MEDICAL CHEMISTRY
MODULE 2

THEME 1. THERMOCHEMISTRY

All objects in physical chemistry are considered as a part of a *system* or the *surroundings*. The *system* is the set of objects under consideration that separated from the surroundings by visual or imaginary boundary.

All systems can be divided into three types according to the flow of matter and energy in and out of systems: *open* systems, *closed* systems and *isolated* systems. A system is described as *open* when both energy and matter of the system can be exchanged with the surroundings. A system is described as *closed* when energy can be exchanged between the system and surroundings but not matter. A system is considered as *isolated* when neither matter nor energy can transfer between the system and surroundings.

The *energy* of a system may be defined as the capacity of the system to perform work. There are some forms of energy and all forms of energy are capable of doing work.

It is assigned that any system possesses an *internal energy* which has two major components: *kinetic energy* of the motion of the system's particles (translations, rotations, vibrations) and *potential energy* of the interaction of all the atoms, ions, and molecules in the system and energy of *chemical bonds.* Internal energy is designated by U. The internal energy of a system cannot be measured directly and it is not a way to calculate absolute value of U from other measured properties. It is possible to find only a change in U value by measurements. But this presents no problems because in most cases we normally are interested in changes in U and not U itself. When a process proceeds in a system it changes the state of the system from state 1 to state 2, as a result the internal energy changes from U_1 to U_2, and the difference is

$$\Delta U = U_2 - U_1. \quad (1.1)$$

The value of internal energy of a system depends on the temperature and the pressure. Internal energy is state function, this means that value of U depends only on state of the system and does not depend on the process path. In other words internal energy depends only on the initial and final states of the system. This implies that for a complete cycle, when system state changes from state 1 to state 2 and back again, ΔU will be zero, regardless of the path of the process. The internal energy of a system may be changed by heating or by doing work on it.

In the simplest case mechanical work may be defined as a product of force and distance, but there are other kinds of work that are more significant for chemists. When gas expands against a constant external pressure p the work done by the gas on the surroundings is

$$A_{exp} = -p\Delta V , \tag{1.2}$$

where ΔV – the change in gas volume. When quantity of compound in system changes the *chemical work* done, its value equals

$$A_{chem} = \mu\Delta n , \tag{1.3}$$

where μ – chemical potential of the compound, Δn – the change in compound quantity. The value of work done by formation of a surface depends on surface tension (σ) and surface area (s)

$$A_{surf} = \sigma\Delta s . \tag{1.4}$$

Energy can be transferred between the system and its surroundings by either performing work or heat exchange. A system does work when the energy transfer is coupled with an act against an opposing force. Heat exchange is observed when the energy transfer is associated with a temperature difference between the system and surroundings. Almost all chemical reactions absorb or release energy in the form of heat. Heat is denoted by Q. The Q value for a process may be calculated using heat capacity

$$Q = C\Delta T , \tag{1.5}$$

where C is heat capacity – the amount of heat required to change temperature of the system on 1 K; ΔT is the change in system temperature.

Heat and *work* are forms of energy that transfer into a system or out of it into the surroundings. In general, heat and work are not state functions because they are not properties of a system. They manifest themselves only during a process and their values depend on the path of the process.

The values of work done and heat depend not only on the initial and final states of system, but also on how the process is carried out, that is, depend on the process path. Signs of the work and heat values are defined such that they are positive if they result in a net increase in the internal energy of the system and negative if they result in a decrease in the internal energy. In other words the sign conventions for A and Q are: heat is positive, if it is absorbed in a process, and heat is negative, if it is released; similarly, the positive work is work done on the system by the surroundings and negative work is work done by the system on the surroundings.

The first law of thermodynamics is based on the *law of conservation of energy*, which states that energy can be converted from one form to another, but cannot be created or destroyed. The *first law of thermodynamics* states that the increase in internal energy of a system is equal to the sum of heat transferred to it and work done on it. This law may be written in integral form

$$\Delta U = Q + A, \tag{1.6}$$

or in differential form

$$dU = \delta Q + \delta A. \tag{1.7}$$

In equation (1.7) we use symbol «d» for designation of infinitesimal change in state function and symbol «δ» – for infinitesimal increment of path-dependent values.

Based upon this law, a perpetuum-motion machine, which produces work without consuming an equivalent amount of energy, is an impossible device to construct. Whenever work is performed by the system, the internal energy must decrease. In biological organisms, energy in the form of food and nutrients is required for sustenance in order to perform the work required to live.

The *thermochemistry* deals with the heat changes accompanying chemical reactions. The chemical change usually is accompanied by the liberation or absorption of energy, which may appear in the form of heat. If heat is liberated in the reaction the process is said to be *exothermic*, but if heat is absorbed it is described as *endothermic*.

Many reactions normally occur at constant (atmospheric) pressure so it is usual practice to record heat of the process by quoting the value of Q_P – the heat absorbed at constant pressure. Using the first law of thermodynamics in form of equation (1.6) for $p = const$ and considering only work of gas expansion done we have

$$Q_p = \Delta U + p\Delta V = (U_2 + pV_2) - (U_1 + pV_1) \tag{1.8}$$

Introducing new function of a system $H = U + pV$ one may rearrange equation (1.8) to form

$$Q_p = \Delta H . \tag{1.9}$$

Function H is the state function called *enthalpy*. According to equation (1.9) the heat of the process at constant pressure equals to the enthalpy change. Although heat is not a state function, the heat of a process at constant pressure is equal to change of state function because in this case «path» is defined and therefore it have only one specific value. Enthalpy changes of constant-pressure processes are sometimes called «heats» of the processes. This quantity is often referred to as the *heat of reaction*; it represents *the difference in the enthalpies of the reaction products and of the reactants, at constant pressure, and at a definite temperature, with every substance in a definite physical state*. Consider an arbitrary reaction of the type

$$a\mathrm{A} + b\mathrm{B} = c\mathrm{C} + d\mathrm{D} \tag{1.10}$$

where a, b, c and d – stoichiometric coefficients. For this reaction the heat of reaction will be

$$\Delta H_{reaction} = \sum H(products) - \sum H(reactants), \tag{1.11}$$

$$\Delta H_{reaction} = (cH_{\mathrm{C}} + dH_{\mathrm{D}}) - (aH_{\mathrm{A}} + bH_{\mathrm{B}}), \tag{1.12}$$

When ΔH for a process is negative the heat is actually evolved and this process is *exothermic*; if ΔH is positive the heat is absorbed and the process is *endothermic*.

At constant volume the work of gas expansion is zero, so at such conditions the heat of a process is equal to the change in internal energy

$$Q_V = \Delta U . \tag{1.13}$$

Using the value of Q_P (or ΔH) the value of Q_V (or ΔU) can be determined if the volume change ΔV at the constant pressure p is known

$$Q_p - Q_V = p\Delta V . \tag{1.14}$$

If the gases are assumed to behave ideally, pV is equal to nRT, and hence

$$Q_p - Q_V = p\Delta V = \Delta n_g RT , \tag{1.15a}$$

$$\Delta H - \Delta U = \Delta n_g RT\,, \tag{1.15b}$$

where Δn_g – the change in the amount of mole of gaseous substances in the reaction.

It is essential to specify a balanced equation when quoting the enthalpy change of a reaction. The chemical equation that is accompanied by corresponding enthalpy change is known as *thermochemical equation*. This equation shows the enthalpy changes as well as the mass relationships. When writing thermochemical equations, one must always specify the physical states of all reactants and products, because they help determine the actual enthalpy changes. For example, the thermochemical equation for the combustion of methane is

$$CH_{4(g)} + 2O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)},\ \Delta H = -802.4 \text{ kJ/mol}.$$

The *heat of formation* (ΔH_f) of a compound is usually defined as the change of enthalpy when 1 mol of the substance is formed from the elements. By convention, the heat of formation of any element in its most stable form is taken as zero. If element forms several allotropic modifications the heat of formation will be zero for more stable form. For example, the element oxygen exists as molecular oxygen (O_2) and ozone (O_3). The first modification is more stable than the second. Thus, we can write

$$\Delta H_f(O_2) = 0, \text{ and } \Delta H_f(O_3) = 142.2 \text{ kJ/mol}.$$

Table 1.1 illustrates the values of standard enthalpies of formation for some organic and inorganic substances.

The enthalpy change accompanying of complete combustion in oxygen of 1 mol of a compound is called the *heat of combustion* (ΔH_c).

The important law of thermochemistry was discovered experimentally by G. H. Hess (1840); it is known as *Hess's law or the law of constant heat summation.* This law states that *the resultant heat change in a chemical reaction is the same whether it takes place in one step or several stages*. This means that the net heat of reaction, at constant pressure or constant volume, depends only on the initial and final states, and not on the intermediate states through which the system may pass.

Table 1.1. Standard enthalpies of formation (p = 1 atm, t = 25°C)

Substance	ΔH_f, kJ/mol	Substance	ΔH_f, kJ/mol

CO (gas)	−110.5	Alanine (CH_3NH_2COOH)	−563
CO_2 (gas)	−393.5	Cysteine ($C_3H_7NO_2S$)	−534
H_2O (gas)	−241.8	Glutamic acid ($C_5H_9NO_4$)	−1010
H_2O (liquid)	−285.84	Leucine ($C_6H_{13}NO_2$)	−647
Glucose ($C_6H_{12}O_6$)	−1273.2	Serine ($C_2H_6ONCOOH$)	−726
Sucrose ($C_{12}H_{22}O_{11}$)	−2222.1	Tyrosine ($C_8H_{10}ONCOOH$)	−672
Ethanol (C_2H_5OH)	−277.0	Palmitic acid ($C_{15}H_{31}COOH$)	−891.6
Glycerol ($C_3H_5(OH)_3$)	−668.6	Stearic acid ($C_{17}H_{35}COOH$)	−947.7

The great practical significance of Hess's law lies in the fact that, as a consequence of this law, thermochemical equations can be added and subtracted like algebraic equations; as a result the heats of reactions which cannot be determined by direct experiment can be calculated from other thermochemical data.

It follows from Hess's law that the heat of a reaction is equal to the difference between the heats of formation of all the substances on the right-hand side of the equation of the reaction and the heats of formation of all the substances on the left-hand side (each multiplied by the stoichiometric coefficient of the equation). For the hypothetic reaction (1.10) the heat of reaction will be

$$\Delta H_{reaction} = [c\Delta H_f(C) + d\Delta H_f(D)] - [a\Delta H_f(A) + b\Delta H_f(B)]. \quad (1.16)$$

It follows from Hess's law that the heat of a reaction is equal to the difference between the heats of combustion of the reactants and the heats of combustion of the products (multiplied, of course, by the proper stoichiometric coefficient)

$$\Delta H_{reaction} = [a\Delta H_c(A) + b\Delta H_c(B)] - [c\Delta H_c(C) + d\Delta H_c(D)]. \quad (1.17)$$

When a solute is dissolved in a solvent to form a solution, there is frequently an evolution or absorption of heat. *The heat absorbed or generated when one mol of solute is dissolved in a certain amount of solvent to form a solution of a particular concentration* is called the *integral heat of solution* at the given concentration.

The enthalpy change when 1 mol of solute is dissolved in such a large volume of solvent, at a particular concentration, that there is no appreciable change in the concentration, is the *differential heat of solution* at the specified concentration.

The heat change associated with any process, physical or chemical usually varies with temperature. Effect of temperature on heat of reaction may be written as

$$\left(\frac{d(\Delta H)}{dT}\right)_P = \Delta C_P, \tag{1.18}$$

where ΔC_P is the difference in the heat capacities at constant pressure of the final and initial states, e.g., products and reactants in a chemical reaction. This expression is generally referred to as the *Kirchhoff's equation*. In order to make practical use of this expression it is integrated between the temperature limits of T_1 and T_2, with the result

$$\Delta H_{T_2} - \Delta H_{T_1} = \int\limits_{T_1}^{T_2} \Delta C_P dT, \tag{1.19}$$

where ΔH_{T_1} and ΔH_{T_2} are the heats of reaction at constant pressure, at the temperatures T_1 and T_2, respectively.

The food which we eat is metabolized in our bodies through several stages by a number of complex biological molecules called enzymes. The energy released at each stage is captured for body function and growth. One interesting aspect of metabolism is that the overall change in energy is the same as it is in combustion. For example, the total enthalpy change for the conversion of glucose ($C_6H_{12}O_6$) to carbon dioxide and water is the same whether we burn the substance in air or assimilate it in our bodies. In all these cases the process is represented by thermochemical equation

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)},\ \Delta H = -2801\ \text{kJ/mol}.$$

Various foods have different compositions and hence different energy contents. The energy content of food is generally measured in calories. The calorie (cal) is a non-SI energy unit that is equivalent to 4.184 J. Energy content of foods, that we can find on food wrappers, are the enthalpies of combustion. Because the composition of particular foods is often not known, energy content values are expressed in terms of kJ/g rather than kJ/mol. In the context of nutrition we often use a «big calorie» instead of calorie that is equal to a kilocalorie

$$1\ \text{Cal} = 1000\ \text{cal} = 4184\ \text{J}.$$

Note, we use capital «C» for representation the «big calorie». Table 1.2 shows the energy content values of some foods and fuels.

Table 7.2. Energy content of foods and some common fuels

Food	ΔH_c, kJ/g	Fuel	ΔH_c, kJ/g
Apple	–2	Charcoal	–35
Beef	–8	Coal	–30
Beer	–1.5	Gasoline	–34
Bread	–11	Kerosene	–37
Butter	–34	Wood	–20
Cheese	–18	Methane	–56
Eggs	–6	Acetylene	–50
Milk	–3	Octane	–48
Potatoes	–3	Methanol	–21

The heat changes involved in chemical reactions are measured by carrying out the process in the suitable vessel surrounded by a definite amount of water; the whole apparatus is known as a *calorimeter.* If heat is liberated in the reaction the temperature of the water rises, but if heat is absorbed the temperature falls. The product of the rise or fall temperature and the heat capacity of the water and other parts of the calorimeter and its contents may be determined from the weights and specific heats of the various parts. A *calorimeter constant* (denoted as K) is a constant that quantifies the heat capacity of a calorimeter in general. It may be calculated by applying a known amount of heat to the calorimeter and measuring the calorimeter's corresponding change in temperature. An alternative method is to place a heating coil in the calorimeter and to generate a definite amount of heat by the passage of an electric current. From corresponding rise in temperature of the water in the calorimeter the heat capacity can be evaluated.

Problems

Examples

Problem 1. The combustion of gaseous C_2H_5OH in a calorimeter at constant volume gives a value of $\Delta U = -1373.16$ kJ/mol. Calculate the value of ΔH for this process at 25 °C.

Solution. For the solution equation (7.15b) is used. The balanced chemical equation for C_2H_5OH combustion is

$$C_2H_5OH_{(g)} + 3O_{2(g)} = 2CO_{2(g)} + 3H_2O_{(g)}.$$

It follows that change in the amount of mole of gaseous substances is

$$\Delta n_g = (3 + 2) - (1 + 3) = 1.$$

Therefore, at standard temperature

$$\Delta n_g RT = 1 \times 8.314 \times (273.15 + 25) = 2478.8 \text{ J/mol} \approx 2.48 \text{ kJ/mol}.$$

$$\Delta H = \Delta U + \Delta n_g RT = -1373.16 - 2.48 = -1370.68 \text{ kJ/mol}.$$

Problem 2. Calculate the standard enthalpy change for the reaction of dissociation of PCl_5 into PCl_3 and Cl_2. Consider all substances are gaseous, use thermochemical data: $\Delta H_f(PCl_5) = -374.89$ kJ/mol, $\Delta H_f(PCl_3) = -287.02$ kJ/mol. Is this reaction endothermic or exothermic?

Solution. Write the balanced chemical equation for this process

$$PCl_5 \rightleftarrows PCl_3 + Cl_2,\ \Delta H_{reaction},$$

in which all stoichiometric coefficients are equal to unity. For this reaction equation (7.16) gives

$$\Delta H_{reaction} = 1 \cdot \Delta H_f(PCl_3) + 1 \cdot \Delta H_f(Cl_2) - 1 \cdot \Delta H_f(PCl_5).$$

By the definition $\Delta H_f(Cl_2) = 0$, consequently

$$\Delta H_{reaction} = -287.02 + 0 - (-374.89) = 87.87 \text{ kJ/mol}.$$

The positive sign of this value indicates that the reaction is endothermic and that the dissociation at 25.0 °C requires 87.87 kJ per mol of PCl_5.

Problem 3. Calculate the heat capacity of a calorimeter that, when containing 250 mL of water, requires a current of 0.650 ampere passing for 5 min 25 sec through the heater with 8.35 ohm resistance in order to raise the water temperature from 25.357 °C to 26.213 °C.

Solution: When current passes through the heater according to the Joule–Lenz law the heat produced is

$$Q = I^2Rt = 0.650^2 \times 8.35 \times 325 = 1146.6 \text{ J}.$$

Heat capacity of the calorimeter is equal

$$C = Q/\Delta T = 1146.6/(26.213 - 25.357) = 1146.6/0.856 = 1339.5 \text{ J/K}^{*}.$$

Problems for self-solving

1. The enthalpy change of combustion of diamond is –395.7 kJ/mol, while the enthalpy change of combustion of graphite is –393.8 kJ/mol. Calculate enthalpy change for the transition from graphite to diamond. *Answer:* $\Delta H = 1.9$ *kJ/mol.*

2. Calculate the heat required to raise the temperature of 1.5 mol of an ideal gas from 15 to 50 °C at fixed volume. What is the change in the internal energy? Use a specific heat value of C_V = 25 J/(K·mol)? *Answer:* $Q = 1.31$ *kJ.*

3. 1.6 g of solid NH_4NO_3 was dissolved in water in the calorimeter. After the salt is dissolved the temperature of water was on 0.28 K lower than the initial temperature. Calculate the integral heat of the dissolution of 1 mol of the salt if calorimeter constant is 1045 J/K. *Answer:* $\Delta H = 14.6$ *kJ/mol.*

4. How much energy must be added to 1.35 kg of water in a pan for it is to be warmed from 20 °C to its boiling temperature of 100 °C. Assume heat capacity of water is 4.18 J/(K·g). *Answer:* $Q = 451.44$ *kJ.*

5. The heat of combustion of ethanol with formation of liquid water and gaseous CO_2 is equal −1370.7 kJ/mol. Write equation of combustion of ethanol on air and calculate the enthalpy of formation of C_2H_5OH using equation (7.16). Use ΔH_f for CO_2 and H_2O (liquid) from Table 7.1. for the calculations. *Answer:* $\Delta H_f = 273.8$ *kJ/mol.*

6. Write a balanced equation for the complete combustion of octane, C_8H_{18} (liq). Determine the value for ΔH_c (298 K) using following data

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[*] *Here we use the difference in temperature expressed in Celsius scale for calculation of* ΔT *because the values of the differences* ΔT *and* Δt *are equal.*

ΔH_f (C_8H_{18} (liq)) = –250 kJ/mol, ΔH_f (CO_2 (gas)) = −393.5 kJ/mol, ΔH_f (H_2O (gas)) = −241.8 kJ/mol. *Answer:* ΔH_c *= –5074.2 kJ/mol.*

7. The standard enthalpy of reaction for the combustion of 1 mol of Ca is –635 kJ/mol. Write a balanced equation for the process to which this value refers. Does the reaction give out or absorb heat?

8. Write a balanced equation for the complete combustion of one mol of liquid propan-1-ol, C_3H_7OH. Use following data ΔH_f (C_3H_7OH (liq)) = –303 kJ/mol, ΔH_f (CO_2 (gas)) = −393.5 kJ/mol, ΔH_f (H_2O (gas)) = −241.8 kJ/mol to find the amount of heat liberated when 3.00 g of propan-1-ol is fully combusted. *Answer:* ΔH_c *= –92.2 kJ.*

9. 100.0 cm^3 of aqueous hydrochloric acid, HCl (2.0 mol/dm^3) were mixed with 100.0 cm^3 of aqueous NaOH (2.0 mol/dm^3) in a simple, constant-pressure calorimeter. A temperature rise of 13.9 K was recorded. Determine the value of ΔH for the reaction in *kJ* per mol of HCl. (C_{water} = 4.18 J/(K·g); density of water = 1.00 g/cm^3). *Answer:* ΔH *= –58 kJ/mol.*

10. Using following data ΔH_f (C_3H_8 (gas)) = –105 kJ/mol, ΔH_f (CO_2 (gas)) = −393.5 kJ/mol, ΔH_f (H_2O (gas)) = −241.8 kJ/mol, determine the standard enthalpy of combustion of propane, C_3H_8. *Answer:* ΔH_c *= –2042.7 kJ/mol.*

THEME 2. CHEMICAL KINETICS

Chemical kinetics is the part of chemistry concerned with the rates, at which a chemical reaction occurs. The word «kinetic» suggests movement or change. In chemistry the kinetics refers to the *reaction rate (velocity)*, which is the change in the concentration of a reactant or a product with time. Thermodynamics is concerned with the overall energy change between the initial and final states for a process. It is unknown, what is the time that is necessary for the occurring of this change. Accordingly, thermodynamics does not deal with the subject of processes rates. There is no direct correlation between thermodynamics and kinetics of a chemical reaction. Some reactions are energetically favorable, but take place very slowly, because there is no low energy pathway by which the reaction can occur.

In a kinetics experiment, a chemist attempts to understand the step-by-step transformation of reactants to products. Taken together these elementary steps give us the mechanism by which the reaction proceeds.

The rate of a chemical reaction is expressed as a change in number of reactive species with time in the unity of system volume

$$v = \frac{1}{V}\frac{\Delta n}{\Delta t}, \tag{2.1}$$

here V – volume of the system in which reaction proceeds, Δn – change in mole number of reagent or product species (molecules, atoms or ions), Δt – time that corresponds to this change. If volume kept constant the rate equals to the change in concentration (Δc) of some species with time

$$v = \left(\frac{\Delta c}{\Delta t}\right)_V \text{ or in more precise form } v = \left(\frac{\mathrm{d}c}{\mathrm{d}t}\right)_V . \tag{2.2}$$

If we consider the generalized reaction proceeding according to equation

$$a\mathrm{A} + b\mathrm{B} \rightarrow p\mathrm{P},$$

the rate of the reaction may be defined as either the rate of disappearance of the reactants or as the rate of appearance of the products. The concentration of reagents (A and B) is decreased as they are consumed and the changes in their concentrations will be negative, the concentration of the product (P) is increased with time and the change in its concentration will be positive. The rate of reaction is a positive value by the definition so, if we calculate the reaction rate observing the change in concentration of reagents, it is necessary to take these facts into consideration. Consequently for the reaction rate we may write

$$v = -\frac{1}{a}\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} = \frac{1}{p}\frac{\mathrm{d}c_\mathrm{P}}{\mathrm{d}t}. \tag{2.3}$$

Note the appearance of negative signs and stoichiometric coefficients in the equation (2.3); «–» corresponds to the change in concentrations of reagents and «+» – to the change in concentrations of products. By defining the rate of reaction in this way the rate will always be a positive number that is independent of whether we observe the change in a reactant or a product concentration in time. In accordance with these definitions the units of the rate must be those of concentration divided by time: mol/(liter·sec) or mol/(liter·min), etc.

The disappearance of reactants over time is proportional to the concentrations of each reactant raised to some power. This power known as the *order of reaction* with respect to the reactant. The sum of the individual orders gives the *overall order* of the reaction. The order of reaction with respect to each reactant, as well as the rate law itself, cannot be determined from the balanced chemical equation; it must be found experimentally. This statement can be written as

$$v = kc_A^{n_A} c_B^{n_B}, \tag{2.4}$$

where k – rate constant, n_A and n_B – orders of reaction on A and B substances, respectively. This equation is known as the reaction's *rate law* and is the *fundamental equation of chemical kinetics*.

Rate laws for the reactions are always determined experimentally. Using the dependence of concentrations of reactants on time we can determine the reaction order and then the rate constant of the reaction. Note that: a) the order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation; b) reaction order can also be zero and a fraction; c) reaction order is always defined in terms of reactant (not product) concentrations.

Once we know from experimental data how the concentration of a reactant or product depends on time we can determine the rate law. Kinetic rules for different reactions are distinguished depending on their order.

First-order reactions. Consider a reaction at constant temperature of a single reactant

A → products.

If there is no significant reverse reaction and if the reaction is first order, the rate law is

$$v = -\frac{dc_A}{dt} = k_I c_A, \tag{2.5}$$

where k_I – first-order rate constant, it has units of reciprocal time. Equation (2.5) is a differential equation that can be solved by separation of variables. Solving it one obtain

$$\ln\frac{c_{A,0}}{c_{A,t}} = k_I t \quad \text{and} \quad k_I = \frac{1}{t}\ln\frac{c_{A,0}}{c_{A,t}}, \tag{2.6}$$

where $c_{A,0}$ – initial reagent concentration, $c_{A,t}$ – reagent concentration at moment of time t.

A classic example of a first-order process is a radioactive decay in which the rate is often expressed as a *half-life*, $\tau_{1/2}$, which represents the time required for decay of the half of a present reagent molecules. The time at which this happens can be written in terms of the rate constant by substituting a value of $c_{A,t} = c_{A,0}/2$ into equation (2.6). This gives

$$\tau_{1/2} = \frac{\ln 2}{k_I}. \tag{2.7}$$

Second-order reactions. As a second-order reaction may be considered some reactions that involve two reagents, A and B, and proceed to form the products

A + B → products.

If initial concentrations of the reagents are equal the rate law may be written in form

$$v = -\frac{dc_t}{dt} = k_{II} c_t^2, \tag{2.8}$$

where k_{II} – second-order rate constant with units of reciprocal time and concentration, c_t – concentration of the reagents that corresponds to time t. Integration of the differential equation (2.8) gives

$$\frac{1}{c_t} - \frac{1}{c_0} = k_{\text{II}} t \text{ and } k_{\text{II}} = \frac{1}{t}\left(\frac{1}{c} - \frac{1}{c_0}\right), \tag{2.9}$$

and for the half-life

$$\tau_{1/2} = \frac{1}{c_0 k_{\text{II}}}. \tag{2.10}$$

The rate constant of a chemical reaction depends on the nature of reagents and changes with temperature, solvent and the presence of catalyst.

With very few exceptions, reaction rates increase with increasing temperature. The temperature dependence of rate constants follows to approximate van't Hoff's rule

$$k_{T_2} = k_{T_1} \cdot \gamma^{\frac{T_2 - T_1}{10}}, \tag{2.11}$$

where k_{T_1} and k_{T_2} – rate constants at different temperatures T_1 and T_2, γ – temperature coefficient that has a value from 2 to 4.

More precisely the temperature dependence of the rate constants can be expressed by the following equation, known as the *Arrhenius' equation*

$$\ln k = A - \frac{B}{T}. \tag{2.12}$$

Thus, a plot of $\ln k$ versus $1/T$ gives a straight line with slope A and y-intercept B. Theoretical interpretation of this dependence gives

$$k = k_0 e^{-E_a/RT}, \tag{2.13}$$

E_a – *activation energy*, which is the minimum amount of energy required to initiate a chemical reaction; k_0 – *preexponential factor* – rate constant that would be observed if $E_a = 0$.

The interrelation between values of the rate constants for a reaction at two different temperatures follows from the Arrhenius' equation

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{2.14}$$

A substance that increases the rate of a chemical reaction but does not appear in its stoichiometric equation is called a *catalyst*. Catalysis can be divided into two classes. In *homogeneous catalysis* all substances involved in the reaction, including the catalyst, occur in the same phase. In *heterogeneous catalysis* the catalyzed reaction occurs at the boundary between two phases (usually on the surface of a solid catalyst). *Enzyme catalysis* is a special case of homogeneous catalysis.

In *catalysis* the increasing of the reaction rate occurs by the lowering the activation energy. A catalyst generally provides an alternative mechanism involving the catalyst that competes with the uncatalyzed mechanism. If the catalyzed mechanism is faster than the uncatalyzed mechanism, the observed rate of the reaction is primarily due to the catalyzed mechanism, although the reaction is also still proceeding by the uncatalyzed mechanism. The catalyst reacts with reactants and forms an intermediate, but it is regenerated in a subsequent step so it is not consumed in the reaction.

Enzymes are biological catalysts. Enzymes can increase the rate of biochemical reactions by factors ranging from 10^6 to 10^{18} and they are also highly specific. An enzyme acts only on certain molecules, called substrates (that is, reactants), while leaving the rest of the system unaffected. It has been estimated that an average living cell may contain almost 3000 different enzymes, each of them catalyzes a specific reaction in which a substrate is converted into the appropriate products. An enzyme is typically a large protein molecule that contains one or more active sites where interactions with substrates take place. These sites are structurally compatible with specific substrate molecules, in much the same way as a key fits a particular lock.

The mathematical treatment of enzyme kinetics is quite complex, even when we know the basic steps involved in the reaction.

A simple theory of enzyme action was proposed by L. Michaelis and M. Menten in 1913. The enzyme catalysed reaction is given by the following scheme

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P},$$

where E, S, and P represent enzyme, substrate, and product, and ES is the enzymesubstrate intermediate; k_1, k_{-1}, k_2 – rate constants for the corresponding elementary steps. This process is shown in Fig. 2.1.

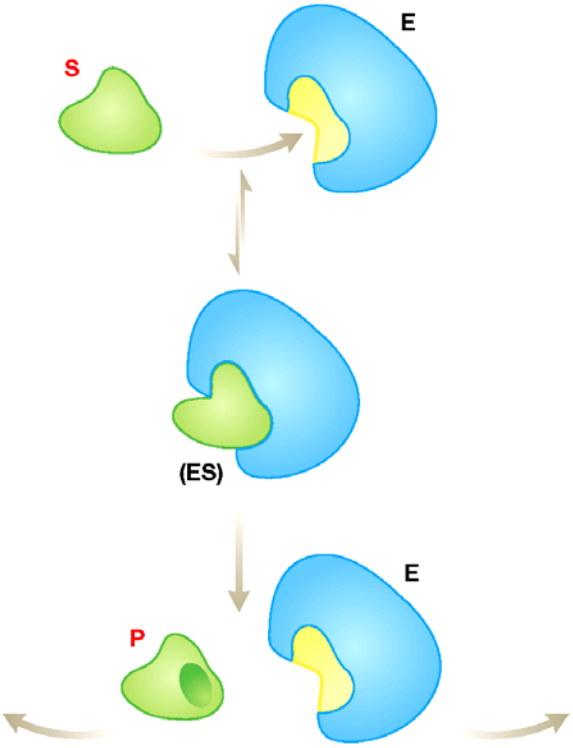


Fig. 2.1. Michaelis–Menten mechanism of enzyme action

It is assumed that the formation of the intermediate ES and its decomposition back to enzyme and substrate molecules occur rapidly and that the rate determining step is the formation of product. Because the rate-limiting step is the second reaction, the rate of the overall reaction is determined by the second step and is proportional to the concentration of the complex

$$v = k_2 c_{\mathrm{ES}} . \qquad (2.15)$$

Experimentally, enzyme reactions are probed by measuring the *initial velocity*, when the concentration of the substrate is much greater than the concentration of the enzyme. The use of the initial velocity allows the use of the assumption that changes of the substrate concentration are negligible. The initial velocity usually has a linear dependence on the substrate concentration at low substrate concentrations and approaches an asymptotic value denoted by $v_{\max}$ at high concentrations (Fig. 2.2). This dependence of the initial velocity on the substrate concentration can be qualitatively understood in terms of the Michaelis–Menten model. At any given time, the enzyme is present as a free enzyme and as a complex with the substrate. At low substrate concentrations, most of the enzyme is present in the free form and the rate is proportional to the substrate concentration because the complex formation is favored as the substrate concentration is increased. The maximum velocity is reached at high substrate concentrations when all of the enzyme is present as the intermediate complex ES. Under these conditions the enzyme is said to be saturated with its substrate, so the increase in the substrate concentration have no effect. This dependence can also be described using the *Michaelis–Menten equation*

$$v = \frac{\mathrm{d}c_P}{\mathrm{d}t} = \frac{v_{\max} c_{S,0}}{c_{S,0} + K_M}, \tag{2.16}$$

where $c_{S,0}$ – initial substrate concentration; $v_{\max}$ – maximum velocity, that occurs when all the enzyme is combined with substrate;

$$v_{\max} = k_2 c_{E,0}, \tag{2.17}$$

$c_{E,0}$ – total enzyme concentration, K_M – Michaelis constant,

$$K_M = (k_{-1} + k_2) / k_1. \tag{2.18}$$

The value of the maximum velocity can be found by an extrapolation of the curve shown in Fig. 2.2. According to Michaelis–Menten equation value of K_M is equal to the substrate concentration at half-maximum velocity.

For enzyme catalyzed reactions following the Michaelis–Menten mechanism, a plot of the reciprocal of the initial velocity against the reciprocal of the substrate concentration, a so-called *double-reciprocal plot*, produces a straight line

$$\frac{1}{v} = \frac{1}{v_{\max}} + \frac{K_M}{v_{\max}} \cdot \frac{1}{c_{S,0}}. \tag{2.19}$$

This equation is known as *Lineweaver–Burk equation*. The y-intercept of the plot gives the value of the maximum velocity and the slope of the plot gives the value of K_M.

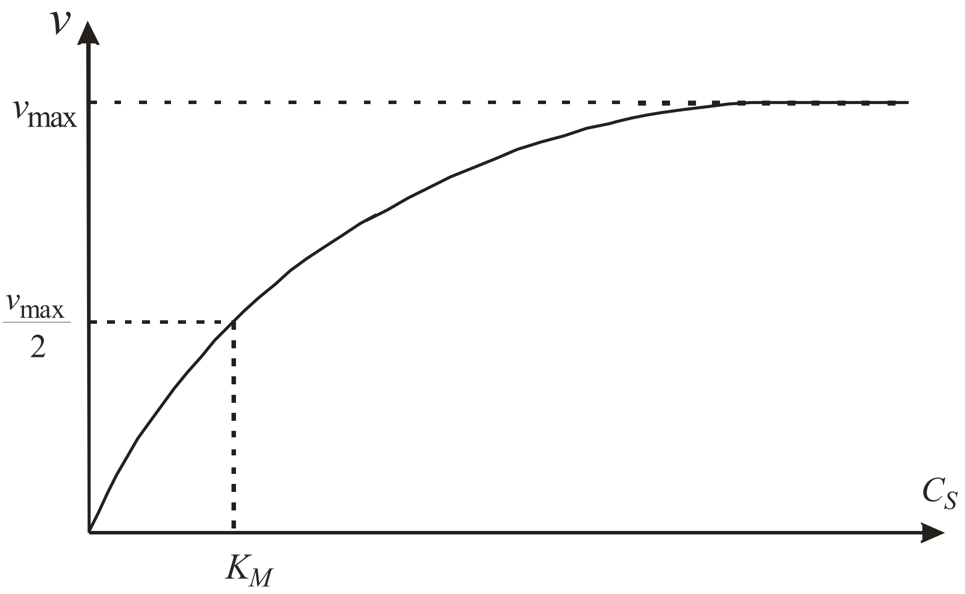


Fig. 2.2. The effect of substrate concentration on the initial velocity for an enzyme-catalyzed reaction

Problems

Examples

Problem 1. For the gas-phase reaction $H_2 + I_2 \rightarrow 2HI$ at 373.15 K, the rate constant is equal to $8.74 \cdot 10^{-15}$ mol/(L·s), at 473.15 K it is equal to $9.53 \cdot 10^{-10}$ mol/(L·s). Find the value of the activation energy and the rate constant at 400 K.

Solution. For any two temperatures T_1 and T_2, equation (8.14) gives

$$E_a = R \ln \frac{k_{T_2}}{k_{T_1}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1}.$$

Substitution of the values gives

$$E_a = 8.314 \cdot \ln \frac{9.53 \cdot 10^{-10}}{8.74 \cdot 10^{-15}} \left(\frac{1}{373.15} - \frac{1}{473.15} \right)^{-1} = 167.9 \cdot 10^3 \text{ J/mol.}$$

For the rate constant at 400 K equation (8.14) gives

$$k_{400} = k_{T_1} \cdot \exp\left(\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{400} \right) \right),$$

$$k_{400} = 8.74\cdot10^{-15}\exp\left(\frac{167.9\cdot10^3}{8.314}\left(\frac{1}{373.15}-\frac{1}{400}\right)\right) = 3.17\cdot10^{-14}\ \text{mol/(L·s)}.$$

Problem 2. Iodine atoms combine to form molecular iodine in the gas phase

$$I(g) + I(g) \rightarrow I_2(g).$$

This reaction follows second-order kinetics and has the rate constant $7.0\cdot10^9$ mol/(L·s) at 23 °C. Consider the initial concentration of I atoms is 0.086 mol/L, calculate the concentration after 2 min. Also calculate the half-life of the reaction if the initial concentration of I is 0.60 mol/L and if it is 0.3 mol/L.

Solution. The relationship between the concentrations of a reactant at different times for a second-order reaction is given by equation (8.9). The applying this equation gives

$$\frac{1}{c_t} - \frac{1}{0.086} = 7\cdot10^9\cdot2\cdot60,\ \ \frac{1}{c_t} = 8.4\cdot10^{11},\ \ c_t = 1.19\cdot10^{-12}\ \text{mol/L}.$$

The concentration obtained is such a low that it is undetectable. The very large rate constant for this reaction means that practically all the I atoms combine after only 2 min of reaction time.

The half-life for a second-order reaction is given by equation (8.10). It gives

$$\tau_{1/2} = \frac{1}{0.6\cdot7\cdot10^9} = 2.38\cdot10^{-10}\ \text{s}$$

and

$$\tau_{1/2} = \frac{1}{0.3\cdot7\cdot10^9} = 4.76\cdot10^{-10}\ \text{s}.$$

These two results confirm that the half-life of a second-order reaction is not a constant and depends on the initial concentration of the reactant.

Problems for self-solving

1. The time dependence of the reactant concentration for a first-order reaction is characterized by a half-life of 150 s. How long time is required for

the concentration of the reactant to decrease from 0.05 to 0.01 mol/L? *Answer:* $t = 348$ *s.*

2. Consider the simple first-order reaction A → B. If you start with solution of 0.1 mol/L A, it takes 10 s to go to a concentration of 0.005 mol/L of A. What is the value of rate constant for this reaction? *Answer:* $k = 0.0693\ s^{-1}$.

3. Calculate the activation energy for a reaction if its rate constant increases from 10 to 20 s^{-1} as the temperature increases from 298 to 315 K. *Answer:* $E_a = 60.7$ *kJ/mol.*

4. The rate for a reaction increases from $7{\cdot}10^{-3}$ to $3{\cdot}10^{-2}$ mol/(L·s) as the temperature increases from 20 to 30 °C. Calculate activation energy. *Answer:* $E_a = 117$ *kJ/mol.*

5. A reaction has a rate constant of 0.01 s^{-1} at 298 K and an activation energy of 35 kJ/mol. Calculate the rate constant when the system is cooled to 277 K. *Answer:* $k = 0.0035\ s^{-1}$.

6. Consider a simple first-order reaction A → B. If you start with solution of 0.1 mol/L A, it takes 20 s to go to a concentration of 0.05 mol/L of A. (a) What is the value of the rate constant for this reaction? (b) Calculate half-life of the reaction. *Answer: (a)* $k = 0.035\ s^{-1}$; *(b)* $\tau_{1/2} = 19.8$ *s.*

7. The experimental rate law of a reaction A + B → C is $v = k[A]^2[B]$. (a) Determine total order of the reaction. (b) Imagine initial conditions at which the rate equals v_0. If the concentration of reagent A is doubled and the concentration of B is halved, what will happen with the reaction rate?

8. A reaction has a rate constant of 0.01 s^{-1} at 300 K and activation energy of 65000 J/mol. Calculate the rate constant when the system is cooled to 273 K. *Answer:* $k_{T_1} = 7.5{\cdot}10^{-4}\ s^{-1}$.

9. The half-life of a second-order reaction A → products is 10 s if the initial concentration of the reactant is 0.1 mol/L. Calculate: (a) the rate constant and (b) the concentration of the reactant at 50 s after the initiation of the reaction, if the initial concentration of the reactant is 0.1 mol/L. *Answer: (a)* $k = 1$ mol/(L·s)*; (b)* $c = 0.017$ *mol/L.*

10. Consider a reaction A + B + C → D, for which the order in respect of each reagent is 1. (a) Write the rate law for the reaction. (b) Imagine initial conditions at which the rate equals v_0. If the concentration of reagent A is tripled and the concentrations of B and C are halved, how will the reaction rate change?

THEME 3. ELECTROCHEMISTRY

3.1. GALVANIC CELLS. POTENTIOMETRY

When a most of chemical reactions occur, the transfer of electrons from one molecule or particle to another takes place. The direction of this transfer is disordered because the molecular collisions are chaotic and equilprobable, and energy that evolved when reaction proceeds dissipates as a heat. In order to convert the heat energy of the chemical reaction to electrical one we must to direct the electron flow. This can be made by separation of reagents and providing the electric contact, for example, metallic conductor, between separated parts.

A galvanic or voltaic cell consists essentially of two electrodes (half cells) combined in such a manner that when they are connected by a conducting material, such as a metallic wire, an electric current will flow. Each electrode, in general, involves an electronic (metallic) and an electrolytic conductor in contact; at the surface of separation between the metal and the solution there exists a difference of electrical potential, called the electrode potential. The algebraic difference of the two electrode potentials equals to the *electromotive force (EMF) of the cell*.

During the operation of a galvanic cell a chemical reaction takes place at each electrode, and it is the energy of these reactions that provides the electrical energy of the cell. If there is an over-all chemical reaction, the cell is referred to as a *chemical cell*. In some cells, however, there is no resultant chemical reaction, but there is a change of energy due to the transfer of solute from the solution with one concentration to another; such cells are called *concentration cells*.

In order that the electrical energy produced by a galvanic cell may be related thermodynamically to the process occurring in the cell, it is essential that the latter should behave reversibly in the thermodynamic sense. A reversible cell must satisfy the following conditions. If the cell is connected to an external source of EMF which is adjusted so as exactly to balance the EMF of the cell, i.e., so that no current flows, there should be no chemical or other change in the cell. If the external EMF is decreased by an infinitesimally small amount, current will flow from the cell, and a chemical or other change, proportional in extent to the quantity of electricity passing, should take place. On the other hand, if the external EMF is increased by a very small amount, the current should pass in the opposite direction, and the process occurring in the cell should be exactly reversed.

It may be noted that galvanic cells can only be expected to behave reversibly when the currents passing are infinitesimally small, so that the system is always virtually in equilibrium. If large currents flow, concentration gradients arise within the cell because diffusion is relatively slow; in these circumstances the cell cannot be regarded as existing in a state of equilibrium. It is important to recall, in this connection, that in the potentiometric method of measuring of EMF, as will be described late, an infinitesimal or zero current is drawn from the cell at the point of balance. The EMF obtained in this way is as close to the reversible value as is experimentally possible. If an attempt had been made to determine the EMF with an ordinary voltmeter, which takes an appreciable current, the result would have been in some error. For reliable measurement of the EMF of a galvanic cell Poggendorff's compensation method is used.

An instance of a reversible cell is the Daniell–Jacobi cell, consisting of a zinc electrode immersed in an aqueous solution of zinc sulfate, and a copper electrode in copper sulfate solution, i.e.,

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \mid \mathrm{CuSO_4} \mid \mathrm{Cu}.$$

The two solutions being usually separated by a porous partition that prevents spontaneous diffusion between solutions. If the external circuit is closed by a source of the EMF just less than that of the Daniell–Jacobi cell, the chemical reaction taking place in the cell is

$$\mathrm{Zn} + \mathrm{CuSO_4} \rightarrow \mathrm{Cu} + \mathrm{ZnSO_4},$$

i.e., zinc dissolves from the zinc electrode to form zinc ions in solution, while copper ions are discharged and deposit copper on the other electrode. On the other hand, if the external EMF is greater than that of the cell, the reverse process occurs; the copper electrode dissolves while metallic zinc is deposited on the zinc electrode.

There are several types of reversible electrodes; in details they will be described later. They differ formally as far as their construction is concerned; nevertheless, they are all based on the same fundamental principle which it is important to understand clearly. A reversible electrode always involves an oxidized and a reduced state, using the terms «oxidized» and «reduced» in their broadest sense. Thus, oxidation refers to the liberation of electrons while reduction implies the taking up of electrons. If the electrode consists of a metal Me and its ions Me^{z+}, the former is the reduced state and the latter is the oxidized state; similarly, for an anion electrode, the A^{-} ions are the reduced state while A represents the oxidized state. For instance, in the silver-silver chloride electrode, the metallic silver and the chloride ions together form the reduced state of the system while silver chloride is the oxidized state. It can be seen, therefore, that all types of reversible electrode are made up from the reduced and oxidized states of a given system, and in every case the electrode reaction may be written in the general form

$$\text{Oxidized State} + z\bar{e} \rightleftarrows \text{Reduced State}$$

or in a brief form

$$\mathrm{Ox}^{z+} + z\bar{e} \rightleftarrows \mathrm{Red},$$

where z is the number of electrons by which the oxidized and reduced states differ. In general the potential of reversible electrode is given by the *Nernst equation*:

$$\varphi = \varphi^{o} + \frac{RT}{zF}\ln\frac{a_{\mathrm{Ox}^{z+}}}{a_{\mathrm{Red}}}, \qquad (3.1a)$$

where $a_{\mathrm{Ox}^{z+}}$, a_{Red} – activities of oxidized and reduced states, respectively, that must be raised to the power of the number of its molecules taking part in the electrode reaction; φ^{o} – standard electrode potential, that is, the potential of the electrode when all the substances concerned are in their standard states of unit activity.

In dilute solutions, where activities are close to concentrations, Nernst equation may be written in form

$$\varphi = \varphi^{o} + \frac{RT}{zF}\ln\frac{c_{\mathrm{Ox}^{z+}}}{c_{\mathrm{Red}}}, \qquad (3.1b)$$

where $c_{\mathrm{Ox}^{z+}}$, c_{Red} – concentrations of oxidized and reduced states, respectively. For the simplicity later in this theme we will mainly use Nernst equation written in concentrations.

A reversible electrode consists of an oxidized and a reduced states, and the reaction which occurs at such an electrode, when it forms part of an operating cell, is either oxidation, i.e.,

$$\text{Reduced state} \rightarrow \text{Oxidized state} + \text{electrons},$$

or reduction, i.e.,

$$\text{Oxidized state} + \text{electrons} \rightarrow \text{Reduced state}.$$

In the first case electrode is negative, in the second electrode is positive. It can be readily seen, therefore, that in a reversible cell, consisting of two reversible electrodes, a flow of electrons, and hence a flow of current, can be maintained if oxidation occurs at one electrode and reduction at the other electrode. The *EMF of the cell* is equal to the difference between the potentials of electrodes

$$E = \varphi_+ - \varphi_-, \tag{3.2}$$

where φ_+ and φ_- – potentials of positive and negative electrodes, respectively. According to the convention widely adopted, the EMF of the cell is positive when in its normal operation oxidation takes place at the left-hand electrode (negative electrode) of the cell as written, reduction occurring at the right-hand electrode (positive electrode). If the reverse is the case, so that reduction is taking place at the left-hand electrode, the EMF of the cell, by convention, will have a negative sign.

Reversible electrodes

The electrodes constituting a reversible cell are reversible electrodes, and several types of such electrodes are known; the combination of any two reversible electrodes gives a reversible cell.

The *first type* of reversible electrode involves a metal in contact with a solution of its own ions, e.g., zinc in zinc sulfate solution, or copper in copper sulfate solution, as in the Daniell–Jacobi cell

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(\text{solution}),$$

$$\mathrm{Cu} \mid \mathrm{Cu}^{2+}(\text{solution}).$$

Electrodes of the first type are reversible with respect to the ions of the electrode material. If the electrode material is a metal, represented by Me, with valence that equals to z, the reaction which takes place at such an electrode, when the cell of which it is part operates, is then

$$\mathrm{Me}^{z+} + z\bar{e} \rightleftarrows \mathrm{Me},$$

where $\bar{e}$ denotes an electron, and Me^{z+} implies a solvated ion in solution. The direction of the reaction depends on the direction of the flow of current through the cell. The potential of electrodes of this kind depends on the concentration (or activity) of the reversible ions in the solution

$$\varphi = \varphi^{o} + \frac{RT}{zF}\ln\frac{a_{\mathrm{Me}^{z+}}}{a_{\mathrm{Me}}} \approx \varphi^{o} + \frac{RT}{zF}\ln c_{\mathrm{Me}^{z+}}, \tag{3.3}$$

where φ^{o} – standard electrode potential; $a_{\mathrm{Me}^{z+}}$ – activity of Me^{z+} ions in solution; a_{Me} – activity of solid metal, this value is taken as unity; $c_{\mathrm{Me}^{z+}}$ – concentration of metal ions in solution.

Electrodes of the *second type* involve a metal and a sparingly soluble salt of this metal in contact with a solution of a soluble salt with the same anion. An example is silver-silver chloride electrode consisting of silver, solid silver chloride and a solution of a soluble chloride, such as hydrochloric acid (or KCl)

Ag | AgCl (solid) | HCl (solution)

The electrode reaction in this case may be written as

$$\mathrm{AgCl} + \bar{e} \rightarrow \mathrm{Ag} + \mathrm{Cl}^{-},$$

its potential is given by the Nernst equation

$$\varphi = \varphi^{o} + \frac{RT}{F}\ln\frac{a_{\mathrm{AgCl}}}{a_{\mathrm{Ag}}\cdot a_{\mathrm{Cl}^{-}}} \approx \varphi^{o} - \frac{RT}{F}\ln c_{\mathrm{Cl}^{-}}, \tag{3.4}$$

where φ^{o} – standard electrode potential; $a_{\mathrm{Cl}^{-}}$ and $c_{\mathrm{Cl}^{-}}$ – activity and concentration of chloride ions in solution, respectively; a_{Ag} and a_{AgCl} – activities of solid substances, these values are conventionally taken as unity.

The second type electrodes behave as if they were reversible with respect to the common anion, namely, the chloride ion in this case. Electrodes of the second type have been made with other insoluble halides, e.g., silver bromide or iodide, and mercurous chloride, and also with insoluble sulfates, oxalates, etc.

Electrodes of a special type are electrodes that are called *gas electrodes*. They may be reversible with respect to cations (hydrogen electrode) or anions (oxygen and the chlorine electrodes). The most important of these electrodes is the hydrogen gas electrode. It consists of a small sheet or wire of platinum coated with the finely divided metal, i.e., «platinized» by electrolysis of a solution of chloroplatinic acid. The platinum foil or wire, attached to a suitable connecting wire, is inserted in the experimental solution, and a stream of hydrogen gas is passed through the solution. It may be schematically written as

$$\mathrm{Pt} \mid \mathrm{H_2(gas)} \mid \mathrm{H^+(solution)},$$

in this electrode the following reversible electrode reaction takes place

$$2\mathrm{H}^+ + 2\overline{e} \rightleftarrows \mathrm{H_2(gas)}.$$

The finely divided platinum permits rapid establishment of the equilibrium between gaseous hydrogen, on the one hand, and hydrogen ions in solution and electrons, on the other hand; the result is that the platinum acquires a potential that is characteristic of the hydrogen gas and hydrogen ion system. Various types of hydrogen electrode vessels have been devised for different purposes; a convenient type of hydrogen electrode is shown in Fig. 3.1. A sheet of platinum is sealed into a glass tube, and platinized in the usual manner; this constitutes the actual electrode. The lower half of the sheet is immersed in the experimental solution, and hydrogen gas is passed in through the side tube; the platinum sheet is surrounded by hydrogen gas. The gas should be purified, so as to remove oxygen and other substances, and its partial pressure should be

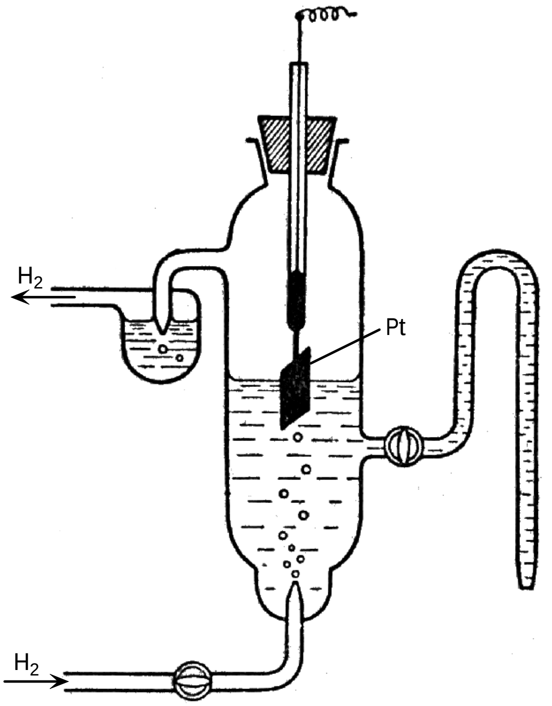


Fig. 3.1. Hydrogen gas electrode

known, after making allowance for the aqueous vapor pressure of the solution. The potential of the electrode, measured by combination with a reference electrode, must be corrected to a pressure of 1 atm. The hydrogen gas electrode cannot be employed in solutions containing oxidizing agents, such as nitrates, permanganates, ferric salts, etc., or other substances capable of reduction by hydrogen in the presence of finely divided platinum. The electrode does not behave satisfactorily in solutions containing ions of metals lying below hydrogen in the table of standard potentials (Table 3.1), e.g., gold, silver, mercury and copper. In addition, traces of compounds of mercury, sulfur and arsenic «poison» the electrode, so that it will not function even in other solutions. In spite of these limitations, the hydrogen gas electrode has been extensively employed for precise measurements in cells with or without liquid junctions, and for the standardization of buffer solutions.

*Table 3.1. Standard electrode potentials at 25 °C**

Electrode half-reaction	φ^o, V
$F_2(g) + 2\overline{e} \rightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2\overline{e} \rightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + \overline{e} \rightarrow Co^{2+}(aq)$	+1.81
$H_2O_2(aq) + 2H^+(aq) + 2\overline{e} \rightarrow 2H_2O$	+1.77
$MnO_4^-(aq) + 8H^+(aq) + 5\overline{e} \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3\overline{e} \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2\overline{e} \rightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6\overline{e} \rightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$O_2(g) + 4H^+(aq) + 4\overline{e} \rightarrow 2H_2O$	+1.24
$Br_2(l) + 2\overline{e} \rightarrow 2Br_2(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3\overline{e} \rightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2\overline{e} \rightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2\overline{e} \rightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + \overline{e} \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + \overline{e} \rightarrow Fe^{2+}(aq)$	+0.77
$C_6H_4O_2(s) + 2H^+ + 2\overline{e} \rightarrow C_6H_4(OH)_2(s)$	+0.70

$MnO_4^{-}(aq) + 2H_2O + 3\overline{e} \rightarrow MnO_2(s) + 4OH^{-}(aq)$	+0.59
$I_2(s) + 2\overline{e} \rightarrow 2I_2(aq)$	+0.53
$O_2(g) + 2H_2O + 4\overline{e} \rightarrow 4OH^{-}(aq)$	+0.40
$Cu^{2+}(aq) + 2\overline{e} \rightarrow Cu(s)$	+0.34
$\frac{1}{2}Hg_2Cl_2(s) + \overline{e} \rightarrow 2Hg(l) + Cl^{-}(aq,$ 0.1 mol/L)	+0.3341
$\frac{1}{2}Hg_2Cl_2(s) + \overline{e} \rightarrow 2Hg(l) + Cl^{-}(aq,$ 1 mol/L)	+0.2812
$\frac{1}{2}Hg_2Cl_2(s) + \overline{e} \rightarrow 2Hg(l) + Cl^{-}(aq,$ saturated solution)	+0.2415

*For all half-reactions the activity (concentration) is 1 mol/L for dissolved species and the pressure is 1 atm for gases; *g* – gaseous substance, *s* – solid, *l* – liquid, *aq* – dissolved in water

Table 3.1. Continued

Electrode half-reaction	φ^o, V
$AgCl(s) + \overline{e} \rightarrow Ag(s) + Cl^{-}(aq)$	+0.2224
$Cu^{2+}(aq) + \overline{e} \rightarrow Cu^{+}(aq)$	+0.15
$Sn^{4+}(aq) + 2\overline{e} \rightarrow Sn^{2+}(aq)$	+0.15
$2H^{+}(aq) + 2\overline{e} \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2\overline{e} \rightarrow Pb(s)$	–0.13
$Sn^{2+}(aq) + 2\overline{e} \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2\overline{e} \rightarrow Ni(s)$	–0.25
$Co^{2+}(aq) + 2\overline{e} \rightarrow Co(s)$	–0.28
$PbSO_4(s) + 2\overline{e} \rightarrow Pb(s) + SO_4^{2-}(aq)$	–0.31
$Cd^{2+}(aq) + 2\overline{e} \rightarrow Cd(s)$	–0.40
$Fe^{2+}(aq) + 2\overline{e} \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3\overline{e} \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2\overline{e} \rightarrow Zn(s)$	–0.76
$2H_2O + 2\overline{e} \rightarrow H_2(g) + 2OH^{-}(aq)$	–0.83
$Mn^{2+}(aq) + 2\overline{e} \rightarrow Mn(s)$	–1.18

$Al^{3+}(aq) + 3\bar{e} \to Al(s)$	–1.66
$Be^{2+}(aq) + 2\bar{e} \to Be(s)$	–1.85
$Mg^{2+}(aq) + 2\bar{e} \to Mg(s)$	–2.36
$Na^{+}(aq) + \bar{e} \to Na(s)$	–2.71
$Ca^{2+}(aq) + 2\bar{e} \to Ca(s)$	–2.87
$Sr^{2+}(aq) + 2\bar{e} \to Sr(s)$	–2.89
$Ba^{2+}(aq) + 2\bar{e} \to Ba(s)$	–2.91
$K^{+}(aq) + \bar{e} \to K(s)$	–2.93
$Li^{+}(aq) + \bar{e} \to Li(s)$	–3.05

The potential of hydrogen electrode is given by the equation

$$\varphi = \varphi^{o} + \frac{RT}{2F}\ln\frac{a_{H^+}^{2}}{p_{H_2}} = \frac{RT}{F}\ln\frac{a_{H^+}}{p_{H_2}^{1/2}} \approx \frac{RT}{F}\ln\frac{c_{H^+}}{p_{H_2}^{1/2}}, \qquad (3.5a)$$

where φ^{o} – standard electrode potential, this value of hydrogen electrode is equal to zero by the convention; a_{H^+} and c_{H^+} – activity and concentration of hydrogen ions in solution; p_{H_2} – pressure of gaseous hydrogen. If the pressure is 1 atm the equation has a simple form

$$\varphi = \frac{RT}{F}\ln c_{H^+}. \qquad (3.5b)$$

Next of important type of reversible electrode consists of on unattackable metal, e.g., gold or platinum, immersed in a solution containing both oxidized and reduced states of an oxidation-reduction system, e.g., Sn^{4+} and Sn^{2+}, Fe^{3+} and Fe^{2+}, or $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$. The purpose of the unattackable metal is to act as a conductor for making electrical contact, just as in the case of a gas electrode. The oxidized and reduced states are not necessarily ionic; for example, an important type of reversible electrode is the *quinhydrone electrode*. It involves the organic compound quinone, together with hydrogen ions, as the oxidized state, while the neutral molecule hydroquinone is the reduced state. Electrodes of the kind under consideration, consisting of conventional oxidized and reduced forms, are sometimes called *oxidation-reduction electrodes*; the chemical reactions taking place at these electrodes are either oxidation of the reduced state or reduction of the oxidized state, e.g.,

$$\mathrm{Sn}^{4+} + 2\overline{e} \rightleftarrows \mathrm{Sn}^{2+} \text{ (tin electrode)},$$

$$\mathrm{C_6H_4O_2} + 2\mathrm{H}^+ + 2\overline{e} \rightleftarrows \mathrm{C_6H_4(OH)_2} \text{ (quinhydrone electrode)},$$

depending upon the direction of the current. In order that the electrode may behave reversibly it is essential that the system contains both oxidized and reduced states. Corresponding electrode potential are given by the equations

$$\varphi = \varphi^o + \frac{RT}{2F}\ln\frac{c_{\mathrm{Sn}^{4+}}}{c_{\mathrm{Sn}^{2+}}}, \qquad (3.6)$$

$$\varphi = \varphi^o + \frac{RT}{2F}\ln\frac{a^2_{\mathrm{H}^+}a_{\mathrm{Q}}}{a_{\mathrm{Hq}}} \approx \varphi^o + \frac{RT}{F}\ln c_{\mathrm{H}^+}, \qquad (3.7)$$

where a_{Hq}, a_{Q} – activities of hydroquinone ($\mathrm{C_6H_4(OH)_2}$) and quinone ($\mathrm{C_6H_4O_2}$) in solution, correspondingly, these two values are equal at pH < 8, so at this condition their ratio is unity.

The quinhydrone electrode potential is evidently dependent on the hydrogen ion activity of the solution, and hence it offers possibilities for the determination of the latter. For this purpose a small quantity of the compound quinhydrone, which consists of equimolar amounts of quinone and hydroquinone, is dissolved in the solution. The ratio of the concentrations of these two substances is thus equal to unity, and if the ratio of the activities is taken as equal to the ratio of the concentrations, equal to unity. The electrode gives accurate results in solutions of pH less than 8; in more alkaline solutions errors arise, first, because of oxidation of the hydroquinone by oxygen of the air, and second, on account of the ionization of the hydroquinone as an acid. The quinhydrone electrode can be used in the presence of the ions of many metals which have a harmful effect on the hydrogen gas electrode. The potential of the electrode is affected, however, by neutral electrolytes which increase the ionic strength of the solution. Because of its simplicity and accuracy the quinhydrone electrode has been widely used for the pH measurements.

The ion-selective electrodes. As an example of this kind of electrodes the glass electrode may be considered. Its construction and using are described in the Laboratory Exercise No. 10. Electrodes sensitive to hydrogen ions, and hence to the pH value of a solution, are typically built from glasses based on lithium silicate doped with heavy-metal oxides. The glass electrodes can also be made responsive to Na^+, K^+ and NH_4^+ ions by being doped with Al_2O_3 and B_2O_3.

Single electrode potentials

There is no known method whereby the potential of a single electrode can be measured. It is only the EMF of a cell, made by combining two electrodes, that can be determined experimentally. However, by choosing an arbitrary zero of potential, as the freezing point of water is chosen as the zero of the centigrade temperature scale, it is possible to express the potentials of individual electrodes. The arbitrary zero of potential is taken as the potential of a reversible hydrogen electrode, with gas at 1 atm pressure, in a solution of hydrogen ions of unit activity. This particular electrode, is known as the *standard hydrogen electrode*. The convention, therefore, is to take the potential of the standard hydrogen electrode as zero; electrode potentials based on this zero are said to refer to the hydrogen scale. If any electrode is combined with the standard hydrogen electrode, so as to make a complete cell, the EMF of this cell is equal to the potential of the chosen electrode on the hydrogen scale. When any reversible electrode is combined with a standard hydrogen electrode, as just indicated, an oxidation reaction takes place at the former, while the hydrogen ions are reduced to hydrogen gas at the latter.

In order to measure the potential of any electrode on the hydrogen scale, it is necessary to combine the electrode with a standard hydrogen electrode, i.e., one with gas at 1 atm pressure and a solution of hydrogen ions of unit activity, and to determine the EMF of the resulting cell. This value is identical with the required electrode potential. For a number of reasons the direct use of the hydrogen electrode is not convenient, and hence several subsidiary reference electrodes have been devised. The potentials of these electrodes have been measured against the standard hydrogen electrode. The most common of these is the *calomel electrode*. It consists of mercury in contact with a solution of potassium chloride saturated with mercurous chloride (calomel). In order to obtain the potential of any given electrode, it is combined with a reference electrode, and the EMF of the resulting cell is measured; the potential of the reference electrode, is then subtracted to give the required electrode potential. Fig. 3.2 shows construction of calomel electrode.

A difficulty that arises in the determination of electrode potentials is that it is frequently necessary to have two different solutions in contact. For example, the potential of zinc electrode

$$Zn \mid ZnSO_4 \text{ (solution)}$$

may be measured by combining it with a calomel electrode

$$KC1 \text{ (solution)} \mid Hg_2Cl_2 \text{ (solid)} \mid Hg.$$

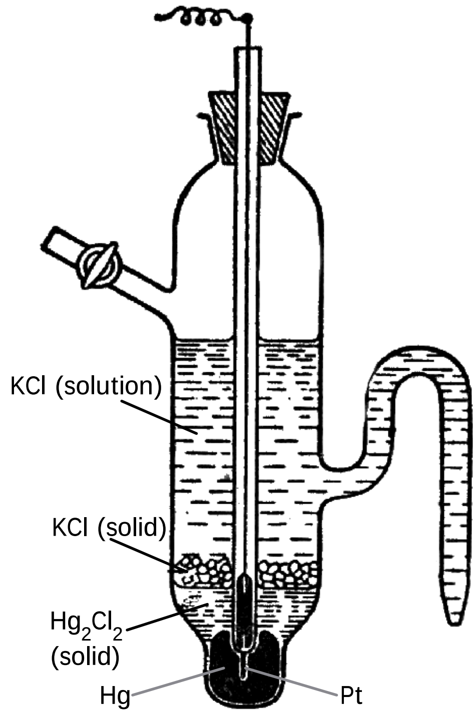


Fig. 3.2. Saturated calomel electrode

In the resulting cell there will be a junction between two different solutions. Such a liquid-liquid contact introduces an additional potential, known as a liquid junction potential. In certain simple cases it is possible to calculate the value of this potential with fair accuracy, but in most instances the calculation is too difficult and uncertain to be significant. It is therefore the general practice to try to reduce the value of the liquid junction potential as much as possible, and this may be achieved by the use of a salt bridge. This generally consists of a tube or a convenient vessel containing a saturated solution of potassium chloride which is employed to connect the solutions in the two electrodes. It is because potassium and chloride ions have almost identical mobilities that potassium chloride possesses the property of being able to minimize liquid junction potentials. When potassium chloride cannot be used, e.g., if one of the electrodes contains a silver salt, a saturated solution of ammonium nitrate is employed as a salt bridge. It is doubtful whether the liquid junction potentials are ever eliminated entirely, but at least they can be reduced in magnitude so that the actual value is negligible for measurements not requiring the highest degree of accuracy. When a salt bridge is used, and it is supposed that the liquid junction potential is eliminated, a double line is inserted between the symbols for the two solutions, e.g.,

$$\mathrm{Zn} \mid \mathrm{ZnSO_4}\ (\text{solution}) \parallel \mathrm{KCl}\ (\text{solution}) \mid \mathrm{Hg_2Cl_2}\ (\text{solid}) \mid \mathrm{Hg}.$$

For work of special accuracy where liquid junctions can be avoided by the use of a single electrolyte, e.g., a chloride solution, the silver-silver chloride electrode has been employed as a reference electrode. It usually consists of a silver wire coated with a layer of silver chloride; this is inserted directly into the solution of the chloride in the experimental electrode. The potential of the silver chloride electrode has been determined from measurements on cells consisting of this electrode combined with a hydrogen electrode in solutions of hydrochloric acid. In this way the EMF of the cell

$$\mathrm{Pt} \mid \mathrm{H_2}(\text{gas}, p = 1\ \text{atm}) \mid \mathrm{H^+}(\text{solution}, a = 1) \parallel \mathrm{AgCl}(\text{solid}) \mid \mathrm{Cl^-}(\text{solution}, a = 1) \mid \mathrm{Ag}$$

has been found to be 0.2224 volt at 25° C. Since the potential of hydrogen electrode is zero, by convention, the potential of the silver chloride electrode is also 0.2224 volt, and hence at any different concentration of the chloride ions in solution, its potential may be calculated by equation

$$\varphi = 0.2224 - \frac{RT}{F} \ln c_{\mathrm{Cl^-}}. \tag{3.8}$$

Standard potentials

The potential of any electrode is determined by the standard potential and by the activity or activities of the ions taking part in the electrode process. These activities are variable, but the standard potential is a definite property of the electrode system, having a constant value at a given temperature. If these standard potentials were known, it would be a simple matter to calculate the actual potential of any electrode, in a solution of given concentration or activity. The standard potentials of many electrodes have been determined, with varying degrees of accuracy, and the results have been tabulated. The principle of the method used to evaluate φ^0 for a given electrode system is to measure the potential of the electrode, on the hydrogen scale, in a solution of known activity; from these two quantities the standard potential φ^0 can be calculated at the experimental temperature, using the Nernst equation. Actually the procedure is more complicated than is indicated, because the activities are uncertain, but the details need not be considered here. It should be remembered that the standard potential refers to the condition in which all the substances in the cell are in their standard states of unit activity; gases such as hydrogen, oxygen and chlorine are thus at 1 atm pressure. With bromine and iodine, however, the standard states are chosen as the pure liquid and solid, respectively; the solutions are therefore saturated with these elements in the standard electrodes. For all ions the standard state of unit activity is taken as the hypothetical ideal solution of unit molarity. Standard potentials for different half-reactions are given in Table 3.1. These φ^o values correspond to the half-cell reactions as read in the forward (left to right) direction. The more positive φ^o value the greater the tendency for the substance to be reduced.

Applications of electrode potentials. There are numerous applications of electrode potentials in various branches of chemistry; some of these will be considered here. The determination of any properties by measuring the EMF of a galvanic cell is known as a *potentiometric determination.* The most widely used potentiometric determinations are pH measurements and potentiometric titration. Potentiometric measurements can also be used to determine various thermodynamic parameters of oxidation-reduction reactions. The most important of these is determination of the equilibrium constants for a reactions proceeding in the cell.

Problems

Examples

Problem 1. The experimentally measured EMF of the cell

$$\text{Ag} \mid \text{AgCl}_{(\text{solid})} \mid \text{KC1 (0.1 mol/L)} \mid \text{Hg}_2\text{Cl}_{2(\text{solid}))} \mid \text{Hg}$$

is 0.0455 volt at 25 °C. Calculate the approximate concentration of the Ag^+ ions in the saturated solution of AgCl in 0.1 mol/L KC1 solution. The potential of calomel electrode equals 0.3341 V.

Solution. If the potential of the right-hand electrode is 0.3341 V, hence, the potential of the silver electrode is equal

$$\varphi_{\text{Ag/Ag}^+} = \varphi_{calomel} - E = 0.3341 - 0.0455 = +0.2886 \text{ V}.$$

Nernst equation for the silver electrode, reversible with respect to Ag^+ ions, gives

$$\varphi_{\mathrm{Ag/Ag^+}} = \varphi^o + \frac{RT}{F}\ln c_{\mathrm{Ag^+}} = \varphi^o + 0.059 \cdot \lg c_{\mathrm{Ag^+}}.$$

From Table 3.1 the φ^o value for the silver electrode is 0.80 volt; hence

$$0.2886 = 0.80 + 0.059 \lg c_{\mathrm{Ag^+}},$$

$$\lg c_{\mathrm{Ag^+}} = -0.5114/0.059 = -8.667,\ c_{\mathrm{Ag^+}} = 10^{-8.667} = 2.15 \cdot 10^{-9}\ \text{mol/L}.$$

Thus, the concentration of the silver ions is $2.15 \cdot 10^{-9}$ mol per liter.

Problem 2. The EMF of the cell

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \parallel 0.1\ \text{mol/L KC1} \mid \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$$

containing solution of $ZnSO_4$ with c = 1 mol/L, was found to be 1.094 volt. Determine the standard potential of the Zn/Zn^{2+} electrode if the potential of the 0.1 mol/L KC1 calomel electrode is +0.334 V.

Solution. Let $\varphi^o_{\mathrm{Zn/Zn^{2+}}}$ be the value of the required potential, i.e., the standard potential of the left-hand electrode of the cell. The total EMF of the cell is thus

$$E = \varphi_+ - \varphi_- = 0.334 - (\varphi^o_{\mathrm{Zn/Zn^{2+}}} + 0.059 \lg c_{\mathrm{Zn^{2+}}}) = 0.334 - \varphi^o_{\mathrm{Zn/Zn^{2+}}},$$

and this is found by direct measurement to be 1.094 volt; hence,

$$0.334 - \varphi^o_{\mathrm{Zn/Zn^{2+}}} = 1.094, \text{ and } \varphi^o_{\mathrm{Zn/Zn^{2+}}} = 0.334 - 1.094 = -0.760\ \text{V}.$$

Problem 3. The Daniel–Jacobi galvanic cell consists of zinc and copper electrodes immersed in zinc and copper sulfate solutions, respectively. In an experiment the concentration of solutions are: $c(\mathrm{Zn^{2+}})$ = 1.0 mol/L and $c(\mathrm{Cu^{2+}})$ = 0.1 mol/L. Calculate the standard EMF of the cell at 25 °C and and the EMF that can be measured experimentally. Use standard electrode potentials given in Table 3.1.

Solution. Electromotive force of the cell equals the difference in standard potentials of the electrodes (equation (3.2))

$$E = \varphi_+ - \varphi_-,$$

where φ_+ and φ_- – potentials of positive and negative electrodes, respectively. Standard electromotive force of the cell equals the difference in standard potentials of the electrodes

$$E^o = \varphi_+^o - \varphi_-^o,$$

where φ^o – standard electrode potentials (given in Table 3.1). The potential of each electrode of the cell is given by Nernst equation

$$\varphi = \varphi^o + \frac{RT}{zF} \ln c_{\mathrm{Me}^{z+}},$$

here $c_{\mathrm{Me}^{z+}}$ – concentration of metal ions in solution.

$$\varphi_{Zn} = \varphi_{Zn}^o + \frac{RT}{2F} \ln c_{\mathrm{Zn}^{2+}} = -0.76 + 0.0295 \lg c_{\mathrm{Zn}^{2+}} = -0.76 \text{ V},$$

$$\varphi_{Cu} = \varphi_{Cu}^o + \frac{RT}{2F} \ln c_{Cu^{2+}} = 0.34 + 0.0295 \lg c_{Cu^{2+}} = 0.3105 \text{ V}.$$

Cupper electrode is positive because its potential is higher than potential of zinc electrode. So,

$$E^o = 0.34 - (-0.76) = 1.10 \text{ V}, E = 0.3105 - (-0.76) = 1.0705 \text{ V}.$$

Problems for self-solving

1. Metallic silver electrode is immersed into solution of silver nitrate and $c(\mathrm{AgNO_3}) = 0.001$ mol/L. Calculate this electrode potential at 298 K, use Nernst equation, standard potential of the electrode is 0.799 V. *Answer:* $\varphi = 0.622$ *V.*

2. Calculate the potential of silver-silver chloride electrode at 298 K. Concentration of potassium chloride solution is $1 \cdot 10^{-3}$ mol/L. Use Nernst equation, standard potential of the electrode is 0.2224 V. *Answer:* $\varphi = 0.401$ *V.*

3. A wire of pure copper is immersed into a solution of copper nitrate at 25 °C. Use Nernst equation and calculate the concentration of copper nitrate in solution if the potential of the electrode is 0.29 V, and standard potential of the electrode equals 0.34 V. *Answer: c = 0.02 mol/L.*

4. A silver-silver chloride electrode is immersed in a solution of KCl with concentration 0.01 mol/L at 20 °C. What is the value of electrode

potential, if the standard electrode potential at this temperature is 0.2256 V? *Answer:* $\varphi = 0.3419$ *V.*

5. A galvanic cell consists of zinc electrode in 0.1 mol/L $Zn(NO_3)_2$ solution and silver electrode in 0.01 mol/L $AgNO_3$ solution. Using standard potentials given in Table 3.1, calculate the standard EMF of this cell at 25 °C, and the EMF that can be measured experimentally. *Answer:* $E^0 = 1.56$ *V;* $E = 1.4715$ *V.*

6. Consider the galvanic cell consists of zinc and hydrogen gas electrodes. In an experiment, the EMF of the cell is found to be 0.54 V at 25 °C. Suppose that in solution of the left-hand electrode $c(Zn^{2+}) = 1.0$ mol/L and the hydrogen pressure is 1.0 atm. Calculate the molar concentration of H^+ ions in the solution of the right-hand electrode and the pH value of the solution. *Answer:* $c(H^+) = 1.86 \cdot 10^{-4}$ *mol/L; pH = 3.73.*

7. The titration of 5 mL of HCl solution was carried out potentiometrically using 0.1 mol/L NaOH solution. The potentiometric titration curves were drawn, the equivalence point was found to be 8 mL. Calculate the HCl concentration in the investigated solution. *Answer: c(HCl) = 0.16 mol/L.*

8. Calculate the electromotive force (EMF) of the galvanic cell consisting of two zinc electrodes immersed in $ZnSO_4$ solutions with different concentrations at $T = 298$ K:

$$Zn \mid ZnSO_4\ (0.01\ mol/L) \parallel ZnSO_4\ (0.1\ mol/L) \mid Zn.$$

Answer: $E = 0.03$ *V.*

9. Metallic zinc electrode is immersed into solution of zinc sulphate with $c(ZnSO_4) = 1 \cdot 10^{-3}$ mol/L. Use Nernst equation and calculate the electrode potential at 298 K if standard potential of the electrode is –0.763 V. *Answer:* $\varphi = -0.852$ *V.*

10. Calculate the electromotive force (EMF) of the galvanic cell consisting of two hydrogen gas electrodes immersed in HCl solutions with different concentrations (the hydrogen pressures are the same and $T = 298$ K):

$$Pt(H_2) \mid HCl\ (0.05\ mol/L) \parallel HCl\ (0.1\ mol/L) \mid (H_2)Pt.$$

Answer: $E = 0.018$ *V.*

THEME 4

THE COLLOIDAL STATE

The concepts of «colloid chemistry» – what colloids are and how they are formed, stabilized, used, and destroyed.

Colloidal systems or colloids (from Greek word «κωλλα», meaning «glue») are a specific state of matter endowed with certain characteristic properties. It is not a given class of substances: for instance, salt (potassium chloride) forms a colloidal solution in benzene, but forms a true solution in water. Examples of colloidal systems from daily life: foams, milk, fog, smoke, detergents, aerogel, blood, paints, cosmetics, etc.

The first important characteristic of the colloidal state is the presence of particles which are larger than molecules, but not large enough to be seen in microscope. The size of particles in the colloidal state is from 10^{-9} to 10^{-7} meter, although those limits are far from rigid. *The second essential property*: the colloidal solutions consist of two or more phases. These two phases may be distinguished by the terms *dispersed phase* (for the phase forming the particles) and *dispersion medium* or *continuous phase* for the medium in which the particles are distributed (or dispersed).

Classification of colloidal systems

All colloidal systems may be classified in the following manner.

1. Classification in accordance with *aggregative state of dispersed phase* and *dispersion medium* (Table 4.1). The medium may be solid, liquid or gaseous; similarly the dispersed phase may be solid, liquid or gaseous, thus leading to a number of possible types of colloidal systems. If the dispersion medium is a liquid and dispersed phase is a solid, such colloidal systems are called *sols*. *Smokes* and *dusts* consist of solid particles dispersed in gaseous medium, whereas in *fog*, *mist* and *cloud* the dispersed phase is liquid and the dispersion medium is a gas. Ruby glass consists of particles of gold dispersed in glass. *Suspension* is obtained if, in a liquid medium, the dispersed phase is solid and the particles are relatively large. If the dispersed phase and medium are immiscible liquids the result is an *emulsion*.

2. Classification in accordance with *interaction between dispersed phase and dispersion medium.* This classification is used only for colloidal solution with *a liquid dispersion medium*. Sols may be divided into *lyophobic* (from

Greek «liquid hating») and *lyophilic* (from Greek «liquid loving») or *hydrophobic* and *hydrophilic*, if dispersion medium is aqueous. The terms lyophilic and lyophobic are frequently used to describe the tendency of a surface or functional group to become wetted or solvated. Lyophobic sols are relatively unstable (particles aggregate and sediment); have low affinity for the solvent; addition of electrolytes causes coagulation and precipitation. *Typical examples of lyophobic sols* are sols of metals, sulfur, sulfides, silver halides, and also inks, paints. Lyophilic sols have strong affinity between dispersed phase and dispersion medium and are stable (particles stay separate). *Typical examples of lyophilic sols* are surfactant solutions at defined concentration and sols of proteins.

Table 4.1. Examples of commonly encountered colloidal systems

System	Type	Dispersed phase	Continuous phase or dispersion medium
Fog, mist	Liquid aerosol	Liquid	Gas
Smoke	Solid aerosol	Solid	Gas
Shave cream	Foam	Gas	Liquid
Styrofoam	Solid foam	Gas	Solid
Milk	Direct emulsion	Liquid (fat)	Liquid (water)
Butter	Reverse emulsion	Liquid (water)	Liquid (fat)
Paint	Dispersion	Solid	Liquid
Suspension	Dispersion	Solid	Liquid
Sol	Dispersion	Solid	Liquid
Opal	Dispersion	Solid	Solid
Jello	Gel	Macromolecules	Liquid
Liquid soaps and detergents	Micellar solution	Micelles (aggregates) of detergent molecules	Liquid

3. Classification in accordance with the *size of particles of dispersed phase*. If diameter of particles is more than 10^{-4} meter, they are *heterogeneous systems*; if diameter of particles lies in the range from 10^{-5} to 10^{-7} meter, they are *microheterogeneous systems*; if diameter of particles less than 10^{-7} meter, but more than 10^{-9} meter they are «*true*» *colloidal systems or ultramicroheterogeneous systems.*

4. Classification in accordance with the *shape of particles of dispersed phase*. For example, shape can be spherical, cylindrical, cubic, needle-like, etc.

Preparation of colloidal systems

Lyophilic systems may be prepared when substances with high molecular weight are warmed with a suitable dispersion medium. For example, gelatin and starch in water, rubber in benzene. *Lyophobic systems may be prepared* by special methods: (1) *condensation methods* and (2) *dispersion methods*.

Condensation methods are:

(1) *physical condensation* is based on physical processes, such as solvent replacement or vapor condensation (for example, the fog formation);

(2) *chemical condensation* is based on different chemical reactions, hydrolysis, ion-exchange reactions, oxidation-reduction, etc. For example, hydrolysis of ferric chloride $FeCl_3$:

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3HCl,$$

by adding boiling water dropwise to a solution of ferric chloride one obtains the dark brown sol of ferric hydroxide.

A common feature of both classes of condensation method is that formation of the colloidal particles in the new phase occurs at moderate supersaturation.

Dispersion methods. In these methods the starting material consists of the substance in the massive form; by means of suitable devices it is disintegrated into particles of colloidal dimensions. Colloidal mill or electrical disintegration (a direct current electrical arc) are used. For example, when a coffee is milled in a grinder, ultrasonic destruction of kidney stones, etc.

Peptization is the direct disintegration or dispersion of the coagulation products (see *Theme 5* about a coagulation process) of a sol into particles of colloidal size by an added *peptizing agent*. The peptizing effect of such agents is based on their specific reaction with the coagulate. For example, a deposit of ferric hydroxide can be peptized by treatment with very small quantities of ferric chloride solution after preliminarily removing of the coagulating substances. In this case peptization is due to adsorption of Fe^{3+} ions which again stabilize the particles.

Tyndal effect. Presence of colloidal particles can be made evident by optical means. If a strong beam of light is passed through a colloidal solution, colloidal particles will scatter the light. True solutions are optically clear, *but colloidal solutions scatter light*, producing *so-called the Tyndall effect.* The path of the light through the sol, which is rendered visible as a result of the scattering, is called the *Tyndal beam.*

Structure of a lyophobic sols. Necessary conditions for the stability of lyophobic sols are 1) the particles must be very small (prevents sedimentation); 2) must carry electrical charges (hinder coagulation); 3) must form solvate shells (hinder coagulation).

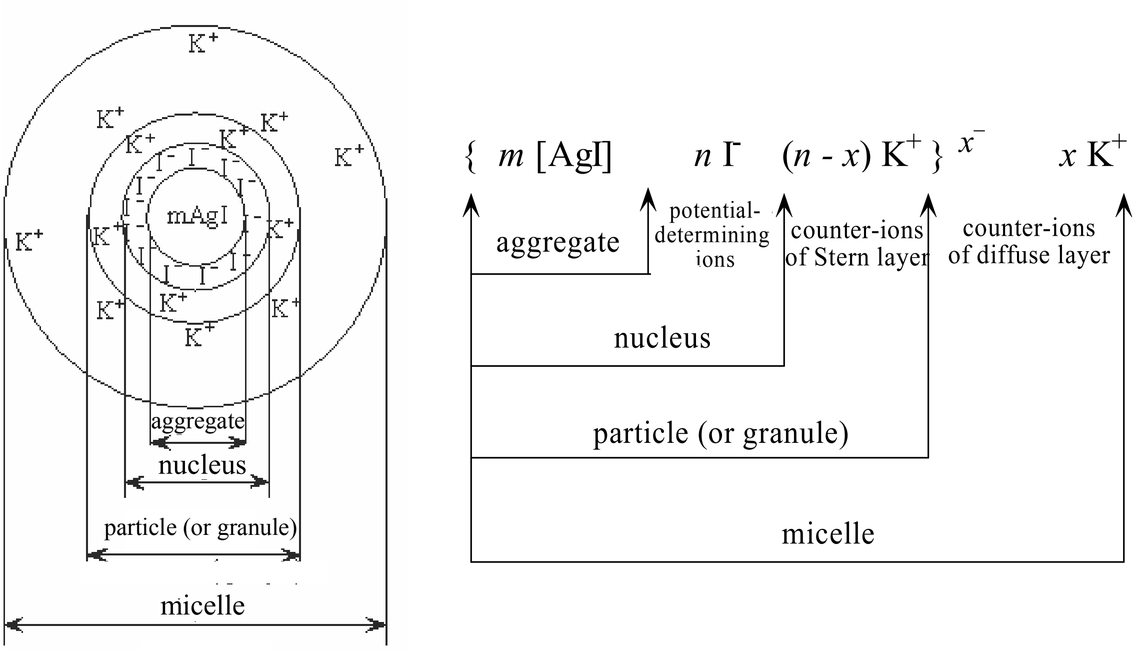


Fig. 4.1. Structure of silver iodide micelle with negatively charged particles (where m – number of AgI molecules in aggregate, n – number of potential-determining ions, x – number of counter-ions, $n << m$)

Electrical charges appear on the colloidal particles as a result of adsorption or dissociation processes.

The particles of a colloid preferentially adsorb ions of a certain species from the electrolyte solution. The entire part, consisting of the particles of the dispersed phase with the *adsorbed ions* (*potential-determining ions*) and *counter-ions* of Stern layer (ions of opposite charge) partially bound to them, migrates through the solution as a single unit so-called *particle* or *granule.* The counter-ions in the surrounding solution experience an attraction to the charged particles. Those nearest to it are more strongly attracted and become bound to the particle. The entire unit with the *counter-ions of diffuse layer* is called a *micelle* (Fig. 4.1).

Problems

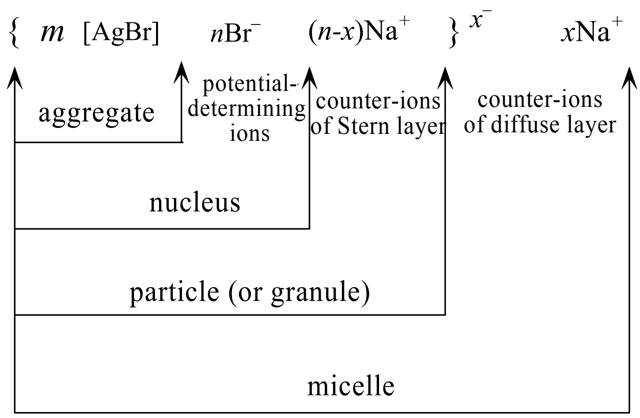
Examples

Problem 1. Sol of AgBr was prepared by mixing of $AgNO_3$ and NaBr solutions. It was found the charge of the particles of dispersed system is negative. Write the structure of the AgBr micelle. Show micelle components: aggregate, potential-determined ions and two parts of counter-ions layer – Stern layer and diffuse layer.

Solution.

$$AgNO_3 + NaBr \rightarrow AgBr\ (\text{aggregate}) + NaNO_3$$

$$Ag^+ + Br^- \rightarrow AgBr\ (\text{aggregate})$$



$$\{\ m\ [AgBr]\quad nBr^-\quad (n\text{-}x)Na^+\ \}^{x-}\quad xNa^+$$

Problem 2. Classify colloidal systems in accordance with the aggregative state of the dispersed phase and the continuous phase: 1) paint, 2) opal, 3) emulsion, 4) fog, 5) gel.

Solution. 1) paint – *s*/*l*, 2) opal– *s*/*s*, 3) emulsion – *l*/*l*, 4) fog – *l*/*g*, 5) gel– *macromolecules*/*l*.

Problems for self-solving

1. A spherical particle of colloid gold has a radius of $1 \cdot 10^{-9}$ m. Density of gold is 19.3 g/cm^3. Calculate the mass of the particle. How many atoms of gold make up the particle? *Answer*: $m = 8.08 \cdot 10^{-20}$ g; $N = 247$.

2. Classify colloidal systems in accordance with the aggregative state of the dispersed phase and the continuous phase: 1) aerosol, 2) smoke, 3) mayonnaise, 4) mist, 5) sol, 6) minerals, 7) dust, 8) fog.

3. Classify colloidal systems in accordance with the aggregative state of the dispersed phase and the continuous phase: 1) suspension, 2) dust, 3) emulsion, 4) ink, 5) foam, 6) milk, 7) sol, 8) mist.

4. Sol of AgCl was prepared by mixing of $AgNO_3$ and KCl solutions. It was found the charge of the particles of dispersed system is positive. Write the structure of the AgCl micelle. Show micelle components: aggregate, potential-determined ions and two parts of counter-ions layer – Stern layer and diffuse layer.

5. Sol of $BaSO_4$ was prepared by mixing of $Ba(NO_3)_2$ and K_2SO_4 solutions. It was found the charge of the particles of dispersed system is positive. Write the structure of the $BaSO_4$ micelle. Show micelle components: aggregate, potential-determined ions and two parts of counter-ions layer – Stern layer and diffuse layer.

6. Sol of $BaCO_3$ was prepared by mixing of $Ba(NO_3)_2$ and K_2CO_3 solutions. It was found the charge of the particles of dispersed system is negative. Write the structure of the $BaCO_3$ micelle. Show micelle components: aggregate, potential-determined ions and two parts of counter-ions layer – Stern layer and diffuse layer.

7. Classify colloidal systems in accordance with the aggregative state of the dispersed phase and the continuous phase: 1) sol, 2) liquid soap, 3) shave cream, 4) fog.

8. Sol of $Fe(OH)_3$ was prepared by hydrolysis of $FeCl_3$ solution. It was found the charge of the particles of dispersed system is positive. Write the structure of the $Fe(OH)_3$ micelle. Show micelle components: aggregate, potential-determined ions and two parts of counter-ions layer – Stern layer and diffuse layer.

9. Classify colloidal systems in accordance with the aggregative state of the dispersed phase and the continuous phase: 1) gel, 2) solid aerosol, 3) reverse emulsion, 4) opal.

10. Sol of AgBr was prepared by mixing of $AgNO_3$ and NaBr solutions. It was found the charge of the particles of dispersed system is positive. Write

the structure of the AgBr micelle. Show micelle components: aggregate, potential-determined ions and two parts of counter-ions layer – Stern layer and diffuse layer.

THEME 5

THE COLLOID STABILITY

Coagulation is the process in which colloidal particles come together to aggregate and form a visible precipitate or *coagulum*. *Coagulum* is an aggregate of colloidal particles having a relatively tight, dense structure formed as a result of the inability of the colloidal system to maintain its dispersed state. Such aggregates are normally formed irreversibly; that is, they cannot be returned to the colloidal state without significant input of work.

Coagulation does not necessarily proceed so far as to cause sedimentation or precipitation or turbidity or, finally, change in color of the solution, although it frequently leads to such consequences. In such cases the effect of coagulation is visible to the naked eye and is known as the stage of *visible coagulation*, in contrast to the stage of *invisible coagulation*, when the process cannot be detected.

One of the most important ways of the coagulation of lyophobic sols is *the addition of an electrolyte*. A certain minimum value of electrolyte concentration in the 1 liter of system at which coagulation begins is called *coagulation threshold,* γ*, or critical coagulation concentration*

$$\gamma = n / V \text{, mol/L} \qquad (5.1)$$

where n – electrolyte moles number where coagulation is observed; V – total volume of solution.

Investigations of the coagulation process of lyophobic sols by electrolytes have led to the formation of the so-called *Schultze-Hardy rule* (H. Schultze, 1882; W.B. Hardy, 1900)

(1) Coagulation of the sol is caused by the ions carrying the charge opposite to that of sol particles.

(2) Coagulating power of ions causing coagulation is directly proportional to the valence of these ions.

For example, to coagulate negative particles of sol of As_2S_3, the coagulation power of different cations has been found to decrease in the order as

$$Al^{3+} > Mg^{2+} > Na^{+}.$$

Similarly, to coagulate positive particles of sol such as $Fe(OH)_3$, the coagulating power of different anions has been found to decrease in the order

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-.$$

According to the theory of coagulation of hydrophobic sol by the electrolytes the coagulation threshold varies as the inverse sixth power of the valence of ions causing coagulation

$$\gamma = \frac{\text{const}}{z^6}. \tag{5.2}$$

For monovalent ions, the effectiveness for coagulating negatively charged colloids has the order

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+,$$

while for divalent cations the order is

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}.$$

At increasing of the concentration of added electrolyte to the sol the diffuse layer of electrical double layer is compressed and zeta potential is decreased. This effect leads to instability of colloidal system and to coagulation process.

Colloidal systems differ widely with respect to stability. Some of them can be preserved unchanged for long periods of time; others are comparatively unstable being more sensitive to various influences. There are two kinds of processes which lead to the destruction of colloidal systems and which under certain conditions can take place spontaneously. These are *sedimentation processes* and *coagulation processes*. *Kinetic and aggregate stabilities* characterize the stability of colloidal systems with respect to sedimentation process and the changing in particle size (coagulation).

Kinetic stability is determined by two conflicting processes: sedimentation of the particles and their thermal motion. The *aggregate stability* is a measure of the ability of a colloidal system to preserve its degree of dispersion. It is due to the fact that the particles of the dispersed phase are electrically charged and are surrounded by a solvate (hydrate) shell.

The addition of a lyophilic substance (protein, surfactant, starch, gelatin, etc.) to a lyophobic sol frequently renders the latter less sensitive to the precipitating effect of electrolytes. This is an illustration of the phenomenon of *protective action* (Fig. 4.1): macromolecules of lyophilic substances are adsorbed onto the colloidal particles of lyophobic sol and provide *steric* or *entropic stabilization*.

In colloidal systems containing *a low concentration of lyophilic substances*, macromolecules can become adsorbed on the surface of two or more particles leading to phenomenon, termed *flocculation* (Fig. 4.1). Flocculation is the process of *flocs* forming. Flocs are an aggregate of individual colloidal particles associated by lyophilic substance to a coagulum but generally having a rather loose, open structure. Flocs may sometimes be formed reversibly and be returned to the dispersed state with minimal energy input.

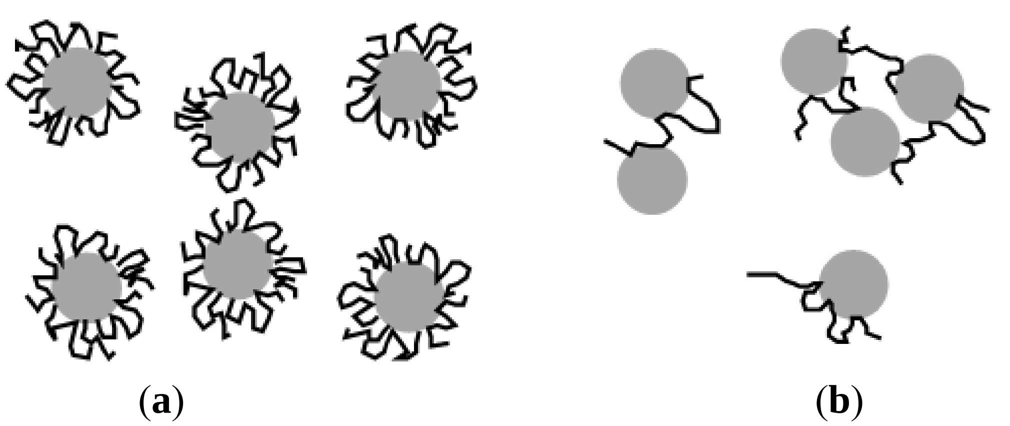


Fig. 5.1. Sterically stabilized systems: a given adsorbed macromolecule is associated with one particle – a protective action (**a**). Process of flocculation (**b**)

The relative protective effects of different substances can be expressed quantitatively in terms of what is known as the *gold number*. This is defined as the dry weight in milligrams of protective material which when added to 10 mL of a standard gold sol is just sufficient to prevent color change from red to blue on the addition of 1 mL of a 10 per cent solution of sodium chloride. The color change referred to is due to coagulation of the particles, and hence the gold number is a measure of the quantity of protective colloid which just fails to prevent precipitation by the electrolyte (sodium chloride). It follows, therefore, that *the smaller the gold number the greater the protective action of the given substance*. Gelatin has a very small gold number, and hence is a very good protective substance; egg albumin and gum arabic are less effective, while potato starch has relatively little protective action.

Introduction to blood coagulation. The ability of the body to control the flow of blood following vascular injury is paramount to continued survival.

The process of blood clotting and then the subsequent dissolution of the clot, following repair of the injured tissue, is termed *hemostasis*. Hemostasis, composed of four major events that occur in a set order following the loss of vascular integrity

1. The initial phase of the process is vascular constriction. This limits the flow of blood to the area of injury.

2. Next, platelets become activated by thrombin and aggregate at the site of injury, forming a temporary, loose platelet plug. The protein fibrinogen is primarily responsible for stimulating platelet clumping. Platelets clump by binding to collagen that becomes exposed following rupture of the endothelial lining of vessels. In addition to induced secretion, activated platelets change their shape to accommodate the formation of the plug.

3. To insure stability of the initially loose platelet plug, a fibrin mesh (also called the clot) forms and entraps the plug. If the plug contains only platelets it is termed a white thrombus; if red blood cells are present it is called a red thrombus.

4. Finally, the clot must be dissolved in order to normal blood flow to resume following tissue repair. The dissolution of the clot occurs through the action of plasmin.

Problems

Examples

Problem 1. Calculate the coagulation threshold of AgCl sol by 1 mol/L $NaNO_3$, if its minimal volume for beginning of coagulation process is 0.002 liter. Initial volume of sol in the test-tube is 0.01 liter.

Solution. The coagulation threshold can be calculated using the equation

$$\gamma = \frac{c_{electrolyte} V_{electrolyte}}{V_{electrolyte} + V_{sol}} = \frac{1 \times 0.002}{0.002 + 0.01} = 0.167 \text{ mol/L.}$$

Problem 2. The charge of the colloidal particles of AgCl sol is positive. Use Schultze–Hardy rule and arrange the electrolytes – KCl, Na_3PO_4 and Na_2SO_4 – in order of increasing of their coagulation power of the sol.

Solution. Because the colloidal particles of AgCl sol are positive, according to Schultze–Hardy rule coagulation of the sol is caused by the ions carrying the charge opposite to that of sol particles. It means by Cl^-, PO_4^{3-} and SO_4^{2-} anions. Coagulating power of these ions is directly proportional to their valence, so, we can arrange the ions in the following order

$$PO_4^{3-} > SO_4^{2-} > Cl^-.$$

Problems for self-solving

1. Calculate the coagulation threshold of $Fe(OH)_3$ sol by 0.003 mol/L K_2SO_4, if its minimal volume for beginning of coagulation process is 0.009 liter. Initial volume of sol in the test-tube is 0.02 liter. *Answer*: γ *= 0.93 mmol/L.*

2. Calculate the coagulation threshold of $Fe(OH)_3$ sol by 0.0005 mol/L K_2SO_4, if its minimal volume for beginning of coagulation process is 0.005 liter. Initial volume of sol in the test-tube is 0.01 liter. *Answer*: γ *= 0.17 mmol/L.*

3. The coagulation threshold of $Al(OH)_3$ sol by addition of KNO_3 solution is equal 60 mmol/L. Calculate the coagulation threshold of sol by addition of $K_3[Fe(CN)_6]$. It is known that the sign of the colloidal particles is positive. Use equation (11.2) for calculations. *Answer*: γ *= 0.082 mmol/L.*

4. Calculate the coagulation threshold of sol by Na_2SO_4, if the addition of 0.003 liter of 0.1 mol/L Na_2SO_4 solution leads to coagulation of 0.015 liter of sol. *Answer*: γ *= 0.017 mol/L.*

5. Calculate the coagulation threshold of sol by K_2SO_4 solution, if the addition of 0.006 liter 0.1 mol/L Na_2SO_4 leads to coagulation of 0.03 liter of sol. *Answer*: γ *= 0.017 mol/L.*

6. It is known that the charge of the colloidal particles is negative. How can the values of coagulation power of the following electrolytes be arranged into series: $CrCl_3$, $Ba(NO_3)_2$, K_2SO_4?

7. Calculate the coagulation thresholds of $Fe(OH)_3$ sol by different electrolytes, if for coagulation of 0.1 liter of this sol it is necessary to add: (a) 0.01 liter of 1 mol/L NH_4Cl solution; (b) 0.063 liter of 0.01 mol/L Na_2SO_4 solution; (c) 0.037 liter of 0.001 mol/L Na_3PO_4 solution. *Answer*: *(a)* γ *= 0.09 mol/L; (b)* γ *= 3.9 mmol/L; (c)* γ *= 0.3 mmol/L.*

8. The charge of the colloidal particles of the AgCl sol is positive. Use the Hardy-Schultze rule and for a given electrolytes – KCl, Na_3PO_4 and Na_2SO_4 – determine the ions that will cause the coagulation of the sol. Also arrange these electrolytes in order of increasing of their coagulation thresholds of the sol.

9. The charge of the colloidal particles of the $Cu_2[Fe(CN)_6]$ sol is negative. Use the Hardy-Schultze rule and for a given electrolytes – $AlBr_3$, $Ca(NO_3)_2$ and KCl – determine the ions that will cause the coagulation of the sol. Also arrange these electrolytes in order of increasing of their coagulation thresholds of the sol.

10. The 0.01 mol/L Na_2SO_4 solution was used for determination of a coagulation threshold of a sol. Calculate the coagulation threshold of the sol, if 5 mL of Na_2SO_4 solution is the minimal amount of the solution required for the coagulation of 20 mL of the sol. *Answer:* $\gamma = 2$ *mmol/L.*

THEME 6

THE ELECTRIC DOUBLE LAYER AND ELECTROKINETIC PHENOMENA

When a hydrophobic sol is placed in an electric field the colloidal particles become moving definitely in one direction or another. This means that colloidal particles are electrically charged with respect to the dispersion medium. The phenomenon of *the migration of colloidal particles under the influence of an electrical potential* is called *electrophoresis*. The movement of particles in an electric field can be easily observed in the apparatus constituting the U-tube with two electrodes. The lower part of the U-tube contains the sol covered by the so-called lateral liquid – pure dispersion medium with small amounts of salts, e.g. KNO_3, NH_4Cl, – into which platinum electrodes connected to a current source are dipped. If sol is colored, the boundary between the sol and lateral liquid is visible, its moving can be observed. The rate of this motion is equal to the speed of electrophoresis of the particles of dispersed phase. The velocity of the particles under a fall of potential of 1 volt per meter, i.e., the electrophoretic mobility, may be calculated. In spite of the varying nature of the dispersed particles, the electrophoretic mobilities for aqueous sols almost always lie within the range of 2 to 4×10^{-4} cm per sec. The sign of the charge carried by the particles can be determined by observing the direction in which the boundary moves.

Electrophoresis and others familiar effects, called *electrokinetic phenomena* – electroosmosis, appearance of sedimentation potential (Dorn effect) and streaming potential (Quincke effect) – can be most clearly understood by consideration of the electrical condition of a boundary of two phases. It was suggested by H. Helmholtz as early as 1879 that *electrical double layer*, of positive and negative ions, exists between two phases at the surface of separation.

According to modern views, developed in works of L. G. Gouy, D. L. Chapman and O. Stern, the electrical double layer at a solid-liquid interface is made up of two parts: the first part is formed by ions (either positive or negative) coincide with the solid surface, the second part is layer of *counter-ions*. The ions situated at the first part of the electrical double layer is known as *potential determining ions*. The layer of counter-ions can be divided on two parts: 1) layer of ions in aqueous solution, which are firmly held to the solid, so-called *Stern layer*, and 2) more mobile *diffuse* *layer*, extending into the solution. The resultant (net) charge of the Stern and diffuse layers is equal in magnitude but of opposite sign to that of the surface of colloidal particle. The electrical double layer described above presumably exists at all solid-liquid interfaces, and it is undoubtedly formed at the surface of a colloidal particle. The surface charge ions, i.e. ions fixed on the surface of colloidal particle part can arise on the surface by two mechanisms: 1) adsorption of ions on the surface of particle and 2) dissociation of substance that forms the solid phase. The counter-ions of Stern layer are attracted by surface charge and adsorption forces, the ions of diffuse layer are undergone by two oppositely directed forces: electrostatic attraction and diffusion process. A simplified schematic representation of the structure of the electric double layer is shown in Fig. 6.1. Because of existence of spatial separation of electrical charges, there is a difference of potential between solid and liquid phases. The electric potential (φ_s) in the Stern layer varies linearly (φ_δ, section *MN*) with the distance (δ); the potential in diffuse layer varies exponentially (section *NK*), Fig. 6.1.

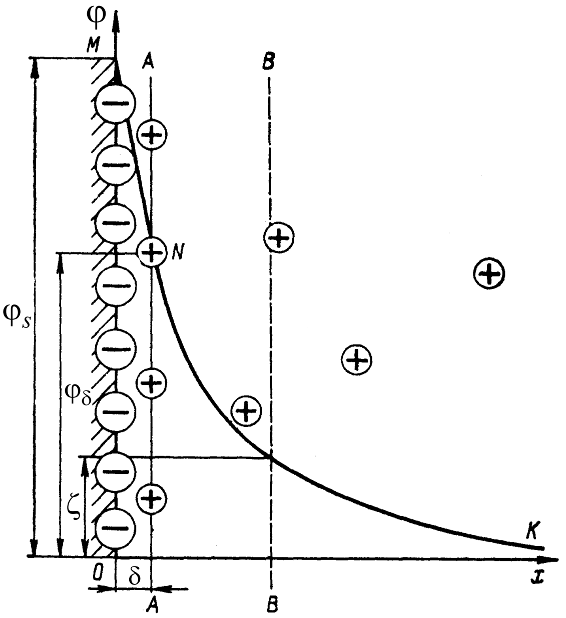


Fig. 6.1. Schematic representation of the structure of the electric double layer

When an electric field is applied to an electrical double layer there must be a displacement of the oppositely charged layers relative to one another; the actual movement will presumably take place in the diffuse layer at the region indicated by the dotted line (*BB*) in Fig. 6.1, this line represents the slip boundary that denotes the separation between two moving parts. In the case of a sol, the layer closely attached to the colloidal particle is free to move, together with the particle itself, in an applied field, thus producing the phenomenon of electrophoresis, described above. It is to be expected that there should be a connection between the velocity of electrophoresis and the potential acting at the slip surface of the moving colloidal particle. This potential has been called the *electrokinetic* *potential* or *zeta potential*, because it is represented by the Greek letter zeta – ζ (Fig. 6.1)

$$velocity = \frac{E\varepsilon\varepsilon_o}{\eta}\zeta, \tag{6.1}$$

where E – electric field intensity; ε – dielectric permittivity of dispersed medium; ε_o – dielectric permittivity of vacuum; η – viscosity of medium.

If a liquid, e.g., water, is separated by a porous diaphragm, and an electric field is applied between electrodes placed on each side of the diaphragm, there will be a flow of liquid from one side to the other. A porous diaphragm is actually a mass of small capillaries, and the same type of electroosmotic flow has been observed through glass capillary tubes. Therefore the phenomenon of electroosmosis consists in *the passage of liquid through a porous diaphragm under the influence of an applied electric field.* In each case, the charged layer attached to the solid cannot move, and so the diffuse layer in the liquid phase, together with the liquid, moves when an electric field is applied. The direction of the electroosmotic flow depends on the charge of the diffuse part of the double layer; in moderately pure water most solids acquire a negative charge, so that the diffuse layer has a resultant positive charge. Thus, the electroosmotic flow of water through the diaphragm is generally directed to the cathode (negative electrode).

Another electrokinetic phenomenon, the *streaming potential* (so-called *Quincke effect*), is *the production of a potential difference when a liquid is forced through a porous membrane or capillary tube.* The separation of the oppositely charged layers of the electrical double layer, due to the forcible passage of liquid, results in a difference of potential between the two sides of the membrane or the ends of the capillary tube. The streaming potential effect may thus be regarded as the reverse of electroosmosis.

The last electrokinetic phenomenon, the *sedimentation potential* (also called *Dorn effect*), *is the potential difference at zero current caused by the sedimentation of particles in the field of gravity between two identical electrodes placed at different levels*. When colloidal particles sediment a potential will arise due to the separation of the charges. This charge separation occurs because of the substantial difference between the rate of sedimentation of particles and the much smaller counter-ions. Colloidal particles move down much more rapidly, leaving the counter-ions behind. This effect may be regarded as the reverse of electrophoresis.

Electrophoresis has a great practical applicability of the electrokinetic phenomena and has been studied extensively in its various forms, whereas electroosmosis and streaming potential have been studied to a moderate extent and sedimentation potential rarely, owing to experimental difficulties.

The fact that different proteins have different electrophoretic mobilities at a given pH has been utilized by A. Tiselius (1937). When an electric field is applied to the solution in Tiselius apparatus, separate boundaries are formed, due to the different speeds of the different protein particles; by the use of special optical devices each boundary produces a characteristic peak (Fig. 6.2). From the position of the peak, which is determined by the electrophoretic mobility, the nature of the protein can be identified; further, the area under of the peak is a measure of the amount present in the solution (Fig. 6.2).

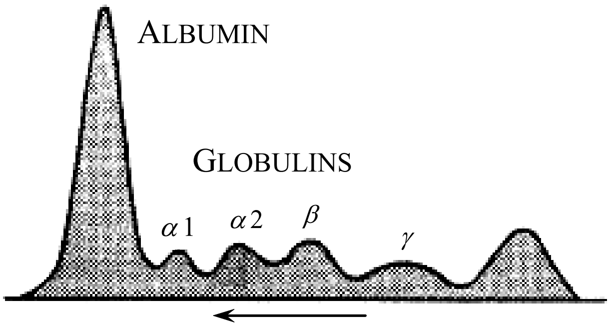


Fig. 6.2. Electrophoretic diagram (ascending) for human blood serum

It is possible to calculate the value of the zeta potential from a study of ever electrokinetic phenomenon, but more convenient methods, used for this purpose, are determination of electrophoretic mobility and measurement of streaming potential. The Fig. 6.3 shows the relationship between four electrokinetic phenomena all related to zeta potential. In the upper quadrants, electrophoresis and electroosmosis, it is the application of an electric field which causes relative movement between the two phases while in the cases of streaming and sedimentation potentials it is the movement resulting from the application of a force which gives rise to the potential.

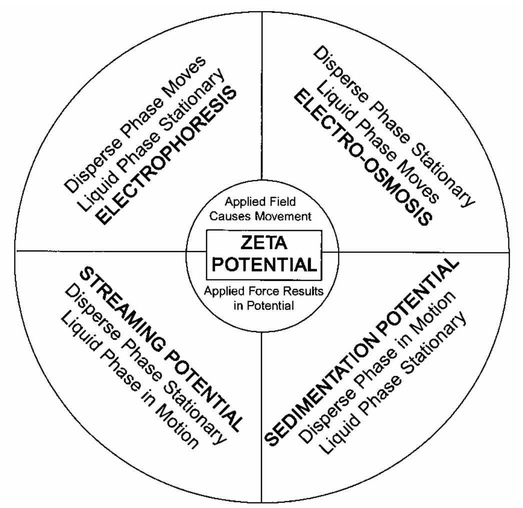


Fig. 6.3. Relationship between the four electrokinetic phenomena and zeta potential

Problems

Examples

Problem 1. Calculate the electrophoretic mobility of sol particles in water at 20 ºC if ζ-potential value and electric field intensity are equal 70 mV and $3.6{\cdot}10^2$ V/m, respectively. Use the values of dielectric permittivity and viscosity of water as those for dispersed medium.

Solution. According to equation (6.1) the velocity of electrophoresis is equal

$$velocity = \frac{E\varepsilon\varepsilon_o}{\eta}\zeta = \frac{3.6\cdot 10^2 \times 80.1 \times 8.85\cdot 10^{-12}}{1.005\cdot 10^{-3}} \times 70\cdot 10^{-3} = 1.78\cdot 10^{-5}\,\text{m/s}.$$

The electrophoretic mobility is equal

$$U_{el.mob.} = velocity\,/\,E = 1.78\cdot 10^{-5}\,/\,3.6\cdot 10^2 = 4.9\cdot 10^{-8}\,\text{m}^2/(\text{s}\cdot\text{V}).$$

Problem 2. Calculate zeta potential of the sol particles at 25 ºC if the velocity of electrophoresis and electric field intensity are equal $2.0{\cdot}10^{-5}$ m/s and $3.6{\cdot}10^2$ V/m, respectively; the values of dielectric permittivity and viscosity of dispersion medium are such as for water.

Solution. For the calculation of ζ-potential value we use the following equation

$$\zeta = \frac{\eta \cdot velocity}{E\varepsilon\varepsilon_o} = \frac{0.894 \cdot 10^{-3} \times 2.0 \cdot 10^{-5}}{3.6 \cdot 10^{2} \times 78.3 \times 8.85 \cdot 10^{-12}} = 0.072 \text{ V.}$$

Problems for self-solving

Note: Use viscosity and dielectric permittivity values from Table 6.1.

Table 6.1. Physicochemical properties of water

t, ^oC	Density ρ, g/cm^3	Viscosity η, mPa·s	Surface tension σ, mJ/m^2	Dielectric permittivity ε
0	0.99984	1.729	75.62	87.74
5	0.99996	1.518	74.90	85.76
10	0.99970	1.307	74.20	83.83
11	0.99960	1.271	74.07	83.52
12	0.99949	1.236	73.92	83.15
13	0.99937	1.203	73.78	82.78
14	0.99924	1.171	73.64	82.40
15	0.99910	1.140	73.48	81.94
16	0.99894	1.111	73.34	81.66
17	0.99877	1.083	73.20	81.28
18	0.99859	1.056	73.05	80.91
19	0.99840	1.029	72.89	80.54
20	0.99820	1.005	72.75	80.10
21	0.99799	0.981	72.60	79.79
22	0.99777	0.958	72.44	79.42
23	0.99756	0.936	72.28	79.05
24	0.99729	0.914	72.12	78.67
25	0.99704	0.894	71.96	78.30
26	0.99678	0.874	71.80	77.93
27	0.99651	0.854	71.64	77.55
28	0.99623	0.836	71.47	77.18
29	0.99594	0.818	71.31	76.81

30	0.99564	0.801	71.15	76.55

1. Calculate ζ-potential value of the sol particles at 20 ºC if distance, on which the boundary sol – lateral liquid displaces, is equal $2.5\cdot10^{-3}$ m; time of boundary displacement – 105 s; voltage is equal 110 V; distance between electrodes is 0.17 m. The values of dielectric permittivity and viscosity of dispersion medium are such as for water. *A*nswer: 0.052 V.

2. Calculate zeta potential of the sol particles at 15 ºC if the velocity of electrophoresis and electric field intensity are equal $1.7\cdot10^{-5}$ m/s and $3.0\cdot10^{2}$ V/m respectively; the values of dielectric permittivity and viscosity of dispersion medium are such as for water. *Answer*: $\zeta = 0.089$ *V.*

3. Calculate ζ-potential value of the sol particles at 20 ºC if distance, on which the boundary sol – lateral liquid displaces, is equal $1.5\cdot10^{-3}$ m; time of boundary displacement – 55 s; voltage is equal 110 V; distance between electrodes 0.17 m. The values of dielectric permittivity and viscosity of dispersion medium are such as for water. *Answer*: $\zeta = 0.060$ *V.*

4. Represent schematically according to Fig. 6.1 the structure of the electric double layer of AgI colloidal particle with positively charged potential determining ions and NO_3^- ions as the counter-ions.

5. Represent schematically according to Fig. 6.1 the structure of the electric double layer of AgI colloidal particle with negatively charged potential determining ions and K^+ ions as the counter-ions.

6. Calculate the thickness of the diffuse electric double layer for a negatively charged solid surface in contact with the aqueous solutions of 0.1 $mol\cdot dm^{-3}$ KCl at 25°C. *Answer: 1 nm.*

7. In a electrophoresis experiment a spherical particle dispersed in aqueous solution of KCI at 25°C takes 8.0 s to cover a distance of $120\cdot10^{-6}$ m along one of the stationary levels of the cell, the potential gradient being 10.0 V cm^{-1}. Calculate (a) the electrophoretic mobility of the particle and (b) an approximate value for the zeta potential of the particle. *Answer: (a)* $1.5\cdot10^{-8}\ m^2\cdot s^{-1}\cdot V^{-1}$; *(b) 19 mV.*

8. Spherical particles suspended in KCl (aq.) are observed to have an electrophoretic mobility of $4.0\cdot10^{-8}\ m^2\cdot s^{-1}\cdot V^{-1}$ at 25°C. Calculate an approximate value for the zeta potential. *Answer: 48 mV.*

9. Calculate the rate of electro-osmotic flow of water at 25°C through a glass capillary tube 10 cm long and 1 mm diameter when the potential difference between the ends is 200 V. The zeta potential for the glass-water interface is –40 mV. *Answer:* $5\cdot10^{-5}$ $cm^3\cdot s^{-1}$ *towards negative electrode.*

10. Calculate the thickness of the diffuse electric double layer for a negatively charged solid surface in contact with the aqueous solutions of 0.001 $mol\cdot dm^{-3}$ KCl at 25°C. *Answer: 10 nm.*

THEME 7
ADSORPTION

Adsorption is a process that occur when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. It also can be defined as the preferential concentration (i.e., location) of one component of a system at an interface, where the local (i.e., interfacial) concentration of one or more components of one or both phases is different from those in the bulk phases.

Adsorption should be clearly differentiated from «*absorption*», in which physical penetration of one substance into another phase is involved. The term *sorption* encompasses both processes. Adsorption can occur at any type of interface, although the distinct characteristics of solid versus liquid interfaces make the analysis of each case somewhat different. Where the interfacial concentration of the adsorbed species is greater than that in the bulk phase(s), one can refer to «*positive*» *adsorption*. In a situation of «*negative*» *adsorption*, the concentration of a system component in the region of the interface will be less than that in one or both bulk phases. The result of negative adsorption can be the increase in the interfacial energy of a system relative to a defined standard state.

The substance that adsorbs is the *adsorbate* and the underlying material that we are concerned with in this section is the *adsorbent* or substrate. The reverse process of adsorption is *desorption*.

Types of adsorption: physical and chemical adsorptions. The forces involved in adsorption processes are nonspecific Van der Waals forces, ionic or electrostatic forces, and specific forces involved in the formation of chemical bonds. Because the nonspecific interactions are orders of magnitude smaller than the chemical forces, adsorption processes that involve only nonspecific Van der Waals (weak intermolecular) interactions are generally referred to as «*physical adsorption*» while those in which stronger chemical interactions occur are termed «*chemical adsorption or chemisorption*».

The process of physical adsorption is reversible and equilibrium is reached rapidly. Physical adsorption is generally a multilayer process (Fig. 7.1). Unlike physical adsorption, chemisorption is limited to the formation of a monomolecular adsorbed layer (Fig. 7.1). Chemisorption processes may be much slower than physical adsorption and are not readily reversible.

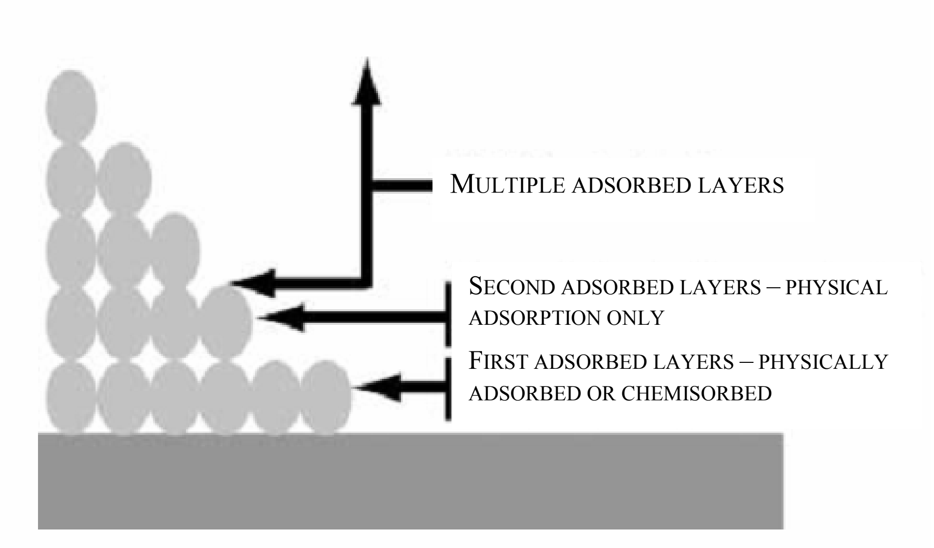


Fig. 7.1. Multilayer adsorption on a solid surface: the first adsorbed layer may be physically adsorbed or chemisorbed; subsequent layers will be physically adsorbed only

Absolute adsorption, A, is quantitative characteristic of adsorption process. It is equal the amount of adsorbed substance (in moles or kg) per unit area of the surface layer or per unit mass of the adsorbent

$$A = n/s \quad \text{or} \quad A = n/m, \tag{7.1}$$

where n – the amount of adsorbed substance; s and m – the adsorbent area and its mass, respectively.

Also adsorption is described quantitatively by *Gibbs's adsorption*

$$\Gamma = n^{s}/s, \tag{7.2}$$

where n^{s} – moles excess of adsorbate in the surface layer with area s as compared to the bulk of solution.

The A and Γ values are related by the following equation

$$A = \Gamma + c \cdot \delta, \tag{7.3}$$

where c – concentration of a component in the bulk phase; δ – thickness of the surface layer.

A molecule in the inner layers of a substance experiences attraction that is equal in all directions by surrounding molecules, so that the net force on it is zero. For a molecule in the surface layer, however, these forces are unbalanced (Fig. 7.2).

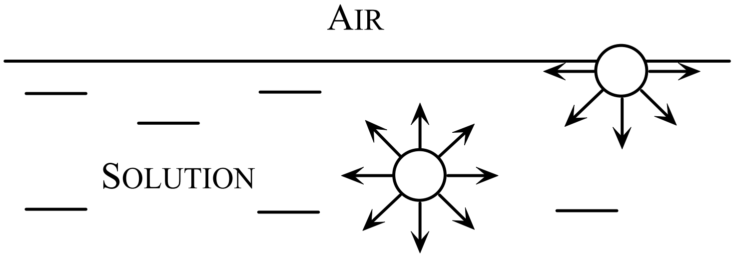


Fig. 7.2. The surface layer of a liquid

At a liquid-air interface the molecules of liquid in the surface layer are attracted more strongly by the underlying molecules than by the molecules of the gas. Due to this the properties of molecules the surface layer differ somewhat from the properties of molecules on the substance in the bulk phase.

Surface tension. Owing to the unique environment of the molecules in the surface layer an increase in surface area requires the work done. This work referred to 1 m^2 is called the *surface tension*, σ. Its units are N/m or J/m^2 (numerically the values in both units are equal). Hence, the surface tension may be regarded as force per unit length ($\sigma = F / l$) or energy per unit area ($\sigma = E / s$).

Substances which greatly reduce the surface tension of a solvent are called *surface active agents* or *surfactants*. The quantity $g = -(d\sigma/dc)_{T,c\to 0}$ is usually taken as the *measure of surface activity*. With rise in temperature the thermal motion of the molecules becomes more energetic and, hence, adsorption decreases. Surfactant molecules consist usually of hydrophobic hydrocarbon chains and hydrophilic groups: –COOH, –OH, $-NH_2$, –SH, –CN, $-NO_2$, –SCN, –CHO, $-SO_3H$, $-SO_3Na$, for instance sodium *n*-dodecylsulfate $C_{12}H_{25}OSO_3Na$ or cetyltrimethylammonium bromide $C_{16}H_{33}N(CH_3)_3Br$.

The longer the hydrocarbon chain, the greater is the tendency for surfactant molecules to adsorb at the air-water surface and, hence, to decrease the surface tension. A rough generalisation, known as *Traube's rule*, is that for a particular homologous series of surfactants the concentration required for an equal lowering of surface tension in dilute solution decreases by a factor of about 3 for each additional $-CH_2-$ group.

Adsorption of a solute in the surface layer of a solution is described quantitatively by *Gibbs's equation*

$$\Gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}, \quad (7.4)$$

where $d\sigma/dc$ is the change in the surface tension of the solution with concentration c; R – gas constant; T – absolute temperature.

This equation shows that when σ value decreases with the increasing of concentration, i.e., $d\sigma/dc<0$, then $\Gamma>0$, and the concentration of solute is greater in the surface layer than in the bulk of solution (*positive adsorption*). It is observed for surfactant solutions. In the opposite case, i.e., when $d\sigma/dc>0$, $\Gamma<0$, and the concentration is lower in the surface layer than in the bulk of the solution (*negative adsorption*).

Theory of monolayer adsorption of Langmuir. Since chemical forces fall off very rapidly with distance, it is probable that chemisorption does not extend beyond a single layer of gas molecules on the surface of the solid. By supposing that a unimolecular layer only of gas can be adsorbed on the surface of a solid, in 1916 I. Langmuir was able to derive *an adsorption isotherm* relating the pressure of the gas to the extent of adsorption, since it is applicable at constant temperature. So, the *adsorption isotherm* shows a dependence of adsorption on the pressure $A = f(p)$ or on the concentration $A = f(c)$ at $T = const$.

The simplest physically plausible isotherm is based on four assumptions.

1. All sites on the surface are equivalent and the surface is uniform (that is, the surface is perfectly flat on a microscopic scale).

2. The ability of a molecule to adsorb at a given site of the surface is independent of the occupation of neighboring sites (that is, there are no interactions between adsorbed molecules).

3. Adsorption cannot proceed beyond monolayer coverage.

4. The free gas and the adsorbed gas are in dynamic equilibrium

$$\text{G (gas)} + \text{M (surface)} \leftrightarrow \text{GM (surface)}$$

with rate constants k_a for adsorption and k_d for desorption. The constant of the adsorption equilibrium is equal

$$K = \frac{k_a}{k_d}. \quad (7.5)$$

The rate of change of surface coverage due to adsorption is proportional to the partial pressure p of gas and the number of vacant sites of the surface.

The *fractional coverage, θ*, equals the ratio of the number of adsorption sites occupied and the number of adsorption sites available of the surface depends on the pressure of the overlying gas. The variation of θ value with pressure (adsorption process from gaseous phase) or concentration (adsorption process from solution) at constant temperature is called the *Langmuir adsorption isotherm*

$$A = A_{\infty}\frac{Kp}{1+Kp} \quad or \quad A = A_{\infty}\frac{Kc}{1+Kc}, \tag{7.6}$$

where A_{∞} – limiting monomolecular adsorption (it means a complete monolayer on the surface, A value reaches A_{∞} and $\theta = 1$); K – constant of adsorption equilibrium; p – the partial pressure of gas; c – the substance concentration in the bulk phase; the p and c values are equilibrium ones.

The linear form of adsorption isotherm is following

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{1}{A_{\infty}K}\frac{1}{c}. \tag{7.7}$$

The plot of Langmuir adsorption isotherm is presented in the Fig. 7.3.

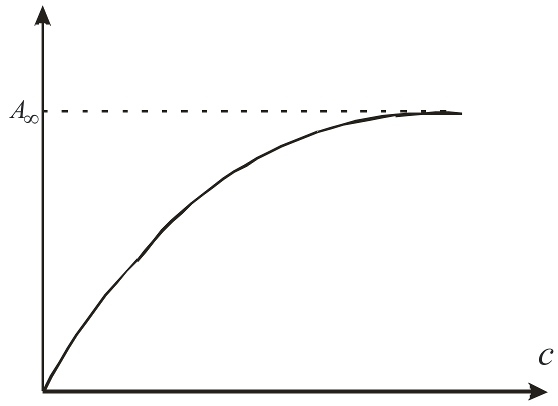


Fig. 7.3. The Langmuir adsorption isotherm

The first place among the adsorbents used in practice belongs to the different kinds of specially prepared carbons with exceptionally high porosity and, hence, a huge surface area. For instance, in 1 g of a highly adsorbing carbon (*activated carbon, also called activated charcoal or activated coal*) the inner surface of the pores has a surface area of 400–900 m^2. Besides the general degree of porosity, its character, i.e., the numbers of pores of different diameters, is of high significance in adsorption processes. In addition to activated carbon, other substances are used as adsorbents for different purposes. Activated carbon is frequently used in everyday life: industry, food production, medicine, pharmacy, military, etc. Other examples of the adsorbent are mostly highly porous or finely divided materials, such as silica gel, alumina, kaolin, and certain alumosilicates.

Medical applications of activated carbon. Activated carbon is used to treat poisonings and overdoses following oral ingestion. It is thought to bind to poison and prevent its absorption by the gastrointestinal tract. In cases of suspected poisoning, medical personnel administer activated charcoal on the scene or at a hospital's emergency department. In rare situations activated charcoal is used in intensive care to filter out harmful drugs from the blood stream of poisoned patients. Activated charcoal has become the treatment of choice for many poisonings, and other decontamination methods.

While activated carbon is useful in acute poisoning, it has been shown it is not effective in long term accumulation of toxins, such as with the use of toxic herbicides.

Tablets or capsules of activated charcoal are used in many countries as an over-the-counter drug to treat diarrhea, indigestion, and flatulence. Activated charcoal is also used for bowel preparation by reducing intestinal gas content before abdominal radiography to visualize bile and pancreatic and renal stones.

Practical application of adsorption. Adsorption has a wide variety of applications. In heterogeneous catalysis, both in the gaseous phase and in solution, adsorption of the reacting substances by a solid catalyst is of decisive importance. Solid adsorbents are also used in various processes of purification of gases or liquids from undesirable admixtures or impurities. Other examples are the many processes of purification and drying of gases in industrial conditions, and the discoloration of solutions in the manufacture of sugar, glucose, petroleum products, certain pharmaceutical products, etc.

Adsorption phenomena play an important part in dyeing processes. For example, when wool is dyed, the dye-stuff is first adsorbed, after which a chemical reaction takes place in the adsorbed layer.

The properties of many powdered materials, in particular building materials, can be radically changed by the adsorption of various substances. This phenomenon, for instance, is at the basis of the hydrophobization of cement upon treatment with solutions of high-molecular organic acids, etc. Soils adsorb various dissolved substances from natural waters.

Problems

Examples

Problem 1. Determine the area per single surfactant molecule in the closely packed monolayer at the interface of surfactant/solution, if the value of limiting monomolecular adsorption (A_∞) is equal $6·10^{-6}$ mol/m^2.

Solution. The area per single molecule in the monomolecular layer is equal

$$S_M = \frac{1}{A_\infty N_A} = \frac{1}{6.02 \cdot 10^{23}\,\mathrm{mol}^{-1} \times 6 \cdot 10^{-6}\,\mathrm{mol/m}^2} = 2.77 \cdot 10^{-19}\,\mathrm{m}^2.$$

Problem 2. Calculate the value of limiting monomolecular adsorption (A_∞) according to the linear form of the Langmuir adsorption isotherm using following data

p, Pa	1.03	1.29	1.74	2.50	6.67
A, mol/kg	0.0157	0.0194	0.0255	0.0351	0.0758

Solution. The linear form of adsorption isotherm is following

$$\frac{1}{A} = \frac{1}{A_\infty} + \frac{1}{A_\infty K}\frac{1}{p}.$$

We draw adsorption isotherm of $1/A$ *vs* $1/p$ (see Fig. 7.4) and determine the $1/A_\infty$ value as intercept on Y-axis ($1/A$). $1/A_\infty$ = 3 kg/mol and A_∞ = 0.33 mol/kg.

Problems for self-solving

1. When $5.19·10^{-5}$ g of palmitic acid ($C_{15}H_{31}COOH$), in the form of a dilute solution in benzene, was spread on the surface of water, it could be compressed to an area of 265 cm^2. Calculate the area occupied by a single molecule in the closely packed layer. *Answer*: $S_M = 2.17·10^{-15}$ *cm*^{2}.

2. A solution of 1 mol of substance in one liter of water was treated with 14 g of activated carbon. The final concentration of the substance in solution after treatment was determined to be 0.3 mol/L. What is the adsorption value? *Answer*: *A = 0.05 mol/g.*

3. How much activated carbon would be needed to reduce the substance concentration of two liters of 0.5 mol/L solution of substance to 0.3 mol/L due to adsorption, if the adsorption value is 0.2 mol/g? *Answer*: *m = 2 g.*

4. Four grams of activated carbon was added to 2 liter of 1.0 mol/L aqueous solution of some substance causing the final concentration of dye is 0.60 mol/L. Calculate the adsorption value per gram of activated carbon. *Answer*: *A = 0.2 mol/g.*

5. Calculate specific area of adsorbent, S, if area per single molecule in the monomolecular layer is equal $0.4{\cdot}10^{-18}$ m^2 and the value of limiting monomolecular adsorption (A_∞) is equal 0.33 mol/kg. *Answer*: $S = 7.946{\cdot}10^4\ m^2/kg$.

6. Calculate the value of limiting monomolecular adsorption (A_∞) and constant of adsorption equilibrium (K) according to the linear form of the Langmuir adsorption isotherm using following data

Gas pressure, Pa	$3.04{\cdot}10^2$	$4.68{\cdot}10^2$	$7.72{\cdot}10^2$	$11.69{\cdot}10^2$	$14.03{\cdot}10^2$	$17.77{\cdot}10^2$
A, mol/kg	4.44	6.28	9.22	11.67	13.22	14.89

Answer: $A_\infty = 29.4\ mol/kg,\ K = 5.66{\cdot}10^{-4}\ Pa^{-1}$.

7. The surface tensions of aqueous solutions of sodium dodecyl sulphate at 20°C are as follows:

c, mmol·dm^{-3}	0	2	4	5	6	7	8	9	10	12
σ, mN·m^{-1}	72	62.3	52.4	48.5	45.2	42.0	40.0	39.8	39.6	39.5

Determine the critical micelle concentration (cmc) and calculate the area occupied by each adsorbed surfactant molecule at the critical micelle concentration. *Answer:* $cmc = 7.8\ mmol{\cdot}dm^{-3}$; $S\ (at\ cmc) = 39{\cdot}10^{-20}\ m^2{\cdot}molecule^{-1}$.

8. The following surface tensions were measured for aqueous solutions of the non-ionic surfactant $CH_3(CH_2)_9(OCH_2CH_2)_5OH$ at 25°C:

c, 10^{-4} mol·dm^{-3}	0.1	0.3	1.0	2.0	5.0	8.0	10.0	20.0	30.0
σ, mN·m^{-1}	63.9	56.2	47.2	41.6	34.0	30.3	29.8	29.6	29.5

Determine the critical micelle concentration and calculate the area occupied by each adsorbed surfactant molecule at the critical micelle concentration. *Answer: cmc* = $9\cdot10^{-4}$ *mol·dm*$^{-3}$*; S (at cmc) = 50·10*$^{-20}$ *m*^{2}*·molecule*$^{-1}$*.*

9. Determine the area per single surfactant molecule in the closely packed monolayer at the interface of butan-1-ol/solution, if the value of limiting monomolecular adsorption (A_∞) is equal $8\cdot10^{-6}$ mol/m^2. *Answer:* $S_M = 2.1\cdot10^{-19}$ m^2.

10. A solution (100 mL) of substance (initial concentration is 0.5 mol/L) was treated with 15 g of activated carbon. The final concentration of the substance in solution after treatment was determined to be 0.3 mol/L. What is the adsorption value? *Answer*: *A = 0.001 mol/g.*

Further readings

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