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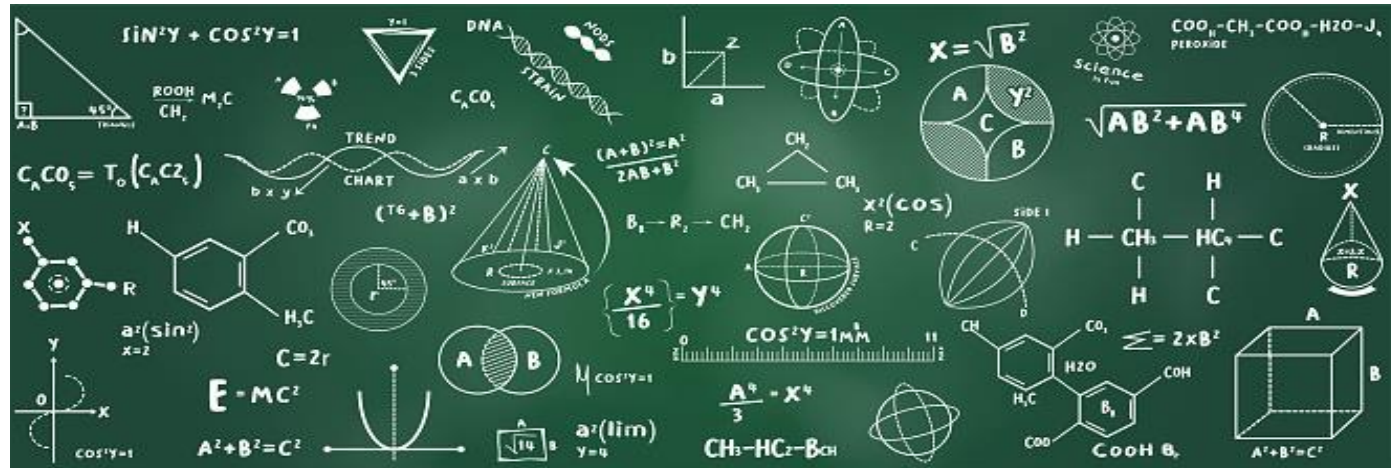
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Entropy in chemical kinetics and physics

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Entropic principles provide the basis for forming functional bonds between many values of chemical kinetics. The equilibrium sum of entropic components of the universal gas constant equal to R/2 has the direct mathematical connection with the geodesic angle tangent. A similar ratio of this parameter is obtained by Arrhenius graphs of reaction rate coefficient dependence on the temperature. When two entropic components move in one format, the equilibrium sum of their energies equals a half of the energy initial value. The established principles are also manifested in other regularities of physical chemistry, for example, by the activation energy in diffusion processes and kinetic energy equation.

Keywords- chemical kinetics, Arrhenius equation graphs, entropy, negentropy, gas constant, diffusion activation energy, kinetic energy equations.

CITATION OF THE ARTICLE

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I. INTRODUCTION

In the course of researches in various fields of chemical physics we can point out high self-organization and connection between many natural phenomena and processes [1],[2]. Thus, several constant and derivative values and parameters, having the mathematical connection but unclear formation nature between them, are successfully used in chemical kinetics. The same situation is also observed in other research areas. It is obvious that definite common principles and regularities act here.

A lot of studies are dedicated to the analysis of global processes in animate and inanimate systems. As an example, we can take the paper by G.R. Ivanitsky [3], in which he developed the method of chemical kinetics for these purposes.

This approach can definitely provide effective results because the nonlinear dynamics of chemical kinetics agrees with the principles of processes' directedness.

For example, it follows from Le Chatelier principle:

"With the external action on the system being in equilibrium, the equilibrium will shift in the direction of the process, which counteracts this action".

It is known that the notion of entropy arising from the second law of thermodynamics is the criterion of the process directedness and degree of the system irregularity. Thus, the problem of multidimensional manifestation of the notion of entropy is also of the considerable interest. Therefore, the attempt to explain the abovementioned problems from the point of concepts on the gradient of directedness of physical-chemical processes with changing entropic components is made in this study.

II. INITIAL PRINCIPLES[4]

The character of the change in the value of potential energy (ΔU) by its sign for different potential fields was analyzed [1] (Table 1).

It was found out that the values of $-\Delta U$ and, consequently, $+\delta A$ (positive work) correspond to interactions proceeding along the potential gradient, and $+\Delta U$ and $-\delta A$ (negative work) take place during the interactions against the potential gradient.

Table 1 – Directedness of the interaction processes

No	Systems	Type of potential field	Process	U	r_2/r_1 (x_2/x_1)	U_2/U_1	Sign ΔU	Sign δA	Process directedness in potential field
1	opposite electrical charges	electrostatic	attraction	$-k\dfrac{q_1q_2}{r}$	$r_2 < r_1$	$U_2 > U_1$	-	+	along the gradient
			repulsion	$-k\dfrac{q_1q_2}{r}$	$r_2 > r_1$	$U_2 < U_1$	+	-	against the gradient
2	similar electrical charges	electrostatic	attraction	$k\dfrac{q_1q_2}{r}$	$r_2 < r_1$	$U_2 > U_1$	+	-	against the gradient
			repulsion	$k\dfrac{q_1q_2}{r}$	$r_2 > r_1$	$U_2 < U_1$	-	+	along the gradient
3	elementary masses m_1 and m_2	gravitational	attraction	$-\gamma\dfrac{m_1m_2}{r}$	$r_2 < r_1$	$U_2 > U_1$	-	+	along the gradient
			repulsion	$-\gamma\dfrac{m_1m_2}{r}$	$r_2 > r_1$	$U_2 < U_1$	+	-	against the gradient
4	spring deformation	field of elastic forces	compression	$k\dfrac{\Delta x^2}{2}$	$x_2 < x_1$	$U_2 > U_1$	+	-	against the gradient
			extension	$k\dfrac{\Delta x^2}{2}$	$x_2 > x_1$	$U_2 > U_1$	+	-	against the gradient
5	Photo effect	electrostatic	repulsion	$k\dfrac{q_1q_2}{r}$	$r_2 > r_1$	$U_2 < U_1$	-	+	along the gradient

Therefore, after analyzing the first law of thermodynamics, we have the following [4]:

1. In the systems in which the interaction proceeds along the potential gradient (positive work), the resultant potential energy, as well as the reduced mass are found based on the principle of adding reciprocals of corresponding values of subsystems. This is a corpuscular process, in which entropy can serve as the theoretical concept.

2. In the systems in which the interactions proceed against the potential gradient (negative work), the algebraic addition of their masses, as well as the corresponding energies of subsystems is performed. This is a wave process, in which negentropy can serve as the theoretical concept.

3. The resonance stationary state of the systems is fulfilled under the condition of equality of degrees of their corpuscular and wave interactions. In thermodynamics of open systems the entropy products in stationary state are completely compensated by the negentropy flow.

4. All phenomena and processes in nature and world, including a human, machines, economics and ecology proceed only in two energy directions: either along the force field gradient with minimum energy input, or against the gradient with maximum energy input. The first direction corresponds to the notion of entropy and the second – to the notion of negentropy (negative entropy). In the dynamics of processes both phenomena are interrelated and complement each other.

III. ENTROPIC NOMOGRAMS

Heisenberg and Dirac [5] proposed the exchange Hamiltonian to evaluate the degree of structural interactions derived in the assumption on direct overlapping of wave functions of interacting centers:

$$\overline{H} = -I_0 S_1 S_2 \; ,$$

Where: $\overline{H}$ – spin operator of isotropic exchange interaction for a pair of atoms, I_0 – exchange constant, S_1 and S_2 – overlapping integrals of wave functions.
Therefore, in this approach the overlapping integrals of wave functions are modeled through the value of relative difference of energy parameters of interacting centers – coefficient α (in %). Such parameter is a direct characteristic of entropic equilibrium degree in the system.

Applying the reliable experimental data we obtain the nomogram of structural interaction degree dependence (ρ in %) on coefficient α in %, the same for a wide range of structures (Fig. 1). Here, the values of α from 0 to 5 correspond to the conditions of entropic equilibrium, at which ρ=100%. This type of nomogram,

as well as its dissymmetric variant (the figure is not given) provide the possibility to evaluate the degree and direction of the structural interactions of phase formation, isomorphism and solubility processes in multiple systems, including molecular ones.

The less is α, the higher is the interaction wave component degree. In Fig. 1 the increase of α characterizes the increase in corpuscular and electrostatic properties in microsystems (entropic curve). Thus, the notion of entropy is numerically modeled via coefficient α and negentropy – via 1/ α.
In general case, during the translational motion of the system of two similar vectors $(\vec{R})$ with the phase difference of 90° their resultant is as follows:

$$\vec{C} = 2^{1/2}\vec{R}, \text{ where for the given angle tg } 45°=1$$

If the rotational or spiral motion takes place, the vector $(\vec{C})$ becomes a tangent vector and forms the rotation angle, for which:

$$tg\varphi = C/R = 2^{1/2}, \dots\dots\dots\dots\dots\dots\dots (1)$$

Where φ – geodesic angle equal to 54.733°. This is the angle at which a silkworm winds a silk thread onto the base.
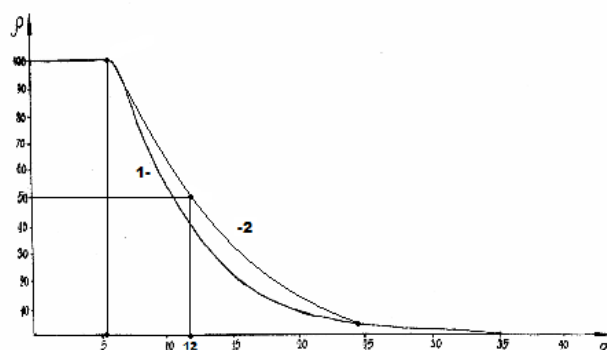

Fig. 1. Nomogram of the dependence of structural interaction degree (ρ) on coefficient α

At ρ=50% the system has the equilibrium entropic state, for which the following equation is fulfilled:

$$\ln(\tfrac{\rho}{\alpha}) = tg\,\varphi \quad \dots\dots\dots\dots\dots\dots (2)$$

When calculating by this equation, we get α=12.1% that corresponds to the given nomogram.

Many phenomena and processes in nature, engineering and even economics are described by the same graphs called S-curves. Such S-curves and initial nomograms are graphical characteristics of non-equilibrium dynamics of changes in entropic components, for example, Lorentz curve [6] of spatial and time dependence (the figure is not given).

IV. ENTROPY AND UNIVERSAL GAS CONSTANT

The gas constant is called universal by its diversified application in chemical kinetics. Thus, according to the gas state equation R equals the work for expanding 1 mole of gas with temperature increase by 1º K. And in a chemical reaction R equals the difference of molecular heat capacities at constant pressure and constant gas volume.

By Boltzmann equation:

$$S=klnw ……………………………..(3)$$

Where S – entropy, k – Boltzmann's constant, w – number of available states.

Substituting lnw for Avogadro's number (A) we have:

$$S=kA=R …………………………(3a).$$

That is, the gas constant can be considered as the parameter with the entropic component maximum value.

But in an open thermodynamic system the negentropy, which numerically equals the entropy, is formed to compensate its growth. Their algebraic sum in the equilibrium state equals R/2 by the reverse addition principle. Similarly to the equation (2) by the entropic nomogram we have:

$$\ln(\tfrac{R}{2}) \approx tg\,\varphi ……………………..(4).$$

The quantum correction $a_0 = 1.00233$ can be introduced to correct the equation (4):

$$\ln\left(\tfrac{R}{2}\right) = a_0^2 tg\,\varphi \ …………………. (4a).$$

Parameter R/2 is the equilibrium entropic component equal to 50% from the maximum R value. By the equations (2 and 4) and the nomogram we have:

$$ln\left(\tfrac{R}{2}\right) \approx ln\left(\tfrac{50}{121}\right) \approx tg\,\varphi = a_0^2 tg\,\varphi ……… (5)$$

In numbers: $1.4248 \left(\frac{J}{mole\cdot K}\right)$; 1.4188; 1.4142, 1.4208.

Only the percentage ratio of the values and international system of units is used in these equations for R/2. Thus, the equations (5) provide the direct physical-chemical and natural bond between the total entropic R/2 value and entropic ratios in dynamics of rotational or spiral motion.

V. ENTROPY BY ARRHENIUS GRAPH EQUATIONS

The average temperature values of the experiment are often used in studies in chemical kinetics. Such technique is used, for example, to evaluate the activation energy and pre-exponential factor in Arrhenius equation. It can be assumed that this approach is equivalent to the application of a similar R/2 value.

Therefore, the dependence similar to the equation (5) should be also demonstrated by the graphs of Arrhenius equation (5).

For this, we will consider the non-logarithmic variant of the graph [7] of the reaction rate coefficient (K) dependence upon the temperature (T).
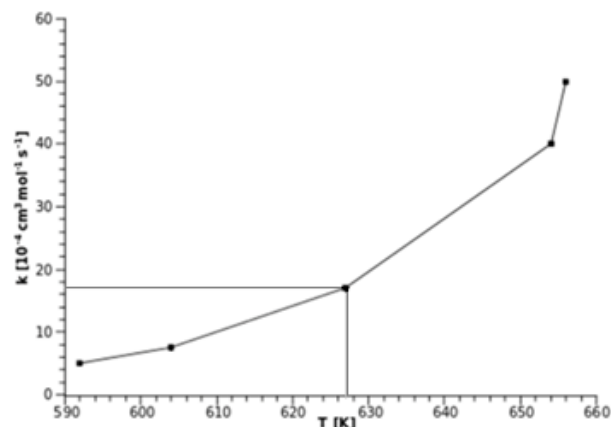

Fig 2. The graph of the reaction rate coefficient (K) dependence upon the temperature (T)

This graph is similar to S-curve with negentropy on X-axis. There is a point in the middle of the graph, with the temperature of approximately 628 K on X-axis. It equals the average temperature in the experiment, i.e. 50% from its maximum value. It corresponds to $K=17\cdot10^{-4}$ on Y-axis.

The value of 50% can be applied in the calculations of entropic ratio but only for the graph negentropic component. And for the rate coefficient it is necessary to have its value in percent for relative values.

For this, we will apply the correlation of coefficient K in Fig. 2 with the value of α on the nomogram. By the ratio of their maximum values the correlation coefficient equals $35/50\approx0.7$, therefore: $17\cdot10^{-4}\cdot0.7\approx11.9\alpha\%$. We get the equation similar to the equation (5):

$$ln\left(\tfrac{50}{119}\right) \approx tg\,\varphi ……………………(6)$$

Thus, the entropic equilibrium value of R/2 is the energy parameter of forming functional dependencies in many phenomena and processes, for example, in activation energies of diffusion and self-diffusion.

VI. EQUATION OF ACTIVATION ENERGY OF DIFFUSION AND SELF-DIFFUSION

Taking into account the entropy principles, we obtain the resultant value of the effective energy of the paired interaction of atoms *A* and *B*, identical to the activation energy of diffusion process, as the sum of the reciprocals of P-parameters:

$$\frac{1}{E_a} = 2\left[\left(\frac{r_i n}{P_o}\right)_A + \left(\frac{r_i n}{P_o}\right)_B\right], \quad \cdots\cdots\cdots\cdots (7)$$

Where E_a – activation energy of the diffusion process of atom *B* in the environment of atoms *A*; *n* – number of all valence electrons or the number of valence electrons of a specific atom, most distant from the nucleus.

Digit 2 in these equations provides the average equilibrium sum by each atom. Here $\frac{r}{P_0} = \frac{1}{P_E}$, where P_E – spatial-energy parameter numerically equal to the effective energy of structural interactions.

P-parameter was obtained [8] by applying principles of adding entropic components of oppositely charged systems (principle of adding reciprocals). In this case, this is the energy of atomic nucleus and orbital energy of electrons.

P-parameter was obtained by applying the entropic principles of adding entropic components of oppositely charged systems (the principle of adding reciprocals). In our case, these are the energy of atom nucleus and orbital energy of electrons.

During the diffusion of atom *B* in the environment with atoms *B* homogeneous in composition and similar to it, E_a takes the meaning of activation energy of atom *B* self-diffusion. Based on (7) it is defined as follows:

$$E_{ac} = \frac{P_o}{4 r_i n}, \qquad (8)$$

Here, one digit 2 in the denominator takes into account the average equilibrium sum for each atom. Another digit 2 in the denominator corresponds to the principle of adding reciprocals of two similar P-parameters.

The comparison of the calculation results with the experimental data demonstrated their good agreement [8].

VII. ON KINETIC ENERGY EQUATIONS

The equation of kinetic energy is also of interest in the view of applying entropic principles:

$$E = \frac{mv^2}{2} \quad \cdots\cdots\cdots\cdots\cdots(9),$$

Where m – body or particle mass, v – its motion speed. Kinetic energy is the energy of motion.

In classical mechanics every motion in one format comprises two components: one along the force field, another one – an inertial part of the motion. Thus, two acceleration types are registered in the rotational motion: tangential acceleration directed tangentially towards the trajectory (negentropy), and centripetal one directed towards the motion center (entropy).

It can be assumed that by analogy with the gas constant the maximum kinetic energy of each motion component equals:

$$E_E = mv^2 \quad \cdots\cdots\cdots\cdots (10).$$

Thus, the centripetal force equation does not have the coefficient 1/2: $F = \frac{mv^2}{r}$,
Where r – rotation radius.

And the kinetic energy corresponding to it can be written as in the formula (10).

The equation (10) is performed similarly for the kinetic energy with tangential acceleration. But during the motion in one format the equilibrium sum of entropic components will have the coefficient 1/2 by the equation (9).

This paper did not take into account entropic principles as applicable to relativistic mechanics but they also work that is demonstrated by the fundamental Einstein equation of mass and energy equivalence:

$$E = mc^2,$$

Where c – speed of light.

VIII. CONCLUSIONS

1. Entropic principles provide the basis for forming functional bonds between many values of chemical kinetics.

2. The equilibrium sum of entropic components of the universal gas constant equal to R/2 has the direct mathematical connection with the geodesic angle tangent.

3. A similar ratio of this parameter is obtained by Arrhenius graphs of reaction rate coefficient dependence on the temperature.

4. When two entropic components move in one format, the equilibrium sum of their energies equals a half of the energy initial value.

5. The established principles are also manifested in other regularities of physical chemistry, for example, by the activation energy in diffusion processes and kinetic energy equation.

IX. REFERENCES

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