect of concentration and acidity at the reduction potential of the following half-reaction:

For example:

$$\underbrace{\mathbf{MnO_4^- + 8H^+}}_{\text{Oxidized form}} \mathbf{+ 5\,\bar{e} \rightarrow} \underbrace{\mathbf{Mn^{2+} + 4H_2O}}_{\text{Reduced form}}$$

$$\varphi_{\text{Ox/Red}} = \varphi^0_{\text{Ox/Red}} + \frac{0.0592}{5} \times \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}][H_2O]^4}$$

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:

$$E = \varphi_{Ox_1/\mathrm{Re}d_2} - \varphi_{Ox_2/\mathrm{Re}d_2} \qquad 12.3$$

For example, for a chemical reaction

$$\underset{Ox_1}{2\,KMnO_4} + \underset{Red_2}{5\,H_2O_2} + 3\,H_2SO_4 \rightarrow \underset{Red_1}{2\,MnSO_4} + \underset{Ox_2}{10\,O_2} + K_2SO_4 + 8\,H_2O$$

the standard reduction potentials for conjugate pairs are:

$$\varphi^0\ MnO_4^- / Mn^{2+} = +\ 1.51\ V$$

$$\varphi^0\ O_2 / H_2O_2 = +\ 0.68\ V$$

Thus emf can be calculated as

$$E^0 = 1.51 - 0.68 = 0.83\ V$$

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 (Δ_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

$$A_{el} = nFE \qquad 12.4$$

On the other hand, A_{el} is a type of useful work produced by a system and it equals to free energy change

$$A_{el} = -\Delta_r G \qquad 12.5$$

Taking together Equations 12.4 and 12.5, we can derive that

$$\Delta G = - n \times F \times E, \qquad 12.6$$

The equation 12.6 gives the linkage between a free energy change and emf of an electrochemical reaction.

If $E > 0$, $\Delta rG < 0$ a reaction is spontaneous;
If $E < 0$, $\Delta rG > 0$ a reaction is nonspontaneous.

It is evident that spontaneous Redox reactions generate a positive emf.

PROBLEM 12.2 Predict whether the following reaction would occur spontaneously under the standard conditions: $Cd (s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu (s)$

Answer:

The two half-reactions for the overall process are

$$\text{Oxidation: } Cd (s) - 2e \rightarrow Cd^{2+} (aq)$$
$$\underline{\text{Reduction: } Cu^{2+} (aq) + 2e \rightarrow Cu (s)}$$
$$\text{Overall: } Cd (s) + Cu^{2+} \rightarrow Cd^{2+} + Cu (s)$$

In Appendix we find the standard reduction potentials for these half-reactions and use the Equation 12.3. to calculate the E^o value for the reaction

$$E^o = = 0.337 \text{ V} - (- 0.403 \text{ V}) = + 0.740 \text{ V}$$

As E^o is a positive quantity, the reaction is spontaneous under the standard conditions.

PROBLEM 12.3 Predict whether the following reaction would occur spontaneously as written at 298 K: $Co (s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe (s)$
given that $[Co^{2+}] = 0.15$ M and $[Fe^{2+}] = 0.68$ M

Answer:

The half-cell reactions are

$$\text{Anode } Co (s) - 2e \rightarrow Co^{2+} (aq)$$
$$\underline{\text{Cathode: } Fe^{2+} (aq) + 2e \rightarrow Fe (s)}$$
$$\text{Overall: } Co (s) + Fe^{2+} \rightarrow Co^{2+} + Fe (s)$$

According to Appendix 2, table 9

$$\varphi^0 (Co^{2+} /Co) = - 0.280 \text{ V}$$
$$\varphi^0 (Fe^{2+} /Fe) = - 0.440 \text{ V}$$

The Nernst Equation for a half-reaction is

$$\varphi = \varphi^0 + \frac{0.0592}{n} \times \lg \frac{[Ox]}{[\mathrm{Re}\, d]}$$

$$\varphi (Co^{2+} /Co) = - 0.280 + \frac{0.0592}{2} \times \lg 0.15 = -0.304\, V$$

$$\varphi\ (Fe^{2+}/Fe) = -\ 0.440 + \frac{0.0592}{2} \times \lg 0.68 = -0.445V$$

$$E = \varphi\ (Fe^{2+}/Fe) - \varphi\ (Co^{2+}/Co) = -\ 0.445 + 0.304 = -\ 0.141\ V$$

Since E is a negative quantity, the reaction is nonspontaneous as written, and the cell reaction must be $Fe\ (s) + Co^{2+} \rightarrow Fe^{2+} + Co\ (s)$

The vast majority of oxidation-reduction reactions are reversible; therefore equilibrium constant (K) is their important characteristics. Because $\mathbf{\Delta_rG^0}$ **is** related to the equilibrium constant by the equation

$$\mathbf{\Delta_rG^0 = -\ R \times T \times lnK} \qquad 12.7$$

we have

$$\mathbf{nFE^0 = R \times T \times lnK} \qquad 12.8$$

or

$$\mathbf{K = e^{nFE^0/\ RT}} \qquad 12.9$$

Thus equilibrium constant of a Redox reaction can be calculated according to the electrochemical data. When a reaction occurs under standard temperature Equation 12.9 can be rearranged as

$$\mathbf{K} = 10^{\frac{n \times E^0}{0.0592}} \qquad 12.10$$

PROBLEM 12.4 For the following redox reaction

$$H_2O_2 + 2\ KJ + H_2SO_4 \rightarrow J_2 + K_2SO_4 + 2\ H_2O$$

(a) Write the half reactions.

(b) Write a balanced equation for the whole reaction.

(c) Calculate emf, free-energy change and equilibrium constant under standard conditions.

Answer:

$H_2O_2 + 2\ KJ + H_2SO_4 \rightarrow J_2 + K_2SO_4 + 2\ H_2O$

$$\begin{array}{l|ll} 2\ J^- - 2\ e^- \rightarrow J_2^0 & 2 & \varphi^0 = +\ 0.54\ V \\ H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O^0 & 2 & \varphi^0 = +\ 1.77\ V \\ \hline 2\ J^- + H_2O_2 + 2\ H^+ \rightarrow J_2^0 + 2\ H_2O^0 & & \end{array}$$

$$E^0 = 1.77 - 0.54 = 1.23\ V$$

$E^0 > 0$, hence this reaction is spontaneous.

$\Delta G^0 = -\ n \times F \times E^0 = -\ 2 \times 96{,}500 \times 1.23 = -\ 237{,}390\ J$

$K = 10^{\frac{2 \times E^0}{0.0592}} = 10^{\frac{2 \times 1.23}{0.0592}} = 10^{41.55} = 3.58 \times 10^{41}$, K >> 0, hence the equilibrium is shifted completely to the right.

12.3 A Galvanic cell

An arrangement that uses redox reactions to generate an electric current is called *a galvanic cell* (figure 12.2). 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 galvanic cell was developed by Italian doctor and physiologist L. Galvani in (1726 - 1798). In 1791 he carried out long series of experiments on the contraction of a frog's leg muscle through electricity and generated a concept about animal origin of electricity.

Electricity production by galvanic cells started since 1800, when A.Volta described his electrochemical cell.

L. Galvani (1726-1798)

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 $Red_1 - ne \rightarrow Ox_1$ travel through the external wire to another electrode, bringing thereduction: $Ox_2 + ne \rightarrow Red_2$

Let us examine the construction of a Daniel cell. It consists of zinc and copper electrodes, immersed into solutions of their salts.

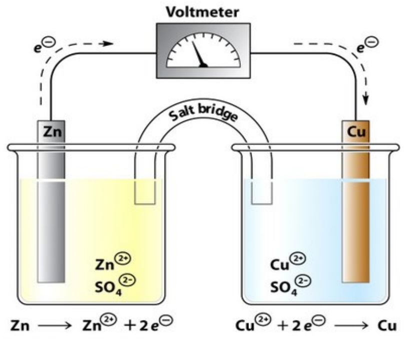


Figure 12.2 — Scheme of Daniel galvanic cell

A Zinc bar is an anode; oxidation occurs on its surface:

$$Zn - 2e \rightleftarrows Zn^{2+}$$

Electrons, lost by zinc, travel through the external wire to copper electrode, while Zn^{2+} cations diffuse into a solution. Aa 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:

$$Cu^{2+} + 2e \rightleftarrows Cu$$

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:

$$(-)Zn / Zn^{2+} // Cu^{2+}/ Cu (+)$$

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 Cu^{2+} ions by Zn metal:

$$\begin{array}{ll|l} \text{Anode:} & Zn - 2e \rightleftarrows Zn^{2+} & 1 \\ \underline{\text{Cathode:}} & \underline{Cu^{2+} + 2e \rightleftarrows Cu1} & \underline{1} \end{array}$$

$$Zn + Cu^{2+} \rightleftarrows Cu^{\cdot} + Zn^{2+}.$$

Emf of a galvanic cell is equal to:

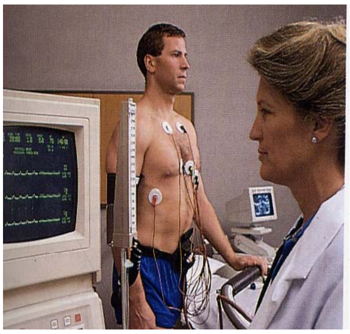
$$E = \varphi \text{ (cathode)} - \varphi \text{ (anode)} \qquad 12.11$$

For Daniel galvanic cell $E^0 = \varphi^0 (Cu^{2+}/Cu) - \varphi^0 (Zn^{2+}/Zn) = + 0.34 - (- 0.76) = = 1.1V$.

Besides the reduction potentials electricity production in galvanic cells can be driven by the so called *membrane potentials.* The membrane potential appearsto respond to the different ionic concentrations across the membrane. The Nernst equation for the membrane potential is

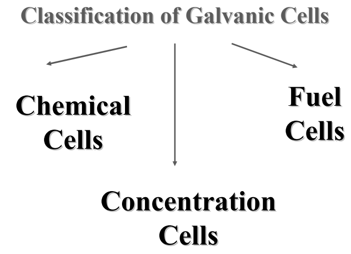
$$\varphi = \frac{R \times T}{n \times F} \times \ln \frac{[X] \cdot external}{[X] \cdot internal} \qquad 12.12$$

where $[X]_{external}$ and $[x]_{internal}$ — 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 K^+ ions than to either Na^+ or Cl^- ions (Appendix 2, table 7). 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.



- Chemical cells are composed of different electrodes.
- Concentration cells consist of two identical electrodes and differ in electrolytes concentrations only:

$$\mathbf{(-)\ Zn / ZnSO_{4aq} // ZnSO_{4aq} / Zn(+)}$$
$$\mathbf{C_M(1) \qquad C_M(2)}$$

- In fuel cells energy of combustion converts into electrical energy. Nowadays the most applied cells are propane-oxygen ones:

$$\mathbf{C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O}$$

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:

$$\text{Anode: } H_2(g) + 2\ OH^-\ (aq) - 2e \rightarrow 2\ H_2O\ (\ell)$$
$$\underline{\text{Cathode: } \tfrac{1}{2}O_2\ (g) + H_2O\ (\ell) + 2e \rightarrow 2\ OH^-\ (aq)}$$
$$\text{Overall: } H_2(g) + \tfrac{1}{2}O_2\ (g) \rightarrow H_2O\ (\ell)$$

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.

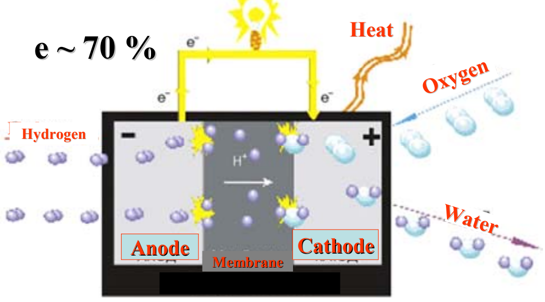


Figure 12.3 — Schematic diagram of a hydrogen-oxygen fuel cell

$$\mathbf{2H_2 + O_2 \rightleftarrows 2\ H_2O}$$

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).

12.4 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:

$$Me^{n+}\,(aq) + ne \rightleftarrows M\,(s)$$

For example Cu / Cu^{2+} (aq); Zn / Zn^{2+} (aq).

Their reduction potentials are given by the Nernst's Equation:

$$\varphi = \varphi^0 + \frac{0.0592}{n} \log\,[Me^{\,n+}]$$

where 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 Ag,AgCl / KCl(aq).

The electrode reaction is: $AgCl + \bar{e} \rightleftarrows Ag + Cl^-$

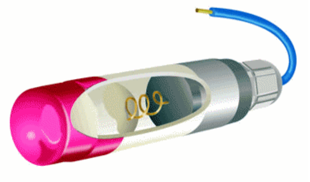


Figure 12.4 — The silver-silver chloride electrode

The Nernst's equation is given by

$$\varphi = \varphi^o - 0.0592 \log\,[Cl^-]$$

(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 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 H_2 into atomic hydrogen and as an electrical conductor to the external circuit. The cell diagram is represented as

$$Pt,\, H_2/\ 2H^+aq$$

The electrode reaction is: $2\,H^+ + 2\,\bar{e} \rightleftarrows H_2$

The Nernst's equation is given by:

$$\varphi=\varphi^o+0.0592\,\log[H^+]$$

or

$$\varphi = -\,0.0592\ pH$$

where φ^o(SHE) is assumed to be zero.

The standard hydrogen electrode (figure 12.5) is applied to determine the standard reduction potential of any other electrodes. Figure 12.6 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.

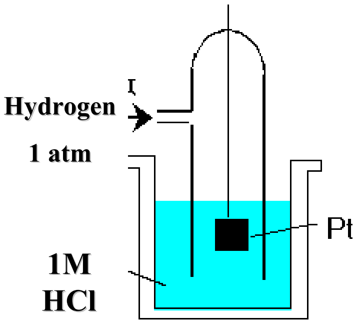


Figure 12.5 — Gas Electrodes

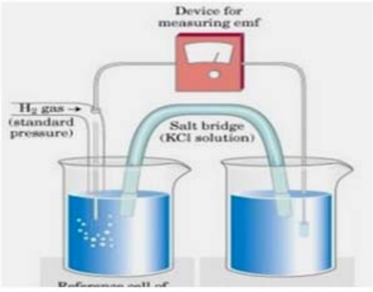


Figure 12.6 — A galvanic cell consisting of a test electrode and standard hydrogen electrode

Every standard reduction potential has a specific sign. When a substance is easier to reduce the hydronium ions under standard conditions, its φ^{o} is positive. When a substance is more difficult to reduce than hydronium ions under standard conditions, its φ^{o} is negative.

The Glass Electrode

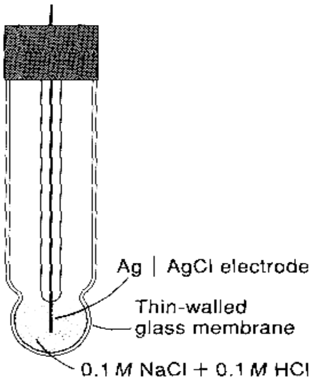


Figure 12.7 — A glass electrode

The glass electrode is an example of widely used ion-selective electrodes, because it is specific for H^+ ions (figure 12.7). 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:

$$\varphi =+ 0.059 \log([H^+]_{ex}/[H^+]_{in}) \qquad 12.13$$

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 12.8)

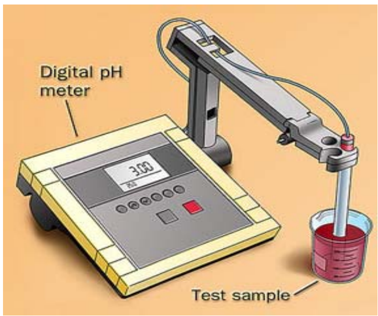


Figure 12.8 — Galvanic cell for pH measuring

$$\underbrace{\textbf{Ag, AgCl / HCl/ glass membrane}}_{\text{Glass electrode}}\;//\;\textbf{Test soln}\;//\;\underbrace{\textbf{KCl / AgCl, Ag}}_{\text{Silver-silver chloride electrode}}$$

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).

PROBLEM 12.5 A galvanic cell for pH determination is composed of a glass electrode and a silver-silver chloride electrode. Calculate pH of a test solution if emf of a galvanic cell is 0.659 V (a potential of a silver-silver chloride electrode is +0.222 V).

Answer:

A glass electrode is an anode and of a silver-silver chloride electrode is a cathode. Hence E = φ (cathode) - φ (anode), thus

$$\varphi\ (\text{anode}) = 0{,}222 - 0{,}659 = -\ 0.437\ \text{V}$$

On the other hand, according to the equation 12.13:

$$\varphi\ (\text{anode}) = 0.0592 \times \log \frac{[H^{+}]_{sol}}{0.1}$$

$$0.0592 \times \log \frac{[H^{+}]_{sol}}{0.1} = -0.437$$

$\log [H^+] = -8.38$

$pH = 8.38$

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 12.9) 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.

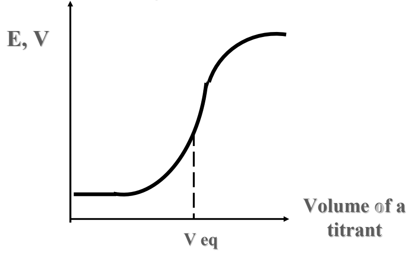


Figure 12.9 — Integral Curve of Potentiometric Titration

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 12.10) is applied for very precise determination of the endpoint of titration. The first derivative, ΔE/ΔV, is the slope of the curve, and the endpoint occurs at the volume, V_{eq}, where ΔE/ΔV has the maximum value.

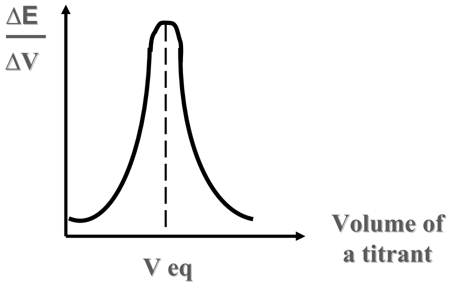


Figure 12.10 — Differential curve of potentiometric titration

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).

12.5 Laboratory work

ELECTROCHEMISTRY

Test 1: Potentiometric titration of a weak acid solution

Chemical devices: a pH-meter, a glass electrode with a hydrogen function, a silver-silver chloride electrode.

Solutions: 0.1M potassium hydroxide solution, acetic acid solution of an unknown concentration.

The aim of a laboratory work is:

- to determine of acetic acid concentration in its dilute solution;
- to determine of acetic acid ionization constant (K_a).

In order to determine CH_3COOH concentration, 10.0 mℓ of its solution are titrated against KOH secondary titrant according to a reaction:

$$CH_3COOH + OH^- \rightarrow H_2O + CH_3COO^-$$

The volume of each KOH added portion is 1.00 mℓ. Potentiometric pH measuring must be done after each portion addition. pH determination is fulfilled by means of a galvanic cell composed of glass and silver-silver chloride electrodes. A scheme of an employed galvanic cell may be represented in the following way:

(-)Ag,AgCl/HCl (0.1M)/glass membrane/CH_3COOH//KCl(sat.)/AgCl,Ag(+)

The endpoint is fixed by a sharp jump in pH values. The obtained data must be put into a table 12.1.

Table 12.1

№	Total volume of KOH solution, mℓ	Volume of KOH solution added portion, mℓ	pH of solution	ΔpH/ΔV
1.	0	0		
2.	1	1		
3.	2	1		
4.	3	1		
5.	4	1		
6	5	1		
7.	6	1		
8.	7	1		
9.	8	1		

The equivalent KOH volume is determined in a graph form. In order to do it you must represent the experimental data as integral or differential curves of potentiometric titration.

CH_3COOH normality may be calculated on the base of an equivalent law:

$$C_N(CH_3COOH) = \frac{C_N(KOH) \times V(KOH)}{V(CH_3COOH)}$$

where C_N(KOH) — normality of KOH solution, mol/ℓ;

V (KOH) — KOH equivalent volume, mℓ;

V (CH_3COOH) — volume of acetic acid, mℓ.

Test 2: Determination of acetic acid ionization constant (K_a)

In order to determine K_a of acetic acid half of KOH equivalent volume must be added to 10.0 mℓ of acetic acid solution. As a result of this procedure half of acid will be neutralized thus half of CH_3COOH will be converted into its salt. Since $[CH_3COOH] = [CH_3COONa]$, thus $K_a = [H^+]$ and pH = pK, (pK = - log K).

Compare K_a value of acetic acid obtained experimentally with K_a value taken from a reference book. Calculate absolute and relative errors of an experiment.

12.6 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 ΔG^o and K to the standard emf of a cell. Define all the terms.
9. Which of the following is the strongest oxidizing agent?

(a) H_2O_2 in acid

(b) H_2O_2 in base

(c) MnO_4- in acid

(d) MnO_4- in base

(e) CrO_4^{2-} in acid.

10. Use the overall cell potentials to predict which of the following reactions are spontaneous.

(a) $Cu(s) + 2\ Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$ $E^o = 0.46$ V

(b) $2\ Fe^{3+}(aq) + 2\ Cl^-(aq) \rightarrow 2\ Fe^{2+}(aq) + Cl_2(g)$ $E^o = -0.59$ V

(c) $2\ Fe^{3+}(aq) + 2\ I^-(aq) \rightarrow 2\ Fe^{2+}(aq) + I_2(aq)$ $E^o = 0.24$ V

(d) $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(aq)$ $E^o = 1.09$ V

(e) $Cu(s) + 2\ H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$ $E^o = -0.34$ V

NUMERICAL EXERCISES

Thermodynamics of electrochemical cells and the Nernst equation

1. For the following redox reaction

(a) Write the half reactions;

(b) Write balanced equations for the overall reactions;

(c) Calculate emf, free energy change and equilibrium constant for each of the given reaction under standard conditions:

(a) $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow$
(b) $K_2SO_3 + KMnO_4 + KOH \rightarrow$
(c) $KMnO_4 + KNO_2 + H_2SO_4 \rightarrow$
(d) $KMnO_4 + KNO_2 + H_2O \rightarrow$
(e) $KMnO_4 + KNO_2 + KOH \rightarrow$
(f) $H_2O_2 + KMnO_4 + H_2SO_4 \rightarrow$
(g) $KMnO_4 + H_2S + H_2SO_4 \rightarrow$
(h) $KMnO_4 + HCl \rightarrow$

2. Use the standard reduction potentials to find the equilibrium constant for each of the following reactions at 25°C:

(a) $Br_2\ (\ell) + 2\ I^-(aq) \rightleftarrows 2\ Br^-(aq) + I_2\ (s)$
(b) $5\ Fe^{2+}\ (aq) + MnO_4^-(aq) + 8\ H^+\ (aq) \rightleftarrows Mn^{2+}\ (aq) + 5\ Fe^{3+}\ (aq) + 4\ H_2O\ (\ell)$
(c) $Sr(s) + Mg^{2+}\ (aq) \rightleftarrows Sr^{2+}\ (aq) + Mg\ (s)$

3. Write the cell reactions and electrode half-reactions for the following cells.

(a) $Zn/ZnSO_4\ (aq)//AgNO_3\ (aq)/Ag$
(b) $Cd/CdCl_2\ (aq)//\ HNO_3\ (aq)/H_2\ (g)/Pt$
(c) $Cu/Cu^{2+}(aq)\ //Mn^{2+}(aq)/MnO_2(s)/Pt$

4. Devise cells in which the following are the reactions:

(a) $Zn(s) + CuSO_4\ (aq) \rightarrow ZnSO_4\ (aq) + Cu(s)$
(b) $2\ AgCl\ (s) + H_2\ (g) \rightarrow 2\ HCl\ (aq) + 2\ Ag\ (s)$
(c) $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (\ell)$

5. Calculate the emf of the Daniel cell at 298 K when the concentrations of $CuSO_4$ and $ZnSO_4$ are 0.50 M and 0.10 M, respectively.

ANSWER: 1.12V

6. Calculate the emf of the following concentration cell at 298 K:
$Mg(s)/Mg^{2+}(0.24\ M)//Mg^{2+}(0.53\ M)/Mg(s)$.

ANSWER: 10 mV

7. A living cell accumulates K^+ ions and removes Na^+ ions. Calculate a transmembrane potential which is generated due to unequal distribution of K^+ ions at 37°C.

ANSWER: -0.17V

8. The emf of the cell $Pt/H_2\ (g)/HCl\ (aq)//AgCl\ (s)/Ag$ is +0.322 V at 298 K. What is the pH of the electrolyte solution? Assume a reduction` potential for a silver-silver chloride electrode equal to 0.222 V.

ANSWER: 1.7

9. Consider a hydrogen electrode in aqueous HCl solution at 25°C operating at 101.3 kPa. Calculate the change in the electrode potential when the molarity of the acid is changed from 5.00 mmol/ℓ to 50.0 mmol/ℓ.

ANSWER: 59 mV

Bioelectrochemistry

10. Can coenzyme NAD·H be oxidized with oxygen gas at 25°C and pH ≈ 7? Assume that reduction potentials are the following:

$$NAD{\cdot}H - 2\,e \rightarrow NAD^+ + H^+ \varphi^o = -\,0.32\ V$$

$$1/2\ O_2 + 2\ H^+ + 2\ e \rightarrow H_2O \quad \varphi^o = +\ 0.82\ V$$

ANSWER: 1.14V, NAD·H is not stability under 25°C

11. The following reaction, which takes place just before the citric acid cycle, is catalyzed by the enzyme lactate dehydrogenase:

$$\underset{\text{pyruvate}}{CH_3COCOO^-} + NADH + H^+ \rightleftarrows \underset{\text{lactate}}{CH_3CH(OH)COO^-} + NAD^+$$

From the data listed in Appendix 2, table 15, calculate the value of ΔG^0 and the equilibrium constant for the reaction at 298 K.

ANSWER: -26.1 kJ; 3.63 ×10^4

12. Look up the standard biochemical reduction potentials in the Table 15 for the reactions: $CH_3CHO + 2\ H^+ + 2e \rightarrow C_2H_5OH$

$$NAD^+ + H^+ + 2e \rightarrow NADH$$

Calculate the equilibrium constant for the following reaction at 298 K

$$CH_3CHO + NADH + 2\ H^+ \rightleftarrows C_2H_5OH + NAD^+$$

ANSWER: 1.45×10^4

13. The oxidation of malate to oxaloacetate is a key reaction in the citric acid cycle:

$$\text{Malate} + NAD^+ \rightarrow \text{oxaloacetate} + NADH + H^+$$

Calculate the value of Δ_rG^0 and the equilibrium constant for the reaction at pH 7 and 298°C.

ANSWER: 2.97×10^4 J/mol, 6.17×10^{-6}

14. The nitrite in soil is oxidized to nitrate by the bacteria *nitrobacter agilis* in the presence of oxygen. The half-reactions are

$$NO_3^- + 2\ H^+ + 2e \rightarrow NO_2^- + H_2O \quad \varphi^o = 0.42\ V$$

$$½\ O_2 + 2\ H^+ + 2e \rightarrow H_2O \quad \varphi^o = 0.82\ V$$

Calculate the yield of ATP synthesis per mole of nitrite oxidized, assuming an efficiency of 55 %. (The Δ_rG^o value for ATP synthesis from ADP and P is 31.4 kJ/mol).

ANSWER: 1.4 mol

APPENDIX 1

Multiple Choice Questions

1. Chemical Thermodynamics

1. The second law may be defined as:

(a) it's impossible to extract an amount of heat from a hot reservoir and use it all to do work;

(b) 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;

(c) the efficiency of heat engines is equal to 100 %;

(d) total disorder increases in any spontaneous process.

2. Enthalpy is a state function, which characterizes:

(a) disorder or randomness in a thermodynamics system;

(b) the amount of thermal energy not available to do work;

(c) the amount of the internal energy available to be converted into heat;

(d) the thermal energy absorbed by a system.

3. An exothermic process proceeds with the decrease in entropy. At what temperature does it run spontaneously?

(a) at low temperature;

(b) at all temperatures;

(c) at high temperature;

(d) at no temperatures.

4. Point out the exothermic processes:

(a) $2\ KNO_3 = 2\ KNO_2 + O_2$,	$\Delta rH = +255$ kJ
(b) $2\ NaOH + H_2SO_4 = Na_2SO_4 + 2\ H_2O$,	$\Delta rH = -290$ kJ
(c) $2\ Mg + O_2 = 2\ MgO$,	$\Delta rH = -\ 1200$ kJ
(d) $CaCO_3 = CaO + CO_2$,	$\Delta rH = +\ 178$ kJ

5. Point out the reactions, which run with increase in entropy:

(a) $2\ KNO_3\ (s) = 2\ KNO_2\ (s) + O_2\ (g)$;

(b) $2\ H_2\ (g) + O_2\ (g) = 2\ H_2O\ (g)$;

(c) $2\ Mg\ (s) + O_2\ (g) = 2\ MgO\ (s)$;

(d) $CaCO_3\ (s) = CaO\ (s) + CO_2\ (g)$.

6. Point out the closed systems:

(a) a thermometer;

(b) the Universe;

(c) an oxygen – filled balloon;

(d) an open glass with water.

7. Change in what state function is equal to the heat effect of a chemical reaction?

(a) internal energy;

(b) free energy;

(c) entropy;

(d) enthalpy.

8. The First Law of Chemical Thermodynamics is defined as:
(a) the entropy of the Universe increases;
(b) the total energy in the Universe remains constant;
(c) the total energy in the Universe increases;
(d) the total energy in the Universe decreases.

9. An endothermic process proceeds with the increase in entropy. At what temperature does it run spontaneously?
(a) at low temperature;
(b) at all temperatures;
(c) at high temperature;
(d) at no temperatures.

10. Which of the following are open systems:
(a) a human being;
(b) the Universe;
(c) a helium – filled balloon;
(d) an open glass with water.

11. What state function determines spontaneity of a chemical reaction?
(a) internal energy;
(b) free energy;
(c) entropy;
(d) enthalpy.

12. Define exorgonic processes:

(a) A process that isaccompanied by a negative change in Gibbs energy and there fore is thermodynamically favored;

(b) A process that is accompanied by a positive change in Gibbs energy and therefore is thermodynamically not favored;

(c) A reaction that absorbs heat from the surroundings;

(d) A reaction that gives off heat to the surroundings.

13. Point out the path functions:
(a) internal energy;
(b) work;
(c) entropy;
(d) heat.

14. Entropy is a state function, which characterizes:
(a) disorder or randomness in a thermodynamic system;
(b) the amount of thermal energy not available to do work;
(c) the efficiency of energy conversion in open systems;
(d) the amount of thermal energy absorbed by a system.

15 Standard heats of combustion of graphite and diamond are equal to -393.5 kJ/mol and -395.4 kJ/mol, respectively. The enthalpy of graphite to diamond transition is:

(a) 0;

(b) 3.8 kJ/mol;

(c) -1.9 kJ/mol;

(d) 1.9 kJ/mol.

Answers «Chemical Thermodynamics»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a, b, d	c	a	b, c	a, d	a, c	d	b	c	a, d	b	a	b, d	a, b	a, c

2. Chemical Kinetics. Catalysis. Chemical Equilibrium

1. The rate of a chemical reaction is defined as:

(a) a period of time, which is required to complete interaction between substances;

(b) a period of time, which is required to decrease the concentration of a reactant to half of its initial concentration;

(c) a change in the concentration of reactants or products per unit time;

(d) an amount of products prepared as a result of a chemical reactions.

2. Point out the correct statements:

(a) mechanism of a chemical reaction is defined as a number of elementary steps by which reactants turn into products;

(b) an elementary step is a reaction that represents the progress at the molecular level;

(c) all chemical reactions involve several elementary steps;

(d) enzymatic reactions involve only one elementary step.

3. Elementary reactions may 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;

(d) tetramolecular: an elementary step involves four molecules.

4. The hydrolysis of acetylcholine is catalyzed by the enzyme acetyl cholinesterase, which has a turnover rate of 25,000 1/s. How long does it take for the enzyme to cleave one acetylcholine molecule?

(a) 0.04 s.;

(b) 0.004 s.;

(c) 0.0004 s.;

(d) 0.00004 s.

5. Catalysts are defined as substances, which

(a) alter the rate of chemical reactions;

(b) shift equilibrium of chemical reactions;
(c) increase the rate of chemical reactions;
(d) decrease the rate of chemical reactions.

6. A change in reactants' concentration doesn't affect the rate of chemical reactions which obeys:
(a) the first order kinetics;
(b) the second order kinetics;
(c) the third order kinetics;
(d) zero order kinetics.

7. Temperature affects the rate of chemical reactions because is responsible for:
(a) increase in activation energy of a process;
(b) increase in a fraction of active molecules in a reactants mixture;
(c) decrease in a fraction of active molecules in a reactants mixture;
(d) decrease in activation energy of a process.

8. Catalysts alter the rate of chemical reactions because they are able to
(a) decrease activation energy of a process;
(b) shift equilibrium of a process toward products;
(c) shift equilibrium of a process toward reactants;
(d) increase activation energy of a process.

9. A turnover number is:
(a) a number of substrate molecules processed by an enzyme molecule per second;
(b) a catalytic rate constant, also referred to as k_2;
(c) an equilibrium constant, which characterizes a stability of enzyme-substrate complexes;
(d) a thermal coefficient of a biochemical reaction.

10. What is the half-life of a compound if 75 % of a given sample of the compound decomposes in 69 min? Assume the first-order reaction.
(a) 79.4 min;
(b) 69.0 min;
(c) 34.5 min;
(d) 17.2 min.

11. The rate of enzymatic reactions depends upon:
(a) temperature;
(b) acidity and basicity of medium;
(c) presence of inhibitors;
(d) atmospheric pressure.

12. The activation energy is defined as:
(a) the energy absorbed at the result of a chemical reaction;
(b) the energy released at the result of a chemical reaction;

(c) the minimum energy required to initiate a chemical reaction;
(d) the energy required to brake a particular chemical bond in one mole of a substance.

13. A certain first-order reaction is 35 % complete in 50 min at 298 K. What is its rate constant?
(a) 0.0086;
(b) 0.086;
(c) 0.0037;
(d) 0.037.

14. An enzyme-catalyzed reactions are examples of:
(a) heterogeneous catalysis;
(b) homogeneous catalysis;
(c) autocatalysis;
(d) inhibition.

15. General principles of catalysis are:
(a) a catalysts changes the equilibrium constant of chemical reactions;
(b) a reaction in which a catalyst is involved is a catalyzed reaction, and a process is called catalysis;
(c) a small quantity of a catalyst should be able to affect the rate of a reaction for a large amount of reactants;
(d) a catalyst is a substance that changes the rate of a reaction without itself being consumed by the process.

Answers «Chemical Kinetics. Catalysis. Chemical Equilibrium»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
c	a, b	a, b, c	d	a, c, d	d	b, c	a, d	a, b	c	a, b, c	c	a	b	b, c, d

3. Introduction to Volumetric Analysis

1. Name the methods of redox titration:
(a) neutralization method;
(b) complexonometric method;
(c) iodometric method;
(d) permanganatometric method.

2. Point out the coefficient before the reducing agent in the following reaction

$$\mathbf{KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + O_2 + K_2SO_4 + H_2O}$$

(a) 2
(b) 5
(c) 10
(d) 3

3. Molarity is defined as:
(a) the number of moles of a solute in 1 liter of a solution;
(b) the number of equivalent moles of a solute in 1 liter of a solution;
(c) a mass of a solute in 1 milliliter of a solution;
(d) the number of moles of a solute dissolved in 1 kg (1000 g) of a solvent.

4. The method, which is widely used in medicine to determine acidity of gastric juice, is known as
(a) alkalimetry;
(b) acidiometry;
(c) direct titration;
(d) displacement titration.

5. Point out the equivalent factor for the oxidizing agent in the following reaction:

$$\mathbf{HBrO_3 + 5\ H^+ + 6e \rightarrow Br^- + 3H_2O}$$

(a) 1/2;
(b) 1/5;
(c) 1/3;
(d) 1/6.

6. Back titration **is** analytical procedure which is defined as:
(a) gradual addition of a titrant to a test solution up to the equivalence point;
(b) the excess of a titrant added to a test solution and measured by some another titrant;
(c) the excess of a reagent is added to a test solution with later measuring of its products by a titration method;
(d) titrate solution against a primary titrant of known purity.

7. An oxidizing agent is an atom, a molecule or an ion, which:
(a) accepts electrons;
(b) donates electrons;
(c) increases its oxidation number;
(d) decreases its oxidation number.

8. Point out the equivalent factor for the oxidizing agent in the following reaction: $\mathbf{MnO_4^- + e \rightarrow MnO_4^{2-}}$
(a) 1/2;
(b) 1/5;
(c) 1/3;
(d) 1.

9. In Redox reactions KI exhibits:
(a) only oxidizing properties
(b) only reducing properties
(c) neither oxidizing nor reducing properties
(d) oxidizing and reducing properties (Redox duality)

10. In Redox reactions HNO_2 exhibits:
(a) only oxidizing properties;
(b) neither oxidizing nor reducing properties;
(c) oxidizing and reducing properties (Redox duality) ;
(d) only reducing properties.

11. The half-reaction $\mathbf{I_2 + 2\ e^- \rightleftarrows 2\ I^-}$ is a basis for:
(a) permanganatometric titration;
(b) iodometric titration;
(c) complexonometric titration;
(d) acid-base titration.

12. The most important reducing agents are
(a) some oxides (CO, NO);
(b) some nonmetals (O_3, I_2);
(c) H_2SO_4 (concentrated), HNO_3;
(d) metals and some nonmetals (H_2, C).

13. Point out the disproportionation reactions:
(a) $Cl_2 + 2KOH \rightarrow KCl + KClO + H_2O$;
(b) $2H_3PO_4 + 5KOH \rightarrow K_3PO_4 + K_2HPO_4 + 5H_2O$;
(c) $4HNO_2 \rightarrow 2HNO_3 + NO + H_2O$;
(d) $2NaNO_3 \rightarrow 2NaNO_2 + O_2$.

14. 15 g of NaCl is dissolved in 85 g of H_2O. The NaCl percent by mass concentration is:
(a) 0.15 %;
(b) 0.15;
(c) 18 %;
(d) 15 %.

15. 0.1 mole of ammonia was dissolved in 500 ml of water. Molarity of the prepared solution is:
(a) 0.2 mol/ℓ;
(b) 0.02 mol/ℓ;
(c) 0.02 mol/ℓ;
(d) 0.002 mol/ℓ.

Answers «Introduction to Volumetric Analysis»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
c, d	b	a	a	d	b	a, d	d	b	c	b	a, d	a, c	b, d	a

4. Physical Properties of Solutions

1. Solutions are:
(a) isolated systems, separated from the surroundings by an interface surface;
(b) homogeneous systems which do not exchange by mass with the surroundings;
(c) homogeneous systems which contain at least two components;
(d) heterogeneous systems which contain at least two components.

2. Solubility of solids depends upon:
(a) temperature;
(b) pressure;
(c) the nature of solutes and solvents;
(d) concentration of other solutes in a solution.

3. In accordance with the state of solvents solutions are:
(a) liquid, transparent, colored;
(b) solid, liquid, turbid;
(c) gaseous, liquid, solid;
(d) liquid, turbid, colored.

4. Name equilibrium constants which characterize homogeneous equilibrium in aqueous solutions:
(a) solubility product constant (K_{sp});
(b) acid ionization constant (K_a);
(c) base ionization constant (K_b);
(d) instability constant (K_{ins}).

5. Colligative (collective) properties of solutions depend upon the number of solute particles and not their nature. They are:
(a) vapor- pressure lowering,
(b) boiling-point elevation,
(c) freezing-point depression,
(d) diffusion

6. The statement that solubility of a gas in a liquid is proportional to its partial pressure above the solution is defined as:
(a) the henry's law;
(b) the sechenov's equation;
(c) the ostvald's dilution law;
(d) the pauli's principle.

7. An erythrocyte placed into 10% NaCl solution undergoes:
(a) hemolysis;
(b) plasmolysis;
(c) shrinking;
(d) precipitation.

8. Compare K_{sp} for the following salts and point out a salt which exhibits the highest solubility in water:

(a) $K_{sp}(SrSO_4) = 3 \times 10^{-7}$; ;
(b) $K_{sp}(CuS) = 6.3 \times 10^{-36}$
(c) K_{sp} $(CaCO_3) = 4.8 \times 10^{-10}$;
(d) K_{sp} $(BaSO_4) = 1.1 \times 10^{-10}$.

9. Point out a solution with the highest boiling point:
(a) 0.01 M sucrose;
(b) 0.01 M sodium phosphate;
(c) 0.01 M potassium chloride;
(d) 0.01 M sodium carbonate.

10. A formula for the main component of bone tissue is:
(a) $Ca_4H(PO_4)_3$;
(b) $Ca_3(PO_4)_2 \cdot 2\ H_2O$;
(c) $CaHPO_4 \cdot Ca(H_2PO_4)_2$;
(d) $Ca_5(PO_4)_3OH$.

11. The Raoult's ebullioscopic law can be defined as:

(a) boiling points of solutions containing nonvolatile solutes are always lower than that of pure solvents;

(b) boiling points of solutions containing nonvolatile solutes are always higher than that of pure solvents;

(c) boiling points of pure solvents are always higher than that of solutions that contain nonvolatile solutes;

(d) boiling points of pure solvents are always lower than that of solutions containing nonvolatile solutes.

12. Solutions which are applied in medicine for intravenous injections are characterized by their osmolarity or osmolality. These concentration units express:
(a) concentration of water;
(b) concentration of substances unable to diffuse through cell membranes;
(c) concentration of substances able to diffuse through cell membranes;
(d) concentration of electrolytes.

13. Point out solutions which are isotonic with blood plasma:
(a) 3 % sodium chloride;
(b) 0.9 % glucose;
(c) 0.9 % sodium chloride;
(d) 4.5 % glucose.

14. Point out a solution with the lowest freezing point:
(a) 0.01M sucrose;
(b) 0.01M potassium chloride;

(c) 0.01M sodium phosphate;
(d) 0.01M potassium sulfate.

15. Point out a solution with the highest osmotic pressure:
(a) 0.1M glucose;
(b) 0.1M potassium chloride;
(c) 0.1M potassium sufate;
(d) 0.1M sodium phosphate.

16. Define the Raoult's cryoscopic law:

(a) freezing points of solutions containing nonvolatile solutes are always lower than that of pure solvents;

(b) freezing points of solutions containing nonvolatile solutes are always higher than that of pure solvents;

(c) freezing points of pure solvents are always lower than that of solutions;

(d) freezing points of pure solvents are always higher than that of solutions.

17. Precipitation of ionic compounds occurs:
(a) from saturated aqueous solutions;
(b) from unsaturated aqueous solutions;
(c) from supersaturated aqueous solutions;
(d) from colored aqueous solutions.

18. The first Raoult's Law is defined as:

(a) he vapor pressure of solutions containing nonvolatile solutes is always less than that of pure solvents;

(b) the decrease in vapor pressure is proportional to the mole fraction of a solute;

(c) the vapor pressure of solutions containing nonvolatile solutes is always higher than that of pure solvents;

(d) the vapor pressure of solutions containing volatile solutes is always less than that of pure solvents.

19. In order to increase solubility of gases in water it is necessary:
(a) to increase gas pressure above water;
(b) to add some electrolytes into a solution;
(c) to decrease temperature;
(d) to increase temperature.

20. Osmosis is a spontaneous process defined as:

(A) a reversible thermodynamic process of water diffusion through semipermeable membrane from a solution of a weak electrolyte into a solution of a strong electrolyte;

(b) a reversible thermodynamic process of water diffusion through semipermeable membrane from a true solution to a colloidal solution;

(c) a reversible thermodynamic process of water diffusion through semipermeable membrane from pure water to a solution;

(d) a reversible thermodynamic process of water diffusion through semipermeable membrane from a dilute solution into a more concentrated one.

Answers «Physical Properties of Solutions»

1	2	3	4	5	6	7	8	9	10
c	a, c, d	c	b, c, d	a, b, c	a	b, c	a	b	d
11	12	13	14	15	16	17	18	19	20
b	b	c, d	c	d	a	a, c	a, b	a,c	c, d

5. Electrolyte solutions. Acid-base equilibrium

1. Give name to positively charged particles
(a) radicals;
(b) molecules;
(c) anions;
(d) cations.

2. What substance is applied in medicine to correct acidosis?
(a) $NaNO_2$;
(b) $NaHCO_3$;
(c) Na_2CO_3;
(d) $KMnO_4$.

3. Water is the best medium for electrolytes dissociation due to its:
(a) high heat capacity;
(b) high polarity of molecules;
(c) low water ionization constant;
(d) low freezing point.

4. Weak electrolytes are characterized by:
(a) Ionization percent;
(b) Acid ionization constant;
(c) Ionic strength;
(d) Base ionization constant.

5. Gastric juice pH is approximately 1. The hydrogen ions molarity in it is:
(a) 0.01M;
(b) 0.001M;
(c) 0.1 M;
(d) 1.0M.

6. Buffer capacity of a solution depends upon:
(a) nature of components;

(b) atmospheric pressure
(c) concentration of buffer components;
(d) the ratio of concentrations of buffer components.

7. According to the Bronsted theory acids are defined as
(a) electrons donors;
(b) electrons acceptors;
(c) protons donors;
(d) protons acceptors.

8. Specify which of the following systems can be classified as a buffer system:
(a) KCl / HCl;
(b) NaH_2PO_4 / Na_2HPO_4;
(c) $KHSO_4$ / H_2SO_4;
(d) NH_3 / NH_4Cl.

9. Strong electrolytes are characterized by:
(a) ionic strength of solutions;
(b) activity coefficient of electrolytes;
(c) acid ionization constant;
(d) activity of ions.

10. Point out the buffer systems of blood plasma:
(a) hydrophosphate buffer system;
(b) hydrocarbonate buffer system;
(c) hemoglobin buffer system;
(d) ammonia buffer system.

11. Point out the buffer systems of blood:
(a) hemoglobin buffer systems;
(b) hydrocarbonate buffer systems;
(c) oxyhemoglobin buffer systems;
(d) acetate buffer systems.

12. According to the Bronsted theory bases are defined as
(a) electrons donors;
(b) electrons acceptors;
(c) protons donors;
(d) protons acceptors.

13. The theory of strong electrolytes was developed in 1923 by peter debye and walter karl huckel. They postulated the following:
(a) strong electrolytes are completely dissociated into ions in solutions;
(b) each ion is surrounded by ions of the opposite charge, forming an ionic atmosphere;

(c) all the ions in a solution contribute to the ionic strength (i), which characterizes the electric field of a solution;

(d) strong electrolytes obey the ostwald's dilution law.

14. Point out the correct statements:

(a) buffer solutions are able to resist in pH change upon the addition of small quantities of acids and bases;

(b) each buffer solution contains a conjugate pair of an acid and a base;

(c) pH of a buffer solution can be calculated by Henderson-Hasselbach equation;

(d) pH of a buffer solution can be calculated by Van't-Hoff's equation.

15. The ionic strength of 0.1 mol/l kbr solution is equal to:

(a) 0.2 mol/ℓ;

(b) 0.3 mol/ℓ;

(c) 0.4 mol/ℓ;

(d) 0.1 mol/ℓ.

Answers «Electrolyte solutions. Acid-base equilibrium»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
d	b	b	a, b, d	c	a, c, d	c	b, d	a, b, d	a, b	a, b, c	a, d	a, b, c	a, b, c	d

6. Electrochemistry

1. Point out the Redox reactions:

(a) $BaO + CO_2 \rightarrow BaCO_3$;

(b) $2H_2S + SO_2 \rightarrow 3S + 2\,H_2O$;

(c) $HNO_3 + K_2CO_3 \rightarrow 2\,KNO_3 + CO_2 + H_2O$;

(d) $Zn + 2\,HCl \rightarrow ZnCl_2 + H_2$.

2. Galvanic cells are classified as:

(a) concentration cells;

(b) chemical cells;

(c) fuel cells;

(d) electrolytic cells.

3. Point out the correct statements:

(a) a conjugate pair of oxidizing and reducing agents is characterized by its reduction potential;

(b) a reduction potential can be calculated by the Nernst equation;

(c) high reduction potentials correspond to strong oxidizing agents;

(d) low reduction potentials correspond to weak reducing agents.

4. Point out the coefficient before the reducing agent in the following equation:

$$\mathbf{K_2Cr_2O_7 + KI + HCl \rightarrow CrCl_3 + I_2 + KCl + H_2O}$$

(a) 1;

(b) 6;
(c) 14;
(d) 3.

5. Point out the correct statements:

(a) a galvanic cell is an arrangement that uses Redox reactions to generate an electric current;

(b) a galvanic cell is an arrangement that uses electric current to promote Redox reactions;

(c) a galvanic cell consists of two electrode compartments connected by a salt bridge and an external metallic wire;

(d) a galvanic cell efficiency is characterized by its electromotive force (emf).

6. A galvanic cell, which is applied for potentiometric pH measuring is composed of:

(a) a standard hydrogen electrode and silver-silver chloride electrode;
(b) the oxygen electrode and glass membrane electrode;
(c) a glass membrane electrode and standard hydrogen electrode;
(d) a glass membrane electrode and silver-silver chloride electrode.

7. Point out the scheme for a galvanic cell that consists from zinc and copper electrodes dipped into their salts solutions:

(a) $Zn \,|Zn^{+2}\,(aq) \,|\, Cu^{+2}\,(aq) \,|\, Cu$;
(b) $Cu \,|\, Zn^{+2}\,(aq) \,\|\, Cu^{+2}\,(aq) \,|\, Zn$;
(c) $Cu \,\|\, Cu^{+2}\,(aq) \,|\, Zn^{+2}\,(aq) \,|\, Zn$;
(d) $Zn \,|\, Zn^{+2}\,(aq) \,\|\, Cu^{+2}\,(aq) \,|\, Cu$.

8. What galvanic cell exhibits the highest emf (electromotive force) under standard conditions?

(a) It consists of zinc and copper electrodes;
(b) It consists of nickel and copper electrodes;
(c) It consists of aluminum and copper electrodes;
(d) It consists of copper and silver electrodes.

9. Beside reduction potentials membrane potentials can drive electricity production in galvanic cells. The membrane potential appears in response to:

(a) the different ionic concentrations across the membrane;
(b) the different solvent concentration across the membrane;
(c) the different osmotic pressure across the membrane;
(d) the different electrophoretic mobility of particles across the membrane.

10. Point out the coefficient before the oxidizing agent in the following equation $\mathbf{FeSO_4 + KClO_3 + H_2SO_4 \rightarrow Fe_2\,(SO_4)_3 + Cl_2 + K_2SO_4 + H_2O}$

(a) 6;
(b) 3;

(c) 1;
(d) 2.

11. The anode is an electrode that:
(a) gains negative charge when galvanic cell is functioning;
(b) gains positive charge when galvanic cell is functioning;
(c) the electrode at which oxidation occurs;
(d) the electrode at which reduction occurs.

12. Emf of a galvanic cell is equal to:
(a) E = nFE;
(b) E = φ (cathode) - φ (anode) ;
(c) E = φ (anode) - φ (cathode) ;
(d) E = $\varphi_{\text{Ox 2/Red 2}} - \varphi_{\text{Ox 1/Red 1}}$.

13. The electrode reaction is for the hydrogen electrode is represented by:
(a) $2\ H^- - 2\ e \leftrightarrow H_2$;
(b) $2\ H^+ + 2\ \bar{e} \leftrightarrow H_2$;
(c) $H^- + H^+ \leftrightarrow H_2$;
(d) $H_2 - 2\ \bar{e} \leftrightarrow 2\ H^+$.

14. The Nernst's equation for the silver-silver chloride electrode is given by:
(a) $\varphi = \varphi^o - 0.0592\ \log[Cl^-]$;
(b) $\varphi = \varphi^o - 0.0592\ \log[Cl^+]$;
(c) $\varphi = \varphi^o + 0.0592\ \log[Cl^-]$;
(d) $\varphi = \varphi^o + 0.0592\ \log[H^+]$.

15. The Galvanic Cell for pH measuring is:
(a) Ag, AgCl / HCl / glass // test soln.// Zn / Zn^{2+}(aq);
(b) Ag, AgCl / HCl /glass//test soln.// KCl / AgCl, Ag;
(c) Ag, AgCl / HCl /glass//test soln.// Cu / Cu^{2+}(aq);
(d)) Ag, AgCl / KCl /glass//test soln.// KCl / AgCl, Ag.

Answers «Electrochemistry»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
b, d	a, b, c	a, b, c	b	a, c, d	d	d	c	a	d	a,c	b	a	a	b

Appendix II

Table 1 — Molar mass of inorganic substances

	OH^-	O^{2-}	Cl^-	Br^-	I^-	S^{2-}	SO_3^{2-}	SO_4^{2-}	NO_3^-	PO_4^{3-}	CO_3^{2-}	SiO_3^{2-}
H^+	18	18	36.5	81	128	34	82	98	63	98	62	78
NH_4^+	35	-	53.5	98	145	68	116	132	80	149	96	112
Na^+	40	62	58.5	103	150	78	126	142	85	164	106	122
K^+	56	94	74.5	119	166	110	158	174	101	212	138	154
Mg^{2+}	58	40	95	184	278	56	104	120	148	262	84	100
Ca^{2+}	74	56	111	200	294	72	120	136	164	310	100	116
Ba^{2+}	171	153	208	297	391	169	217	233	261	601	197	213
Al^{3+}	78	102	133.5	267	408	150	294	342	213	122	234	282
Cr^{3+}	103	152	158.5	292	433	200	344	392	238	147	284	332
Zn^{2+}	99	81	136	225	319	97	145	161	189	385	125	141
Mn^{2+}	89	71	126	215	309	87	135	151	179	355	115	131
Fe^{2+}	90	72	127	216	310	88	136	152	180	358	116	132
Fe^{3+}	107	160	162.5	296	437	208	352	400	242	151	292	340
Cu^{2+}	98	80	135	224	318	96	144	160	188	382	124	140
Ag^+	125	232	143.5	188	235	248	294	312	170	419	276	292
Pb^{2+}	241	223	278	367	461	239	287	303	331	811	267	283

Table 2 — Solubility of inorganic substances in water

Cations	**Anions**												
	OH^-	F^-	Cl^-	Br^-	I^-	S^{2-}	SO_3^{2-}	SO_4^{2-}	NO_3^-	PO_4^{3-}	CO_3^{2-}	SiO_3^{2-}	CH_3COO^-
NH_4^+	—	s	s	s	s	—	s	s	s	s	s	—	s
Na^+ K^+	s	s	s	s	s	s	s	s	s	s	s	s	s
Mg^{2+}	L	**in**	s	s	s	s	**in**	s	s	**in**	**in**	**in**	s
Ca^{2+}	L	**in**	s	s	s	L	**in**	L	s	**in**	**in**	**in**	s
Ba^{2+}	s	L	s	s	s	s	**in**	**in**	s	**in**	**in**	**in**	s
Al^{3+}	**in**	L	s	s	s	—	—	s	s	**in**	—	**in**	L
Cr^{3+}	**in**	in	s	s	s	—	—	s	s	**in**	—	**in**	s
Zn^{2+}	**in**	L	s	s	s	**in**	**in**	s	s	**in**	**in**	**in**	s
Mn^{2+}	**in**	L	s	s	s	**in**	**in**	s	s	**in**	**in**	**in**	s
Co^{2+} Ni^{2+}	**in**	s	s	s	s	**in**	**in**	s	s	**in**	**in**	**in**	s
Fe^{2+}	**in**	**in**	s	s	s	**in**	**in**	s	s	**in**	**in**	**in**	s
Fe^{3+}	**in**	**in**	s	s	s	—	—	s	s	**in**	**in**	**in**	s
Cd^{2+}	**in**	s	s	s	s	**in**	**in**	s	s	**in**	**in**	**in**	s
Hg^{2+}	—	—	s	L	n	**in**	**in**	s	s	**in**	**in**	—	s
Cu^{2+}	**in**	**in**	s	s	s	**in**	**in**	s	s	**in**	**in**	**in**	s
Ag^+	—	s	in	**in**	in	**in**	**in**	L	s	**in**	**in**	**in**	s
Sn^{2+}	**in**	s	sp	s	s	**in**	—	s	—	**in**	—	—	s
Pb^{2+}	**in**	**in**	L	L	in	**in**	**in**	**in**	s	**in**	**in**	**in**	s

where **s** — soluble;
in — insoluble;
L — soluble, but it is low.

Table 3 — 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_A	6.0220	10^{23}mol^{-1}
Atomic mass unit	amu[a]	1.6606	10^{-27}kg
Electron rest mass	m_e	9.1095	10^{-31}kg
Proton rest mass	m_p	1.6726	10^{-27}kg
Neutron rest mass	m_n	1.6750	10^{-27}kg
Planck constant	h	6.6262	10^{-34} J×s
Rydberg constant[b]	R_∞	1.0974	10^{7} m^{-1}
Gas constant	R	8.3144	J/mol×K
Gas molar volume	V_m	2.2414	10^{-2}m^{3}/mol

[a] The symbol amu is commonly used in this country, but u is the official symbol.
[b] The symbol R_∞ refers to the Rydberg constant for infinite nuclear mass.

Table 4 — Molar boiling-point elevation and freezing-point depression constants of several common liguids

Solvent	Normal freezing point (°C)*	K_f (°C/m)	Normal boiling point (°C)*	K_b (°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 1 atm.

Table 5 — Some common acid-base indicators

Color Indicator	In acid	In base	pH rage*
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 the range over which the indicator changes from the acid color to the base color.

Table 6 — Density and concentration of aqueous solutions (20°C)

g/mℓ	**Concentration**		**g/mℓ**	**Concentration**	
	w, %	**C_M, mol/ℓ**		**w, %**	**C_M, mol/ℓ**
SODIUM CHLORIDE					
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	5	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
HYDROCHLORIC ACID					
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 7 — Distribution of Major Ions on Opposite Sides of the membrane of a Typical Nerve Cell

Ion	**Concentration/ m*M***	
	Intracellular	**Extracellular**
Na^+	15	150
K^+	150	10
Cl^-	10	110

Table 8 — K_a AND pK_a FOR ACIDS

Acid	**pK_a**	**K_a**
HClO	7.25	5.6×10^{-8}
HCl	-7	1.0×10^{7}
H_2SO_4	-3	1.0×10^{3}
H_3O^+	-1.74	55
HNO_3	-1.32	21
H_2SO_3	1.92	0.012
HF	3.13	7.2×10^{-4}
HNO_2	3.15	7.1×10^{-4}
HCOOH	3.70	2.2×10^{-4}

Acid	**pK_a**	**K_a**
CH_3COOH	4.75	1.8×10^{-5}
HCN	9.00	1.0×10^{-9}
H_3BO_3	9.14	7.3×10^{-10}
NH_4^+	9.25	5.6×10^{-10}
H_2SiO_4	9.5	3.2×10^{-10}
H_2CO_3	6.52	3.0×10^{-7}
HCO_3^-	10.4	4.0×10^{11}
H_3PO_4	1.96	0.011
$H_2PO_4^-$	7.12	7.6×10^{-8}
HPO_4^{2-}	12.3	4.8×10^{-13}
H_2S	6.92	1.2×10^{-7}
HS^-	13	1.0×10^{-13}

Table 9 — Standard reduction potentials for metals

Half-Reaction	**φ°, V**	**Half-Reaction**	**φ°, V**
$Li^+ + e^- \rightarrow Li$	-3.045	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.250
$K^+ + e^- \rightarrow K$	-2.925	$Mo^{3+} + 3e^- \rightarrow Mo$	-0.200
$Ba^{2+} + 2e^- \rightarrow Ba$	-2.900	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.136
$Ca^{2+} + 2e^- \rightarrow Ca$	-2.870	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
$Na^+ + e^- \rightarrow Na$	-2.714	$2H^+ + 2e^- \rightarrow H_2$	0.000
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.370	$Bi^{3+} + 3e^- \rightarrow Bi$	+0.215
$Al^{3+} + 3e^- \rightarrow Al$	-1.660	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.180	$Ru^{2+} + 2e^- \rightarrow Ru$	+0.450
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.762	$Ag^+ + e^- \rightarrow Ag$	+0.799
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.740	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.854
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440	$Pd^{2+} + 2e^- \rightarrow Pd$	+0.987
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403	$Pt^{2+} + 2e^- \rightarrow Pt$	+1.190
$Co^{2+} + 2e^- \rightarrow Co$	-0.280	$Au^{3+} + 3e^- \rightarrow Au$	+1.500

Table 10 — K_{sp} for inorganic substances

Substances	**K_{sp}**	**Substances**	**K_{sp}**
Ag_3AsO_3	$1.0 \cdot 10^{-17}$	AgBr	$5.3 \cdot 10^{-13}$
AgNSC	$1.1 \cdot 10^{-12}$	$CaHPO_4$	$2.7 \cdot 10^{-7}$
AgCl	$1.78 \cdot 10^{-10}$	$Ca(H_2PO_4)_2$	$1.0 \cdot 10^{-3}$
Ag_2CrO_4	$1.1 \cdot 10^{-12}$	$Ca_3(PO_4)_2$	$2.0 \cdot 10^{-29}$
$Ag_2Cr_2O_7$	$1.0 \cdot 10^{-10}$	$Ca(OH)_2$	$2.0 \cdot 10^{-14}$
AgI	$8.3 \cdot 10^{-17}$	CdS	$1.0 \cdot 10^{-29}$
$AgIO_3$	$3.0 \cdot 10^{-8}$	$Co(OH)_2$	$2.0 \cdot 10^{-16}$
$AgNO_2$	$1.6 \cdot 10^{-4}$	$CuSO_3$	$2.5 \cdot 10^{-10}$
Ag_3PO_4	$1.3 \cdot 10^{-20}$	CuS	$6.3 \cdot 10^{-36}$
Ag_2S	$6.3 \cdot 10^{-50}$	$Cu(OH)_2$	$5.0 \cdot 10^{-20}$
Ag_2SO_4	$1.6 \cdot 10^{-5}$	$Cr(OH)_3$	$6.3 \cdot 10^{-31}$
$Al(OH)_3$	$1.0 \cdot 10^{-32}$	$Fe(OH)_2$	$1.0 \cdot 10^{-15}$

Substances	**K_{sp}**	**Substances**	**K_{sp}**
$AlPO_4$	$5.7\cdot10^{-19}$	$Fe(OH)_3$	$3.2\cdot10^{-38}$
$BaCO_3$	$5.1\cdot10^{-9}$	$FeCO_3$	$3.5\cdot10^{-11}$
BaC_2O_4	$1.1\cdot10^{-7}$	$FePO_4$	$1.3\cdot10^{-22}$
$BaCr_2O_4$	$1.2\cdot10^{-10}$	FeS	$5.0\cdot10^{-18}$
BaF_2	$1.1\cdot10^{-6}$	Hg_2Cl_2	$1.3\cdot10^{-18}$
$Ba_3(PO_4)_2$	$6.0\cdot10^{-39}$	HgS	$4.0\cdot10^{-53}$
$BaSO_3$	$8.0\cdot10^{-7}$	Hg_2SO_4	$6.8\cdot10^{-7}$
$BaSO_4$	$1.1\cdot10^{-10}$	Li_2CO_3	$3.98\cdot10^{-3}$
$Ba(OH)_2$	$5.0\cdot10^{-3}$	LiF	$3.8\cdot10^{-3}$
$Ca(OH)_2$	$5.5\cdot10^{-6}$	Li_3PO_4	$3.2\cdot10^{-9}$
$CaCO_3$	$4.8\cdot10^{-10}$	$MgCO_3$	$4.0\cdot10^{-5}$
CaC_2O_4	$2.3\cdot10^{-9}$	MgC_2O_4	$8.6\cdot10^{-5}$
$CaSO_4$	$9.1\cdot10^{-6}$	$Mg(OH)_2$	$6.0\cdot10^{-10}$
CaF_2	$4.0\cdot10^{-11}$	$Mg_3(PO_4)_2$	$1.0\cdot10^{-13}$
$MnCO_3$	$1.8\cdot10^{-11}$	PbS	$2.5\cdot10^{-27}$
$Mn(OH)_2$	$4.5\cdot10^{-13}$	$PbSO_4$	$1.6\cdot10^{-8}$
MnS	$2.5\cdot10^{-10}$	$SrCO_3$	$1.1\cdot10^{-10}$
$Na[Sb(OH)_6]$	$4.0\cdot10^{-8}$	$SrCrO_4$	$3.5\cdot10^{-5}$
$Ni(OH)_2$	$2.1\cdot10^{-16}$	$SrCr_2O_4$	$5.5\cdot10^{-8}$
$PbBr_2$	$9.1\cdot10^{-6}$	$Sr_3(PO_4)_2$	$1.0\cdot10^{-31}$
$PbCO_3$	$1.0\cdot10^{-13}$	$SrSO_4$	$3.2\cdot10^{-7}$
$PbCl_2$	$1.6\cdot10^{-5}$	$ZnCO_3$	$1.4\cdot10^{-11}$
$PbCrO_4$	$1.8\cdot10^{-14}$	ZnC_2O_4	$1.5\cdot10^{-9}$
PbI_2	$1.1\cdot10^{-9}$	$Zn(OH)_2$	$7.1\cdot10^{-18}$
$Pb(OH)_2$	$1.1\cdot10^{-20}$	ZnS	$1.6\cdot10^{-24}$

Table 11 — Ionic strength and ions activity coefficients of the ions

Ions	**Ionic strength of a solution**								
	0.0005	**0.001**	**0.01**	**0.02**	**0.1**	**0.2**	**0.3**	**0.5**	**1.0**
H^+	0.98	0.97	0.91	0.90	0.87	0.81	0.80	0.79	0.85
NH_4^+, K^+, Li^+, Cl^-, Br^-, I^-, NO_2^-, NO_3^-	0.98	0.96	0.90	0.87	0.75	0.67	0.62	0.55	0.44
OH^-, F^-, ClO_4^-	0.98	0.96	0.90	0.87	0.76	0.68	0.63	0.56	0.46
Na^+, $H_2PO_4^-$	0.98	0.96	0.90	0.87	0.77	0.73	0.70	0.67	0.63
Ca^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}	0.90	0.87	0.68	0.64	0.41	0.33	0.28	0.25	0.21
Mg^{2+}, Be^{2+}	0.91	0.87	0.69	0.65	0.45	0.37	0.34	0.28	0.23
PO_4^{3-}	0.80	0.73	0.40	—	0.10	—	—	—	—
Al^{3+}, Fe^{3+}, Cr^{3+}	0.80	0.74	0.45	—	0.18	—	—	—	—

Table 12 — Selected thermadynamic data at 1 atm. and 25ºC

Substances	**State**	**ΔH^0f (kJ/mol)**	**ΔG^0_f (kJ/mol)**	**S^0 (J/K×mol)**
AgCl	s	-127	-109.7	96.1
$AgNO_3$	s	-123	-32.2	141
Ag_2O	s	-30.6	-10.8	122
Al	s	0	0	28.4
Al^{3+}	l	-524.7	-481.2	-313.4
Al_2O_3	s	-1670	-1576	51
$Al_2O_3 \cdot 3H_2O$	s	-656	-575	107
B_2O_3	s	-1264	-1184	54
H_3BO_3	s	-1088	-963	89.6
	solution	-1067	-963	160
Ba^{2+}	l	-538	-561	12.6
$BaCl_2$	s	-860	-811	126
$BaCl_2 \cdot 2H_2O$	s	-1460	-1300	203
$BaSO_4$	s	-1464	-1353	132
Br_2	l	0	0	152
Br_2^-	l	-121	103	81
C	s	0	0	5.7
CO	g	-111	-137	198
CO_2	g	-394	-394	214
	l	-413	-386	121
H_2CO_3	l	-700	-623	187
HCO_3^-	l	-691	-587	95
CO_3^{2-}	l	-676	-528	-53
Ca^{2+}	l	-543	-553	-55
CaO	s	-636	-604	40
$Ca(OH)_2$	s	-987	-897	76
$CaSO_4$	s	-1430	-1320	107
$CaSO_4 \cdot 2H_2O$	s	-2020	-1790	194
$CaCl_2$	s	-795	-750	114
$CaCl_2$	l	-877	-815	55
$CaCl_2 \cdot 6H_2O$	s	-2600		
$CaCO_3$	s	-1207	-1129	93
Cl_2	g	0	0	223
HCl	g	-92.3	-95.3	187
HCl	l	-167	-131	55
CrO_4^{2-}	l	-863	-706	38.5
$Cr_2O_7^{2-}$	l	-1461	-1257	214
Cu^{2+}	l	64.4	65	99
CuCl	s	-135	-119	92
$CuCl_2$	s	-206		
$CuSO_4$	s	-770	-662	113
$CuSO_4 \cdot 3H_2O$	s	-1680	-1400	225
$CuSO_4 \cdot 5H_2O$	s	-2280	-1880	306
F^-	l	-329	-276	-10

Substances	**State**	**$\Delta H^0 f$ (kJ/mol)**	**ΔG^0_f (kJ/mol)**	**S^0 (J/K×mol)**
HF	g	-269	-271	174
Fe	s	0	0	27.2
Fe^{2+}	l	-88	-85	-113
Fe^{3+}	l	-48	-11	-293
$FeCl_3$	s	-405		
$FeCl_3 \cdot 6H_2O$	s	-2220		
$FeSO_4$	s	-923	-820	108
$FeSO_4 \cdot 7H_2O$	s	-3000		
H_2	g	0	0	131
H^+	l	0	0	0
HO^-	l	-230	-157	-10.5
H_2O	l	-286	-238	70
H_2O	g	-242	-229	189
H_2O_2	l	-188	-118	
H_2O_2	solution	-191		
Hg	l	0	0	77
Hg	g	61	32	175
Hg^{2+}	l		-164	
$HgCl_2$	s	-230	-176	
Hg_2Cl_2	s	-264	-211	196
HgO	s	-90	-58.4	73
K^+	l	-251	-282	103
$KAl(SO_4)_2 \cdot 12H_2O$	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
$KClO_3$	s	-391	-290	143
KI	s	-328	-322	104
KI	l	-307	-334	112
KNO_3	s	-492	-393	133
KNO_3	l	-458	-393	290
$KMnO_4$	s	-814	-714	172
Li^+	l	-278	-294	14
LiOH	s	-487	-444	50
Li_2CO_3	s	-1215	-1130	90
Mg^{2+}	l	-462	-456	-118
$MgCO_3$	s	-1110	-1030	66
$MgCl_2$	s	-641	-592	90
$MgCl_2 \cdot 6H_2O$	s	-2500	-1280	366
MgO	s	-601	-570	27
$Mg(OH)_2$	s	-925	-834	63
$MgSO_4$	s	-1280	-1170	92
$MgSO_4 \cdot 7H_2O$	s	-3380		
Mn^{2+}	l	-219	-223	-84

Substances	**State**	**$\Delta H^0 f$ (kJ/mol)**	**ΔG^0_f (kJ/mol)**	**S^0 (J/K×mol)**
Mn^{3+}	l	-100		
$MnSO_4$	s	-1060	-956	112
N_2	g	0	0	191
NH_3	g	-46.2	-16.6	192
NH_3	l	-80.7	-26.6	110
N_2H_4	l	50.6	149.4	121.2
NH_4^+	l	-133	-80	113
NH_4Cl	s	-315	-204	94.6
$(NH_4)_2SO_4$	s	-1180	-900	220
NH_4NO_3	s	-365.6	-183.9	151.1
N_2O	g	81.6	104	220
NO	g	90	87	211
NO_2	g	34	52	240
N_2O_4	g	9.2	97.9	304.3
HNO_3	l	-173	-80	156
NO_3^-	l	-207	-114	146
Na	s	0	0	51
Na^+	l	-240	-262	60
Na_2CO_3	s	-1130	-1060	136
$Na_2CO_3 \cdot 10H_2O$	s	-4080	-3906	
$NaHCO_3$	s	-948	-852	102
NaF	s	-569	-541	58
NaCl	s	-411	-384	50
$NaNO_2$	s	-360		
$NaNO_3$	s	-425	-366	116
NaOH	s	-425	-380	60
Na_2SO_3	s	-1110	-1000	146
Na_2SO_4	s	-1380	-1270	149
$Na_2SO_4 \cdot 10H_2O$	s	-4320	-3640	592
$Na_2S_2O_3 \cdot 5H_2O$	s	-2600		
O_2	g	0	0	205
O_3	g	142	163	238
P_4(white)	s	0	0	44.4
P(red)	s	-18.4		
PCl_3	g	-306	-286	312
PCl_5	g	-398	-324	352
HPO_4^{2-}	l	-1299	-1094	-36
PO_4^{3-}	l	-1284	-1026	-218
$P_2O_4^{2-}$	l	-2276		
Pb^{2+}	l	1.6	24.3	21.3
PbO	s	-218	-188	69
PbO_2	s	-277	-219	77
$Pb(CH_3COO)_2$	s	-965		
$Pb(CH_3COO)_2 \cdot 3H_2O$	s	-1870		
S	s	0	0	32
SO_2	g	-296	-300	249

Substances	**State**	**$\Delta H^0 f$ (kJ/mol)**	**ΔG^0_f (kJ/mol)**	**S^0 (J/K×mol)**
SO_3	g	-395	-370	256
H_2S	g	-20	-33	206
H_2SO_4	l	-907	-742	17
HSO_4^-	l	-886	-753	127
SO_4^{2-}	l	-907	-742	17.2
SiO_2	s	-859	-805	42
Zn^{2+}	l	-152	-147	106
ZnO	s	-348	-318	44
$ZnCl_2$	s	-416	-369	108
$ZnSO_4$	s	-979	-872	125
$ZnSO_4 \cdot 7H_2O$	s	-3080	-2560	386
Organic compounds				
CH_4	g	-75	-51	186
C_2H_2	g	207	209	201
C_2H_4	g	52	68	219
C_2H_6	g	-85	-33	229
C_6H_6	s	49	173	125
CH_3Cl	g	-82	-59	234
CH_2Cl_2	g	-88	-59	270
$CHCl_3$	g	-100	-67	296
CCl_4	l	-107	-64	310
CH_3Br	g	-27	-26	246
CH_2Br_2	g	-4.2	-6	294
$CHBr_3$	g	25	16	331
CBr_4	g	50	36	358
CH_3OH	l	-239	-166	127
C_2H_5OH	l	-277	-174	161
$C_3H_8O_3$ (glycerol)	l	-671	-479	205
CH_2O	g	-116	-110	218
CH_3CHO	g	-247	-139	264
CH_3COCH_3	l	-247	-154	199
HCOOH	l	-409	-346	129
$HCOO^-$	l	-410	-335	92
CH_3COOH	l	-484	-389	160
CH_3COO^-	l	-485	-404	205
C_3H_7COOH	l	-535	-376	226
$C_3H_7COO^-$	l	-536	-372	202
$C_{15}H_{32}COOH$	s	-891	-315	455
$C_{15}H_{32}COO^-$	l		-259	
Glucose	s l	-1274 -1263	-911 -915	212 264
Glucoso-1-phosphoric acid	l		-1790	
Glysine	s l	-537 -523	-378 -380	104 159
Cystein	s	-533	-343	170

Table 13 — Selected standard enthalpy of combustion for organic substances at 1 atm. and 25ºC

Substances	**State**	**$\Delta_{com}H^\circ_{298}$, kJ/mole**	**Substances**	**State**	**$\Delta_{com}H^\circ_{298}$, kJ/mole**
CH_4	g	-882	C_2H_4	g	-1390
CH_3Br	g	-770	C_2H_2	g	-1304
CH_3Cl	g	-686	C_2H_5OH	s	-1370
CH_3I	l	-814	NH_2CH_2COOH	s	-981
CH_3NH_2	solution	-1070	$CO(CH_3)_2$	l	-1780
CH_3OH	l	-715	C_6H_6	l	-3170
CH_2O	g	-561	$C_6H_5NH_2$	l	-3400
HCOOH	l	-262	$C_6H_5NO_2$	l	-3080
$CO(NH_2)_2$	s	-634	C_6H_5OH	l	-3060
$CHCl_3$	l	-346	glucose	s	-2810
CHI_3	s	-677	fructose	s	-2820
C_2H_6	g	-1540	CH_3COOH	l	-872

Table 14 — Standard reduction potentials at 25°C*

Half-Reaction	**φ°, V**	**Half-Reaction**	**φ°, V**
$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$	+0.373	$Cu^{2+} + Cl^- + e^- \rightarrow CuCl$	+0.54
$AlO_2^- + 2H_2O + 3e^- \rightarrow Al + 4OH^-$	-2.35	$Cu^{2+} + I^- + e^- \rightarrow CuI$	+0.86
$H_3AsO_4 + 2H^+ + 2e^- \rightarrow HAsO_2 + 2H_2O$	+0.56	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$[Au(CN)_2]^- + e^- \rightarrow Au + 2CN^-$	-0.61	$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.356
$BiO_3^- + 6H^+ + 2e^- \rightarrow Bi^{3+} + 3H_2O$	+1.80	$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$	-0.56
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.065	$Fe(OH)_2 + 2e^- \rightarrow Fe + 2OH^-$	-0.877
$BrO^- + 2H_2O + 2e^- \rightarrow Br^- + 2OH^-$	+0.76	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.77
$2BrO_3^- + 6H_2O + 10e^- \rightarrow Br_2 + 12OH^-$	+0.50	$H_2O_2 + 2e^- \rightarrow 2OH^-$	+0.88
$2BrO_3^- + 3H_2O + 6e^- \rightarrow Br^- + 6OH^-$	+0.61	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	+0.68
$BrO_3^- + 6H + 6e^- \rightarrow Br^- + 3H_2O$	+1.45	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.359	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.88	$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92
$ClO_3^- + 3H_2O + 6e^- \rightarrow Cl^- + 6OH^-$	+0.63	$2HgCl_2 + 2e^- \rightarrow Hg_2Cl_2 + 2Cl^-$	0.62
$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$	+1.45	$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.84	$IO_3^- + 3H_2O + 6e^- \rightarrow 2I^- + 6OH^-$	+0.26
$[Co(NH_3)_6]^{3+} + e^- \rightarrow [Co(NH_3)_6]^{2+}$	-0.43	$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$	+1.08
$CrO_2^- + 2H_2O + 3e^- \rightarrow Cr + 4OH^-$	-1.2	$2IO_3^- + 2H_2O + 10e^- \rightarrow I_2 + 12OH^-$	+0.21
$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$	-0.13	$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33	$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	+0.60
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.153	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	+1.455	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.23
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	+1.68	$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96
$S + 2e^- \rightarrow S^{2-}$	-0.48	$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$	+0.94
$SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$	+0.17	$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$	0.99
$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$	+0.311	$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$	-0.93
		$S_2O_8^{2-} + 4e^- \rightarrow 2SO_4^{2-}$	+2.01
		$SeO_8^{2-} + 4H^+ + 2e^- \rightarrow SeO_4^{2-} + H_2O$	+1.15
		$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
		$C_6H_4O_2 + 2H^+ + 2e^- \rightarrow C_6H_4(OH)_2$	+0.7

* For all half-reaction is 1M for dissolved species and the pressure is 1 atm for gases

Table 15 — Standard Reduction Potentials for Some Biological Half-Reactions at 298K (pH = 7)

System	Half–Cell Reactions	φ°, V
O_2 / H_2O	$O_2(q) + 4H^+ + 4e^- \rightarrow 2H_2O$	+0.816
Cu^{2+} /Cu^+ hemocyanin	$Cu^{2+} + e^- \rightarrow Cu^+$	+0.540
Cyt f^{3+} /Cyt f^{2+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.365
Cyt a^{3+} /Cyt a^{2+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.29
Cyt c^{3+} /Cyt c^{2+}	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.254
Fe^{3+} /Fe^{2+} hemoglobin	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.17
Fe^{3+} /Fe^{2+} myoglobin	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.046
Fumarate/Succinate	${}^-OOCCH{=}CHCOO^- + 2\ H^+ + 2e^- \rightarrow$ $\rightarrow {}^-OOCCH_2CH_2COO^-$	+0.031
MB /$MBH_2{}^b$	$MB + 2H^+ + 2e^- \rightarrow MBH_2{}^b$	+0.011
Pyruvate /Lactate	$CH_3COCOO^- + 2H^+ + 2e^- \rightarrow$ $CH_2CHOHCOO^-$	-0.185
Acetaldehyde/ Ethanol	$CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_2OH$	-0.197
FAD /$FADH_2$	$FAD + 2H^+ + 2e^- \rightarrow FADH_2$	-0.219
NAD^+ /NADH	$NAD^+ + H^+ + 2e^- \rightarrow NADH$	-0.320
$NADP^+$ /NADPH	$NADP^+ + H^+ + 2e^- \rightarrow NADPH$	-0.324
CO_2 /Formate	$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$	-0.414
$2H^+$ /H_2	$2H^+ + 2e^- \rightarrow H_2$	-0.421
Fe^{3+} /Fe^{2+} ferredoxin	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	-0.432
Acetic acid/ Acetaldehyde	$CH_3COOH + 2H^+ + 2e^- \rightarrow CH_3CHO + H_2O$	-0.581
Acetate /Pyruvate	$CH_3COOH + CO_2 + 2\ H^+ + 2e^- \rightarrow$ $\rightarrow CH_3COCOOH + + H_2O$	-0.700

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 pre-exponential 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 Consecutive reactions are reactions of the type A→B→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 (ε) 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 ε is ~ 81, for ethyl alcohol ε ~ 24, for most organic solvents ε 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 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 reactes with or neutralized by the base.

Exorgonic 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 J $K^{-1}mol^{-1}$.

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

$$\mathrm{I} = \frac{1}{2}\Sigma C_i \times Z_i^2$$

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:

$$\varphi_{\mathbf{Ox/Red}} = \varphi^{0}_{\mathbf{Ox/Red}} + \frac{R \times T}{n \times F} \times \ln \frac{[Ox]}{[\mathrm{Re}d]}$$

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; pH = - log a_{H+}. In dilute solutions pH is defined as - log[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);
- 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 $aA + bB \rightleftarrows cC + dD$.

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 half-reaction

$$2\,H^+\,(1\,M) + 2e \rightleftarrows H_2\,(g).$$

It is assigned a zero electrode potential when the gas is at 101.3 kPa pressure and concentration of the H^+ ions is at 1 M at 298 K.

Standard reduction potential. The electrode potential of a substance for the reduction half-reaction $Ox + \upsilon e^- \rightleftarrows Red$, where Ox and Red are oxidized and reduced forms of the substance and υ 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.

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