Ukraine Ministry of Education
Kharkov Aviation Institute

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LECTURE NOTES IN CHEMISTRY

for the first year students

Kharkov
1997

УДК 54 (075).8

Конспект лекций по химии для студентов первого курса. /Д. Е. Коваленко. - Харьков: Харьковский авиационный институт, 1997. - 104 страницы.

Изложены разделы курса химии, преподаваемые студентам первого курса в Харьковском авиационном институте: термодинамика, кинетика, электрохимия и строение вещества. Конспект может быть полезен иностранным и украинским студентам изучающим химию на английском языке.

Иллюстраций: 23. Библиография : 6 названий

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Introduction

1) "*Chemistry* is the science of the transformation of substances. It studies the composition and structure of substances, the relation between the properties of substances and their composition and structure, the conditions and ways of changing substances into one another " [1, p. 17]

Chemistry helps to understand the nature, to choose materials and fuels, to predict their properties, to create technologies.

Thermodynamics

"*Thermodynamics* is a science that deals with:
(1) the conversion of energy from one form to another; (2) the energy effects in physical and chemical processes and their dependence on the conditions under which the processes take place; and (3) the possibility, direction and limits of spontaneous processes (i.e., processes in which work is not supplied from outside the system) under given conditions." [3, p. 156]

"*Basic Concepts*:

A system is a body or group of interacting bodies that we consider apart from its surroundings." [3, p. 157]

"*An isolated system* is one that cannot exchange energy or matter with its surroundings and that has a constant volume." [3, p. 157]

A closed system is one that can not exchange matter with its surroundings. *An open system* is one that can exchange both energy and matter with its surroundings.

Parameters - are quantities which determine the state of the system.

There are *intensive parameters* (P, T) which does not depend on mass of substances, and *extensive parameters* (V, m, l) which value depends on mass of substances.

Process is any change of the state of the system, during which the parameters change. Processes in which heat is evolved are called *exothermic*, those in which heat is absorbed are called *endothermic*.

"Thermodynamic functions whose value depends only on the state of the system are called functions of state (U, H, S, G, F) The change of such functions in a process depends only on the initial (1) and final (2) states of the system; it does not depend on the path by which the system is brought from one state to the other." [3, p. 157]

For example we can write:

$$\Delta U = U_2 - U_1 \text{ or } \Delta S = S_2 - S_1$$

Where U is the *internal energy*. Thermodynamically, it is strictly determined by the first law. Physically, the internal energy of a system is the total energy it has, including the energy of the translational and rotational motions of its molecules, the intermolecular vibrations of atoms and atomic groups, the motion of the electrons in the atoms, the energy of the atomic nuclei, and other forms of energy. It does not include the kinetic energy of motion of the system as a whole or its potential energy due to position" [3, p. 158]

"First Law of Thermodynamics

It is intimately related to the law of conservation of energy." [3, p. 163]

"A great part in the formulation of the first law, as we know it today was played by G. Hess (1836), I. Mayer (1842), J. Joule (1847), H. Helmholtz (1847), and others...

The first law can be formulated in several ways.

The following formulation is a highly important one: *in any process the change in the internal energy of a system* ($\Delta U = U_2 - U_1$) *is equal to the heat Q imparted to the system minus the work A done by the system*

$$\boxed{\Delta U = Q - A}$$ " [3, p. 164]

This equation is a mathematical expression of the first law of thermodynamics.

"For process involving only infinitesimally small changes, it is convenient to write previous equation in the form:

$$\boxed{dU = \delta Q - \delta A}$$

where dU is the total differential of the internal energy of the system; and δQ and δA are infinitesimally small amounts of heat and work." [3, p. 165]

We write dU because the internal energy is a function of state and it does not depend on the path of the process.

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We write dU because the internal energy is a function of state and it does not depend on the path of the process.

But heat (Q) and work (A) are not the functions of state. They depend on the path of the process. Because of it we write δQ and δA.

"By means of previous equations we can define the concept of internal energy thermodynamically as a quantity, the increase in which during a process is equal to the heat absorbed by the system plus the work done on the system by external forces" [3, p. 164-165]

$$\Delta U = Q + A$$

In this equation we write plus before work because it done on the system by external forces. *It is not done* by the system.

"In many processes work is done only against the external pressure. In such cases for an isothermal process

$$\delta A = PdV$$

, and

$$A = P\Delta V$$

$$dU = \delta Q - PdV$$

$$\Delta U = Q - P\Delta V$$

where P is the pressure, and V is the volume of the system.

1) Hence, for *isochoric processes (dV=0)*.

$$\boxed{\delta Q = dU}$$

V=const

$$\boxed{Q_v = \Delta U}$$

2) For *isobaric process* (P=const)

$$Q_P = \Delta U + P\Delta V = U_2 - U_1 + P(V_2 - V_1) = \underbrace{U_2 + PV_2}_{H_2} - \underbrace{U_1 + PV_1}_{H_1} = \Delta H$$

$$\boxed{Q_p = \Delta H} \text{ if P=const}$$

where

Q_p -heat effect of the process at P=const

Q_v -heat effect of the process at V=const

"Enthalpy H is widely used thermodynamic function. It is defined by

$$\boxed{H = U + PV}$$

The enthalpy, like the internal energy, is a function of state." [3, p. 159]

"Attention! In thermodynamics a positive value of Q means that heat is absorbed by the system, while a negative value denotes heat that is evolved". [3, p. 159]

"The reverse sign convention, called thermochemical, is also frequently used!" [3, p. 160]

The heat effect of a process is defined as the sum of the absorbed heat and the total work done by the surroundings on the system, minus the work of the external pressure." [3, p. 160] For the processes at constant temperature

$$Q_V = \Delta U = U_2 - U_1$$
$$Q_P = \Delta H = H_2 - H_1$$

"The above relations show that at constant temperature the heat effect of isochoric and isobaric processes does not depend on the path of the process, but is uniquely determined by the initial and final states of the system." [3, p. 160]

$$\boxed{Q_P - Q_V = \Delta H - \Delta U = P\Delta V = \Delta nRT}$$

For ideal gases at constant temperature PV=nRT. Hence, if in a reaction n_1 moles of gaseous substance are used up and n_2 moles of gaseous products are formed then $\Delta(PV) = \Delta nRT$ and $\Delta H = \Delta U + \Delta nRT$. For example:

$$2H_2+O_2=2H_2O_{(l)}$$

$$\Delta n = 0 - 2 - 1 = -3$$

Hess's Law (1840)

"*The heat effect of a chemical reaction is independent of the path of th reaction and depends only on the initial and final states of the system*. Thi law is strictly valid only for isochoric processes (heat effect equal to ΔU) o for isobaric processes(heat effect equal to ΔH).For these processes it is easily deduced from the first law of thermodynamics" (see above). [3, p. 167]

Heat effect of the chemical reaction is heat absorbed or involved during the chemical process, if the temperature of initial substances equal to the temperature of final substances.

Problem which deal with Hess's law.

Example 1:

There are two chemical reactions :

$$1)\ C + \tfrac{1}{2}O_2 = CO + 110.5\ \text{kcal}$$

$$2)\ CO + \tfrac{1}{2}O_2 = CO_2 + 283\ \text{kcal}$$

Calculate the heat effect of reaction :

$$3)\ C + O_2 = CO_2 + Q_3$$

Solution (see Fig. 1):

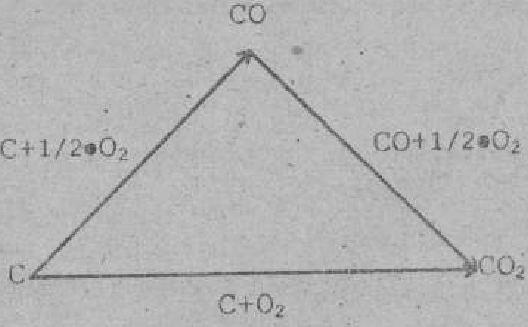


Fig. 1

$$Q_3 = Q_1 + Q_2 = 393.5\ \text{kcal}$$

"*The heat of formation* is the heat effect of the reaction of formation of a given compound from its constituent elements when the latter are in the stablest state for the given temperature." [3, p. 170]

There are 3 consequences of Hess's law.

1) It follows from Hess's law that the heat effect 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, of course, by the proper coefficient (n) of the equation).

$$\Delta H^0_{ch.r.} = \sum(n\Delta H^0_f)_{prod} - \sum(n\Delta H^0_f)_{react},$$

where $\Delta H^0_{ch.r.}$ - heat effect of the chemical reaction, ΔH^0_f - heat of formation at p = const, prod - products of reaction, react - initial substances.

In handbooks there are values of the heat of formation (H^0_f) for many substances.

Example 2:

Determine heat effect of reaction

$$2H_{2(gas)} + O_{2(gas)} = 2H_2O_{(liquid)},$$

if

$$\Delta H^0_{f(H_2)} = 0$$

because hydrogen is a simple substance in the stablest form,

$$\Delta H^0_{f(O_2)} = 0,$$

$$\Delta H^0_{f(H_2O(liquid))} = 286 \, J/_{mol}$$

Solution:

$$\Delta H_{ch.r} = 2\Delta H^0_{f(H_2O(liquid))} - (2\Delta H^0_{f(H_2)} + 2\Delta H^0_{f(O_2)}) = 2 \cdot 286 = 572\,J$$

2) The 2nd consequence of Hess's law.

"It follows from Hess's law that the heat effect 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 coefficients)." [3, p. 174]

$$\Delta H^0_{ch.r.} = \sum(n\Delta H^0_{com})_{react} - \sum(n\Delta H^0_{com})_{prod}.$$

where ΔH^0_{com} - heat of combustion, that defined as the heat effect of the reaction of oxidation of a substance by oxygen to the higher oxides of the corresponding elements or to compounds of these oxides.

3) The 3rd consequence of Hess's law.

"The amount of heat evolved (absorbed) in decomposition of a compound into simple substances is the same as that absorbed (evolved) during formation of this chemical compound from the initial simple substances." [6, p. 74]

Efficiency of Fuel

Example 3:

Determine the heat effect per 1 kilo of reactants (C_7H_{16} and O_2) for reaction:

$$C_7H_{16} + O_2 \longrightarrow H_2O + CO_2$$

Solution:

1) We must balance the equation

$2C^{3-} - 14e \rightarrow 2C^{4+}$ $5C^{2-} - 30e \rightarrow 5C^{4+}$	44	1
$O_2 + 4e \rightarrow 2O^{2-}$	4	11

$$C_7H_{16} + 11O_2 = 7CO_2 + 8H_2O$$

2) We must determine heat effect of the reaction

$$\Delta H^0_{ch.r} = \sum(n\Delta H^0_f)_{prod} - \sum(n\Delta H^0_f)_{react} =$$
$$= 7\Delta H^0_{f(CO_2)} + 8\Delta H^0_{f(H_2O)} - \Delta H^0_{f(C_7H_{16})}$$

3) We must determine the heat effect of the reaction per 1 kilo of the reactants

$$= \frac{\Delta H^0_{ch.r.} \cdot 1000}{\sum(nM)_{react}}$$

where n = coefficient of the equation, M = molar masses of the reactants."

$$\sum(nM)_{react} = M_{C_7H_{16}} + 11M_{O_2} = 100 + 11\cdot 32 = 452\,g.$$

Dependence of Heat Effect of Reaction on Temperature

"In the general case true heat capacity is defined as the ratio between an infinitesimal amount of heat imparted to the system and the change in temperature which this brings about, i.e.,

$$C=\delta q/dT.$$

Hence it follows that for isochoric processes

$$C_V = (dU/dT)_V$$

and for isobaric processes

$$C_P = (dH/dT)_P.$$

Differentiating the equation

$$\Delta U = U_2 - U_1$$

with respect to the temperature at constant volume, we obtain

$$[\partial(\Delta U)/\partial T]_V = (\partial U_2/\partial T)_V - (\partial U_1/\partial T)_V = C_{V2} - C_{V1} = \Delta C_V,$$

where C_{V_1} - heat capacity at constant volume of the system in the initial state. C_{V_2} - heat capacity at constant volume of the system in the final state, ΔC_V - change in the heat capacity at constant volume of the system upon transition from state 1 to state 2".

$$\Delta C_V = \sum(nC_V)_{prod} - \sum(nC_V)_{react}.$$

"For constant pressure processes we obtain in similar manner:"

$$[\,\partial(\Delta H)/\partial T\,]_P = \Delta C_P.$$

"These equations are mathematical expressions of the same *Kirchhoff's law*, that can be formulated as follows: the temperature coefficient of the heat effect of a process is equal to the change in the heat capacity of the system caused by the process." [3, p. 176]

$$\Delta U_{T_2} = \Delta U_{T_1} + \int_{T_1}^{T_2} \Delta C_V dT$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_P dT$$

These equations are the same law.

"**Example 4**:

Determine how the heat effect ΔH of the reaction

$$CO_{(gas)} + H_2O_{(gas)} = CO_{2(gas)} + H_{2(gas)}$$

depends on the temperature and find its value at 1000 °C, if at 25.01 °

ΔH_{298} =9,838 cal and

$$C_{P_{CO}} = 6.3424 + 1.8363 \cdot 10^{-3} T - 0.2801 \cdot 10^{-6} T^2$$
$$C_{P_{H_2O}} = 7.219 + 2.374 \cdot 10^{-3} T + 0.267 \cdot 10^{-6} T^2$$
$$C_{P_{CO_2}} = 6.396 + 10.1 \cdot 10^{-3} T + 3.405 \cdot 10^{-6} T^2$$
$$C_{P_{H_2}} = 6.9469 + 0.1999 \cdot 10^{-3} T + 0.4808 \cdot 10^{-6} T^2$$

Solution:

From these equations we obtain

$$\Delta C_P = C_{P_{H_2}} + C_{P_{CO_2}} - C_{P_{H_2O}} - C_{P_{CO}} =$$
$$= -0.219 + 5.69 \cdot 10^{-3} T - 2.911 \cdot 10^{-6} T^2$$

$$\Delta H_T = -9.838 + \int_{298}^{T} (-0.219 + 5.69 \cdot 10^{-3} T - 2.911 \cdot 10^{-6} T^2) dT =$$
$$= -9.838 - (0.219T + 2.845 \cdot 10^{-3} T^2 - 0.9703 \cdot 10^{-6} T^3)\Big|_{298}^{T} =$$
$$= -10.0 - 0.219T + 2.845 \cdot 10^{-3} T^2 - 0.9703 \cdot 10^{-6} T^3$$
$$\text{and } \Delta H_{1273K} = -7.67\text{cal} \approx -32.2\text{ J"}$$

[3, p. 178]

Second Law of Thermodynamics

Introduction. The first law of thermodynamics determine energy parameters of processes and the second law of thermodynamics determine directions of the processes. "The second law of thermodynamics has a more limited field of application than the first law. It is of a statistical nature and is therefore applicable only to systems composed of a large number of particles, i.e., to systems whose behavior can be described by the laws of statistics." [3,p.182]

Basic concepts.

"*Spontaneous processes* are ones that take place without work being done on the system and as a result of which useful work can be obtained in amount proportional to the change that takes place.

Processes in which work must be done on the system in an amount directly proportional to the resulting change also exist." [3,p.181.]

"*A reversible thermodynamic* process is defined as a process in which the system reverts to its initial state without having caused any changes in its surroundings." [3,p.158.]

"*The second law of thermodynamics states* that *in isolated systems* only such processes can occur spontaneously in which the entropy of the system increases; a process can proceed spontaneously until the entropy reaches its maximum value for the given conditions." [3, p. 183]

$$\boxed{\Delta S \geq 0}$$

"For every thermodynamic system under given conditions there exists a general criterion that characterizes the permissibility, direction and limit of spontaneous thermodynamic processes. For example, for isolated systems this criterion is a thermodynamic parameter called the entropy S." [3, p. 183]

"*Entropy* is a thermodynamic function which is a function of state and whose change for a reversible isothermal process of heat transfer is equal to the reduced heat of the process." [3, p. 189]

$$\Delta S = \frac{Q}{T} \qquad \text{or} \qquad dS = \frac{\delta Q}{T}$$

These formulae can be used in calculations of ΔS in processes of phase transitions.

For irreversible processes

$$dS \rangle \frac{\delta Q}{T}$$

In general case mathematical expression of the 2nd law of thermodynamics is

$$dS \geq \frac{\delta Q}{T}$$

"Entropy is a function of state, hence an infinitesimal change in entropy is expressed by the total differential dS, and the change in entropy in a given process depends only on the initial and final states and is independent of the path." [3, p. 190]

$$\boxed{\Delta S = S_2 - S_1}$$

For a chemical reaction

$$\boxed{\Delta S_{ch.r} = \sum\left(n\Delta S_f^0\right)_{prod} - \sum\left(n\Delta S_f^0\right)_{react}}$$

where S_f^0 is entropy of formation. One can find it in handbooks.

the substance.

__Example 5__:
Is reaction

$$2HCl_{(g)}+Mg(OH)_{2(c)}=MgCl_{2(c)}+2H_2O_{(g)}$$

spontaneous in isolated system in standard conditions (P=1 atm T=298 K)?

__Solution__.

$$\Delta S^o_{ch.r} = \overset{2}{\Delta S}{}^o_{fH_2O(g)} + \Delta S^o_{fMgCl_2(c)} - 2\Delta S^o_{fHCl(g)} - \Delta S^o_{fMg(OH)_2(c)} =$$
$$= 45.1 + 21.4 - 2\cdot 44.6 - 15.1 = +37.8\text{cal} = +13$$

__Answer:__
This reaction is ~~not~~ spontaneous one in this conditions because

$$\Delta S^0_{ch.r} > 0$$

"The establishment of the statistical nature of the second law led L. Boltzmann (1896) to the *__statistical interpretation of entropy.__*

It can be shown that

$$S = k \cdot \log_e P_{th}$$

Where k = Boltzmann's constant

$$(k = \frac{R}{N_A})$$

P_{th} = thermodynamic probability of the given state of the system.

Plank's Postulate (1912)
(3rd Law of Thermodynamics)

$$\boxed{\lim_{T \to 0} S = 0}$$

"At absolute zero the entropy of a perfect crystal of an element or compound in the pure state is zero, while in any other state it is greater then zero." [3,p.249]

Physical interpretation of entropy.

"Entropy can be considered as a measure of disorder in the arrangement of the particles of a substance. This is why entropy has the lowest value for a perfect crystal." [3, p. 249]

"*Characteristic Functions and Thermodynamic Potential*

A characteristic function is such a function of the state of a system that by means of this function or its derivatives the thermodynamic properties of the system can be expressed in explicit form. The following five characteristic functions are most widely applied in thermodynamics: (1) Gibbs free energy, (2) Helmholtz free energy, (3) internal energy, (4) enthalpy, and (5) entropy.

The first four are also known collectively as thermodynamic potentials. To be true, this term is frequently used in a narrower sense to denote the Gibbs and Helmholtz energies or only the former." [3, p. 195]

The Maximum and Maximum Useful Work in a Process

From the 2nd law of thermodynamics

$$dS \geq \frac{\delta Q}{T}$$

It is useful to observe that for isothermal processes it follows from this relation that

$$TdS \geq \delta Q$$

From the first law of thermodynamics

$$dU = \delta Q - \delta A$$

and from these two

$$dU \leq TdS - \delta A$$

or

$$\delta A \leq TdS - dU$$

"In these relations the equality sign refers to equilibrium and to reversible processes; the inequality sign refers to irreversible processes.

The last relation shows that the work which a system can do is maximum for reversible processes. It is called the *maximum work*, A_{max} (W_{max})" [3, p. 192]

$$\delta A_{max} = TdS - dU.$$

For isothermal processes one obtains from the previous expression for a finite change:

$$A \leq T(S_2 - S_1) - (U_2 - U_1)$$

or

$$A \le (\underset{+F1}{\underline{U_1-TS_1}})-(\underset{+F2}{\underline{U_2-TS_2}})=-\Delta F$$

$$\boxed{\begin{gathered} F = U - TS \\ dF = dU - TdS \\ \Delta F = \Delta U - T\Delta S \end{gathered}}$$

"The function U-TS plays an important role in the study of equilibrium in isothermal processes. It is called the Helmholtz free energy and is denoted by the symbol F" [3,p.195]

"It is clear that'

$$A_{max}=-\Delta F$$

Entropy changes, as has been shown, determine the direction and extent of spontaneous processes in isolated systems. The Helmholtz free energy provides a similar criterion for systems at constant volume and temperature." [3,p.196]

If $\Delta F \le 0$ the process is spontaneous under constant V, T.

"A function similar to the Helmholtz free energy is the Gibbs free energy or (Gibbs energy) that provides a criterion for spontaneous processes in systems at constant pressure and temperature. This function is denoted by the symbol G and defined by the expression

$$\boxed{G = H - TS}$$

or which is the same

$$G=U-TS+PV$$

and also

$$G=F+PV$$

For any process $\Delta G=\Delta A+\Delta(PV)$.

It follows, hence, for an isobaric process

$$\Delta G=\Delta F+P\Delta V$$

For an isothermal process

$$\boxed{\begin{array}{l} dG = dH - TdS \\ \Delta G = \Delta H - T\Delta S \end{array}}$$

The maximum useful work A'_{max} in an isothermal process is defined by

$$A'_{max}=-\Delta G$$

According to $A_{max}=-\Delta F$ and $\Delta G=\Delta F+P\Delta V$:

$$A'_{max} = A_{max} - P\Delta V$$

i.e. *__the maximum useful work__* A'_{max} is equal to the maximum work A_{max} minus the work done against external pressure." [3, p. 196]

"In systems at constant temperature and pressure only such spontaneous processes can take place that lead to a decrease in G;

$$\boxed{\Delta G \leq 0}$$

the process goes to equilibrium when the function G reaches a minimum value for the given conditions i.e., the criterion for equilibrium is

$$dG=0$$
$$d^2G>0$$

It follows from the formula:

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

that at low temperature ($T\to0$) ΔG is less than zero ($\Delta G<0$) if ΔH is less than zero ($\Delta H<0$), and ΔG is less than zero if ΔS is bigger than zero ($\Delta S>0$) at the high temperature ($T\to\infty$).

Because of it exothermic processes are spontaneous one at low temperature, and spontaneity of some processes can depend on temperature.

__Example 6.__

Is reaction

$$2HCl_{(g)}+Mg(OH)_{2(c)}=MgCl_{2(c)}+H_2O_{(g)}$$

spontaneous or not (a) at constant pressure and temperature (P=1 atm, T=298K), and (b) at constant volume and temperature (T=298K, initial pressure P_i=1 atm)?

Solution.

a)

$$\Delta G_{ch.r.} = \sum(n\Delta G_f^0)_{prod} - \sum(n\Delta G_f^0)_{react} = \Delta G^0_{f(H_2O(g))} +$$

$$+\Delta G^0_{f(MgCl_2(c))} - 2\Delta G^0_{f(HCl(g))} - \Delta G^0_{f(Mg(OH)_2(c))} = -54.6 + (-141.5) -$$

$$-2\cdot(-22.8) - (-199.3) = +48.8\,\text{kcal} > 0$$

hence, the reaction is not spontaneous;

b)

$$\Delta F_{ch.r} = \Delta G_{ch.r} - \Delta nRT = 48.8\cdot4180 - (1-2)\cdot8.31\cdot298 =$$
$$=204000 + 2470 > 0$$

hence, the reaction is not spontaneous in these conditions.

Example 7. Can be the previous reaction spontaneous at other temperature?

Solution.

$$\Delta G_{ch.r} = \Delta H_{ch.r} - T\Delta S_{ch.r}$$

Let us assume that $\Delta H_{ch.r}$ and $\Delta S_{ch.r}$ do not depend on temperature

$$\Delta H^0_{ch.r.} = \Delta H^0_{f(H_2O(g))} + \Delta H^0_{f(MgCl(c))} - 2\Delta H^0_{f(HCl(g))} - \Delta H^0_{f(Mg(OH)_2(g))} =$$

$$= -57.796 + (-153.35) - 2\cdot(-22.062) - (-221.0) = 53.978\,\text{kcal}$$

$$\Delta S_{ch.r} = \Delta S^0_{f(H_2O(g))} + \Delta S^0_{f(MgCl_2(c))} - 2\Delta S^0_{f(HCl(g))} - \Delta S^0_{f(Mg(OH)_2(g))} =$$

$$= 45.106 + 21.422 - 2\cdot44.64 - 15.1 = -37.8\,\text{cal}$$

$$\Delta G_{ch.r.} = 53978 - T\cdot(-37.8)$$

It is clear that $\Delta G_{ch.r}$ is always bigger than zero because temperature is always bigger than zero T>0.

Hence reaction

$$2HCl_{(g)} + Mg(OH)_{2(c)} = MgCl_{2(c)} + H_2O_{(g)}$$

is not spontaneous at any temperature. But it is known from experience. that this reaction is spontaneous in water solution. Because of it one must pay attention to the state of substance (gas, liquid or solid (crystal)) during the calculations.

Dependencies of $\Delta S_{ch.r}$ and $\Delta G_{ch.r}$ on Temperature

During heating of substance entropy increases

$$\Delta S^0 = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

hence, if one knows $\Delta S^0_{ch.r}$ at T=298 K, it is possible to calculate $\Delta S_{ch.r}$ at other temperature.

$$\boxed{\Delta S^0{}_{T_2} = \Delta S^0{}_{298} + \int_{298}^{T} \frac{\Delta C_p}{T} dT}$$

You know that

$$\Delta G = \Delta H - T\Delta S \qquad \text{and}$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT \qquad \text{(Kirchhof's law)}$$

Hence

$$\Delta G^0_T = \Delta H^0_{298} - T\Delta S^0_{298} + \int_{298}^{T} \Delta C_p dT - T\int_{298}^{T} \frac{\Delta C_p}{T} dT$$

[3, p. 258]

There are dependencies of isobaric heat capacities (Cp) of many substances on temperature and data $(H^0_T - H^0_{298}),(S^0_T - S^0_{298})$ in handbooks.

Hence, one can calculate.

$$\Delta H^0_T = \Delta H^0_{298} + \Delta(H^0_T - H^0_{298}) \qquad \text{and}$$

$$\Delta S^0_T = \Delta S^0_{298} + \Delta(S^0_T - S^0_{298})$$

Example 8. Determine $\Delta G^0{}_{1273}$ of the reaction.

$$CO+H_2O=CO_2+H_2$$

(See example 4.)

Solution.

$$\Delta G^0_{1273} = -7.67 - 1273 \cdot \Delta S^0_{298} - 1273 \cdot \int_{298}^{1273} (-\frac{0.219}{T} + 5.69 \cdot 10^{-3} -$$

$$- 2.911 \cdot 10^{-6} T)dT = -7.67 - 1273 \cdot (S^0_{298_{H_2}} + S^0_{298_{CO_2}} - S^0_{298_{H_2O}} - S^0_{298_{CO}}) -$$

$$-1273 \cdot (-0.219 \ln T + 5.69 \cdot 10^{-3} T - \frac{2.911 \cdot 10^{-6}}{2} T^2)\Big|_{298}^{1273} = \ldots$$

and so on, and so forth.

Dependencies of G=f(P,T) and F=f(V,T)

"Regarding F as a function of T and V, and G as a function of T and P, we can express their total differentials in the form:

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \qquad (1)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \qquad (2)$$ " [3,p.203]

Remember that

$$F=U-TS$$
$$G=H-TS=U-TS+PV$$

and

$$dU \le TdS - \delta A = TdS - PdV$$

if work is done only against external pressure (or by it), then $\delta A=Pd$ [3,p.192]

Hence,

$$dF=dU-TdS-SdT\leq -SdT-PdV \tag{3}$$
$$dG=dU-TdS-SdT+PdV-VdP\leq -SdT+VdP \tag{4}$$

"Comparing the expression (3) and (4) with Eqs. (1) and (2), we conclude that

$$\left(\frac{\partial F}{\partial T}\right)_V=-S \qquad \left(\frac{\partial F}{\partial V}\right)_T=-P$$

$$\left(\frac{\partial G}{\partial T}\right)_P=-S \qquad \left(\frac{\partial G}{\partial P}\right)_T=V$$

Inserting in Eqs. :

$$G=H-TS \text{ and } F=V-TS$$

in place of entropy the derivatives of the thermodynamic functions, we obtain the relations:

$$\begin{aligned} F&=U+T\left(\frac{\partial F}{\partial T}\right)_V \\ G&=H+T\left(\frac{\partial G}{\partial T}\right)_P \end{aligned} \tag{5}$$

or

$$\begin{aligned} \Delta F&=\Delta U+T\left(\frac{\partial(\Delta F)}{\partial T}\right)_V \\ \Delta G&=\Delta H+T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P \end{aligned} \tag{6}$$

or

$$\begin{aligned} A_{MAX}&=-\Delta U+T\left(\frac{\partial A_{MAX}}{\partial T}\right)_V \\ A'_{MAX}&=-\Delta H+T\left(\frac{\partial A'_{MAX}}{\partial T}\right)_P \end{aligned} \tag{7}$$

Equations (5-7) are called the *Gibbs-Helmholtz equations*". [3, p. 203-204]

Phase Equilibria

"*Basic Concepts.*

A system is called *homogeneous* if it does not contain any boundary surfaces separating parts of the system with different properties. If the system does contain such boundary surfaces it is called *heterogeneous*. *A phase* is a part of a system that is homogeneous throughout (i.e., its physical and chemical properties independent of the mass are uniform) and is separated from other parts of the system by a boundary surface (interface). Phases consisting of single chemical substance are called *simple* (or pure) phases; those containing two or more substances are called *mixed* phases."[3,p.157]

"We call a *component or constituent* of a system any chemically homogeneous substance that can be separated from it and is capable of existence in the isolated state some length of time.

The equilibrium in a heterogeneous system in which the components do not interact chemically, but only pass over from one phase to another phase or phases (phase transitions) are called *phase equilibrium*." [3,p.215]

"The least number of components (constituents) of a system sufficient to form all its phases is called the *number of independent components K_{ind}*. This number differs from *the total number of components* when the components interact chemically and equilibrium is being established. For example, the system in which the reaction

$$H_2+I_2 \rightleftarrows 2HI$$

occurs consists of three components: H_2, I_2 and HI, but only two of them (any two) are independent. In the general case the number of independent components equals the total number of components minus the number of reactions expressing the chemical equilibria:

$$K_{ind}=K_{tot}-X$$ "

[3,p.217-218]

"The quantity *C*, called *the number of degrees of freedom* or *variance*, is the number of parameters (temperature, pressure, concentration) that can be arbitrary varied (within certain limits) without changing the number or kind of phases in system." [3,p.219]

Gibbs Phase Rule (1876):

The number of degrees of freedom of a system plus the number of phases equals the number of independent components plus the number of external factors that affect the equilibrium of the system.

$$\boxed{C + F = K_{ind} + n}$$

Phase Diagrams

"The diagram showing how the state of the system (and its phase equilibrium) depends on external conditions or on the composition of the system is called the diagram of state or phase diagram (Fig. 2).

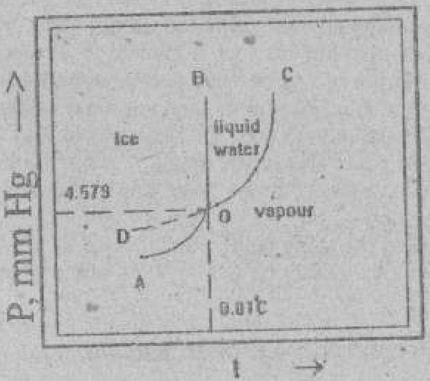


Fig. 2. Diagram of state of water in the moderate pressure region." [3.p.220]

$$C = K_{ind} - F + n$$

$$K_{ind} = 1 \text{ (water)}$$

$$n = 2 \text{ (temperature and pressure)}$$

$$C = 1 - F + 2 = 3 - F$$

"One-phase states of water have two degrees of freedom (bivariant system).

$$F=1 \text{ (ice or liquid, or vapor)}$$

$$C=3-1=2$$

Here both the temperature and pressure can be varied independently within fixed limits without causing any change in the number or kind of phases of the system." [3, p. 221]

The two-phase states of water are represented by curves dividing the diagram into areas each of which corresponds to one of the states of aggregation of water: vapor, liquid, and solid (ice).

$$C=3-F=3-2=1$$

The number of degrees of freedom in the two-phase case diminishes to one (monovariant system); i.e., only the temperature or the pressure can be varied arbitrarily without causing a change in the number or kind of phases, and the variation of one of these parameters entails a corresponding variation of the other. Equilibrium in the two-phase system water-ice is described by curve OB that shows how the freezing point of water depends on pressure. The dotted curve OD in the diagram is a continuation of OC and gives the saturated vapor pressure over supercooled water (metastable equilibrium)" [3, p. 221]

"Point O, called the *triple point*, corresponds to a state of equilibrium between all three phases. In this case the system has zero degrees of freedom (i.e. it is invariant).

$$C=3-F=3-3=0.$$

There is only one combination of temperature and pressure -0.01C and 4.579 mm Hg at which all three phases can exist in equilibrium. The slightest change in either of these parameters causes one or two of the phases to disappear." [3,p.222]

Phase diagrams are widely employed for investigating metal alloys, silicate systems, aqueous salt solutions and various system of organic and other compounds (Fig. 3).

The regions α and β on this diagram correspond to the existence of solid solutions, of tin in lead (α) and of lead in tin (β), respectively.

Slight pressure changes do not practically affect the state of the system; hence, applying the phase rule to determine the *conventional variance of the system*, one can make use of the relation

$$C_{con}=K-F+1$$

$$n=+1 \text{ (only temperature)}$$

$$K=2 \text{ (Sn and Pb)}$$

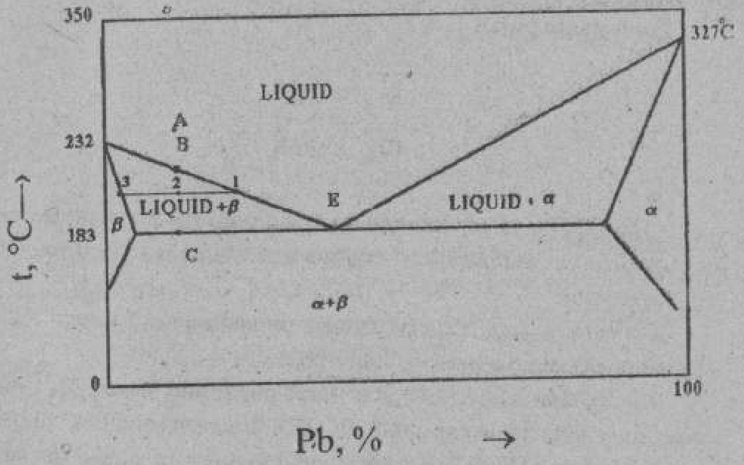


Fig. 3. Phase diagram for the system lead-tin. [3, p. 305]

Thus, a liquid melt (single phase) is a conventionally bivariant system ($C_{con}=2$). The composition of the melt and its temperature can be changed independently (within the corresponding limits). Let an alloy with 17% of lead be initially at a higher temperature than the melting point of tin, for instance in the state corresponding to point A. Its cooling is shown in our diagram by vertical line AB; no change in state occurs at 232 °C and only when the temperature is lowered to 208 °C will tin crystals containing a small (about 2%) amount of dissolved lead be deposited." [3, p. 306]

("*Law of Raoult*: The lowering of the freezing point is proportional to the quantity of substance dissolved in a given mass of the solvent." [1, p. 222])

Chemical Kinetics

"Introduction. *Chemical kinetics* is a branch of chemistry that deal with reaction rates and their dependence on various factors (reactant concentration, temperature, catalysts, etc.)." [3, p. 413]

"*The rate of a chemical reactions* is quantitatively characterized by the change in concentration of the reactants in a unit of time." [3, p. 414]

$$v = \pm \frac{dC}{dt} = \pm \frac{dn}{dtV}$$

$V \geq 0$ always.

Where n is quantity of substance.

The rate of a heterogeneous reaction is

$$v = \pm \frac{dn}{dtS}$$

Where S- is area of boundary surfaces.

Dependence of Reaction Rate on Concentration of Reactants

The law of mass action (C. Guldberg and P. Waage (1867)) "For the kinetically simplest homogeneous reactions the rate of a given reaction at constant temperature is proportional to the product of the reactant concentrations, each concentration being raised to a power that in the simplest case is equal to the coefficient before the formula of the corresponding substance in the equation of the reaction." [3, p. 417]

Mathematically, as applied, for instance to the reaction

$$2NO+H_2=N_2O+H_2O$$

it is expressed in the form of

$$v = k \cdot C_{NO}^2 \cdot C_{H_2}$$

"The proportional factor k is a constant for a given temperature and a given reaction and is called the <u>*rate constant of the reaction*</u>. It is numerically equal to the rate of the reaction when the concentrations of the initial components equal <u>*unity*</u>." [3, p. 418] ("For gas reaction the law is strict only in limits of validity of the ideal gas laws. It is also applicable to reactions in dilute solutions." [3, p. 418]

"*Kinetic Classification of Chemical Reactions*

With respect to their kinetics, chemical reactions are classified either according to their <u>*molecularity*</u> or according to their <u>*order*</u>." [3, p. 418]

"<u>*The molecularity of a reaction*</u> is determined by the number of molecules that simultaneously take part in the reaction. Accordingly reactions are classified as unimolecular, bimolecular and trimolecular."[3, p. 419] For example:

1) $I_2=2I$ This is a unimolecular reaction ○ = ○○

2) $H_2+I_2=2HI$ This is a bimolecular reaction ○○ = ○○

3) $\underset{\text{3MOLECULS}}{\underline{2NO+H_2}} = N_2O+H_2O$ This is a trimolecular reaction ○○○ ⟶ ○○

"<u>*The order of a reaction*</u> equals the sum of the exponents of the concentrations in the equation for the dependence of the rate on the concentrations of the reactants. Reactions are classified as <u>*first order*</u>, <u>*second order*</u>, <u>*third order*</u>. (reactions of a higher order are not encountered.) In addition there are so-called *zero order* reactions and reactions of a *fractional order*." [3, p. 420]

"First Order Reactions

$$v = -\frac{dC}{d\tau} = kC$$

where C-concentration of a reactant.

On separating the variables in this equation

$$-\frac{dC}{C} = kd\tau$$

and integrating, we obtain

$$\log_e C = -k\tau + B$$

Designating the initial concentration (at $\tau=0$) by C_0 (Fig. 4), we determine the constant of integration B

$$B = \log_e C_0, \text{ whence } \log_e \frac{C}{C_0} = -k\tau$$

$$\text{or } C = C_0 \cdot \exp(-k\tau)$$

[3,p.421]

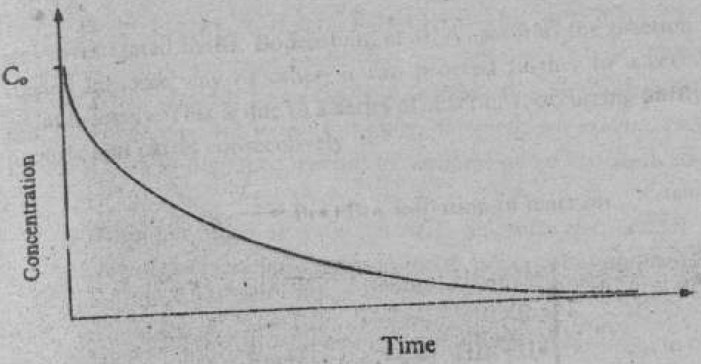


Fig. 4

Let us determine the time when $C=C_0/2$.

$$\log_e \frac{c}{c_0} = -k\tau$$

$$\log_e 2 = -k\tau$$

$$\tau = \frac{\log_e 2}{k}$$

"[3,p.421]

"This relation shows that the rate constant of a first order reaction is inversely proportional to the *half life*.[3, p. 422]

"*The half life ($\tau_{1/2}$)* is equal to the time required for half of the initial substance to react."[3, p. 422]

One also can obtain similar equations for the reactions of higher order but it is more difficult.

The order of reaction is not equal to the molecularity if:

a) "One of reactants present in such excess that its consumption will have practically no effect on its concentration. Thus in the hydrolysis of an ester in a dilute aqueous solution, taking place to the equation

$$CH_3COOC_2H_5+H_2O=CH_3COOH+C_2H_5OH$$

the concentration of water changes negligibly and the rate of the reaction will depend only on the change in concentration of the *ester*. As a result the rate will be described by an equation of the first order although it is actually bimolecular

b) Reaction is complex. Usually in these cases the equation of a chemical reaction reflects only the total effect of these interactions

$$2N_2O_5 \rightarrow 4NO_2+O_2 \text{ molecularity}=2$$

but $v=k\cdot[N_2O_5]$ and order=1 because this reaction has two stages,

1) $N_2O_5 \rightarrow N_2O_3+O_2$

2) $N_2O_3 + N_2O_5 \rightarrow 4NO_2$

The first stage is slower and determine the rate of sum reaction

c) Heterogeneous reactions. For example:

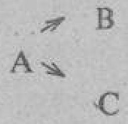
$$2Zn + O_2 = 2ZnO \quad \text{molecularity}=3$$

but $v = kCo_2$ and order=1

Zn is solid. It has no concentration. O_2 is gas.

"Complex Reactions

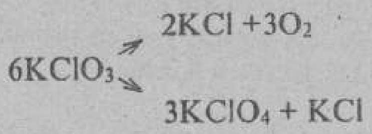
The kinetics of *complex reactions consisting of one or more simple reactions related to one another in one way or another* depends on the nature of their interrelation and on the ratio of their reaction rates. Typical forms of such interrelation are *simultaneous, consecutive, conjugate and reversible* *reactions*. The theory of these reactions is based on the principle that when several reactions occur simultaneously, each takes place independently and each obeys the kinetic equation of the simple reaction. *Simultaneous* reactions are those of the type



$$A \nearrow B, \quad A \searrow C$$

In such reactions the initial substance or substances can react simultaneously in different directions.

An example:



$$6KClO_3 \nearrow 2KCl + 3O_2, \quad 6KClO_3 \searrow 3KClO_4 + KCl$$

Consecutive reactions are those of the type

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C\,.$$

Where B is intermediate product in the formation of C, and K_1 and K_2 are the rate constants of the two stages of the reactions."[3, p. 424]

"If one of the stages proceeds at a considerably lower rate than all others, the overall rate of the reaction will be determined by the rate of this stage."[3, p. 425]

"*Sympathetic (or conjugate)* reactions are defined as reactions of the type

$$A + B \rightarrow M \qquad (b)$$

$$A + C \rightarrow N \qquad (c)$$

of which one, for example (b), takes place only together with the other, i.e., is induced by the other."[3, p. 426]

"*Reversible reactions*.

The rate of reversible reaction equals the difference between the rates of the forward and reverse reactions."[3, p. 426]

$$H_2 + J_2 \overset{v_1}{\underset{v_2}{\rightleftarrows}} 2HJ$$

$$v = v_1 - v_2$$
$$v_1 = k_1 \cdot C_{H_2} \cdot C_{J_2}$$
$$v_2 = k_2 \cdot C_{HJ}^2$$

"If only reactants (H_2 and J_2) were present in the initial state of the system, the rate of the forward reaction will diminish with a decrease in the concentrations of these substance (Fig. 5).

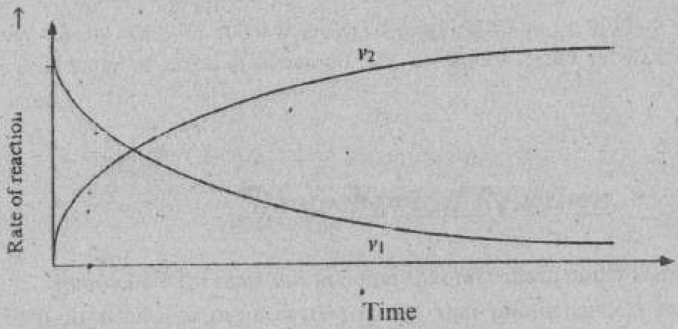


Fig. 5

Curve V_2 depicting the rate of the reverse reaction begins at the origins of the coordinates (since according to the conditions initially $C_{HI}=0$) and grows as the forward reaction takes place with the resultant augmentation of the concentrations."[3, p. 427]

"Hence a state of equilibrium will be reached when the absolute values of the forward and reserve rates will be equal."[3, p. 427]

$$v = 0$$

$$v_1 = v_2$$

$$k_1 \cdot C_{H_2} \cdot C_{J_2} = k_2 \cdot C^2_{HJ}$$

$$\frac{k_1}{k_2} = \frac{C^2_{HI}}{C_{H_2} C_{I_2}} = K_c$$

Where K_c is the concentration equilibrium constant of the reaction. When previous equation is applied to reactions of non-ideal gases or not very dilute solutions, one must substitute the activities for the concentrations, and K_a for K_c. K_p is pressure equilibrium constant

$$K_p = \frac{p^2_{HI}}{p_{H_2} p_{I^2}}$$

Where P are partial pressures.

"The ***partial pressure*** of a gas in a mixture is equal to the pressure which that gas would exert if it were present alone, at the same temperature in the volume occupied by the mixture."[3, p. 81]

$$K_p = K_c \cdot (R \cdot T)^{\Delta n}$$

because [3. p. 82]

$$p_i = \frac{n_i RT}{V} = C_i RT$$

where [3, p. 232] n_i is the number of moles of the component i, and Δn is a difference between the stoichiometric coefficients of gaseous products and reactants

$$\Delta n = c + d - a - b$$

for reaction:

$$aA + bB = cC + dD + eE$$

if all substances (A, B, C, D) are gases and E is a liquid or solid substance.

"One can calculate K_p from equation:

$$\Delta G^o_{ch.r.} = -RT\log_e K_p$$

When the reaction takes place at constant temperature and constant partial pressure of all the substances, and the ideal gas laws are applicable"[3, p. 235]

"Effect of a Change in External Conditions on Equilibrium

In 1885 *Le Chatelier* formulated a general *principle* expressing the influence of changes in various factors on equilibrium. This principle, known as *Le Chatelier's principle*, can be stated as follows:

> any change in the parameters that determine the state of a system in equilibrium causes a shift in the position of equilibrium in a direction that tends to counteract the change produced"[3, p. 209-210]

"For example: 1) a rise in temperature always intensifies the endothermic process"[3, p. 211]; 2)"a rise in pressure favors the formation of products that under the given conditions occupy a smaller volume."[3, p. 212]

Effect of Temperature on Reaction Rate

"For ordinary temperatures, the approximate rule has long been used, according to which the rate of reaction increases about two to fourfold with each 10^0 rise in temperature (Van't Hoff's law)"[3, p. 433]

$$\frac{v_2}{v_1} = \frac{K_2}{K_1} = \gamma^{\frac{t_2 - t_1}{10}}$$

γ -is called the temperature coefficient of the reaction rate $\gamma \in [2;4]$

Arrhenius Equation (1889)

$$K = A \cdot e^{-\frac{Ea}{RT}}$$

"The *energy of activation* (Ea) is the excess energy that a molecule must have at the time of collision to be able to enter into the given chemical reaction."[3, p. 430]

"*A* is constant characteristic of the given reaction"[3, p. 428]

"The above is illustrated by Fig. 6.

In the figure the energy of the molecular system is plotted on the axis of ordinates and the course of the reaction on the axis of abscissas. If the forward reaction (transition from state I to state II) is exotermal, the overall energy of the products is less than that of the reactants i.e., as a result of the reaction the system passes to a lower energy level (from level I to level II). The difference between the levels I and II is equal to the reaction heat effect (ΔU). The level N determines the least amount of energy that the molecules must have for their collision to result in chemical reaction. The difference between the level N and the level I is the activation energy of the forward reaction E_1, and the difference between the levels N and II is the activation energy of the reverse reaction E_2. Hence in its path from the initial to the final state, a system must pass through a sort of *energy barrier*."[3, p. 429-430]

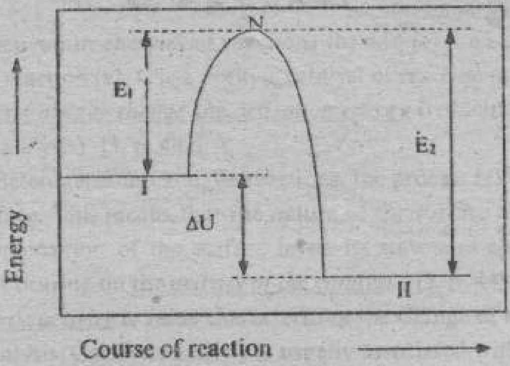


Fig. 6. Energy change in a reaction system.

Chain Reactions

"A feature of chain reaction is that the activation of a particle in some way or other leads to reaction not only of the given particle, but also, consecutively, of a number of other such particles"[3, p. 434]

"In chain reactions the initial molecules react with active particles (free atoms and radicals with unsaturated valences, ions, excited molecules, etc.) to give through a series of intermediate steps, the final products and the same kind of active particles. The latter, interacting with new molecules of the initial substances, ensure the further course of the reaction.

Initiation of such a chain, i.e., the formation of active particles may take place in various ways."[3, p. 434]

Example. "The kinetics of the reaction between gaseous bromine and hydrogen expressed by the ordinary equation

$$H_2+Br_2=2HBr$$

was investigated by M. Bodenstein, et al. As soon as the reaction has been started in some way or other, it can proceed further to a certain extent spontaneously. This is due to a series of reactions, occurring partly simultaneously and partly consecutively

$$Br_2 \longrightarrow Br\bullet + Br\bullet \quad \text{initiation of reaction}$$

$$\left.\begin{array}{lcl} Br\bullet + H_2 & \longrightarrow & HBr + H\bullet \\ H\bullet + Br_2 & \longrightarrow & HBr + Br\bullet \\ Br\bullet + H_2 & \longrightarrow & HBr + H\bullet \\ H\bullet + HBr & \longrightarrow & H_2 + Br\bullet \end{array}\right| \qquad \text{chain of reaction}$$

$$Br\bullet + Br\bullet \longrightarrow Br_2 \quad \text{termination of chain}$$

[3, p. 435]

"One of the most important characteristics of chain reactions, considerably affecting their rate is the *chain length*, i.e., the number of molecules of a given substance entering into reaction as the result of a single act of chain initiation.

Besides being used up in the main reaction, the active particles may also be consumed in side reactions among which an important pert is often played by *collision* of the particles *with the walls of the container or with molecules of inert substances* contained in it. In such collisions most of the active particles lose their excess energy and become inactive; so called *chain termination* takes place. Hence in chain reactions such factors as the *shape of the vessel* may become very important.

Chain termination may also be promoted by the presence in the vessel of inert solid material, even dust particles. Chain reactions are highly sensitive to changes in concentrations of both reactants and *foreign gases*. In particular, this has to be taken into account when investigating the combustion of fuel in the cylinders of an engine."[3, p. 436]

There are chain reactions in which one active molecule may lead to the formation of two or more new active molecules. In such cases the rate of the reaction may quickly grow, the process usually ending in an explosion. Such reactions are called *chain branching reactions* (Fig. 7).

Their quantitative theory is quite involved.

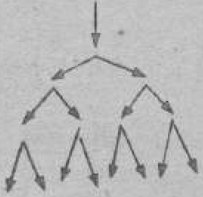


Fig. 7. Schematic diagram of branching chains.

Kinetics of chain reactions

Kinetics of chain reactions is based on general chemical kinetics and on equations of chains initiation and termination. Velocity of chains initiation is of great importance in cases of little chains length, and its importance diminishes in cases of reactions which have long chains.

Example. (Elementary ABC of theory) In case of line chains

$$V = \dot{n}_0 \cdot \nu$$

Where V is reaction rate; n_0 is rate of chains initiation and ν is average chains length. Let $\beta = \frac{1}{\nu}$ is a probability of the terminations of chains after the present link.

In this case

$$V = \frac{n_o}{\beta}$$

Let $\beta=\beta_1+\beta_2$

Where β_1 is a probability of the chains terminations without foreign substance admixture, and β_2 is a probability of the chains terminations in interactions of the chains with molecules of foreign substance.

Let $\beta_2 = KC$ where C is concentration of foreign substance and K is a constant. In this case

$$V = \frac{n_0}{\beta_1 + KC}$$

In case of the branching chains

$$V = \frac{n_0}{\beta - \delta}$$

where δ is a probability of branching on the given step.

If $\beta > \delta$ the reaction is stationary, i.e. it has definite rate. From the last equation one can obtain.

$$V = \mathrm{const}(1 - e^{-\varphi t})$$

where

$$\varphi = \frac{\beta - \delta}{\Delta\tau}$$

where $\Delta\tau$ is time, during which the reaction is on one link.

φ dependents on pressure and temperature.

$$\varphi = CP^n e^{-\gamma/T}$$

where C, n and γ are constants.

If the probability of branching is equal to the probability of the termination of the chain.

$$\beta \approx \delta$$

and

$$V = \frac{n_0}{\beta - \delta} = \frac{n_0}{0} = \infty$$

It is corresponds to the lowest limit of self-inflaming. The rate of the reaction increases quickly.

$$V = \text{const} \cdot e^{\varphi t}$$

where t is time of the reaction.

Above relations do not take into account changing of concentrations during the reaction. That is why this equations can be applied only to the initial stage of reaction (when 20-30% or less of initial substances have reacted.)

"Photochemical Reactions

Photochemical reactions are ones that take place under the influence of light. It would be more correct to say that photochemical reactions are those for which the energy necessary for their initiation or prolongation is supplied in the form of electromagnetic vibrations - visible light, ultraviolet, or more seldom infrared rays. (photosynthesis, photographic processes, luminescence phenomena, decolorization of dyes.) [3, p. 448-449]

Photochemical reactions may be classified into two groups:

1. Reactions that can occur thermodynamically without the agency of light. (for instance the reaction $H_2 + Cl_2 = 2HCl$). In such cases light plays the part only of an initiator of the reaction, promoting the overcoming (or lowering) of the high activation energy of the reaction. Such reactions are often called *photocatalytic*.

2. Reaction that thermodynamically cannot occur under the given conditions and "require work to be supplied from an outside source" [3,p.449]

In every photochemical reaction one must distinguish (differentiate) a primary stage which is directly caused by light and other stages that can occur without light.

"The relation between the amount of absorbed energy and the amount of substance undergoing primary photochemical transformation is expressed in the *law of photochemical equivalency* deduced (1912) by A. Einstein. According to this law, *each molecule undergoing reaction under the influence of light absorbs one quantum of the radiation causing the reaction*" [3, p. 449]

$$N = \frac{E}{h \cdot \nu}$$

Where

N is quantity of molecules that react

E is amount of light energy absorbed by substance.

ν= frequency, s^{-1}

h= Planck's constant.

$h \cdot \nu$ = energy of one quantum.

N differs essentially from n. n is a total quantity of molecules that react in all stages of photochemical reaction.

$$\varphi = \frac{n}{N}$$

φ can be less than 1 or more than 1 (for example φ can be 10^5)

If $\varphi > 1$, the process is a chain one.

Kinetics of Photochemical Reactions

The rate of a consecutive reaction is equal to the rate of the slowest stage of the reaction.

The rate of a primary photochemical stage is proportional to the brightness of light (I_0). If all light is absorbed,

$$v = \frac{dn}{d\tau} = \frac{\varphi \cdot I_0}{h \cdot \nu}$$

In general case

$$v = \frac{\varphi \cdot I_0}{h \cdot \nu}\left(1 - e^{-\alpha CD}\right)$$

Where

α =coefficient of absorption of light by given substance.

C is a concentration of the substance.

D is a length of the path of light in the solution.

If the primary photochemical stage is not the slowest one, brightness does not influence on the reaction rate so much.

The temperature (Van't Hoff's) coefficients of photochemical reactions equal 1.2-1.5.

Catalysis

"Catalysis is the phenomenon in which certain substances, called *catalysts.*, change the rate of or initiate a reaction while they themselves, although participating in the reaction, in the end remain chemically unchanged.

Catalysis in which the catalyst accelerates the reaction is called *positive*, and in which the catalysts (inhibitor or catalytic poison) retards the reaction *negative*. Reactions that are catalitically accelerated by their own products are called *autocatalytic*." [3, p. 441]

"*Homogeneous catalysis* include reactions in which the catalyst is in a uniform gaseous or liquid mixture with the reactants.

In *heterogeneous catalysis* the catalyst is present as a separate phase, and the reaction takes place on its surface." [3, p. 443]

"Catalysts do not affect the equilibrium of a given reaction, but only facilitate or hinder its establishment." [3,p.442]

"Catalysts often display high *specificity*. This means that they will often preferentially accelerate only one of a number of possible reactions of the reactants.

Example

$$C_2H_5OH \xrightarrow{\text{alumina}} C_2H_4 + H_2O$$

$$2C_2H_5OH \xrightarrow{H_3PO_4} (C_2H_5)_2O + H_2O \quad [3,p.444\text{-}445]$$

$$C_2H_5OH \xrightarrow{\text{Cu,Ni}} CH_3CHO + H_2$$

Catalysis Mechanism

"Catalysis deals with effects that may have widely different mechanisms. Thus, in chain reactions a positive catalyst may facilitate chain initiation." [3, p. 441] For example

$$H_2 + Cl_2 \xrightarrow{Na_{\text{vapour}}} 2HCl \qquad\qquad Na + Cl_2 = NaCl + \dot{Cl}$$

"Negative catalysts in chain reactions may act as chain terminating agents. This is the mode of action of the decomposition products of tetraethyl lead or iron carbonyl that are added to petrol to avoid premature *detonation* in engine cylinders.

In other reactions the catalyst may form intermediate products with the reactants, facilitating the formation of the end products by lowering the activation energies. Let us assume, for example, that in reaction

$$A + B = AB \tag{a}$$

the catalyst C may react with A to form intermediate product AC :

$$A + C = AC \tag{b}$$

The compound AC reacts with B, forming AB and liberating the catalyst C :

$$AC + B = AB + C \tag{c}$$

If the activation energies of reactions (b) and (c) are significantly less than that of reaction (a), C is a positive catalyst of reaction (a)" [3 p.442]

"*Catalysts always change the activation energy* (reducing it in the case of positive catalysis)" [3, p. 442]

"In all heterogeneous catalytic reactions, the process takes place on the catalyst surface. This means that the nature of the surface and its size, the chemical composition of the surface layer, its state and structure should have a direct bearing on the *activity of the catalyst*." [3, p. 444]

"*Catalytic activity* is value characterizing the change of reaction rate in result of catalysis. Catalytic activity is usually associated with *adsorption* of the reactants on the most active sites (for the given process) of the catalyst". [3, p. 444]

"The difference in concentration of a component in the surface layer and in the bulk of the solution (mixture of gases) is called adsorption". [3,p.325]

"We differentiate between *positive adsorption*, when the solute concentration in the surface layer is greater than in the bulk, and *negative adsorption* when it is less". [3, p. 325]

"*Physical adsorption* is due to the three components of intermolecular attraction - dispersive, orientational, and inductive interactions". [3, p. 334]

Chemical adsorption (chemisorption) is due to chemical interactions between the adsorbent and adsorbate. "The amount of gas or dissolved substance adsorbed by a given amount of adsorbent depends on the nature of the gas or solution and on the conditions under which the process takes place, above all, on the pressure of the gas or concentration of the solute and on the temperature. All other conditions being equal, the effect of pressure or concentration on the amount of gas adsorbed can be depicted by curves, which are called adsorption isotherms." [3, p. 329]

Various analytical expressions exist for the adsorption isotherm. A widely used one, in particular, is the empirical *Freundlich equation*

$$a = k \cdot p^{1/n}$$

where a - amount of adsorbed gas (adsorbate),

p - equilibrium pressure of the gas,

k and n - empirical parameters, constant for given adsorbent and gas at constant temperature. This equation is in good agreement with experimental data over a wide range of intermediate pressures." [3, p. 330]

"Another equation of the adsorption isotherm (*Langmuir equation*) can be deduced on the basis of the molecular-kinetic theory :

$$a = k \cdot \frac{b \cdot p}{1 + b \cdot p}$$

where k and b are constants for the given isotherm.

This equation gives a good description of the isotherm in the low and high pressure regions." [3, p. 331]

Diffusion

"Diffusion in solutions, gases or solids is a natural process due to heat motion of particles of substances that leads to the distribution of the components throughout the solution, gas or solid". [3, p. 458]

The First Fick's law (1855)

"The rate of diffusion is determined by the following relation:

$$dm = D \cdot A \cdot \frac{dc}{dx} dt$$

where dm is the amount of matter passing through a cross section A in a time interval dt when the concentration changes by dc through a distance dx". [3, p. 459]

The dependence of concentration in given point on time is determined by *the second Fick's law*:

$$\frac{dc}{dt} = D \cdot \frac{d^2c}{dx^2}$$

"The proportionality constant D is called the *diffusion coefficient*. It is numerically equal to the quantity of matter that diffuses in unit time (1s) through a cross section of 1 sq. cm. when the concentration decreases by one unit per cm of path."[3, p. 459]

Diffusion coefficient depends on the nature of substances, on temperature and less on concentration and pressure. In case of gas diffusion:

$$D = 0.043 \cdot \frac{T^{2/3}}{p\left(V_{mA}^{1/3} \cdot V_{mB}^{1/3}\right)} \cdot \sqrt{\frac{1}{Ma} + \frac{1}{Mb}}$$

where V_{mA} and V_{mB} are molar volumes of components, M_a and M_b are molecular masses of the components A and B.

The Stokes-Einstein's equation is applicable to diffusion in liquids:

$$D = \frac{R \cdot T}{N_A} \cdot \frac{1}{6\pi\eta r}$$

where π=ratio of the circumference of a circle to its diameter (3.14..),

η=coefficient of viscosity of the medium r=radius of the particles.

This relation shows that the rate of diffusion increases in direct proportion to the temperature, and in inverse proportion to the viscosity of the medium and the size of the particles."[3, p. 459]

The diffusion coefficient in solids is determined by the following relation:

$$D_T = D_0 \cdot \exp\left(-\frac{\Delta E_m}{R \cdot T}\right)$$

Where ΔE_m is energy of activation of diffusion, i.e. energy which is necessary to move a particle of admixture from the equilibrium position to the intermediate one (Fig. 8)

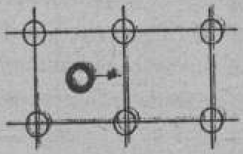


Fig. 8

"Kinetics of Heterogeneous Processes

A heterogeneous process always takes place at an interfacial boundary or in its immediate vicinity."[3, p. 437]

"To estimate the effectivity of possible ways of affecting the rate of a heterogeneous reaction, it is very important to know which of its stages is the slowest under the given conditions, and hence determined the rate of the reaction as a whole. In some cases this stage is diffusion of one of the reaction components from the bulk to the interfacial boundary or vice versa. In others it is the chemical interaction at the interface. The difference between the two is expressed most clearly in the temperature dependence of the reaction rate, because diffusion process changes comparatively little with temperature (about 1-3% per degree). While the rate of chemical reactions is much more temperature-sensitive (about 10% or more per degree depending on the activation energy)"[3, p. 439]

"In the majority of the heterogeneous processes, the overall rate depends greatly on stirring. Because the stirring diminishes ***diffusion layer*** (ΔX) and increases the rate of diffusion.

$$\Delta m = D \cdot A \cdot \frac{\Delta c}{\Delta x} \Delta t$$

Other stages of heterogeneous processes (for example, formation of new phases or electrochemical reaction) also can be the slowest ones, and determine the rates of the processes. Due to the fact that heterogeneous process take place at the interfacial boundary, the rate of such a process, all other conditions being constant will depend on the area and state of the surface." [3, p. 439]

Theories of Heterogeneous Catalysis

"The theories of heterogeneous catalysis issued from the concept that the reaction occurs in some way through the formation of intermediate surface compound. A catalyst forms surface compounds mainly with such substances with which it is capable of reacting in bulk (perhaps under other conditions).

Concerning the nature of the active centers, N. Zelinsky was first to regard them as complex formations consisting of several atoms, so that the deformation of bonds that takes place in a reacting molecule is caused not by a single, but by several atoms on the catalyst surface constituting the active center.

In 1925 H. Taylor introduced the concept according to which the active centers consist of atoms located on the peaks and corners of crystals of the catalyst and therefore unsaturated from the viewpoint of valence.

The multiplet theory (1929, A. BaLandin).

Multiplets are the names given to associations on the catalyst surface of several atoms or ions regularly arranged in correspondence with the structure of the crystal lattice of the catalyst. Catalytic activity appears when the arrangement of the atoms or ions is in geometric conformity with the arrangements of the atoms in the molecules of the reactants.

When the reactant molecules are adsorbed on the catalyst surface, the bonds in the molecule are weakened owing to the influence of and partial binding by the corresponding atoms of the catalyst." [3, p. 446]

"Among other theories of heterogeneous catalysis are the electron-chemical theory, the reaction chain theory, etc." [3, p. 447]

"Experience shows that incorporation of certain substances which themselves are catalytially inactive may greatly augment the activity of a catalyst. Such additions are called *promoters*". [3, p. 445] "Their action is due largely to their effect on the surface structure of the catalyst." [3, p. 445]

"Some substances, even if present in insignificant quantities, greatly decrease the activity of the catalyst or even completely inhibit its action. Like the catalyst itself, these *catalytic poisons* are specific in their action. Poisoning is probably due to adsorption of the catalytic poison by the surface of the catalyst, as a result the reactant molecules are blocked out." [1, p. 334]

Desorption of the catalytic poisons is possible.

Double Electric Layer and Potential Jump

Let us imagine that a metal plate, for instance iron, is immersed in water. The iron ions, owing to the action of the highly polar water molecules, are pulled off from the metal and begin to pass into the layer of water adjoining the surface of the plate (Fig. 9).

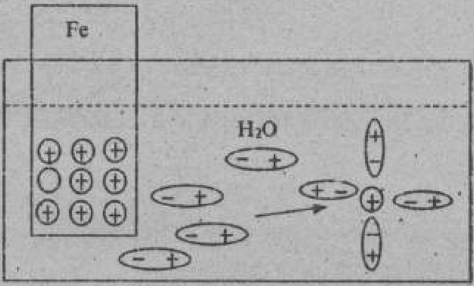


Fig. 9

$$\mathrm{Fe} - 2e \rightleftarrows \mathrm{Fe}^{2+}$$

"The electrostatic attraction which now arises between the ions passing into solution and the oppositely charged metal plate will inhibit this process and equilibrium will set in. A potential difference will thus arise between the metal and the surrounding aqueous medium". [3, p. 373] (Fig. 10)

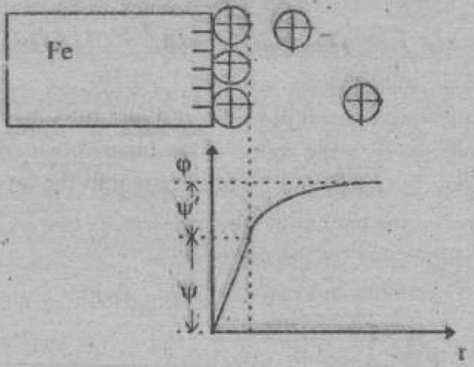


Fig. 10. Double electric layer and the potential difference (jump)

φ-potential
ψ-potential difference (jump) in *dense layer*
ψ'-potential difference in *diffuse layer*

"Similar effects are obtained when the metal is immersed not only in pure water but in a solution. An increase in concentration of the metal ions will promote transition of the ions from the solution to the metal, and equilibrium will set in at another potential of the metal charge. Metals whos ions have little tendency to pass over into solution may even become p tively charged (Fig. 11).

$$Ag^+ + e \rightarrow Ag$$

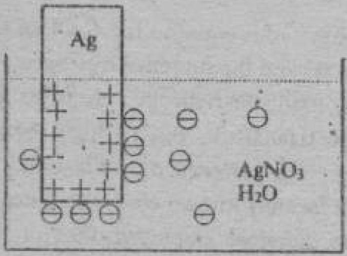


Fig. 11

⊖ -is ions NO_3^-

The position of equilibrium depends primarily on the ratio of the energy required to pull of an ion from the metal and the energy liberated by hydration of the ion." [3, p. 373]

Measurement of Electrode Potential

"There are at the present no methods for determining the absolute value of the potential of a separate electrode, but the conventional quantities characterizing the potentials of different electrodes with respect to the potential of an electrode chosen as reference can be determined. The reference electrode now universally used is the *standard hydrogen electrode*." [3, p. 381]

"This electrode usually consists of a platinized platinum foil immersed in a solution containing hydrogen ions and around which a current of hydrogen gas flows.

The hydrogen gas pressure is one atmosphere and the activity of the hydrogen ion in the solution is unity ($a_{H^+} = 1$). (The activity depends on concentration).

The following reaction occurs in the hydrogen electrode:

$$\frac{1}{2}H_2 \overset{\rightarrow}{\leftarrow} H^+ + e$$ "[3.p.388]

The electrode potential is equal to the e.m.f. of the galvanic cell which consists of this electrode and the standard hydrogen electrode.

"When correctly used, the hydrogen electrode gives very accurate results, reproducible to 0,00001 V. But its high sensitivity to the environmental conditions greatly hampers its utilization. Other, less capricious electrodes with an accurately known electrode potential relative to the hydrogen electrode are therefore employed. One of the most important of such electrodes is the *silver chloride electrode*. [3, p. 389] (silver with deposit of AgCl immersed in saturated solution of KCl).

"A galvanic cell consists of two *half cells* each containing one electrode. By means of these half cells one can set up widely different galvanic cells." [3, p. 381]

"*The e.m.f. of a galvanic cell* is the maximum potential difference between the electrodes:

$$E = \varphi_c - \varphi_a \qquad \text{E is always} \geq 0$$

where φ_c is potential of the cathode, and φ_a is potential of the anode.

Oxidation takes place on the anode, and reduction takes place on the cathode.

The maximum useful work done by the cell equals its e.m.f. (E) multiplied by the quantity of electricity that has passed. We shall refer all quantities to the conversion of the gram-atom of an element (or of one gram-ion of a complex ion). The quantity of electricity associated with this conversion will then be $n_e \cdot F = 96487 \cdot n_e$ coulombs (n_e is the charge of the ion)." [3, p. 379]

$$W'_m = -\Delta G_{ch.r} = n_e \cdot F \cdot E$$

For the reaction

$$b\cdot B+d\cdot D\rightleftarrows q\cdot Q+r\cdot R$$

$$-\Delta G=R\cdot T\left(\log_e K_c-\log_e\frac{c_Q^q\cdot c_R^r}{c_B^b\cdot c_D^d}\right)$$

$$E=-\frac{\Delta G}{n_e\cdot F}=\frac{R\cdot T}{n_e\cdot F}\left(\log_e K_c-\log_e\frac{c_Q^q\cdot c_R^r}{c_B^b\cdot c_D^d}\right)=$$

$$=E^{\circ}-\frac{R\cdot T}{n_e\cdot F}\log_e\frac{c_Q^q\cdot c_R^r}{c_B^b\cdot c_D^d}$$

This is *the Nernst's equation*. E^0 is the e.m.f. of the cell referred to standard conditions, i.e., when

$$C_B=C_D=C_Q=C_R=1$$

The quantity E^0 is called the normal (or standard) e.m.f. of the cell". [3,p.380]

It is clear that the potential of the metal electrode

$$\boxed{\varphi=\varphi^{\circ}+\frac{RT}{nF}\log_e C_{M^{n+}}}$$

"*The standard potential of an electrode* (φ^0) is the potential appearing when the activity (concentration) of the ions determining the electrode reaction is unity". [3, p. 384]

There are standard electrode potentials in handbooks.

"Knowing the standard electrode potentials φ^0, one can readily calculate the electrode potentials of a metal in solution of any concentration by means of last equation". [3, p. 385]

"The standard electrode potentials for selected electrodes are given in *electromotive series*". [3, p. 384]

Polarization

Polarization is a difference between the potential of electrode when an electric current flows and the potential of electrode without electric current.

Polarization diminished the e.m.f. of the galvanic cells and rate of electrolysis. A distinction is made between chemical and concentration polarization.

Concentration polarization is due to the change of concentration during the electrochemical reaction:

$$Zn - 2e \rightarrow Zn^{2+}$$

Concentration of Zn^{2+} increases

$$\Delta\varphi = \varphi^{\circ} + \frac{RT}{nF}\log_e C'_{Zn^{2+}} - \varphi^{\circ} + \frac{RT}{nF}\log_e C_{Zn^{2+}} = \frac{RT}{nF}\log_e \frac{C'_{Zn^{2+}}}{C_{Zn^{2+}}}$$

Chemical polarization is due to the change of the nature of the electrode by the products of the electrochemical reaction:

$$2H^{+} + e \rightarrow H_2\uparrow$$

This reaction can change metal electrode (Cu) into hydrogen one

$$\Delta\varphi^{\circ} = \varphi^{\circ}_{H_2} - \varphi^{\circ}_{Cu} = 0 - 0.337 = -0.337\,V$$

"Both types of polarization can usually be diminished in various ways called *depolarization*.

Concentration polarization can be greatly reduced by vigorous mixing of the solution. Chemical polarization can be weakened by adding substances that will react with those responsible for its appearance." [3, p. 403]

$$H_2 + H_2O_2 = 2H_2O$$

Other types of polarization also exist.

Quantitative Laws of Electrolysis

"According to *Faraday's first law*, for any electrode reaction the amount of substance decomposed is directly proportional to the quantity of electricity which has passed.

$$\boxed{\Delta m = kq = kJ\tau}$$

According to *Faraday's second law*, when equal amounts of electricity pass through solutions of different electrolytes, the amounts of the substance undergoing conversion are proportional to their chemical equivalents.

The evolution of *1 gram-equivalent* of any substance requires the passage of *F=96487 coulombs*. This is a fundamental constant of modern physics and is known as *Faraday's constant*." [3, p. 400]

$$\Delta m = \frac{\text{Э}}{F} J\tau$$

Where Δm is the mass of the substance undergoing conversion,
Э is the equivalent weight of the substance and
$I\cdot\tau$ is the quantity of electricity which has passed.

"*The equivalent weight of an element* is the weight of that element which will combine with eight parts by weight of oxygen (or 1 part of hydrogen) or will displace these amounts from their compounds." [1, p. 33]

"*The equivalent weight of a complex substance* is the weight of the substance which will react without residue with one equivalent weight of hydrogen (1 part by weight) or oxygen (8 parts by weight) or, in general, with one equivalent of any substance." [1, p. 34]

The equivalent weight of a simple substance equals its atomic mass divided by its valence.

"*The equivalent weight (Э) of an acid* equals its molecular weight divided by its basicity, i.e., by the number of atoms of replaceable hydrogen in the acid molecule.

The equivalent weight of a base equals its molecular weight divided by the valence of the metal atom in it.

As to salts, their equivalent weights are found by dividing the molecular weight of the salt by the number of atoms of the metal in its molecule and by the valence of the metal." [1, p. 205]

"Chemical Reactions in Electrolysis

Chemical transformations in electrolysis may very widely differentiate depending mainly on the nature of the electrolyte and solvent and also on the material of the electrode." [3, p. 399]

"When an electric current passes through an electrolytic solution or molten electrolyte, the positive ions move towards the cathode, and the negative towards the anode, where they are discharged. The resulting neutral atoms and atomic groups either separate out of solution or react with each other, forming what is known as *secondary electrolysis products*.

Example 1:

Electrolysis of molten NaCl *on inert electrodes* (such as Pt) *that undergo no chemical change during the reaction*.

Electrolyte dissociates:

$$NaCl \rightarrow Na^+ + Cl^-$$

On the cathode (-) $Na^+ + e \rightarrow Na$

On the anode (+) $2Cl^- - 2e \rightarrow Cl_2\uparrow$

Whole process $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2\uparrow$.

Oxidation process is always takes place on the anode and reduction process is always takes place on the cathode. But in electrolysis the cathode is negative electrode and the anode is positive one, and in galvanic cell the anode is negative electrode and the cathode is positive one.

Example 2:

Electrolysis of the solution of $NiCl_2$.

Electrolyte dissociates:

$$NiCl_2 \overset{\rightarrow}{\underset{\leftarrow}{}} Ni^{2+} + 2Cl^-$$

[1, p. 482]

$$H_2O \overset{\rightarrow}{\underset{\leftarrow}{}} H^+ + OH^-$$

"In considering the mechanism of electrolysis it must not be forgotten that besides the ions of the electrolyte all aqueous solutions also contain H^+ and OH^- ions from the water. These ions migrate in an electric field just like the electrolyte ions, the hydrogen ions moving towards the cathode, and the hydroxyl, towards the anode. Thus, two kinds of ions can be discharged simultaneously at the cathode:

$$Ni^{2+} + 2e \rightarrow Ni^0$$

$$2H^+ + 2e \rightarrow H_2 \uparrow$$

Which of them will actually be discharged depends, above all, on their relative position in the e.m.f. series, then on the concentration of the ions, and in some cases, on the material of the electrode at which they are discharged.

The ion of any metal below hydrogen (in the e.m.f. series) is more easily discharged that the hydrogen ion, *the electrolysis of aqueous solution of salts of Cu, Hg, Ag, Au, Pt, etc. will result in deposition of the corresponding metals on the cathode:*

$$M^{n+} + ne \rightarrow M^0$$

When the salts of the more active metals, sodium, potassium and calcium, as well as magnesium and aluminium, whose electrode potentials differ greatly from that of hydrogen, are electrolyzed, almost exclusively hydrogen ions are discharged, and gaseous hydrogen is liberated at the cathode:

$$2H^+ + 2e = H_2 \uparrow$$

OH^- ions accumulate at the cathode, and solution becomes alkaline.

A different thing happens when aqueous solutions of the salts of the less active metals, situated above hydrogen (in the e.m.f. series), such as *zinc, iron, nickel, etc.*, are electrolyzed. Although theoretically hydrogen ions here too should have been the first to be discharged, practically, the metals are deposited at the cathode:

$$M^{n+} + ne \rightarrow M^0$$
$$\Delta m_M = k_M \cdot q \cdot (0.5 \div 0.97)$$

Hydrogen ion discharges simultaneously at the cathode:

$$2H^+ + 2e = H_2 \uparrow$$
$$\Delta m_{H_2} = k_{H_2} \cdot q \cdot (0.5 \div 0.03)$$

Now let us see what happens at the anode. The negative ions of the electrolyte and hydroxyl ions of water move towards it. If the negative ions do not contain oxygen, e.g., Cl^-, Br^-, S^{2-} ions, these ions, and not the hydroxyl, are discharged, as the latter give up their charge with much greater difficulty, the result being that chlorine, bromine, or sulfur are liberated at the anode.

$$2Cl^- - 2e \rightarrow Cl_2 \uparrow$$

If, however, the negative ions contain oxygen (SO_4^{2-}, NO_3^-.etc.), gaseous oxygen is liberated at the anode.

$$.4OH^- - 4e = 2H_2O + O_2$$

Hydrogen ions accumulate at the anode." [1, p. 483]

"In the above examples of electrolysis the electrodes were assumed to be made of an inert material, such as graphite. When such electrodes are used, ions are discharged both at the cathode and at the anode. But if the anode is an active metal, the process takes a different course. In this case ions will be discharged only at the cathode; at the anode, on the other hand, metal ions will pass into the solution. For instance, if a solution of nickel sulfate $NiSO_4$ is electrolyzed using a plate of metallic nickel as the anode, nickel will be deposited as usual at the cathode, but no hydroxyl ions will be discharged at the anode and there will be no liberation of oxygen, nickel gradually dissolving instead:

Scheme of Electrolysis of $NiSO_4$ solution (with Nickel Anode)

$$NiSO_4$$

$$\underline{\quad\wedge\quad}$$

$$\text{Cathode} \leftarrow Ni^{2+}SO_4^{2-} \rightarrow \text{Anode}$$

$$Ni^{2+} + 2e = Ni \qquad\qquad Ni - 2e = Ni^{2+}$$

The amount of nickel salt in solution is remaining unchanged." [1, p. 485]

"In electrolysis the current intensity (and hence the amount of substance produced in unit time) depends on the voltage (potential difference) applied to the electrodes. On increasing the voltage the current intensity is increased. For a given electrolytic process to occur, however, the applied voltage must be not less than a certain value characteristic of the given process. *This lowest voltage required for a given electrolytic reaction is called the decomposition voltage or decomposition potential*. (E_{dec}) [3, p. 404]

"Practical Application of Electrolysis

Electrolysis has received wide and varied application in industry.

1) *The production of* hydrogen, oxygen, chlorine, caustic soda, aluminium, Mg, Na, K, $KClO_3$, $KClO_4$ etc. is carried out by the electrolysis.

2) *Electrolytic metal coating* became very widespread in the following period. Electrolytic nickel, cadmium, tin, silver and copper plating, etc., is employed for a variety of purposes." [3, p. 402]

3) *Galvanoplastics* is a method of obtaining exact metallic replicas of relief objects by depositing a more or less thick layer of metal electrolytically on their surface. [1, p. 485-486]

4) Electrolysis finds application in the *refining purification of metals*. This applies in particular to copper and lead.

5) *Anodic oxidation (anodizing)* is a method of producing oxide films on Al, Ta, Ti, Nb, etc., which can protect metal against corrosion, abrasion etc.

6) *Electrochemical polishing of metals* by means of anodic dissolution in special electrolytes with *high current density*. Current density is the current intensity referred to a unit of surface area of the electrode

$$j = \frac{I}{S}$$

It is usually expressed in amperes per square decimeter.

Corrosion of Metals and Alloys

Corrosion is the breakdown of a material due to chemical or electrochemical interaction with the environment.

Types of Corrosion

1) *Chemical corrosion* is a corrosion which takes place in non-conductive medium.

a) "The simplest case of the corrosion is that which occurs when metal come into contact with gases (*gas corrosion*). The surface of the metal becomes coated with the corresponding compounds, namely, oxides, sulfides, basic carbonates, which often form a compact layer protecting the metal from further attack by the gases". [1, p. 477]

b) Corrosion in medium of liquid non-electrolyte.

2) "*Electrochemical corrosion* is due to electrochemical interaction between the various constituents of a metal or metal article. Such interaction is largely the result of the formation and functioning of galvanic cells. Cor-

rosion of this type is observed both on contact of the metal with water and an electrolyte solution (liquid corrosion), or on contact with moist air (atmospheric corrosion)". [3, p. 409]

All sorts (chemical and physical) of surface heterogeneities of the metal lead to electrode potential difference and formation of *microcells*. The dissolution of metal takes place on the anodic sites:

$$M - ne \rightarrow M^{n+}$$

At the *cathodic sites* the process of reduction of any oxidant (depolarization) takes place:

$$Ox + ne \rightarrow Red$$

3) *Biological corrosion*. Some microorganisms can destroy metals.

Other principle of classification of corrosion is character of destruction. In accordance with it corrosion can be:

1) Local corrosion.

a) "Intercrystallite corrosion, when the thin layers between the crystals comprising the alloy are the first to break down." [3, p. 408]

b) point corrosion (pitting),

c) selective corrosion, when one of the components of the alloy are the first to break down;

d) subsurface corrosion, the destruction begins on the surface of the metal, but after that the subsurface layer breaks down;

e) crevice corrosion;

2) Continuous corrosion.

a) uneven,

b) even,

Thermodynamics of Corrosion

"At the basis of the commonly encountered processes of metal corrosion lies the fact that most metals (excepting the least active such as Au and Pt) are less stable in the free state under atmospheric conditions than in the state of their ions in compounds." [3, p. 408]

The possibility of spontaneous process can be determined thermodynamically:

$$H_2O + Fe + \frac{1}{2}O_2 = Fe(OH)_2$$

If ΔG of the reaction is less then zero, the process is spontaneous (at constant pressure and temperature) but

$$\Delta G_{ch.r} = -nFE$$

and

$$E = \varphi_c - \varphi_a \approx \varphi^\circ_{Fe/Fe^{2+}} - \varphi^\circ_{O_2/OH^-}$$

if E>0 the corrosion of iron is possible with the oxygen depolarization:

(A) $Fe - 2e \rightarrow Fe^{2+}$

(C) $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

If $\varphi_M < \varphi_{H_2}$ the corrosion of the metal is possible with hydrogen depolarization also:

(A) $M - ne \rightarrow M^{n+}$

(C) $2H^+ + 2e \rightarrow H_2 \uparrow$

Do not remember that electrode potential depends on concentration:

$$\varphi_{H_2} = \varphi^\circ_{H_2} + \frac{RT}{nF} \log_e C_{H^+}$$

Because of this the corrosion with hydrogen depolarization takes place in most cases in acid medium but only for active metals.

e.m.f. series Li . . . H . . . Ag, Pt, Au

'———v———'

hydrogen depolarization is possible

'——————v——————'

oxygen depolarization is possible

Kinetics of Corrosion

Corrosion process is a heterogeneous one, and heterogeneous kinetics is applicable to it.

$$\upsilon = \frac{\Delta m}{\tau \cdot S}$$

In case of electrochemical corrosion

$$\Delta m = k \cdot J \cdot \tau$$

and

$$\upsilon = \frac{k \cdot J \cdot \tau}{\tau \cdot S} = \frac{k \cdot J}{S} = \frac{k}{S} \cdot \frac{U}{R} = \frac{k}{S} \cdot \frac{E - \Delta E}{R}$$

Because of it the rate of the corrosion depends on:

1) The e.m.f. of galvanic cells (E)
2) The electrode polarization (ΔE)
3) The resistance of electrolyte (R)

Factors affecting on corrosion:

1) Chemical nature of metal (its electrode potential)
2) Heterogeneity of the metal surface (it increases e.m.f. of microcells)
    a) Admixtures
    b) Differences in temperature
    c) Mechanical stresses in metal
    d) Mechanical defects of the surface of the metal
    e) Different contact with electrolyte
3) Properties of the corrosion medium:
    a) Electric conductivity;
    b) Concentration of oxidants (O_2, H^+, and others).
    c) Ability to dissolute the products of the corrosion.

For instance:

$$Al_2O_3 + 3H_2O + 6NaOH = 2Na_3[Al(OH)_6]$$

$$Al + 3H_2O \overset{NaOH}{=} Al(OH)_3 + \frac{3}{2}H_2\uparrow$$

$$Al(OH)_3 + 3NaOH = Na_3[Al(OH)_6]$$

$$Al_2O_3 + H_2O \overset{pH=7}{\neq}$$

In the neutral medium thin film of Al_2O_3 protect Al against corrosion, but in alkaline one corrosion of the metal takes place. (What type of depolarization? Write anodic and cathodic reactions.)

Protection of Metals Against Corrosion

Since great losses are incurred in the corrosion of metal components, special measures have long been taken to combat this phenomenon. The most wide spread method is the creation of a *protective coating* on the surface of the metal:

1. Oil paints coatings, lacquer, enamels and bitumen coatings.
2. Metal coatings are divided into anodic and cathodic ones.

a) Cathodic coatings have a more positive electrode potential than the metal being protected (for instance, iron coated with tin, copper or nickel).

All such coating (1, 2a) are effective as long as they retain their continuity. If a crack occurs in the coating, corrosion will occur on the exposed surfaces.

b) Anodic coatings have a more negative electrode potential than the metal being protected. When the coating e.g., zinc on iron is impaired it will still protect the basic metal:

A (Zn) $Zn - 2e = Zn^{2+}$

C (Fe) $Ox + ne \rightarrow Red$

Hence continuity is not a very strict requirement of an anodic coating.

3) *The protection afforded by films formed on metals by chemical reaction* with the environment led to the development of methods for the artificial formation and strengthening of such films to augment their protective

action. *Besides* oxide films, *oxide-chromate*, *phosphate*, *sulfide* and other films are produced.

Oxidation (burnishing, bluing) of iron and steel is carried out by dipping the article in highly concentrated alkali baths which oxidizing agents such as MnO_2 and $NaNO_3$ are added to.

In recent years oxiaation by electrolysis has come into favour (*anodic oxidation, anodizing*).

4) It is general knowledge that different additives introduced into the composition of special (alloyed) steels have a different influence on their resistance to corrosion process. Thus, chromium-nickel and chromium steels have found widespread use as *stainless steels*.

5) Addition of *inhibitors* to the solution.

6) Special electrochemical methods are also used to control corrosion. These are based on cathodic polarization of the protected metal. Thus in methods known as *cathodic protection*, a more active metal (*protector*) is connected to the metal being proterted and, becoming the anode, converts the anodic sites of the metal surface to cathodic (Fig. 12).

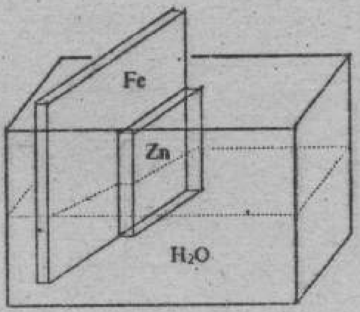


Fig. 12

A(Zn) $\quad Zn - 2e \rightarrow Zn^{2+}$

C(Fe) $O_2 + H_2O + 4e \rightarrow 4OH^-$

Cathodic protection may also be achieved by connecting the metal to the negative terminal of an external direct current source. The protection action is due to the increase in concentration of the electrons in the surface layer of the metal, thus hindering its solution (Fig. 13).

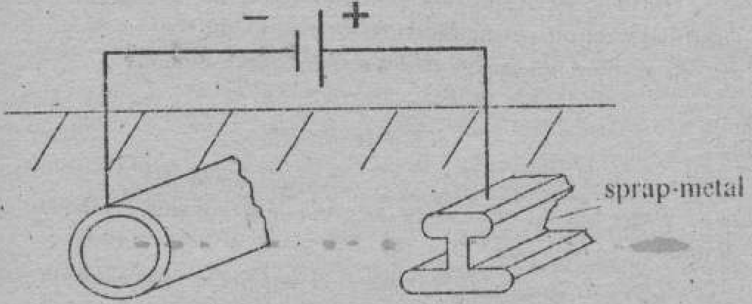


Fig. 13

(C) $O_2 + H_2O + 4e = 4OH^-$ (A) $Fe - 2e \rightarrow Fe^{2+}$

Structure of the Substance. Structure of the Atom

Atomic structure (especially electronic configuration) is of great importance to chemistry because of its connection to properties of substance.

"In 1900, when studying some features of spectra, *M.Planck postulated* that electromagnetic radiation is emitted not continuously, but in discrete portions not smaller than a certain definite quantity

$$\varepsilon = h \cdot \nu \quad (1)$$

Where h is the elementary quantum of action and ν is the frequency of the emitted radiation." [3, p. 19]

"*Louis de Broglie (1924)* suggested that just as light has both particle and wave nature, matter in general, and electron in particular, might also exhibit this dual behavior. The mass m of a photon is given by Einstein's mass-energy equation

$$\varepsilon = m \cdot c^2 \quad (2)$$

From these two equations

$$m \cdot c^2 = h \cdot \nu$$

$$m \cdot c = \frac{h \cdot \nu}{c}$$

$$p = m \cdot c = \frac{h}{\lambda}$$

Where P is momentum of the photon.

$$\lambda = \frac{h}{m \cdot c} \quad (3)$$

According to de Broglie, for a particle of mass m moving with a velocity v, *the de Broglie equation*, Eqn. (3) becomes

$$\lambda = \frac{h}{m \cdot v} \quad (4)$$

In Eqn. (4) λ is the de Broglie wavelength. The experimental proof of the wave character of electrons was provided by C. J. Davisson and L. H. Germer (1927) and independently by G. P. Thompson (1927), who obtained diffraction patterns using accelerated electrons. Equation (4) relating the wave character with momentum (mv) can be considered to be a compromise between the wave and particle aspects of matter." [5, p. 20]

The concept of a de Broglie wave associated with a particle like an electron means that the particle cannot be located precisely. According to *Heiseberg's principle of uncertainty* enunciated in 1927, it is not possible to state, simultaneously and precisely, both the position and momentum of an electron, and other similar particles. If Δp and ΔX represent the uncertainties in the momentum and the position respectively, then, according to Heisenberg,

$$\Delta p \cdot \Delta X \geq \frac{h}{4 \cdot \pi}$$

" [5, p. 21]

"De Broglie suggested that a particle, like an electron, has an associated wave of wavelength defined by the de Broglie equation.

In 1926 *Schredinger* developed a differential *equation* for such a wave

$$\boxed{-\frac{h^2}{8 \cdot \pi^2 \cdot m} \nabla^2 \psi + U \cdot \psi = E \cdot \psi}$$

Where $\nabla^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$ is the Laplasian operator. In this equation, the known quantities are:

m = mass of the particle

U = potential energy of the particle as a function of the coordinates X, Y and Z

h = Planck's constant.

The unknowns to be determined by solving this equation are

E = allowed total energies of the particle or <u>*eigen values*</u> and

ψ = wave function or <u>*eigen function*</u>.

The physical significance of ψ^2 is that ψ^2 dV measures the probability of the electron being found in the volume element dV surrounding a point whose coordinates are known". [5, p. 22-23]

"Solutions of this equation lead to quantization of energy levels, i.e. an electron can assume only discrete values for its energy" [5, p. 22]

<u>*Quantum Numbers*</u>

"Solution of the equation contains the <u>*quantum numbers*</u> n, l, m. Dirac showed that in a wave equation based on the theory of relativity, the fourth quantum number (S) is also introduced. Four quantum numbers have thus been found necessary to describe an electron in an atom completely. These are the <u>*principal quantum number n*</u>, <u>*the azimutal quantum number l*</u>, <u>*the magnetic quantum number m*</u> and the <u>*spin quantum number S*</u>." [5, p. 26]

<u>*Principal quantum number*</u> was introduced in Bohr's theory in 1913.

"Wave mechanics explains why only certain definite electron orbits are stable. Only those orbits are "stable" which can accommodate a whole number of waves. Since the length of a circular orbit of radius r equals $2 \cdot \pi \cdot r$ and

$$\lambda = \frac{h}{m \cdot v}$$

the stability of the orbit is determined by the equation

$$2\cdot\pi\cdot r=\frac{n\cdot h}{m\cdot v}$$

Where n is an integer. This is the mathematical expression of Bohr's first postulate, on which he based his calculation of the motion of the electron in the hydrogen atom in 1913. *The principal quantum number defines the energy level* corresponding to any given orbit *and the distance* of the latter from the nucleus. The value n=1 corresponds to the lowest energy level (electron shell), designated K; the value n=2, to the energy level L, etc." [1, p. 108]

The quantity of electron shells in an atom is equal to the number of the period in which element situated in the Periodic Table."

"Transitions of electrons from inner shell to outer shells require an expenditure of energy and can take place only if the atom absorbs electromagnetic radiation of the proper frequencies. The reverse transitions are accompanied by the emission of electromagnetic radiation of the same frequencies. All this was confirmed by spectroscopic data." [3, p. 26]

Orbital Quantum Number

"The spectral lines that correspond to the transition of an electron from one level to another for the most part consist of several separate close-lying lines (fine structure), indicating that some of the electrons of the given energy level have different binding energies." [3, p. 26]

"*The binding energy* of an electron in an atom is defined as the energy required to remove it from the atom." [3, p. 21]

The electrons of a given shell are accordingly divided into subgroups (sub-levels), denoted by s, p, d, f. To take into account this difference in the binding energy, a second quantum number was introduced into the theory of the atom. This second number is called the *orbital quantum number l*, or *azimutal quantum number* (l also characterizes orbital form).

According to quantum mechanics, it can have any integral value from 0 to (n-1), where n is the principal quantum number." [3, p. 27]

(0=s; 1=p; 2=d; 3=f)

Magnetic Quantum Number

"The further resolution of the spectral lines observed when the spectral source is in a magnetic field-*Zeeman effect (1896)*, necessitated the postulation of the magnetic quantum number m." [5, p. 19]

"The third quantum number characterizes the position of the orbit of the given electron in the atom. This number may have any integral value between +*l* and -*l*, including 0." [3, p. 27]

Spin Quantum Number

"By studying the effect of an inhomogeneous magnetic field on silver vapor in a specially designed and evacuated apparatus, Stern and Gerlach (1921) observed that the beam of silver atoms was split into two separate beams in opposite directions. This could be attributed to the electron spin, an idea which was first put forward by Uhlenbeck and Goudsmit (1925) in order to explain the fine structure of spectral lines and the Zeeman effect. The two different beams in the case of silver correspond to silver atoms with electrons of opposite spins. The fine structure of spectral lines was attributed to the small energy changes that result from the interactions between the two different magnetic moments, one due to the orbital motion of the electron and the other due to its spin around its own axis. According to the quantum theory, the spin number S can assume a value of $+\frac{1}{2}$ and $-\frac{1}{2}$" [5, p. 19]

"Pauli's Principle, or Exclusion Principle

It is impossible for any two electrons in an atom have identical sets of all four quantum numbers."[3, p. 27]

"A pair of electrons differing only in their spins is said to occupy *an orbital*. The type of sub-level (s, p, d, f) gives a general indication of the shape of the orbital (Fig. 14)." [5, p. 27]

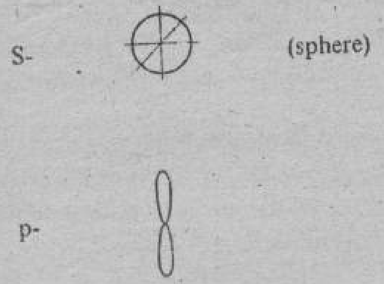


Fig. 14

"The clouds of the p- electron pairs have the symmetry of a body of revolution with a cross section in the form of a "figure-of-eight". *The long axis of the clouds for the three p- electron pairs are mutually perpendicular* (Fig. 15).

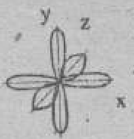


Fig. 15

Periodic Law

"*The physical and chemical properties of elements and their compounds are periodic functions of their atomic numbers.*" [5, p. 34]

Periodic Classification and Electronic Configuration

"In the periodic table, the elements are arranged in the order of increasing atomic number in such a manner, that elements with similar chemical and physical properties are grouped together. Since the properties of an element depend on the atomic number and the arrangement of electrons, each group of elements might be expected to have a similar electronic configuration. The electronic configuration can be written using the following principles.

1. The electrons are accommodated in the subshelles and orbitals in the order of increasing energy. An approximate indication of the relative energies of the various subshells is given by the energy level diagram (Fig. 16). This gives the sequence in which the subshells are occupied:

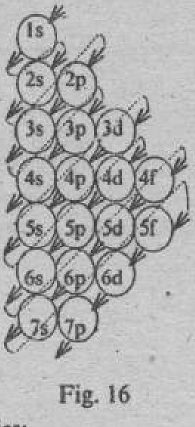


Fig. 16

Or by Klechkovsy's rules:

1) In order of increase (n+*l*)

2) If n+*l* of two subshells are equal one to other, in order of increase of "n"

3) In the case of a "p" subshell there are three orbitals of the same energy. These are called *degenerate orbitals*. Similarly, there are five and seven degenerate orbitals in d and f subshells respectively. According to *Hund's rule* of maximum multiplicity, when electrons are present in a number of

degenerate orbitals they occupy all the orbitals singly, with parallel spins, before pairing in any one orbital occurs.

4) To obtain the electronic configuration of any element of atomic number Z one has to obtain that of the preceding element (atomic number Z-1) and allot the single electron to the appropriate orbital". [5, p. 38]

"The arrangement of electrons in the atoms can be conveniently written in the form of short formulas as follows. First we write the figure indicating the principal quantum number; this is followed by a letter denoting the secondary quantum number, the number of electrons on each corresponding orbit being written as a superscript at the right of this letter. For example, the "electron formula" of the hydrogen atom is $1s^1$, that of the helium atom-$1s^2$, of the lithium atom-$1s^2 2s^1$, of the oxygen atom-$1s^2 2s^2 2p^4$, of the neon atom-$1s^2, 2s^2 2p^6$, of the aluminium atom $1s^2 2s^2 2p^6 3s^2 3p^1$, etc." [1, p. 110]

"The elements in the periodic table can be classified and referred to as s-block, p-block, d-block and f-block elements, depending upon whether electrons are filling up s,p,d or f orbitals. The transition elements (d block) have incomplete d shells with the general electron configuration (n-1) d nS (n≥4). The electrons in the nS level may be drown into the (n-1)d level in order to achieve a d^5 or d^{10} configuration. (Cu, Au etc.)"

Ionization Potential (I)

The minimum energy required to promote the most closely bound electron in a neutral gaseous atom from its ground state to infinity is called the first ionization potential I_1, since it refers to the process $M \rightarrow M^+ + e^-$, I_2 and I_3 refer to processes involving the removal of two and three electrons respectively.

Electron Affinity (E)

The electron affinity can be defined as the energy released when a neutral gaseous atom in its ground state aquires an electron to become an anion. The values are determined indirectly by using the Born-Haber cycle.

Electronegativity (X)

Pauling defines electronegativity as the power of an atom in a molecule to attract electrons to itself.

$X = \frac{1}{2} * (E + I)$ by Mulliken. Other electronegativity scales have also been proposed but the one devised by Pauling has received the widest acceptance. If E_c is the bond energy of a purely covalent bond between A and B and if E is actual bond energy, it is usually found that $E > E_c$. E_c is assumed to be the geometric mean of the bond energies of bond A-A and B-B.

i.e. $E_c = (E_{A-A} \cdot E_{B-B})^{1/2}$

The difference, $\Delta = E - E_c$, is supposed to be a measure of the ionic contribution to the covalent bond. The ionic contribution is due to a polar structure, the polarity being due to unequal sharing of the electron pair. Δ is thus a measure of electronegativity. Pauling set up the empirical relation,

$$X_A - X_B = 0.208(\Delta)^{1/2}$$

Where X_A and X_B refer to the electronegativities of A and B respectively. Since only the difference in electronegativities is given by this Eqn. Pauling choose a value of 2.1 for H so as to get values 2,5 to 4.0 from C to F." [5, p. 45]

Structure of Molecules and Nature of the Chemical Bond

"*Introduction*. The combination of atoms to form molecules involves valency forces and these forces are related to the electronic configuration of the atoms concerned. The motivation for formation of a molecule is the greater stability of the molecule compared to the atoms. The lack of reactivity among the inert gases indicates that the atoms of these elements are quite stable; and this has been attributed to the presence of eight electrons in their outermost shell, the only exception is the first shell which has a stable structure of two electrons.

$^{+10}Ne \qquad 1s^2\underline{2s^2 2p^6}$

$^{+2}He \qquad \underline{1s^2}$

This electron octet is considered to be an exceptionally stable arrangement. One of the postulates of the electronic theory of valency is that, as far as possible, in the process of chemical combination, each atom tends to attain a stable electron octet. This is referred to as the octet theory. Depending on how this octet is achieved we have different types of valency.

Electrovalency and Ionic Compounds

Kossel and Lewis (1916) independently pointed out that the elements immediately preceding the inert gases in the periodic table are electronegative and those following the inert gases are electropositive. In order to attain a stable arrangement, the elements of group VII can gain one electron and those of group VI two electrons respectively, where as the elements of group I must lose one electron and these of group II two electrons for the same purpose." [5, p. 67]

$$\mathrm{Na}\ 1s^2 2s^2 2p^6 3s^1, \qquad \mathrm{Na} - 1e = \mathrm{Na}^+\left(1s^2 2s^2 2p^6\right)$$

$$\mathrm{Cl}\ 1s^2 2s^2 2p^6 3s^2 3p^5, \qquad \mathrm{Cl} + 1e = \mathrm{Cl}^-\left(1s^2 2s^2 2p^6 3s^2 3p^6\right)$$

$$2\mathrm{Na} + \mathrm{Cl}_2 = 2\mathrm{NaCl}.$$

"*Ionic bond* occurs between oppositely charged ions and is due to simple electrostatic attraction between the ions " [1, p. 113]

"If a large number of positive and negative ions are brought close together, the result is a crystal in which each ion of one sign is surrounded by ions of the opposite sign. Obviously, the conception molecule is inapplicable to crystals made up of ions. Molecules appear only in the vapors of ionic compounds." [1, p. 117]

"When the difference between the electronegativities of the elements is great ($\Delta X>1.8$) their atoms form an ionic bond; when the difference is zero, the bond is non-polar covalent; in the intermediate case the bond is polar covalent." [3, p. 46]

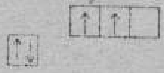
Covalent Bond

"According to the theory of covalence, (Lewis), when a molecule forms (just as in the case of ionic compounds), the atoms of the chemical elements acquire stable electron shells similar to those of noble gas atoms. However, this stability is not attained by transferring electrons from one atom another, but by the formation of one or more electron pairs which become common to the combining atoms, i.e., belong to the electron shells of both the atoms. A chemical bond which is due to the presence of electron pairs is called a *covalent or atomic bond*." [1, p. 117]

Properties of Covalent Bond

1."Only unpaired electrons in the atom can take part in covalent bond formation.

^{+14}Si $\quad\quad$ $1s^2 2s^2 2p^6 \underline{3s^2 3p^2}$



The covalence of the Si is equal 2

$Si{=}0$ $\quad\quad$ $\ddot{Si}::\ddot{\underset{..}{O}}:$

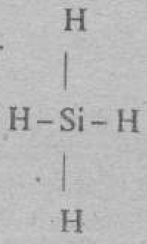
The formation of higher valence often requires *excitation* of the atom with the transition of the electron to a higher energy sublevel." [3, p. 53]

$^{+14}Si^*$ $\quad\quad$ $1s^2 2s^2 2p^6 \underline{3s^1 3p^3}$

The covalence of the Si* is equal 4. (The asterisk is the sign of excited state.)

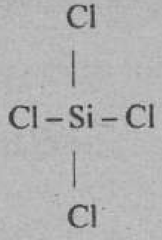
SiO_2 $\quad\quad$ $0{=}Si{=}0$

SiH_4



$$\begin{array}{c} H \\ | \\ H-Si-H \\ | \\ H \end{array}$$

SiCl$_4$

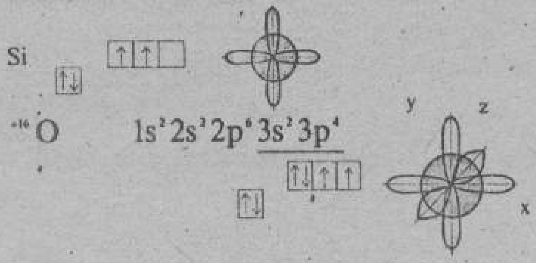


$$\begin{array}{c} Cl \\ | \\ Cl-Si-Cl \\ | \\ Cl \end{array}$$

2. "Orientation of Bond.

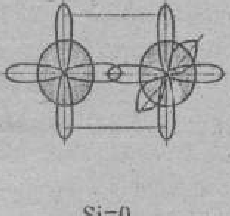
For purely ionic bonds the question of their orientation usually does not arise, since the ions having an electron shell similar to that of the inert gas atoms generate an electric field with spherical symmetry (i.e., the same in all directions). For covalent bonds involving s-electrons, all the directions of the bond are also equivalent owing to the spherical symmetry of the s-electron cloud. But *p-electrons (and d-electrons) form bonds that are definitely oriented in space relative to one another*." [3, p. 59]

Example 1. SiO



$_{+16}$O $1s^2 2s^2 2p^6 \underline{3s^2 3p^4}$

π - bond



Si=0

The linear overlap between the orbitals is called σ-bond.

The lateral overlap between the p orbitals is called π-bond. [5,p.80]

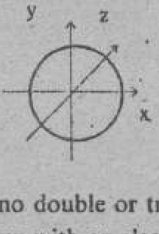
"Since the lateral overlap is less extensive than the linear overlap", π-bond exists only in cases of double or triple bonds as addition to σ-bond.

<u>Example 2.</u> molecule SiH_4

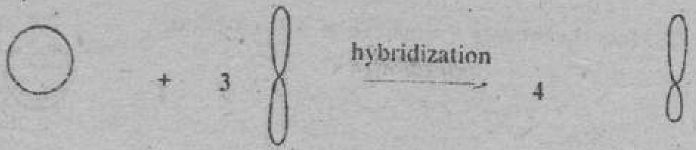
·" Si˙ $3s'3p^3$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

$\boxed{\uparrow}$

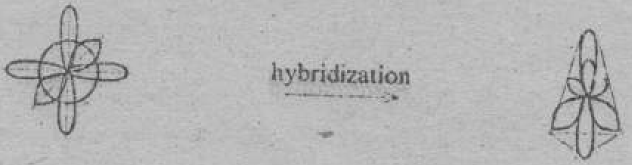
H 1s' $\boxed{\uparrow}$



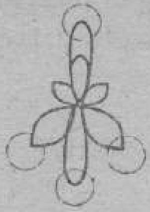
"If a given Si* atom has no double or triple bonds, each of its four valence electrons *($3s'3p^3$)* pairs up with an electron of the interacting atom (H), and as a result of *<u>hybridization</u>* of the bonds all four electrons become equivalent in a number of properties (binding energy, interatomic distance, etc.) If the substituents are identical, the σ-bonds of the atom are arranged in space at the tetrahedral angle 109° 28' to each other.



or

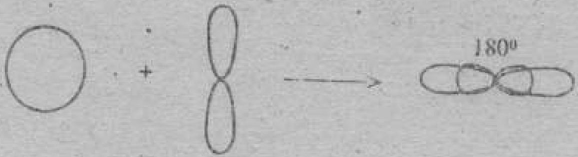


In result of this process the form of the molecule of SiH_4 is tetrahedr.



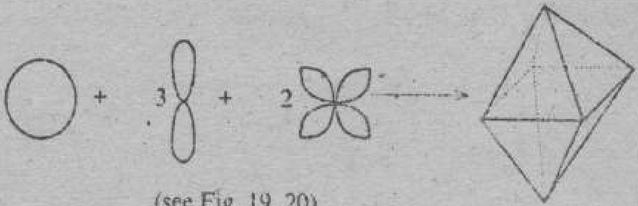
This type of hybridization is called sp³. Other types are:

1) sp



2) sp²

3) sp³d²



(see Fig. 19, 20)

In general, when p- and s- (or p-, s- and d-) electrons simultaneously take part in the forming of valence bonds in an atom, the difference between them disappears, and they all interact similarly. This is known as *hybridization*. [3, p. 46]

3. Polarity of the bond.

"As a result of the difference in electronegativity of the two atoms involved in covalent bond formation, the electron pair may not be equally shared between the two. The polarity of a molecule (or a bond) is expressed quantitatively by its *dipole moment (μ)*, which is equal to the product of the charge and the distance separating the centers of charges." [5, p. 84]

. "Since the dipole moment is a quantity characterized by direction, the dipole moment of the molecule is determined by taking the vector sum of the dipole moments of the separate bonds." [3, p. 65]

"Such polarity affects many properties of molecules." [3, p. 64]

Valence Bond (VB) Method

"The quantitative theory of chemical bonding is developing at present on the basis of the conclusions and methods of quantum mechanics. The theory of covalent bonding suggested by Heitler and London (1927) initially to describe the H_2 molecule, was subsequently extended to cover other cases of covalent bonding. It describes covalent bonding by examining the state of the electron of a given electron pair with the aid of Schrodinger's wave function. This method was called the valence-bond method (VB) or *method of localized electron pairs*. It can be shown if a bond is formed by S-electrons, the electrons forming the bond must have opposite spins (in accordance with Pauli's principle). In the opposite case no bond will form (Fig. 17)." [3, p. 54-55]

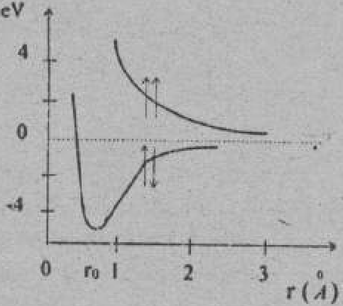


Fig. 17. The potential energy of a system of two hydrogen atoms as a function of r, the distance between them.

You can see that in case of *anti-parallel* spins calculated energy curve has minimum at r_0 which corresponds to the experimental H-H bond distance (0,74 Å).

Molecular Orbital (MO) Method

R.S. Mulliken (1931) and F. Hund (1928)

"Another method that is finding ever wider applications is the method of molecular orbitals (MO method), which is the most general one covering both covalent, and ionic and donor-acceptor (see below) bonds. In this method the formation of a chemical bond is regarded as a result of the collective motion of all the electrons in the field of all the atomic nuclei and all the electrons of the molecule in question. In practice the examination is usually confined to valence electrons, and various simplifying assumptions are introduced. The most common assumption is that the wave function showing the state of the electron in the given bond can be expressed as a linear combination of wave functions characterizing its state in the respective atoms (the method of linear combination of atomic orbits - LCAO method)." [3, p. 55]

The explanation of the paramagnetism of oxygen was one of the early triumphs of the MO theory.

Bond Characteristics

"*The bond energy* is defined as the average amount of energy per mole required to break a particular bond in a molecule into its constituent atoms or radicals." [5,p.267]

The chemical bond energy is 20-200 kcal/mol or 1-10 eV per one bond. Covalent bond energy is bigger than ionic one. Other important characteristic is bond length (distance).

Donor-Acceptor Bonds. Complex Compounds

"In a covalent bond between two atoms the shared electron pair is contributed by both the atoms. In certain cases the octet can also be achieved by both the electrons being supplied by one of the atoms. The resultant covalent bond is called a *coordinate bond* or donor-acceptor bond." [5, p. 69]

"The particle that supplies the electron pair is called the *donor*, and that which the bond is established with is called the *acceptor*. The donor may be a particle containing an electron pair on its outer energy level that does not participate in the formation of the bond with the other particles (unshared electron pair). Donors are mostly molecules containing the atoms N, O, F, P, S or Cl linked in them with atoms of other elements. An acceptor may be a particle having vacant (unfilled) electron levels. *Acceptors are often atoms of transitional metals having unfilled d-sublevels.*" [3, p. 57]

In each case, a lone pair of electrons belonging to the molecule or ion is utilized in the formation of each coordinate bond. Such molecules (ions) are called *ligands* and the compounds formed are called *coordination compounds* or *complex compounds*. The ligands are said to be coordinated to the central metal ion, e.g. (Fig.18)

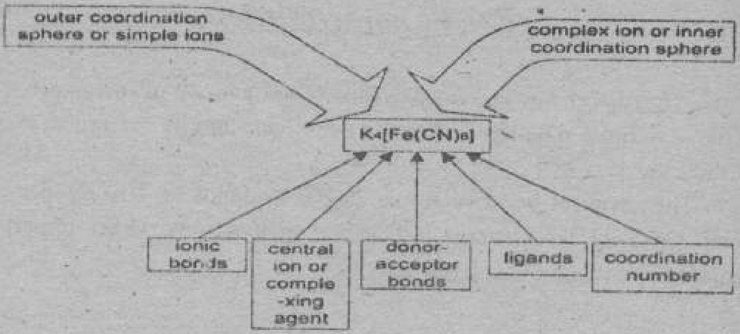


Fig. 18. Structure of complex compound.

Electronic formula of iron is

^{26}Fe $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Electronic formula of Fe^{2+} in accordance with Hund's rule is

Fe^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{3d^6}$

$\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

But electronic formula of the central ion Fe in this complex compound is

Fe^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{3d^6}$

$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{}\boxed{}$

This is a property of such ligands as CN^-, CO, NO_2^-.
They change electronic structure of a central ion
Electronic structure of the complex ion $[Fe(CN)_6]^{4-}$ is (Fig. 19)

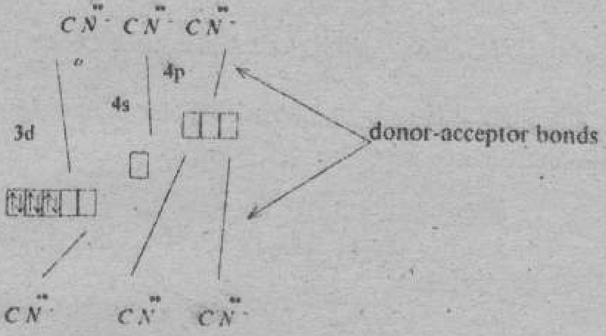


Fig. 19

Because of hybridization d^2sp^3 all donor-acceptor bonds are equal and shape of the ion is octahedron (Fig. 20).

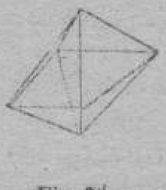


Fig. 20

Magnetic Properties of the Complex Compounds

"On the basis of their behavior in a magnetic field, substances can be classified as *ferromagnetic* (strongly attached into the magnetic fields), *paramagnetic* (attached into the magnetic field) and *diamagnetic* (repelled by the magnetic field). Paramagnetism which arises due to the presence of one or more unpaired electrons in the atom, ion or molecule, has been largely used to deduce the structure of metal complexes." [5, p. 45-46]

For example, $K_4[Fe(CN)_6]$ is diamagnetic, because the central ion electronic structure has no unpaired electrons.

Electrolytic Dissociation of the Complex Compounds

1) First step of ionization of the complex compounds does not destroy complex ions, e.g.

$$K_4[Fe(CN)_6] \rightleftarrows 4K^+ + [Fe(CN)_6]^{4-}$$

Due to ionic character of chemical bond between ions, the first step degree of ionization is 100%. Second step is dissociation of the complex ion, e.g.

$$[Fe(CN)_6]^{4-} \rightleftarrows Fe^{2+} + 6CN^-$$

Due to covalent (donor-acceptor) bond between central ion and ligands, the second step degree of ionization is very little.

"According to above equation, the ionization of $[Fe(CN)_6]^{4-}$ ions, like the ionization of any other weak electrolyte, obeys the law of Mass Action and can be characterized by a corresponding constant referred to as the instability constant of the complex ion". [1, p. 522]

$$K_{inst} = \frac{C_{Fe^{2+}} \cdot C^6_{CN^-}}{C_{[Fe(CN)_6]^{4-}}} = 10^{-24}$$

The instability constants of various complex ions differ greatly and may serve as a measure of stability of the complex" [1, p. 522]

"Ions which are formed by the addition of neutral molecules or other ions capable of existing independently in solution to the ions in question, are called *complex ions*. Compounds containing such ions are referred to as *complex compounds*.

"*Double salts* are the same as complex salts with the difference that their inner coordination sphere is rather unstable, for instance, ordinary alum:

$$KAl(SO_4)_2 \cdot 12H_2O \quad \text{or} \quad K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

$$KAl(SO_4)_2 \rightleftarrows K^+ + Al^{3+} + 2SO_4^{2-}$$

A greater or smaller amount of complex ions are always present in a solution of any double salt." [1, p. 531]

"At present the question of the participation of donor-acceptor bonds in the formation of certain common simple molecules is being studied" [3, p. 57]

According to the *electrostatic theory*, the bond between the central atom or ion and its ligands is due to electrostatic attraction between the particles and is of nature analogous to ionic bonds." [1, p. 532]

"General Properties of Ionic and Covalent Compounds

It is not always possible to differentiate strictly between ionic and covalent compounds. However, there are some striking differences in their properties:

1) Ionic compounds have high melting and boiling points compared to covalent compounds;

2) ionic compounds conduct electricity in the fused state whereas covalent compounds are poor conductors of electricity;

3) ionic compounds are generally more soluble in solvents such a water, than are covalent compounds. On the other hand, the covalent compounds are more soluble in solvents such as carbon tetra-chloride, benzene, etc. while ionic compounds are generally insoluble in these:

4) reaction involving ionic compounds are generally quite rapid, whereas covalent compounds usually react slowly. In electrovalent compounds the constituent elements are present as ions and are held together by electrostatic forces. In covalent compounds, the constituent elements are held together by sharing of electrons. As a consequence, in electrovalent compounds, the ions just depart from each other, the process being aided by the energy of hydration of the ions. In covalent compounds, there has to be an unpairing of the electrons that have been shared. This latter process is what is conventionally understood as bond breaking. For reactions of covalent compounds bond breaking is a prerequisite and this makes the reactions relatively slower compared to those of ionic compounds." [5, p. 81-82]

"The Metallic Bond

Metals are characterized by high electrical conductivity, thermal conductivity, characteristic lustre, malleability, etc. Metals also crystallize as structures with high *coordination numbers*, (number of nearest neighbors in a crystal) such as 8 or 12. According to the free electron theory of metals a *metal crystal consists of a closepacked structure of positive metal ions and the electrons are free to move about in the combined periodic potential field due to the positive ion* (metal ions in a sea of electrons). This model is capable of explaining qualitatively the metallic properties." [5, p. 87]

"The metallic bond is usually a very strong bond: hence, most metals are characterized by great hardness, high melting and boiling points and low volatility. If we exclude mercury and gallium, then the lowest melting points are those of the alkali metals, since the atoms of these metals give up only one electron for bond formation. d-electrons of the transitional elements form additional covalent bonds." [3, p. 110]

"*It is the high mobility of the electrons that gives metals their characteristic properties*. These include physical properties such as high electric and thermal conductivity, ductility (plasticity, malleability), and metallic lustre; and chemical properties, such as the basic character of the lower oxides." [3, p. 118]

"It is the non-directional nature of electron bonding that gives metals their capacity for non-destructive change of form under the action of mechanical forces." [3, p. 121]

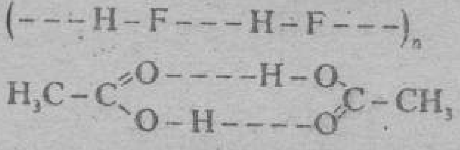
Metals dissolve in polar solvents due to the presence of metal ions in the crystal lattice.

"A quantitative approach which can be extended to insulators and semiconductors is provided by the MO-based *band theory*." (see course in physics) [3, p. 119-120; 5, p. 88]

"*Hydrogen Bond*

The formation of the hydrogen bond is a consequence of bond polarity. When hydrogen is covalently linked to highly electronegative elements such as fluorine, nitrogen or oxygen, the hydrogen atom is capable of forming a weak bond (The hydrogen bond energy is 5-7 kcal/mol) with another atom of the electronegative element. This weak bond is called the hydrogen bond. For example the existence of molecules such as $(H_2O)_n$, $(HF)_n$, $(CH_3\ COOH)_2$, etc. is explained on the basis of hydrogen bonding (indicated by the dotted lines in the examples given)

$$(---H-F---H-F---)_n$$



$$H_3C-C\begin{matrix}\nearrow O----H-O\searrow \\ \searrow O-H----O\nearrow\end{matrix}C-CH_3$$

The abnormal behavior of NH_3,H_2O and HF is due to the hydrogen bonding. The intermolecular forces of attraction together with hydrogen bonding in these cases require a larger amount of energy to overcome these attractive forces. This is reflected in the higher values of melting points and boiling points for these compounds." [5, p. 85]

"Intermolecular Attraction.

1) The mutual attraction of molecules (cohesion) is a complex phenomenon. With the discovery of the polar structure of molecules it became possible to explain the mutual attraction of polar molecules as due to electrostatic interaction between the oppositely charged parts of two molecules. The opposite mutual orientation of molecules gives rise to attractive forces and corresponds to a more stable state. This form of interaction between polar molecules is known as *orientation interaction* (Fig. 21).

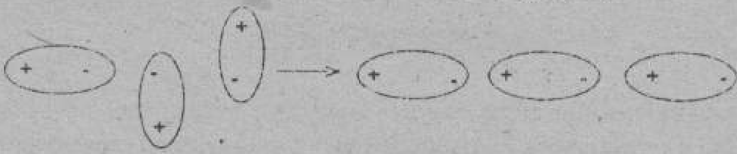
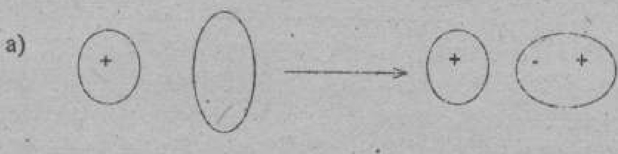


Fig. 21

2) The molecules of most substances are comparatively easily *polarized* under the influence of neighboring molecules or ions, especially upon close approach. The interaction of such induced dipoles gives rise to forces of intermolecular attraction that are similar to, but weaker than the forces between permanent dipoles. Such interaction is known as *distortion interaction* (Fig. 22).



b) 

Fig. 22

3) As was shown by F. London (1930) on the basis of quantum mechanics, the instantaneous dipoles that appear in atoms and molecules owing to the motion of their electrons also give rise to forces of attraction between them. Such forces are called *dispersion forces.* (Fig. 23).

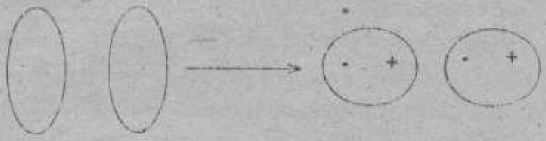


Fig. 23

It is evident from foregoing that polar substances should have stronger forces of intermolecular attraction, higher boiling points and greater heats of vaporization than non-polar substances with weakly polarizable molecules, since the polarity of the molecules gives rise to an additional force of attraction between them. When molecules closely approach one another, there arises a repulsive force due to mutual repulsion of the electrons and to other effects. The forces of attraction and repulsion between molecules are collectively known as intermolecular, or van der Waals forces." [3, p. 73-75]

Structure of Matter

"In the foregoing chapters we have become acquainted with the structure of atoms and molecules, the minutest particles of which all substances consist. To get a complete picture of the structure of matter we have still to see how these particles are arranged in different substances." [1, p. 128]

"In the *gaseous* state molecules have complete freedom of movement. In the *solid* state this movement is absent, even though the molecules, ions or atoms that are held together may vibrate about their equilibrium positions. The forces that hold together the constituent species in a *liquid* are sufficiently strong to prevent complete chaos from reining and yet sufficiently weak to permit a certain amount of disorder. X-ray diffraction studies of liquids show that there is *short range* order extending to 5 to 10 Å in the liquid state." [5, p. 134]

Glassy State

"When order which is the characteristic feature of a crystalline solid extends only to less than 5 or 10 Å the cristallinity is lost. If at the temperature T_f, at which a liquid should crystallize, sufficient nuclei are not present to induce crystallization, *supercooling* can take place and the material is now in a *metastable* state. The continued cooling below T_f may increase the viscosity of the material to such an extent that at a temperature T_g (glass transition temperature) its structure becomes frozen for all practical purposes. This structure will be akin to that of a liquid. The material is now in a glassy (amorphous) state. The chief characteristics of a glass are rigidity ability to withstand shearing stress and hardness, all of which are properties of solids. However, like liquids they are optically isotropic and transparent." [5. p, 156]

Liquid Crystals

Certain solids, when heated, melt sharply to form a turbid liquid, and on further heating undergo an equally sharp change to a clear liquid. The turbid liquid, like *anisotropic* crystals is doubly refracting and gives interference patterns in polarized light. The turbid liquids which exhibit these properties even though they have surface tension like liquids and flow like liquids were given name _liquid crystals_." [5, p. 157]

Crystals

Substances in the solid state may be divided into crystalline and amorphous. Some substances, in addition, can exist in several different crystalline forms, or modifications. This phenomenon is known as _polymorphism_. It must be borne in mind that the properties of substances in the crystalline state depend not only on their composition and the external condition, but also on their internal structure. Every crystalline modification of a substance is characterized by a definite geometrical form of its crystal.

Crystals are classified according to different features. In _crystallography_ the classification is based on the arrangement of the particles in space. E. Fedorov worked out (1910) a general classification of crystal lattices for all the 230 possible types, and founded _crystallochemical analysis_-the science of determining substances by the form of their crystals. In physical chemistry it is more convenient to classify crystals according to the _type of bond_ between the particles forming the crystals. The particles forming the crystal lattice may be ions, _neutral atoms_ or whole _molecules_." [3, p. 106-109] .

Real Crystals

"The perfectly ordered arrangement of the constituents of a crystal is only an idealized situation and is possible only at absolute zero. At all other temperatures, due to thermal vibration some constituents may be missing or misplaced. The term "imperfection" or "defect" is used to denote such departures from regular periodic arrangement of the crystal constituents. These defects have important influence on the electrical, mechanical and optical properties of the solid." [5, p. 230]

"*Frenkel defects* consist in the displacement of some ions from their normal sites in the lattice.

Schottky defects are vacant sites in the lattice. [3, p. 125]

The material used in practice, even when they are purely crystalline in structure, are generally either fine crystalline powders, or systems composed of a great number of small crystals (*polycrystallinity*). The crystals of the main substances are often separated by a thin layer containing various impurities. Certain deviations from the regular structure of a crystal appearing in the process of growth, or as a result of subsequent mechanical deformation or other causes are called *dislocations*. They may have a strong effect on the properties of the crystal.

Many properties of materials may depend to a great degree on the nature of the bond *between* the individual crystals than on the properties of the crystals themselves. As a result of the study of the influence of composition and structure on the properties of different materials, it has become possible to create new kinds of materials exhibiting novel properties." [3, p. 124-126]

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Contents

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КОНСПЕКТ ЛЕКЦИЙ ПО ХИМИИ

для студентов первого курса

Компьютерная верстка:
К. Голобродский
Д. Фирсов
Р. Сухобрус

План, 1997
Подписано в печать
Формат $60 \times 80\ 1/16$ Бум. офс. №2. Офс. печ.
Усл. печ. л. 6.5. Уч.-изд. л. 100 экз. Заказ 22
Цена свободная.

Харьковский авиационный институт
310070, Харьков, ул. Чкалова, 17