Non-Equilibrium Thermodynamics with Linear Modes in Tribocouplings (Part III)

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Abstract

A decrease in the surface temperature of friction pairs contributes to the intensification of the exothermic reaction with the dissociation of ions of the surface layer of the polymer lining. The electrons formed in the electrolyte are strongly oriented and their effective dipole moment is large, which leads to the inversion of many currents according to the "polymer - metal" scheme; triboadsorbed gas is adsorbed by the working surface of the metal, after which its chemical transformations occur; at the speed of tribosorption and triboreaction of the same order, the chemical reaction is shifted towards the working surface of the metal friction element; a change in the degree of dispersity and compactness of the phases that appear in the upper layer of the polymer lining, containing amorphous and vitreous substances, significantly affects their chemical activity; in this case, it is necessary to take into account the change in the Gibbs energy of the surface layer of the polymer lining, which is associated with its temperature and heat content, which affect the direction of shifting the equilibrium of the chemical reaction. When evaluating chemical reactions in tribocouples of friction pairs, the following were determined mathematically: entropy production at their elementary stages; forward and reverse reaction rates, equilibrium and affinity parameters with access to the Onsager relations.

Keywords: *braking device, friction pair, friction lining, chemical reactions and their sequences.*

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Triboqovşaqların xətti rejimli qeyri-müvazinat termodinamikası (III hissə)

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Xülasə

Məqalədə, əyləc qurğularının triboqovşaqlarında xətti rejimli qeyri-müvazinat termodinamikasının tədqiqinin nəticələri təqdim olunub. Sürtünmə cütlərinin səthi temperaturunun azalması polimer kündənin səth təbəqəsinin ionlarının dissosiasiyası ilə ekzotermik reaksiyanın güclənməsinə kömək edir. Elektrolitdə əmələ gələn elektronlar güclü oriyentasiyalıdır və onların effektiv dipol momenti böyükdür ki, bu da “polimer-metal” sxeminə görə bir çox cərəyanların inversiyasına gətirib çıxarır; triboadsorbsiya edilmiş qaz metalın işçi səthi tərəfindən adsorbsiya olunur ki, bunun da nəticəsində, kimyəvi çevrilmələr baş verir; eyni qaydada, tribosorbsiya sürəti və triboreaksiya zamanı kimyəvi reaksiya metal sürtünmə elementinin işçi səthinə doğru sürüşür; amorf və şüşəvari maddələri ehtiva edən polimer kündənin üst təbəqəsində əmələ gələn fazaların disperslik və yığcamlıq dərəcəsinin dəyişməsi, onların kimyəvi fəaliyyətinə əhəmiyyətli dərəcədə təsir göstərir. Bu zaman polimer kündənin səth təbəqəsinin Gibbs enerjisinin dəyişməsini nəzərə almaq lazımdır, hansı ki, onun kimyəvi reaksiyanın tarazlığının yerdəyişmə istiqamətinə təsir edən temperatur və istilik tərkibi ilə bağlıdır. Sürtünmə cütlərinin triboqovşaqlarında kimyəvi reaksiyalar qiymətləndirilərkən onların elementar mərhələlərində entropiya istehsalı və Onsager nisbətlərinə yaxınlığı ilə birbaşa və əks reaksiya sürətləri, müvazinat parametrləri riyazi yolla müəyyən edilib.

Açar sözlər: *əyləc qurğuları, sürtünmə cütü, friksion kündə, kimyəvi reaksiyalar və onların ardıcıllıqları.*

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Неравновесная термодинамика с линейными режимами в трибосопряжениях (часть III)

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Аннотация

Приводятся результаты исследования неравновесной термодинамики с линейными режимами в трибосопряжениях тормозных устройств. Снижение поверхностной температуры пар трения способствует интенсификации экзотермической реакции с диссоциацией ионов поверхностного слоя полимерной накладки. Образующиеся в электролите электроны сильно ориентированы и их эффективный дипольный момент велик, что ведет к инверсии множества токов по схеме «полимер – металл»; трибоадсорбированный газ адсорбируется рабочей поверхностью металла, после чего происходят его химические превращения; при скорости трибососрбции и триборeакции одного порядка химическая реакция смещается в сторону рабочей поверхности металлического элемента трения; изменение степени дисперсности и компактности фаз, возникающих в верхнем слое полимерной накладки, содержащих аморфные и стекловидные вещества, существенно влияет на их химическую активность; при этом необходимо учитывать изменение энергии Гиббса поверхностного слоя полимерной накладки, которое связано с его температурой и теплосодержанием, влияющие на направление смещения равновесия химической реакции. При оценке химических реакций в трибосопряжениях пар трения математическим путем определялось: производства энтропии на элементарных их стадиях; скорости прямой и обратной реакции, параметры равновесия и сродства с выходом на соотношения Онсагера.

Ключевые слова: *тормозное устройство, пара трения, фрикционная накладка, химические реакции и их последовательности.*

Introduction

Irreversible processes, phenomena and effects accompany the electrothermomechanical frictional interaction of brake friction pairs.

The distinction between reversible and irreversible processes first entered thermodynamics through the concept of "entropy". The relationship between the irreversible processes occurring in tribo-couples of friction pairs, for example, between chemical reactions and thermal conductivity, on the one hand, and the rate of entropy increase, on the other, remains hidden from researchers of thermodynamics. Strongly non-equilibrium situations lead to new space-time structures. For this reason, the limitation of equilibrium situations, some essential features of the behavior of matter and energy. An example is the role of fluctuations. The atomic structure of matter leads to fluctuations. But at or near equilibrium, these fluctuations do not have any important consequences.

Indeed, a characteristic feature of equilibrium thermodynamics is the existence of principles of extrema. For isolated systems, entropy increases and therefore reaches a maximum at equilibrium. In other situations (for example, at constant temperature) there are fluctuations called thermodynamic potentials, which also have extremes (maxima or minima) in equilibrium.

State of the problem

The materials of the article [1] refer to the testing technique used to study the processes of tribocracking of friction pairs. These processes are accompanied by the release of gas-vapor mixtures and water, which, at high temperatures exceeding the allowable for polymer lining materials, intensify the hydrogen wear of the working elements of friction pairs. According to the results of studies of tribocracking of contact spots of microprotrusions of metal-polymer friction pairs, their energy load was estimated taking into account the redox processes occurring on the working surfaces. Regularities have been established for changing the dynamic coefficient of friction depending on the energy load of metal-polymer friction pairs exposed to electric, thermal and chemical fields. It is shown that tribocracking has a complex tribochemical nature with burnout of formaldehyde resin from the surface layer of the polymer lining. This process is accompanied by the release of water, hydrogen, oxygen and other gas mixtures. The article [2] gives an analysis and synthesis of thermoelectric processes characterizing the electrothermomechanical frictional interactions of friction pairs of braking devices. The upper layer of the polymer lining is isolated at temperatures above the allowable for its material, when the cracking process begins. Thermokinetic models of the interaction of a metallic friction element during its operation in various media are considered. The influence of surface and bulk temperatures, specific loads, coefficient of mutual overlap of friction pairs, the ratio between the amount of reagents, the presence of inert gases and the type of reactions on the rate of chemical reactions during the cracking process in the upper layer of polymer linings of friction units of brake devices has been established. It is shown that when estimating the equilibrium of a chemical reaction, it is necessary to take into account the change in the Gibbs energy. Non-equilibrium tribology in friction friction pairs of brake devices is expressed in a continuous change in internal and external operational parameters in their surface and near-surface layers during electrothermomechanical friction [3]. It is known that in order to find equilibrium conditions, it is necessary to determine the minimum value of the desired function, and any variables in the system can change, except for fixed ones [4]. If we take the Gibbs energy as an equilibrium criterion, then we should find its minimum, assuming that it is not temperature and pressure that change in the system, but other parameters (for example, concentration) of the substance. Then the Gibbs energy of the system will decrease until it reaches a minimum due to the occurrence of chemical reactions. Similar reasoning is applicable in other cases [5]. The number of dependencies linking various quantities and parameters is qualitatively and quantitatively large. In this publication, we consider some of them and highlight the principles of reciprocity and symmetry using the Onsager relations [6]. The main issues of the article: the influence of various factors on the cracking process in the upper layers of friction linings; chemical reactions in tribocouplings; linearity of successive reactions in tribocouplings; the discussion of the results [7-9].

Objective – substantiation of the possibility of using non-equilibrium thermodynamics with linear regimes in triboconjugation of friction pairs of brakes.

Let us analyze the influence of various factors on the rate of chemical reactions during the cracking process occurring in the surface layers of polymer linings of brake friction units. Among the factors, we single out: surface and bulk temperatures, specific loads, coefficient of mutual overlap of friction pairs, the ratio between the amount of reagents, the presence of inert gases, and the type of reaction [10].

An increase in the surface temperature of the metal-polymer friction pair increases the yield of endothermic reaction products. The more intense the change in entropy ($\varDelta H$) of the upper layer of the polymer lining, the faster the equilibrium constant increases with increasing temperature and, consequently, the yield of reaction products. The reaction during electrothermomechanical friction is accompanied by the release of heat, the temperature drops. In this regard, in accordance with the principle of van't Hoff's movable equilibrium, elastic-plastic deformation of the microprotrusions of the metal friction element occurs. A decrease in the surface temperature of a friction pair favors the passage of an exothermic reaction (in particular, dissociation). With an increase in specific loads p in a friction pair, the temperature T increases, the composition of the equilibrium system changes, and the coefficient also changes with it $K_\nu(K_\vartheta = \varphi(t, p))$.

According to the equation $\varDelta G = \varDelta T - T\varDelta S$ (where $\varDelta G$ is Gibbs energy change; T – temperature; $\varDelta S$ – entropy change) the effect of temperature can also be judged by the sign $\varDelta S$: at $\varDelta S > 0$ heating favors the process $\varDelta S < 0$ – vice versa. Both criteria ($\varDelta H$ and $\varDelta S$) lead to similar results, since we are talking about the effect of T on the thermodynamic equilibrium of the tribosystem, when $\varDelta G = 0$. At $T \neq 0$ fair equality $\varDelta H = T\varDelta S$. Expression sign $\varDelta S(\varDelta \mathrm{H})$ determines the direction of equilibrium shift, its absolute value $\varDelta S(\varDelta \mathrm{H})$ – degree of displacement. It is often easier to focus on ΔS than on ΔH, since the sign of ΔS is often easier to determine than the sign of ΔH.

The nature of the influence of pressure on the equilibrium yield, in accordance with the dependence given in [11], is determined by the sign of the difference in the number of moles of gaseous reagents $\varDelta n$ and the dependence of K_γ on pressure [12, 13].

If the absolute value of Δn is large, then the first factor is decisive; at $\varDelta n>0$, an increase in pressure adversely affects the intensity of the yield of reaction products, and at $\varDelta n < 0$, it is favorable. During cracking of the upper layer of the polymer lining, an increase in pressure leads to a decrease in the yield of gaseous products, including unsaturated hydrocarbons that combine with hydrogen. When $\Delta n=0$, the effect of pressure on thermodynamic equilibrium is determined only by the dependence of K_γ on pressure, and it is not possible to establish it in a general form. However, it is quite obvious that the influence of pressure on K_γ is significant only at high pressures, when the difference in the compressibility of different gases becomes more significant.

When $\Delta n=0$, a change in pressure shifts the equilibrium. But this is a seeming contradiction to Le Chatelier's principle, since the effect of pressure is determined by the sign of the change in volume. At low pressures, the signs of ΔV and Δn coincide, at high pressures $\Delta V \neq 0$ (this possibility has to be taken into account also in cases where the absolute value of Δn is small). For example, if for the reaction $CO_2 + H_2 = CO + H_2O$ (g) at $T = 90°C$.

$$\left(K_\gamma\right)_{p=1} = \frac{\gamma_{CO}\gamma_{H_20}}{\gamma_{CO_2}\gamma_{H_2}} = \frac{1\cdot1}{1\cdot1} = 1{,}0\ ;$$

then

$$\left(K_\gamma\right)_{p=50} = \frac{1{,}26\cdot0{,}76}{1{,}15\cdot1{,}12} = 0{,}74\ ,$$

those the equilibrium of the reaction shifts in the direction of formation CO and H_2O (g) (displacement due to steam condensation is excluded, since $\left(T_{кр_{H_2O}}\right) < 90$ °C).

The influence of P on γ_i sometimes has to be taken into account even at low pressures, especially if the reaction proceeds without a change in volume at the beginning of the electrothermomechanical frictional interaction of microprotrusions of friction pairs. In this case, the change in output can be caused by a relatively small change in p. The calculation of such an equilibrium should be carried out more carefully than for cases with $\Delta n \neq 0$, when by a slight change in pressure it is easy to shift the equilibrium in the desired direction and thereby “correct” the calculations.

A change in the degree of dispersity and compactness of the phases in the upper layer of the polymer lining has a significant effect on the chemical activity of its substances. Therefore, when calculating the equilibrium of reactions involving finely crystalline, amorphous, and glassy substances, it is necessary to take into account the additional change in the Gibbs energy $dG_{sur} = \sum(\sigma_i\omega_i)$ (where σ_i – surface tension of the side surfaces of microprotrusions of friction pairs; ω_i – i-th thermodynamic probability), and the equilibrium satisfies the condition $dG + dG_{sur} = 0$ (where dG – change in the Gibbs energy without taking into account the considered factor).

Since the surface tension during the course of the reaction can be considered constant, the change in the Gibbs energy caused by varying the size of all microprotrusion interfaces is equal to:
$dG_{sur} = \sum\sigma_i \Delta\omega_i = \Delta H_{sur} - T\Delta S_{sur} = RTln(K_\alpha / K_a)$, where R – universal gas constant; K_α, K_a is the chemical equilibrium constant and its values, taking into account the effect of surface energy; ΔH_{sur} and ΔS_{sur} – change in enthalpy and entropy per unit surface area per mole of a given phase.

To obtain the maximum yield of reaction products from the top layer of the lining during electrothermomechanical frictional interaction with a metal friction element, a stoichiometric mixture of starting materials is needed. To achieve the maximum degree of the transformation reaction, an excess of starting materials is necessary. Therefore, if the consumption of one of them is limited for operational reasons, then an increase in the initial concentration of other reagents increases the number of moles of the resulting products and, thereby, the degree of the reaction. In this case, one should take into account the ease of removal of the unreacted excess of reagents from the resulting mixture from the contact gap of friction pairs due to washing them with circulating air flows.

An increase in the degree of conversion can also be achieved if the reaction products are removed from one zone by binding them into poorly dissociated, hardly soluble or non-volatile substances. This approach is quite rational in view of the fact that there is no need for a large excess of the reagent. So, if during the formation of CO_2 without changing the partial pressure of water vapor located between the microprotrusions of the contact gap of friction pairs, then with a decrease in the concentration of this gas, the mixture will be enriched with hydrogen [5].

The presence of reaction products in the initial mixture leads to a decrease in the degree of conversion of the upper layer of the polymer lining. Consider the influence of inert gases (Ar – argon, Ne – neon, He – helium, Kr – krypton, Xe – xenon, Rn – radon) [5] at the beginning and at the end of electrothermomechanical friction, when for some time it can be assumed that the specific loads in the friction pair are constant (p = const). Inert gases act as a diluent for other gases (H_2, O_2, N_2, CO и CO_2) at the beginning of braking, located in the intercontact gap. Towards the end of deceleration, the contact gap decreases as the specific load increases and the effect of dilution with inert gases decreases. A good means of removing inert gases from the contact gap is to purge it with ambient air.

Therefore, for chemical cracking reactions of the upper layer of the polymer lining, which proceed with a decrease in the volume of evolved gases, the effect of dilution with inert gases is undesirable. With an increase in the volume of a mixture diluted with inert gases, the degree of reaction proceeds.

The simplest example of reactions in which one of the reacting components is a solid is probably the dissolution of the surface and near-surface layer of a polymer lining during frictional interaction with a metal element at surface-volume temperatures above 350 °C. In this case, surface processes occurring at a rate directly proportional to the specific surface of the polymer lining. The rate-determining stage of the dissolution process can be either a chemical reaction on the surface or the diffusion of a substance from the surface layer, which is discussed in the materials of the second part of the article.

Let us dwell on the Onsager relations as applied to chemical reactions. This is due to the fact that the implementation of the principle of detailed balance, or microscopic reversibility, inevitably leads to Onsager's relations. The main problem is to determine the relationship between the Onsager coefficients and the experimentally established reaction rate constants L_{ij}.

The production of entropy due to chemical reactions is determined by the dependence [6]:

$$S = \sum_k \frac{A_k}{T}\left(\frac{d\xi_k}{dt}\right) = \sum_k \frac{A_k}{T}\upsilon_k \qquad (1)$$

where υ_k - k-th reaction rate. Here the reaction rates are defined in unit volume. In this case, the thermodynamic forces are defined as $F_k = (A_k/T)$, and streams like $J_k = \upsilon_k$. It is known that for chemical reactions that can be defined as elementary steps, the rate υ and affinity A can be related to the forward and reverse reactions by the following relationships:

$$\upsilon_k = \left(R_{kf} - R_{kr}\right); \qquad (2)$$

$$A_k = RT\ln\left(\frac{R_{kf}}{R_{kr}}\right), \qquad (3)$$

where R_{kf} and R_{kr} – rates of direct and reverse *k*-th reaction, *R* – gas constant.

Using (2) and (3), the speed υ_k can be imagined as

$$\upsilon_k = R_{kf}\left(1-e^{A_k/RT}\right) \tag{4}$$

The last expression serves to establish linear relationships near thermodynamic equilibrium. It is believed that (4) is valid only for the elementary stage. Note that (3) contains the principle of detailed equilibrium, or microscopic reversibility, according to which, in equilibrium, the rates of forward and reverse reactions of each elementary stage are equal (which leads to the Onsager reciprocity relations). Besides, lim $A_k \to \infty$ means that the speed is completely due to the direct reaction.

Since the coefficient R_f has yet to be established, equation (4) does not determine the reaction rate υ_k as a function of the A_k affinity. There is no general thermodynamic relation between rates and affinity. Reaction rates depend on many non-thermodynamic factors, such as, for example, the presence of catalysts. (Catalysts do not affect the equilibrium state, since the catalyst changes the forward and reverse speeds by the same number of times, it does not affect the affinity). However, near thermodynamic equilibrium, there are general linear relationships between these quantities. In this context, the general form of the linear relation takes the form

$$\upsilon_k = \sum_f L_{kj}\frac{A_j}{T}. \tag{5}$$

As shown below, the coefficients L_{kj} can be related to experimentally established quantities such as reaction rates.

At the same time, reactions proceeding in one stage and complex are distinguished.

Consider a reaction that proceeds in one step. Then (4) takes the form

$$\upsilon = R_f\left(1-e^{-A/RT}\right). \tag{6}$$

In balance $A = 0$. Denote by $R_{f.eq}$ equilibrium rate of the forward reaction. Far from balance *A* has a value of zero. By the term "close to equilibrium" it should be understood that

$$\frac{A}{RT} \ll 1. \tag{7}$$

When *A* is small compared with *RT* and $R_f = R_{f.eq} + \Delta R_f$, then (6) can be expanded in a series and get a linear relationship between υ and *A*, neglecting such small quantities as the product ΔR_f and *A*:

$$\upsilon = R_{f.eq}\frac{A}{RT} + \ldots \tag{8}$$

Comparing (8) with the relation $\upsilon = LA/T$, we get

$$L = \frac{R_{f.eq}}{R} = \frac{R_{r.eq}}{R}. \tag{9}$$

At the same time, it was taken into account that in equilibrium the rates of direct and reverse reactions in each elementary stage are equal. When a system contains many reacting components and many reactions take place between them, not all reactions are independent. Consider the following reactions taking place on the surface of the polymer lining:

$$O_2(g) + 2C(h) \rightleftarrows 2CO(g); \tag{10}$$

$$O_2(g) + 2CO(g) \rightleftarrows 2CO_2(g); \tag{11}$$

$$2O_2(g) + 2C(h) \rightleftarrows 2CO_2(g). \tag{12}$$

The third reaction is the sum of the first two reactions. As a result, these three reactions are not independent. Thermodynamically, this means that the affinity of the third reaction is the sum of the affinities of the first two for an arbitrary number of reactions. Since the ratios are expressed in terms of independent thermodynamic forces, only independent affinity values should be used. Without loss of generality, only the affinity of elementary steps can be considered, since any reaction can be reduced to them.

If all chemical reactions in the system are independent, then near equilibrium, each rate υ_k depends on the corresponding affinity, and the equilibrium reaction rate is determined by relation (8). The latter lacks cross-linked terms. In the general formalism, cross terms in chemical reactions appear when the total number of reactions does not coincide with the number of independent reactions. In this case, the affinities for some reactions can be expressed as linear functions of the affinities of other reactions. Without loss of generality, consider a simple system of monomolecular reactions:

$W \rightleftarrows (X, R_{1f}, R_{1r}, A_1, \upsilon_1)$; (13 *a*)

$W \rightleftarrows (Y, R_{2f}, R_{2r}, A_2, \upsilon_2)$; (13 *b*)

$W \rightleftarrows (Y, R_{3f}, R_{3r}, A_3, \upsilon_3)$; (13 c)

where indices *f* and *r* refer to forward and backward reactions.

Only two of these three reactions are independent, since the third is expressed as the sum of the first two. Hence,

$$A_1 + A_2 = A_3. \tag{14}$$

The entropy production per unit volume in these three reactions is given by

$$S = \upsilon_1 \frac{A_1}{T} + \upsilon_2 \frac{A_2}{T} + \upsilon_3 \frac{A_3}{T}. \tag{15}$$

Using the relation between the affinity of reactions (14), we write this expression in terms of two independent affinities A_1 and A_2:

$$S = (\upsilon_1 + \upsilon_3)\frac{A_1}{T} + (\upsilon_2 + \upsilon_3)\frac{A_2}{T} = = \upsilon_1' \frac{A_1}{T} + \upsilon_2' \frac{A_2}{T} > 0, \tag{16}$$

where $\upsilon_1' = \upsilon_1 + \upsilon_3$ and $\upsilon_2' = \upsilon_2 + \upsilon_3$.

Linear relationships are written in terms of these independent rates and affinity [7]:

$$\upsilon_1' = L_{11} \frac{A_1}{T} + L_{12} \frac{A_2}{T}; \tag{17}$$

$$\upsilon_2' = L_{21} \frac{A_1}{T} + L_{22} \frac{A_2}{T}. \tag{18}$$

Using the general relation (4) between the rates υ_k and the A_k affinity, we obtain the relation between the L_{ik} coefficients and the experimentally determined reaction rates. So near the equilibrium at $(A_k / RT) << 1$, the condition is used that near the equilibrium $R_{kf} \approx R_{kf,\,eq}$ is the rate of the direct reaction in equilibrium, we write υ_1' as

$$\begin{aligned} \upsilon_1' = \upsilon_1 + \upsilon_3 &= R_{1f}\left(1 - e^{-A_1/RT}\right) + \\ &+ R_{3f}\left(1 - e^{-A_3/RT}\right) \\ &\approx R_{1f,eq}\frac{A_1}{RT} + R_{3f,eq}\frac{A_3}{RT} = \\ &= \left(\frac{R_{1f,eq} + R_{3f,eq}}{R}\right)\frac{A_1}{T} + \frac{R_{3f,eq}}{R}\frac{A_3}{T}. \end{aligned} \tag{19}$$

Comparing (19) with (17), we obtain

$$L_{11} = \left(\frac{R_{1f,eq} + R_{3f,eq}}{R}\right) \text{ и } L_{12} = \frac{R_{3f,eq}}{R}. \tag{20}$$

Similarly, we have

$$L_{22} = \left(\frac{R_{2f,eq} + R_{3f,eq}}{R}\right) \text{ и } L_{21} = \frac{R_{3f,eq}}{R}. \tag{21}$$

So, it can be seen that the L_{ik} coefficients are in equilibrium with the reaction rates. Obviously, $L_{12} = L_{21}$. Since the principle of detailed equilibrium, or microscopic reversibility, is included in the formalism through $R_{3f} = R_{3r} = R3_{f,eq}$, Onsager's reciprocity relations are satisfied.

It follows from the above that the production of entropy can be expressed in terms of A_2 and A_3 instead of A_1 and A_2. There is no single way to record entropy production. Whichever way the independent affinities and rates were chosen, the corresponding ratios were obtained. The entropy production S can be written in terms of different sets of independent reaction rates and affinities:

$$S = \sum_k \upsilon_k \frac{A_k}{T} = \sum_k \upsilon'_k \frac{A'_k}{T} > 0\,. \qquad (22)$$

Examples of such a record are equations (15) and (16). The number of independent reactions is limited by the number of reacting components. In homogeneous systems, in which the change in the concentrations of all reacting components is determined only by chemical reactions, to determine the state of the system, instead of the concentration n_k, one can choose the degree of completeness of the reaction ξ_k. The chemical potential μ_k is a function of ξ_k, p and T. However, since the degree of completeness of the reaction relates changes in at least two components, in systems containing r reactants, there is a maximum (r-1) of independent degrees of completeness of reactions ξ_k. Thus, all chemical potentials are expressed in terms of the function μ_k (ξ_1, ξ_2, ξ_3, . . . , ξ_{r-1}, p, T). Whence it follows that at any given pressure p and temperature T there are only (r-1) independent degrees of completeness of reactions. Since the affinity A_k is a linear function of chemical potentials, in a system with r reacting components, they can have a maximum (r-1) of independent affinity values. (Sometimes this is derived using the "law of conservation of mass" in chemical reactions. Although this may be true in ordinary chemical reactions. In reality, mass is associated with a chemical reaction, the main consequence of which is a change in the number of molecules of various reacting components.)

It was shown that linear relationships are valid for chemical reactions with affinity A, conditionally satisfying A/RT<<1. However, if the complete chemical reaction

$$\mathrm{X} \rightarrow \mathrm{Y} \qquad (23)$$

contains m intermediate stages W_1, W_2, … ,W_m, the use of linearity can still be justified even if the condition A/RT<<1. Let us assume that the complete reaction (23) proceeds through the sequence of reactions:

$$\mathrm{X} \rightleftarrows \mathrm{W}_1 \rightleftarrows \mathrm{W}_2 \rightleftarrows \mathrm{W}_3 \rightleftarrows$$

$$\rightleftarrows \ldots \mathrm{W}_m \overset{(m+1)}{\rightleftarrows} \mathrm{Y}. \qquad (24)$$

The entropy production for this set of (m+1) reactions is

$$TS = A_1\upsilon_1 + A_2\upsilon_2 + \ldots A_{m+1}V_{m+1}. \qquad (25)$$

If the intermediate components W_k rapidly interconvert, then the rate of each of these reactions is determined by the rate of the slowest reaction, which is called the limiting rate. Let the last reaction $W_m \rightleftarrows$ Y be the limiting rate. Let us write the kinetic equations:

$$\frac{d\{X\}}{dt} = -\upsilon_1; \qquad \frac{d\{W_1\}}{dt} = \upsilon_1 - \upsilon_2;$$

$$\frac{d\{W_2\}}{dt} = \upsilon_2 - \upsilon_3, \ \ldots\ , \frac{d\{Y\}}{dt} = \upsilon_{m+1}. \qquad (26)$$

Due to the rapid interconvertibility, it can be assumed that a stationary state is established for $\{W_k\}$, so $d\{W_k\}/dt \approx 0$. (so Such an assumption is used, for example, in the derivation of the Michaelis-Menten law in enzymatic kinetics). It means that

$$\upsilon_1 = \upsilon_2 = \ldots = \upsilon_{m+1} = \upsilon. \qquad (27)$$

Then the entropy production of the system takes the form

$$TS = (A_1 + A_2 + \ldots + A_{m+1})\upsilon = A\upsilon. \qquad (28)$$

where is the total affinity

$$A = A_1 + A_2 + \ldots + A_{m+1}. \qquad (29)$$

If a A_k/RT << 1 for each of (m+1) reactions, then we are in the range of applicability of linear laws, so from (8) we obtain

$$\upsilon_1 = R_{1f,eq}\frac{A_1}{RT};\ \upsilon_2 = R_{2f,eq}\frac{A_2}{RT}\ \ldots;$$

$$\upsilon_{m+1} = R_{(m+1)f,eq}\frac{A_{m+1}}{RT}, \qquad (30)$$

where $R_{1f,eq}$ – the equilibrium rate of the direct reaction, according to dependence (24), etc.

In this case, even if $A=\sum_{k=1}^{m+1}A_k \gg RT$, linear relationships apply. Using (27), (28), and (30), with the help of simple transformations, we obtain

$$\upsilon=\frac{R_{ef}}{RT}A, \tag{31}$$

where "effective reaction rate" R_{ef} defined as

$$\frac{1}{R_{эф}}=\frac{1}{R_{1f,eq}}+\frac{1}{R_{2f,eq}}+\frac{1}{R_{3f,eq}}+\ldots+\frac{1}{R_{(m+1)f,eq}}. \tag{32}$$

Since a complete reaction is the result of many elementary steps, the ratio
$\upsilon = R_{ef}\,(1 - e^{-A/RT})$ not fulfilled.

Although the derivation of (31) considered the system of monomolecular reactions (24), the result obtained has a more general substantiation. Thus, a linear relationship is valid for a complete reaction if $A/RT \ll 1$ for each elementary step and if the concentrations of substances in the intermediate steps do not change.

The discussion of the results

When evaluating chemical reactions in tribocouples of friction pairs, the following was mathematically determined: the production of entropy at their elementary stages, the rates of the forward and reverse reactions, the parameters of equilibrium and affinity, with access to the Onsager relations. The following is established:

- an increase in the surface-volume temperature contributes to an increase in the volume of the output of endothermic reaction products from the upper layer of the polymer lining, as well as the equilibrium constant, which is accompanied by the release of heat. In this case, in accordance with the principle of van't Hoff's mobile equilibrium, elastic-plastic deformation of the microprotrusions of the working surface of the metal friction element occurs. A decrease in the surface temperature of friction pairs contributes to the intensification of the exothermic reaction with the dissociation of ions of the surface layer of the polymer lining;

- the electrons formed in the electrolyte are strongly oriented and their effective dipole moment is large, which leads to the inversion of many currents according to the "polymer-metal" scheme; triboadsorbed gas is adsorbed by the working surface of the metal, after which its chemical transformations occur; at the rate of tribosorption and triboreaction of the same order, the chemical reaction is shifted towards the working surface of the metal friction element; a change in the degree of dispersity and compactness of the phases that appear in the upper layer of the polymer lining, containing amorphous and vitreous substances, significantly affects their chemical activity; in this case, it is necessary to take into account the change in the Gibbs energy of the surface layer of the polymer lining, which is associated with its temperature and heat content, which affect the direction of shifting the equilibrium of the chemical reaction;

- an increase in specific loads in a friction pair leads to a decrease in the output of gaseous products, including unsaturated hydrocarbons, combined with hydrogen, from their contact gap; in this case, the specific loads in friction pairs directly depend on their mutual overlap coefficient;

- linearity patterns were established in successive reactions in tribocouplings using the production of entropy, creating it from the affinity and the allowable reaction rate, which allows us to consider the ratio correct for the complete reaction if $A / RT \ll 1{,}0$ (where A is affinity; R is gas constant; T is the surface-volume temperature) for each elementary stage and if the concentration of substances in the intermediate stages does not change.

Conclusion

It is established that increase in the surface-volume temperature contributes to an increase in the volume of the output of endothermic reaction products from the upper layer of the polymer lining, as well as the equilibrium constant, which is accompanied by the release of heat. In this case, in accordance with the principle of van't Hoff's mobile equilibrium, elastic-plastic deformation of the microprotrusions of the working surface of the metal friction element occurs.

A decrease in the surface temperature of friction pairs contributes to the intensification of the exothermic reaction with the dissociation of ions of the surface layer of the polymer lining. In this case, it is necessary to take into account the change in the Gibbs energy of the surface layer of the polymer lining, which is associated with its temperature and heat content, which affect the direction of shifting the equilibrium of the chemical reaction.

Linearity patterns revealed in successive reactions in tribocouplings using the production of entropy, creating it from the affinity and the allowable reaction rate, which allows us to consider the ratio correct for the complete reaction if a / rt << 1,0 (where a is affinity; r is gas constant; t is the surface-volume temperature) for each elementary stage and if the concentration of substances in the intermediate stages does not change.

Conflict of Interests

The authors declare there is no conflict of interests related to the publication of this article.

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