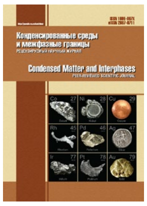

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Substances and the transformations they undergo: basic concepts

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Abstract

We formulated the specific features for the notions of substances and transformation of substances. A substance is a set of interacting particles characterised by the following parameters 1) composition, or the type and ratio of amounts of particles that form the substances, 2) the energy of their interactions, 3) their structure and, finally, 4) the size of particles (dispersion). Transformations of substances occur when these properties change. Such processes are called chemical reactions. To control the transformation of a substance from the thermodynamic point of view, we need to evaluate: 1. The possibility of spontaneous processes (without energy consumption). 2. The thermal effect of the chemical reaction. 3. The equilibrium composition of the reaction medium.

We solved these problems using a mathematical model based on the improved notions (substance, energy, work, supersaturation) and the known laws of thermodynamics.

Keywords: Substances, Transformation of substances, Thermodynamics, Energy, Work, Chemical reactions, Chemical equilibrium, Spontaneous process, Thermochemistry, Supersaturation

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1. Introduction

A notion is a set of specific properties and relations between the subjects under consideration that exists in our thinking as a thought. Words and phrases that describe notions are called terms. Like notes in music and words in people's conversations, notions form the basis of science. As new data are accumulated, sometimes we need to generalise scientific facts, improve the old ones, and introduce new notions, According to the decision of the "Third national meeting of heads of departments of inorganic chemistry" that took place between 9 and 12 October 2016 in Ivanovo, professors V. Zlomanov, P. Kazin, and A. Yatsenko of Lomonosov Moscow State University, and professor E. Rumyantsev of Ivanovo State University of Chemistry and Technology, were given the task of improving the basic notions of chemistry. The results of their work are presented in a brief glossary [1]. It does not replace the information in existing textbooks but complements them and expands knowledge in the field of chemistry. The glossary includes the most important notions at the modern level of comprehension of chemistry that allow defining the conditions required to control the transformation of substances based on thermodynamics. We will analyse the specifics of some notions related to substances and their transformations.

2. Chemistry and substance

Chemistry holds an important place among natural sciences. It is also of economic significance and it generally has an impact in our everyday life. Chemistry does not come to the fore in our lives. However, without chemistry, it would have been impossible to achieve many great things in this field and create new substances that are necessary for human life, such as materials for the production and transformation of energy, for creating vehicles, communication systems, food, medicines, clothing, etc. As chemistry is present everywhere, people often forget about it and underestimate some of its important notions. Chemistry is the science that deals with substances and the transformations they undergo. However, there is no clearly understanding of what substances actually are and what transformations they undergo. According to the philosophical definition of a substance as a form of matter or physical essence, it objectively exists but this definition does not allow the conditions required to control the composition, structure, and, consequently, the properties of substances to be determined. The notion of a substance can be specified based on the atomic structure model. **We will define substances (chemical) as a** set of interacting particles that are characterised by four features: 1) composition, or the type and ratio of amounts of particles forming the substance (atoms, molecules, ions), 2) energy of their interaction, 3) structure and, finally, 4) dispersion or, in other words, the size of particles. The specified features determine the physical and chemical properties of substance. It should be noted that the suggested definition of substances is newer and clearer as compared to those existing in academic and scientific papers.

3. Transformation of substances

When changes occur in the composition, structure, interaction energy, and size of particles of substances and, as a result, in their physical and chemical properties, these processes are called chemical reactions. Sometimes the processes of electron density redistribution between atomic nuclei are called chemical reactions, which is not really correct since the changes of all substance properties are not taken into account. Unlike nuclear reactions, in chemical reactions the atomic nuclei of substances do not change, although electrons and nuclei are redistributed.

First, we will analyse the specifics of substance properties, and then we will consider the thermodynamics of the transformation processes they undergo.

4. Substance features

Composition is a type and qualitative ratio of the particles of atoms, molecules, ions, etc., that substances are made of.

When characterising the composition, it is important to decide which substances should be considered pure. Pure substances are a relative notion which is associated with the functional applications of substances. For example, the properties of semiconductors are determined by the concentration of charge carriers, such as electrons and holes, and their mobility. The criterion of purity of semiconductors is the ratio between the required functional concentration of charge carriers and that determined by the properties of substances. For instance, when using a $Hg_{1-x}Cd_xTe$ solid solution to detect infra-red radiation, the concentration of uncompensated carriers should not exceed 10^{16} cm^{-3}. Therefore, only substances with a total concentration of carriers due to impurities, nonstoichiometry, etc. of less than 10^{16} cm^{-3}, or 10^{-4} at. % can be considered as pure.

***Energy** of the interaction of particles that form substances* is a quantitative measure of the movement and interaction between particles in a system that determines its ability to operate is the most important notion in all natural sciences. An **interaction** is a form of energy exchange that occurs when systems (substances) come into contact. There are electrical, magnetic, gravitational, weak, and strong interactions. Chemistry is limited by the analysis of electrostatic (and in some cases, magnetic) interactions between nuclei and electrons, atoms, and molecules. The energy of such interactions can be described using the Gibbs energy function $G = f(T, p, n_i)$, as its arguments or such natural variables as temperature T, pressure p, and the amount of moles of the components n_i can be measured and recorded in order to control chemical transformations. The change of Gibbs energy (ΔG) includes the enthalpy (ΔH) and the entropy (ΔS) components: $\Delta G = \Delta H - T\Delta S$. The first of them ($\Delta H$) describes the common chemical bond which occurs due to the electrostatic interaction between electrons and atomic nuclei. Depending on the distribution of electron density, there are different types of chemical bonds, including ionic, covalent, and metallic. The type of chemical bond determines the physical and chemical properties of substances. The significant role of the entropy component can be seen in complex cyclic compounds "without" chemical bonds, for example, in catenanes and rotaxanes. The molecules of these compounds consist of two or more cycles that put one through the other like chain links (Fig. 1). The interaction between atoms in cycles is determined by the covalent bond, that is by the value ΔH. The interaction between the same cycles is due to the entropy component ΔS. The molecules of the studied compounds undergo structural changes under the action of light and start rotating like a wind turbine blade in a strictly defined direction. Based on this effect, Jean-Pierre Sauvage (France), James Fraser Stoddart (USA), and Bernard Feringa (Netherlands) designed and manufactured molecular machines and received the 108th Nobel Prize for their work.

Molecular Borromean rings and cyclic DNAs are also examples of other compounds "without" chemical bonds.

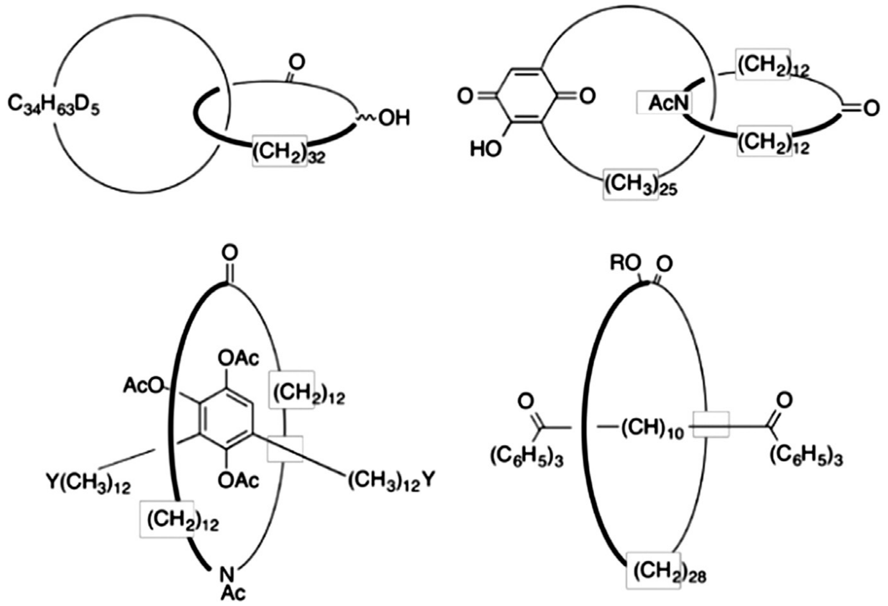

Fig. 1. The scheme of the structure of catenanes (top) and rotaxanes (bottom). Shill G. Catenanes, Rotaxanes, and Knots: transl. from English. M.: Mir, 1973. 211 p. (ill.: p. 202-208)

The interaction between particles in substances leads to the formation of a structure of short-range and long-range order in their spatial distribution.

Chemical and crystal chemical structure is a well-ordered spatial arrangement of particles that form substances. The properties of a crystal, such as the energy of the crystal lattice, as well as electrical, optical, chemical, and other properties, are determined by the composition and structure of the crystal. Different arrangement of the same particles in space, for example, of carbon atoms in diamonds and graphites, results in different properties, including the energy of the crystal lattice that determines the melting and boiling points, hardness, etc.

***Size*,** or the linear (geometric) size of the particles of substances, influences the ratio of the surface and volume energies. Substance particles with a size of 1–100 nm are called **nanoparticles**. Their surface and volume energies are compatible. This leads to the emergence of essentially new properties.

5. Thermodynamics of substance transformation

We study chemistry as a science in order to understand how to synthesise substances with the required functional properties. We can find the solution to this problem in chemical thermodynamics (we will call it thermodynamics from now on in this paper). The transformations themselves are determined by the kinetics of processes. ***Thermodynamics*** (from Greek θέρμη meaning "warmth" and δύναμις meaning "strength") studies the methods of transformation (and transmission) of energy. Thermodynamics has some special features because it focuses only on the macroscopic properties relating to a rather great amount of substances. What's more, it studies only equilibrium processes and it does not study processes over the course of time. The issues of non-equilibrium thermodynamics have been considered in [3].

What do we teachers have to know and what do we have to teach our students in order to control the transformation of substances? Thermodynamics provides the following answer to this question. We need to know how to evaluate the following:

1. The possibility of spontaneous occurrence of processes (without any ambient energy consumption).
2. The sign and value of the thermal effect of a chemical reaction.
3. The equilibrium composition of the reaction medium.

The answers to these questions can be given using a mathematical model based on the notions and laws of thermodynamics. Therefore, at first we will consider the basic concepts and laws of thermodynamics.

6. Basic concepts of thermodynamics

Thermodynamics is a study of ***systems***. Everything that is outside a system is called the ***environment***. The system and the environment can exchange energy and substances. A system that can exchange both substances and energy with the environment is called an ***open system***. If it is impossible for the system to exchange substances with the environment, such a system is called a ***closed*** system. In ***isolated*** systems there is no exchange of substances or energy with the environment.

The state of the system is determined by several variables. They are all interconnected. To make the construction of mathematical models easier, they are provisionally divided into independent variables and their functions. Similar to mathematics, the former are called *arguments* or *state coordinates*. There are two types of variables: *intensive* and *extensive*. Intensive parameters, such as temperature and pressure, reflect the individual properties of substances and do not depend on the quantity of substances. Extensive parameters describe a particular sample of substances and are proportional to their quantity. To determine their values, for example, volume or weight, we need to totalise them in all parts of the system. To determine the state of the system, we need at least one extensive variable among the coordinates (parameters).

The variables that describe the quantitative composition of the system take a special place among the coordinates that determine the state of the system. The minimal set of substances that are enough to characterise the composition of the system is called the ***components.*** To perform a definite qualitative and quantitative characterisation of the composition, they must satisfy the following requirements [2]: a) they must be independent, which means that it is impossible to obtain certain components from others, b) the concentration dependence of the substance properties must be fully described, c) the conditions of electrical neutrality and material balance in the system must be maintained.

Work is the form (method) of transmission of energy. For the work to be performed, the resistance of the external force F must be overcome. If the system is not affected by external forces, it does not perform work. The value of work δW is represented as the product of the overcomable force F on the change of dX of the corresponding coordinate X: $\delta W = FdX$. The symbol of variation δ stands for infinitely small amounts of work W. There are different types of work, such as mechanical, thermal, “chemical”, and so on. It should be noted that unlike internal energy, work is not a function of state, it depends on the course of the process. Work is measured in the same units as energy U. In the SI this unit is the joule (J). Sometimes the values of U and W are expressed in calories (cal). 1 cal = 4.1840 J.

Heat* is a form (**method) of transmission of energy from a more heated system to a less heated one through heat exchange, i.e. as a result of a chaotic collision of particles. Unlike thermodynamics, in thermochemistry heat is considered positive if it is released into the environment and negative if it is absorbed. If we consider temperature (T) as a force (measure of effect) and entropy (S) (the definition of which will be given in article 7) as a coordinate, then the product $TdS = \delta W_{\text{heat}}$ can be considered as ***heat work, or the amount of transmitted heat.

“Chemical work”[*] $\delta W_{\text{chem}} = \sum_i \mu_i dn_i$, W_{chem} is performed upon the transformation (***chemical reaction***) of a certain amount of moles (n_1) of one substance into n_2 moles of another substance. In this case, the chemical potential μ_i, acts as force F (see article 6.), while a change of the amount of moles (dn_i) acts as the change of coordinate X.

Chemical potential μ_i describes the “rate” of change in the internal energy U (enthalpy H, Helmholtz energy F, and Gibbs energy G) of the system that occurs when one mole of the i^{th} component is added to it (see article 6.) while the values of other arguments remain the same.

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,k\neq i}. \tag{1}$$

7. Basic laws of thermodynamics

The logic of the structure of notions and definitions of thermodynamics may seem difficult at first but it can be explained if we see how it works, for example, when solving the main problem of chemistry, which is predicting the result of the transformation of initial substances into products when the substances are provided in a certain ratio and placed under certain conditions. The mathematical model that allows solving the basic problems of thermodynamics can be constructed using the basic laws of thermodynamics.

The first law of thermodynamics is usually represented as follows:

$$dU = \delta Q + \delta W. \tag{2}$$

According to this law, the internal energy U of the isolated system is constant. In a non-isolated system it may change due to the fact that the environment performs work dW upon the system and transmits heat δQ to it. It should be noted that according to IUPAC, those[**] changes that increase the internal energy of the system are considered to be positive.

As it was mentioned previously, *heat* is a form **(**method) of transmission of energy through heat exchange, and the product of $TdS = \delta W_{\text{heat}}$ can be considered as ***heat work*** δW_{heat} or the amount of transmitted heat. Therefore, the first law concerning the constant internal energy of the system can be expressed as follows:

$$dU = \sum W_i, \tag{3}$$

i. e., due to changes in internal energy dU, the system can perform various types of work W_i.

As for the open systems, the first law of thermodynamics is represented as an equation (4):

$$dU = \delta Q + \delta W_{\text{mech}} + \sum \mu_i dn_i, \tag{4}$$

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[*] We use this notion with quotation marks to show that it is a relatively conditional notion since the transformation of substances includes not only chemical work but also heat and mechanical work.

[**] Sometimes another system of signs is used. For instance, if work is considered positive, it is performed by the system upon the environment.

where the latter sum is called "chemical work" (see article 6.). It describes the process of the transmission of substances between the system and its environment.

The first law of thermodynamics shows that processes may occur but it does not mention anything about their direction or which of the processes occur spontaneously. These issues are explained by the ***second law of thermodynamics***. For this purpose, a new variable, ***entropy*** *S*, is introduced. It is used as one of the parameters (coordinates) that determine the state of the system. It changes dS in case of a revertable process can be expressed as the ratio of heat effect δQ of the process to temperature T, and according to the recommendation of IUPAC, the value δQ is considered to be positive if the system obtains heat from the environment:

$$dS = \frac{\delta Q}{T}. \tag{5}$$

In SI, entropy (energy divided by temperature) is expressed as follows: $\mathrm{J \cdot K^{-1}}$. The sign and the value of entropy change determine the direction of the process. If the entropy increases $dS > 0$ in an isolated system, the process occurs spontaneously, which means that it is irreversible. The maximum of entropy and its constant state show that the system is in equilibrium.

What does ***entropy*** mean? We can answer this question using statistical thermodynamics. **Thermodynamic probability *w*** is used to evaluate the measure (value) of probability of a particular state. Its value equals the number of ways in which N particles can be placed in available microstates N_1, N_2, N_4, …, N_i *:

$$w = \frac{N!}{N_1!N_2!....N_i!}, \tag{6}$$

where the factorial sign stands for the product $N! = 1 \cdot 2 \cdot 3 \cdot \ldots \cdot N$ *and* $0! = 1$. To illustrate the notion of thermodynamic probability w, we will consider two macrostates** of a system consisting of six particles ($N = 6$) that can be distributed by three ($i = 3$) microstates (cells). Let us consider the first macrostate with all six particles in one cell. It is a case of thermodynamic probability $w_1 = \frac{6!}{6!0!0!} = 1$.

In the second macrostate, all six particles will be distributed evenly by three cells. The probability of the second macrostate equals $w_2 = \frac{6!}{2!2!2!} = 90$. It is obvious that the probability of an even distribution is 90 times higher as compared to an uneven distribution. According to L. Boltzmann, spontaneous processes occur when the final state is more probable than the initial one, in other words, when the final macrostate can be achieved with a larger number of microstates. Let us remember that a spontaneous process in an isolated system is characterised by increased entropy $dS > 0$.

Thermodynamic probability w is associated with entropy S in the following ratio (7):

$$S = k \ln w, \tag{7}$$

where k is the Boltzmann constant. Thus, we have explained the physical sense of entropy. Similar to thermodynamic probability, it is a **measure** of the system's tendency towards equilibrium. Increased entropy corresponds to the system's transformation into the most probable state.

As opposed to internal energy U, we can find an absolute value for entropy. It becomes possible when we use ***the third law of thermodynamics***, which is formulated as follows: at 0 K the entropy of an ideal crystal (the one without any structural violations or defects) is zero.

To construct a mathematical model that allows solving the main problems of thermodynamics, we need to choose the state function and the arguments that determine it, for example, $G = f(T, p, \text{composition})$. Then, we must analyse its form and determine its extremum coordinates (minimum and maximum values), and thus solve the specified problems. To choose the required function, we combined equations (J. Gibbs) (2), (4), and (5), representing the first and the second laws, into one fundamental equation (8).

$$dU = TdS - pdV + \sum \mu_i dn_i. \tag{8}$$

Equation (8) has two important features.

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* Microstate is the state of the system that is determined by the simultaneous specification of three coordinates x, y, z and three impulses p, or three products of mass m by the velocity vector: $\vec{p}_x = m\vec{v}_x$, $\vec{p}_y = m\vec{v}_y$, $\vec{p}_z = m\vec{v}_z$ of all the particles comprising the system.

** Macrostate is a state of the system consisting of a large number of particles.

1. Energy change dU is expressed through the sum of uniformly constructed products of forces F, represented by T, p, μ_i, by the changes of coordinates dS, dV, and dn_i. Each product represents work: the product of $TdS = W_{\text{heat}}$ represents heat work, the product of $pdV = W_{\text{mech}}$ represents mechanical work, and the product of $\Sigma\mu_i dn_i = W_{\text{chem}}$ represents "chemical" work. Thus, the first law of thermodynamics as the law of conservation of energy can be formulated as follows: internal energy U of the system is constant and it can be transformed into thermal, mechanical, chemical, and other types of work:

$$U = \Sigma W_i. \tag{3}$$

2. In equation (8) internal energy $\boldsymbol{U}$ acts as the function of arguments, such as entropy S, volume V, and number n_i of moles of the components. However, some of the arguments are not convenient to work with in practice. For example, it is impossible to measure and control entropy S, therefore, in order to use the arguments that can be measured and recorded as well as to solve practical problems, we introduced new functions that are related to internal energy:

enthalpy $H = U + pV$, (9)

Helmholtz energy $F = U - TS$, (10)

and ***Gibbs energy*** $G = H - TS$. (11).

Once the equations (9)–(11) were differentiated and dU changed with the expression (8) in the obtained ratios, we obtained new state functions $H = f(S, p, n_i)$, $F = f(T, V, n_i)$, and $G = f(T, p, n_i)$:

$$dH = TdS + Vdp + \sum \mu_i dn_i, \tag{12}$$

$$dF = -SdT - pdV + \sum \mu_i dn_i, \tag{13}$$

$$dG = -SdT + Vdp + \sum \mu_i dn_i. \tag{14}$$

The Gibbs energy function $G = f(T, p, n_i)$ is important for practical thermodynamic calculations, as its arguments, or natural variables, T, p, n_i in equation (14) can be measured and recorded in order to control chemical transformations.

Next, we will consider the application of equations (11)–(14) in the solution of three main problems of thermodynamics. Let us start with the first problem.

8. Possibility of spontaneous process flow (without consumption of any external energy)

If we change equation (8) so that entropy S becomes a state function and internal energy U, volume V, and the amount of moles of n_i components become arguments, that is, if $S = f(U, V, n_i)$, then the first sufficient condition for the spontaneous flow of the process is formulated as follows: if the entropy of an isolated system increases $(dS)_{U,V,n_i} > 0$, the process may occur spontaneously. In the state of equilibrium this function reaches its maximum and remains constant $(dS)_{U,V,n_i} = 0$.

The Gibbs energy function $G = f(T, p, n_i)$ can be used to evaluate the probability of a spontaneous process, as its arguments (or natural variables), such as temperature T, pressure p, and the amount of moles n_i, can be measured and recorded in order to control chemical transformations. Why does it happen? It happens due to the fact that spontaneous processes are those that can perform work W. If it is impossible, equilibrium $\Delta G = 0$ occurs. But when $\Delta G < 0$ with constant T, p, n_i, the system may perform "chemical" work of transformation of n_1 moles of initial substances into n_2 moles of final substances: $(\Delta G)_{p,T} = (W_{\text{chem}})^{\max}_{p,T} = \Sigma\mu_i dn_i$, and the process occurs spontaneously, $dn_2 > 0$. As the process occurs and the system reaches the equilibrium, its "performance" decreases.

9. Thermal effect of a chemical reaction. Thermochemistry

Since internal energies of products and initial substances are different, changes in energy occur during chemical transformations (chemical reactions). It may happen as a release or absorption of heat δQ and the performance of heat work. There is considerable heat in the reaction (see article 6), so it can be measured. ***Thermochemistry*** deals with the study of the heat of chemical reactions. The issues of thermochemistry are considered in detail in [3–5].

10. Calculation of equilibrium composition of the reaction medium. Chemical equilibrium

The most important task in chemistry is to determine the composition of an equilibrium mixture during the transformation of one substance into another. We will consider its solution at a constant temperature T = const based on the example of the interaction of ideal gases (reaction (15))*:

$$\mathrm{aA + bB = cC + dD}. \tag{15}$$

To solve this problem, let us assess the dependence of the change of Gibbs energy $\Delta_r G$ of reaction (15) on real conditions, including partial pressures p_i^* (composition), general pressure p, and temperature T. With the assumptions made, the chemical potential of each participant of reaction (15) can be expressed by equation (16):

$$\mu_i(p,T) = \mu_i^0(T) + RT\ln p_i^*, \tag{16}$$

where p_i^* is the specified pressure: $p_i^* = \dfrac{p_i}{p^0}$, where p^0 is 1 bar. Then the change of Gibbs energy $\Delta_r G$ of process (15) will be expressed as follows (17):

$$\begin{aligned}\Delta_r G &= \mathrm{c}\mu_\mathrm{C} + \mathrm{d}\mu_\mathrm{D} - \mathrm{a}\mu_\mathrm{A} - \mathrm{b}\mu_\mathrm{B} = \\ &= \mathrm{c}\mu_\mathrm{C}^0 + \mathrm{d}\mu_\mathrm{D}^0 - \mathrm{a}\mu_\mathrm{A}^0 - \mathrm{b}\mu_\mathrm{B}^0 + RT\ln\frac{p_\mathrm{C}^\mathrm{c} p_\mathrm{D}^\mathrm{d}}{p_\mathrm{A}^\mathrm{a} p_\mathrm{B}^\mathrm{b}} = \\ &= \Delta_r G^0 + RT\ln\frac{p_\mathrm{C}^\mathrm{c} p_\mathrm{D}^\mathrm{d}}{p_\mathrm{A}^\mathrm{a} p_\mathrm{B}^\mathrm{b}}.\end{aligned} \tag{17}$$

Expression (17) is called an **isotherm reaction equation.** The term isotherm stands for the equality of the temperatures during the initial and final states of the process. However, the temperature may change when the system transits from one state to another. The first summand in equation (17) is the change of standard Gibbs energy of reaction (15). With equilibrium $\Delta_r G = 0$, we determine that:

$$\Delta_r G^0 = -RT\ln\frac{p_\mathrm{C}^\mathrm{c} p_\mathrm{D}^\mathrm{d}}{p_\mathrm{A}^\mathrm{a} p_\mathrm{B}^\mathrm{b}}. \tag{18}$$

The symbol of the logarithm in the last expression is the ratio of the products of the equilibrium partial pressures of final and initial substances in reaction (15). This value is called the **equilibrium constant** of a reaction in the gaseous phase. It describes the depth of the process flow. If $K_p > 1$, then equilibrium (15) is shifted towards the products of the reaction and, vice versa, if $K_p < 1$, it is shifted towards the initial substances. The introduction of the K_p equilibrium constant allows changing equations (18) and (17) as follows:

$$\Delta_r G^0 = -RT\ln K_P, \tag{19}$$

$$\Delta_r G = -RT\ln K_P + RT\ln\frac{p_\mathrm{C}^\mathrm{c} p_\mathrm{D}^\mathrm{d}}{p_\mathrm{A}^\mathrm{a} p_\mathrm{B}^\mathrm{b}}. \tag{20}$$

The specified ratios are important for the solution of practical problems of thermodynamics, such as:

(1) Assessing the direction of the transformation process.

(2) Determining the equilibrium composition.

(3) Changing the composition of the equilibrium reaction mixture with variations in external conditions, including temperature, pressure, and the ratio of interacting substances.

These problems are solved in the following way:

1. The direction of the process can be assessed by the sign of $\Delta_r G$, if we know the equilibrium constant (or the standard thermodynamic properties of the process participants) and the partial pressures of the initial substances upon their mixing.

2. Without an experiment, we can determine the equilibrium composition of the mixture if there are reference thermodynamic data for the calculation of $\Delta_r G$.

3. The sign of the logarithm in expressions (17) and (20) stands for the ratio of the products of the current partial pressures that are recorded and controlled by the experimenter. Taking this into account as well as the known temperature and baric dependences of the equilibrium constants, it should be noted that equation (20) allows controlling the composition of the reaction mixture using external conditions.

Equation (20) has two important features:

a) If we change the ratio of the current partial pressures, we can evaluate the temperature when the sign changes from $\Delta_r G > 0$ to the condition of $\Delta_r G < 0$, i. e., when a non-spontaneous process becomes a spontaneous one.

b) The difference between the summands in equations (17) and (20) shows that the system deviates from equilibrium and it can be considered as **supersaturation**. It is a very important

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* Due to the amounts of substances A, B, C, and D, the decrease and the formation of different substances do not change the composition and the conditions of the system's existence.

feature, since a connection is established between thermodynamics and kinetics. For example, supersaturation values can help in assessing the rate of formation and growth of nuclei of a new phase, which is required for the synthesis of materials with the specified composition and properties.

Depending on the conditions of the process, the equilibrium constant can be expressed not only through partial pressures (activities) but also through other variables, for instance, through the mole fraction or molarity, which is studied in [3].

As it was mentioned before, the equilibrium of the process of substance transformation corresponds to the minimum of the Gibbs energy of the system, which corresponds to the condition of $\Delta_r G = 0$. Modern computational programs allow finding the minimum of the Gibbs energy of the system and, correspondingly, assessing the composition of the equilibrium reaction mixture for a large number of variables. This allows calculating chemical equilibria in general. To do this, we only need to specify the elemental composition of the system and indicate all possible substances that can be formed from the specified elements [3].

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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