Triboqovşaqlarda xətti rejimli qeyri-müvazinat termodinamikası (II hissə)

Ə.X. Canəhmədov[1], D.Y. Juravlev[2], V.N. Volçenko[3], V.T. Balonnıy[4], V.Y. Malık[4]

[1]*Azərbaycan Milli Aviasiya Akademiyası (Mərdəkan pr. 30, Bakı, AZ1045, Azərbaycan)*
[2]*İvano-Frankivsk Milli Texniki Neft və Qaz Universiteti (Karpatska küç.15, İvano-Frankivsk, 76019, Ukrayna)*
[3]*Kuban Dövlət Texnologiya Universiteti (Moskovskaya küç. 2, Krasnodar, 350072, Rusiya)*
[4]*Droqobıç İxtisaslaşdırılmış Neft və Qaz Kolleci (Qruşevskiy küç. 57, Droqobıç, 82100, Ukrayna)*

Yazışma üçün:
Canəhmədov Əhəd / e-mail: dzhanakhmedov@yahoo.com

Xülasə

Məqalədə, əyləc qurğularının triboqovşaqlarında xətti rejimli qeyri-müvazinat termodinamikasının tədqiqi Furye istilikkeçiricilik qanunundan və Fik effektindən, eləcə də friksion kündənin üst təbəqələrində diffuziya və termodiffuziya qeyri-tarazlıq proseslərinin axını ilə əlaqədar olan Sor və Dyufur effektlərindən istifadə etməklə aparılmışdır. Göstərilmişdir ki, polimer kündənin üst təbəqəsindən endotermik reaksiya məhsullarının çıxış həcminin artmasına kömək edən səthi-həcmi temperaturun, həmçinin istilik ayrılması ilə müşaiyət olunan tarazlıq sabitinin artması müşahidə olunur. Eyni zamanda, Vant Hoffun hərəkətli tarazlıq prinsipinə uyğun olaraq, metal sürtünmə elementinin işçi səthinin mikroçıxıntılarının struktur-plastik deformasiyası baş verir.

Açar sözlər: əyləc qurğuları, sürtünmə cütü, friksion kündə, diffuziya və termodiffuziya, Onsager qarşılıqlı nisbəti.

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Неравновесная термодинамика с линейными режимами в трибосопряжениях (часть II)

А.Х. Джанахмедов[1], Д.Ю. Журавлев[2], В.Н. Вольченко[3], В.Т. Балонный[4], В.Я. Малык[4]

[1] *Азербайджанская Национальная академия авиации (Мардакянский пр. 30, Баку, AZ1010, Азербайджан)*
[2] *Ивано-Франковский национальный технический университет нефти и газа (г. Ивано-Франковск, Украина)*
[3] *Кубанский государственный технологический университет (ул. Московская, 2, Краснодар, 350072, Россия)*
[4] *Дрогобыческий специализированный колледж нефти и газа (ул. Грушевского, 57, г. Дрогобыч, 82100, Украина)*

Для переписки:
Джанахмедов Ахад / e-mail: dzhanakhmedov@yahoo.com

Аннотация

Проводится исследование неравновесной термодинамики с линейными режимами в трибосопряжениях тормозных устройств с привлечением закона теплопроводности Фурье и эффекта Фика, а также эффектов Сора и Дюфура применительно к протеканию неравновесных процессов диффузии и термодиффузии в поверхностных слоях фрикционных накладок. Показано, что наблюдается увеличение поверхностно-объемной температуры, способствующей росту объема выхода продуктов эндотермических реакций из верхнего слоя полимерной накладки, а также константы равновесия, что сопровождается выделением теплоты. При этом в соответствии с принципом подвижного равновесия Вант-Гоффа происходит упругопластическая деформация микровыступов рабочей поверхности металлического элемента трения.

Ключевые слова: тормозное устройство, пара трения, фрикционная накладка, диффузия и термодиффузия, соотношения взаимности Онсагера.

Introduction

In tribology, three consecutive and interconnected friction process: frictional interaction of microprotrusions of rubbing surfaces, change in the properties of surface and near-surface layers as a result of interaction and destruction of surfaces due to the two previous stages. These stages of friction occur in the following fields: mechanical, electrical and electromagnetic. The driving force is the redox potential with its gradients. Its value is estimated for a polymer friction element in the longitudinal and transverse directions. For flows of the washing medium, the transverse temperature gradient is taken into account (determined by the ratio C_p/C_V; heat capacity at constant pressure to heat capacity at constant volume).

Any stable structural-phase state exists for a short period of time, passing to a new level of instability due to processes, phenomena and effects that increase the total entropy and, accordingly, reduce the free energy of materials. As a result, the next transition to a new quasi-stable state is provoked. In this case, the process continues for some time, which is determined by the physicochemical characteristics of the corresponding transformations, as well as the ability to create conditions under which these transitions will occur with the least possible frequency.

Analysis of literary sources and the state of the problem

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 tribocouples of friction pairs, between diffusion, thermal diffusion and thermal conductivity, on the one hand, and the rate of entropy increase, on the other.

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 [1].

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 a constant temperature) there are functions called thermodynamic potentials, which also have extrema (maxima and minima) in equilibrium [1]. The paper [2] gives an analysis and synthesis of thermoelectric processes characterizing electrothermomechanical frictional interacttions of friction pairs of brake 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].

The materials of work [4] 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.

In studies [1], it is noted that the adsorption effect, which is characterized by the number of grooves *N*, made in one of the friction elements of a direct or reverse friction pair, has a predominant role in the delivery of an active gas mixture. However, in the area between the grooves, the gas introduced from the outside due to the adsorbing effect is consumed when interacting with the friction surfaces, and a point (zone) may appear in which the active component of the gaseous medium is almost completely consumed, as a result of which the so-called gas starvation may occur [5]. A similar phenomenon can occur with the slit effect.

However, in the considered works [1-5], no attention was paid to diffusion and thermal diffusion processes, as well as the Onsager reciprocity relations as applied to triboconjugations of friction pairs of brake devices.

Formulation of the problem

The main issues of the article: general principles of energy processes in the fields of frictional interaction of friction pairs of brake devices; diffusion and thermal diffusion in tribocouplings; the discussion of the results.

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

General principles of energy processes in the fields of frictional interaction of friction pairs of braking devices

To clarify the meaning of the totality of concepts, we consider each type of energy as a product of two quantities: intensity (factor of intensive property) and capacity (factor of extensive property). So, mechanical energy is determined by the value of Fdl, i.e., the product of the force and the increment of the path; electric - Edq, i.e., the product of emf. on the amount of electric charge carried; magnetic - Bdl, i.e., the product of magnetic induction and magnetization; volumetric - PdV; surface energy - $\sigma d\omega$, i.e., the product of surface tension and the change in surface area; potential - $mgdh$; kinetic – $(\upsilon^2/2)dm$; chemical - μdn, it determines the change in the chemical potential over the thickness of the substance. Intensity factors are often combined under the general name of generalized forces, and the capacity factor is called the generalized path. So, in the case of mechanical energy, the magnitude of the force is a stress factor (just like p, σ, μ, etc. in the corresponding types of energy), and the magnitude of the distance traveled (i.e. changes in υ, ω, n, etc.) shows the extent to which the action of force is manifested. Energy in general can be written as follows:

$$dU = TdS - (Xdx + Ydy + \ldots), \tag{1}$$

where X, Y …. – intensity factors; x, y … - their respective capacitance factors. If we assume that $dx{=}dy{=}\ldots{=}0$, those. the system is not subject to the action of any external forces, then equation (1) takes the form: $dU = TdS$. In this case, the friction pairs in the brake are open. The intensity factors are potentials (T is the potential of thermal energy; μ is the potential of chemical energy, etc.), i.e. voltages of the acting type of energy.

Every time two systems with different potentials interact, potential equalization occurs by changing the corresponding capacitance factors. So, pressure is equalized due to a change in volume, temperature - due to a change in entropy, etc.

Value $(\partial u / \partial n_i)_{V,S,n_j}$ is the chemical potential (μ_i). This is true for the case when the internal energy of the liquid phase of the tribosystem increases with a decrease in the mass of the surface and near-surface layer of the polymer lining during the cracking process by unity at constant entropy, and the volume and masses of the lining components are variable. The heat flow is the driving force in heat transfer, and the chemical potential is the driving force in the phase transition of the mass of the upper layer of the polymer lining. The phase transition leads to the establishment of chemical equilibrium (and phase transition, if the mass decrease occurs in a heterogeneous system, i.e. between phases). Like other intensity factors in the cracking process, the chemical potential of the substances levels off as the process proceeds. At the moment of equilibrium, it becomes the same in all existing phases in which the components of the upper layer of the polymer lining are located. Thus, the chemical variable is the amount of lining components interacting with the material of the metallic friction element. Unlike other intensity factors, it is impossible to directly measure the chemical potential, which makes this concept not as clear as, for example, specific load, surface and bulk temperatures, etc. Below are equations describing an infinitesimal change U, H, F and G for a phase whose mass and concentration may change as a result of exchange with other phases.

If we assume that during frictional interaction only specific loads act on the tribosystem, then with independent variables S, V and n_1, n_2, n_3 ... we obtain the equation:

$$dU = TdS - PdV + \sum \mu_i dn_i. \tag{2}$$

With independent variables S, P and n_1, n_2, n_3 ... we have:

$$dH = TdS - VdP + \sum \mu_i dn_i. \tag{3}$$

Applying T, V and n_1, n_2, n_3 ... as variables, we have:

$$dF = - SdT - PdV + \sum \mu_i dn_i. \tag{4}$$

Finally, with independent variables P, T and n_1, n_2, n_3 ... we have:

$$dG = -SdT - VdP + \sum \mu_i dn_i. \qquad (5)$$

Taking partial derivatives from equations (2)-(5), we obtain analytical expressions for various thermodynamic parameters. In addition, these expressions imply:

$$\mu_i = \left(\frac{\partial u}{\partial n_i}\right)_{V,S,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_j} = \qquad (6)$$
$$= (\partial F/\partial n_i)_{V,T,n_j} = (\partial G/\partial n_i)_{P,T,n_j},$$

those, the chemical potential of the upper layer of the working surface of the polymer lining during frictional interaction with a metal friction element is equal to the partial derivative of any thermodynamic potential of a given phase with respect to the number of moles of this component, provided that the corresponding thermodynamic parameters and the number of moles of the remaining components of the lining remain constant. In other words, the chemical potential is a partial molar value of the thermodynamic potential, provided that the corresponding parameters of the state of the tribosystem remain unchanged.

Diffusion and thermal diffusion in tribocouplings

Diffusion and thermal diffusion flows of liquid, vapor and gas play a significant role in the equilibrium state of tribocouples of friction pairs of braking devices.

On fig. 1 shows the algorithm of nonequilibrium thermodynamics in triboarrangements of friction pairs of brakes.

In table 1 shows the laws and effects as applied to diffusion and thermal diffusion in tribocouplings. As for chemical reactions, the material on them will be placed in the third part of the article.

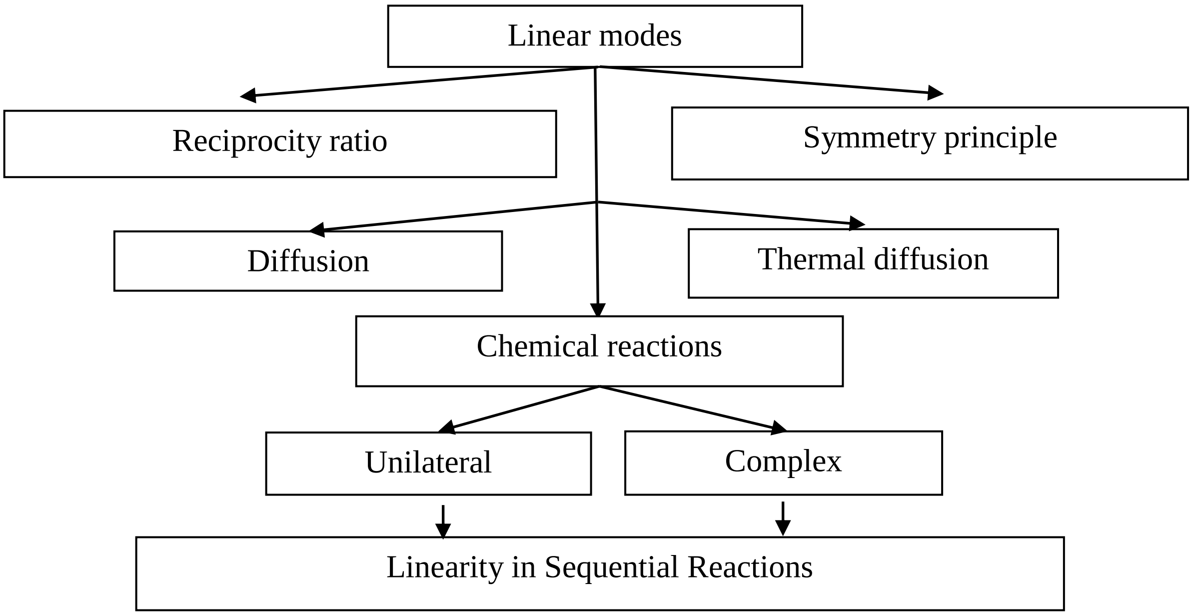

Figure 1 – Algorithm of nonequilibrium thermodynamics with linear regimes in tribocouplings

Table 1 – Laws and effects accompanying diffusion and thermal diffusion in tribocouplings

Laws and effects	
Name	Content
Fourier's law of heat conduction	Establishes a relationship between the temperature gradient of the medium and the heat flux density.
Fick's Laws: first second	 Sets the proportionality of the diffusion flow of liquids and gases to their concentration gradient. It is characterized by the diffusion equation at its constant value.
Effects: Soret Dufour	 The flow of heat generates a flow of liquid and gases. The mixing of liquid and gases contributes to the release of heat

When solving this problem, we apply the theory of linear nonequilibrium thermodynamics to the diffusion process. Depending on the energy load of the working layer of the polymer lining, a weak and strong electrolyte forms on its surface when the formaldehyde resin burns out [4].

In the region of low concentrations, the concentration increases with increasing concentration (since the number of ions in 1 cm3 of solution increases with increasing concentration), reaches a maximum value, and then decreases. In solutions of strong electrolytes, this decrease is explained by a slowdown in the movement of ions due to the relaxation effect and the effect of electrophoretic braking, and in solutions of weak electrolytes, it is explained by a decrease in the degree of dissociation.

Consideration of the influence of the concentration of the solution on the value of λ is more convenient to start with an analysis of the dependence of the equivalent electrical conductivity on the dilution of the solution (Fig. 2). Dilution (dilution) of a solution *V=1/C* is the reciprocal of concentration *C*. As experiments show, with increasing dilution (decreasing concentration), the equivalent electrical conductivity increases and reaches a certain limit value, as shown in fig. 2. This limit value λ is called the electrical conductivity at infinite dilution and is denoted λ_∞.

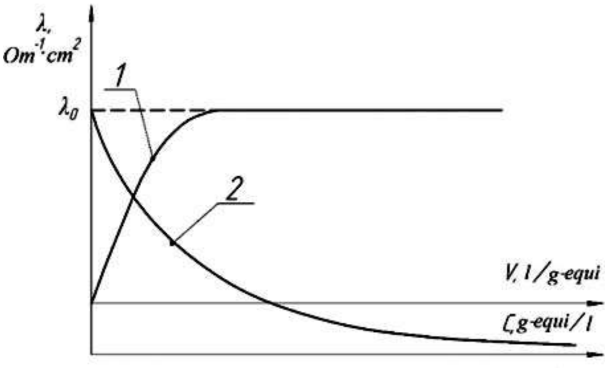

Figure 2 – Dependence of equivalent electrical conductivity λ on dilution (curve 1) and on solution concentration (curve 2)

When several components diffuse simultaneously from the surface layers of the FK-24A lining and the flow of one component affects the flow of another. The entropy production per volume unit due to multicomponent diffusion is:

$$S = -\sum_k J_k \cdot \nabla\left(\frac{\mu_k}{T}\right), \qquad (7)$$

where J_k – flow of matter; μ_k – component chemical potential k and his temperature T.

Under isothermal conditions, the corresponding linear relations have the form:

$$J_k = -\sum_k \frac{L_{ik}}{T} \nabla \mu_k . \qquad (8)$$

The first task is to find a relationship between the linear coefficients L_{ik} and the experimentally measured diffusion coefficients D_{ik}. For multicomponent diffusion (under isothermal conditions), the "generalized Fick's law" can be represented as

$$J_i = -\sum_k D_{ik} \nabla n_k(x). \qquad (9)$$

where $n_k(x)$ – component concentration k at the point x; D_{ik} – diffusion coefficients.

Having written down the dependences for a two-component and multi-component mixture, after performing a series of substitutions and transformations, we obtained the relationship between the coefficient L_{11} and the diffusion coefficient

$$L_{11} = \frac{D_1 T}{\left(1 + \dfrac{\nu_1 n_1}{\nu_2 n_2}\right)\left(\dfrac{\partial \mu_1}{\partial n_1}\right)} . \qquad (10)$$

For the diffusion of a substance in a solution, n_1 and n_2 are the number of moles of the solvent and dissolved substance per unit volume, and for a dilute solution $\mu_1 = \mu_0(p,T) + RT \ln x_1$, where R – gas constant; p – pressure; $x_1 = n_1/(n_1 + n_2) \approx n_1/n_2$, and $n_1 << n_2$. These conditions simplify the relationship between L_{11} and D:

$$L_{11} = \frac{D_1 n_1}{R} . \qquad (11)$$

This formula establishes the relationship between the usual diffusion coefficient and the corresponding coefficient μ. To test the Onsager reciprocity relation, it is necessary to have at least three components in the system. For three-component isothermal diffusion, the entropy production per unit volume is

$$S = -\frac{J_1}{T} \cdot \nabla \mu_1 - \frac{J_2}{T} \cdot \nabla \mu_2 - \frac{J_3}{T} \cdot \nabla \mu_3 . \qquad (12)$$

Let us write for the three-component system the Gibbs-Duhem equations and the condition of the absence of a volumetric flow

$$n_1 \nabla \mu_1 + n_2 \nabla \mu_2 + n_3 \nabla \mu_3 = 0; \qquad (13)$$

$$J_1 \nu_1 + J_2 \nu_2 + J_3 \nu_3 = 0 . \qquad (14)$$

Let's pretend that J_3 and μ_3 are solvent variables, and J_1, μ_1; J_2, μ_2 are variables of two solutes whose cross-diffusion is of interest. Using (13) and (14), J_3 and μ_3 can be eliminated from the entropy production expression. The entropy production is then written only in terms of the two solute variables J_1, μ_1 and J_2, μ_2:

$$S = F_1 \cdot J_1 + F_2 \cdot J_2 . \qquad (15)$$

where the thermodynamic forces F_1 and F_2 have the form

$$F_1 = -\frac{1}{T}\left[\nabla \mu_1 + \frac{n_1 \nu_1}{n_3 \nu_3} \nabla \mu_1 + \frac{n_2 \nu_2}{n_3 \nu_3} \nabla \mu_2\right]; \qquad (16)$$

$$F_2 = -\frac{1}{T}\left[\nabla \mu_2 + \frac{n_2 \nu_2}{n_3 \nu_3} \nabla \mu_2 + \frac{n_1 \nu_1}{n_3 \nu_3} \nabla \mu_1\right]; \qquad (17)$$

So let's write the ratios:

$$J_1 = L_{11} F_1 + L_{12} F_2 ; \qquad (18)$$

$$J_2 = L_{21} F_1 + L_{22} F_2 . \qquad (19)$$

To check the reciprocity relations, it is necessary to relate L_{ik} and the experimentally measured diffusion coefficients D_{ik} of the generalized Fick law:

$$J_1 = -D_{11} \nabla n_1 - D_{12} \nabla n_2 ; \qquad (20)$$

$$J_2 = -D_{21} \nabla n_1 - D_{22} \nabla n_2 . \qquad (21)$$

It should be noted that for $J_2 = 0$ these equations lead to the fact that the constant flow J_1=const associated with the concentration gradient n_1 causes the concentration gradient n_2. Let us continue that fluxes and concentration gradients are directed along the same direction, say *x*, so that all gradients correspond to derivatives with respect to *x*. Since the chemical potentials μ_k are functions of n_k, one can represent the forces F_k in terms of the concentration gradients of the two diffusing components. Thus, we get

$$\frac{\partial \mu_1}{\partial x} = \frac{\partial \mu_1}{\partial n_1}\frac{\partial n_1}{\partial x} + \frac{\partial \mu_1}{\partial n_2}\frac{\partial n_2}{\partial x}. \qquad (22)$$

We write a similar relation for the gradient μ_2. Using these relations in (16) and (17) and substituting them into (18) and (19), we write the fluxes J_k in terms of the gradients n_k. After calculations, the following relations between the diffusion coefficients and linear Onsager coefficients are obtained:

$$L_{11} = \frac{dD_{11} - bD_{12}}{ad - bc}, \quad L_{12} = \frac{aD_{12} - cD_{11}}{ad - bc} \qquad (23)$$

$$L_{21} = \frac{dD_{21} - bD_{22}}{ad - bc}, \quad L_{22} = \frac{aD_{22} - cD_{21}}{ad - bc} \qquad (24)$$

where a, b, c, d are coefficients.

Obviously, the meaning of the reciprocity relations $L_{12} = L_{21}$ is reduced to the following:

$$aD_{12} + bD_{22} = cD_{11} + dD_{21}. \qquad (25)$$

The results of experimental studies of changes in the amount and composition of the gas-vapor mixture formed in the intercontact space of friction pairs indicate that the friction process is of a complex tribochemical nature (Table 2) [4].

The amount of water that ended up in the measuring tube of the vacuum pump was 35.4 ml.

Experimental and calculated data of the multicomponent system are given in Table 3.

Table 2 – The percentage ratio of the components of the gas mixture formed in the intercontact space of the friction pair steel 30KhGSA - FK-24A

Sample number	Composite brand	Temperature, °C	Gas content, wt. share, %						
			H_2	O_2	N_2	CO_2	CO	ΣC_nH_m	Other gases***
1	ФК-24А	150	*	19,8	78,8	0,28	*	*	Rest
2	-	215	*	19,8	78,8	0,23	*	*	
3**	-	420	0,123	19.1	79,5	0,13	*	*	
4**	-	500	0,171	16,3	81,6	0,24	0,24	0,24	
5	-	750	0,308	9,8	81,2	0,08	0,08	1,06	

Note:*Presence of traces of specified gases; **Sampling was carried out from four zones (points) simultaneously; ***Others mean Ar, Ne, He, Kr, N_2O, Xe, O_2, Rn.

Table 3 – Experimental and calculated values of diffusion coefficients for a multicomponent friction lining in the temperature range and verification of relationships

Sample number	Friction material	Temperature, °C	X_1	X_2	D_{11}x*10*, м^2/с	D_{12}x*10*, м^2/с	D_{21}x*10*, м^2/с	D_{22}x*10*, м^2/с	L_{12}/L_{21}
1	ФК-24А	150	0,25	0,50	1,848	-0,063	-0,052	1,797	1,052
2	"	215	0,26	0,03	1,570	-0,077	-0,012	1,606	0,980
3	"	420	0,70	0,15	2,132	0,051	-0,071	2,062	0,942
4	"	500	0,15	0,70	1,853	0,049	-0,068	1,841	0,915
5	"	730	0,25	0,75	1,79	0,043	-0,07	1,80	1,1

*Note: before the line, the exponent near the number ten is equal to two, and after it, it is equal to minus three.

The relationship between chemical potentials and concentrations is not always known exactly, and reliable measurements of diffusion coefficients are quite difficult.

Nevertheless, it can be seen that, within the limits of experimental errors, the reciprocity relations hold very well. In thermal diffusion, the interaction between heat flows and liquid and gas causes two separate Soret and Dufour effects (see Table 1).

In this case, reciprocity relations can be obtained using the expression for the production of entropy during diffusion and heat conduction:

$$S = \left(J_u - \sum_{k=1}^{w} J_k \mu_k \right) \cdot \nabla \left(\frac{1}{T} \right) - \sum_{k=1}^{w} J_k \cdot \frac{1}{T} \nabla \mu_k \qquad (26)$$

After complete separation of the temperature and concentration gradient, determination of the molar entropy under the condition of equalizing the specific loads in the tribocoupling and, using a series of transformations, an expression was obtained that determines the heat flux, taking into account the flow of liquid and gas

$$S = \left(J_u - \sum_{k=1}^{w} J_k (\mu_k + TS_k) \right) \cdot$$

$$\cdot \nabla \left(\frac{1}{T} \right) - \sum_{k=1}^{w} J_k \cdot \frac{1}{T} (\nabla \mu_k)_{p,T} \qquad (27)$$

Now, using $G = H\text{-}TS$, it is easy to see that $\mu_k + TS_k = H_k$, where is the partial molar enthalpy $H_k = (\partial H / \partial n_k)_{p,T}$.

Using this definition, the heat flux, taking into account the flow of matter, can be defined as

$$J_q \equiv J_u - \sum_{k=1}^{w} H_k J_k . \qquad (28)$$

In a closed system at constant volume, the change in enthalpy due to a change in composition is equal to the exchange of heat interacting with the external environment. In an open system with a fixed amount of heat, the difference between the changes in energy and enthalpy due to the flow of liquid and gas is determined. In what follows, the resulting expressions are associated with Fourier's heat conduction laws and Fick's diffusion laws, but in this case we write the gradients as

$\nabla \mu_1 = (\partial \mu_1 / \partial n_1) \nabla n_1$;

$\nabla (1/T) = -(1/T^2) \nabla T$,

so the two streams take the form:

$$J_q = -\frac{L_{qq}}{T^2} \nabla T - L_{q1} \frac{1}{T} \left(1 + \frac{\nu_1 n_1}{\nu_2 n_2} \right) \frac{\partial \mu_1}{\partial n_1} \nabla n_1 ; \qquad (29)$$

$$J_1 = -\frac{L_{1q}}{T^2} \nabla T - L_{11} \frac{1}{T} \left(1 + \frac{\nu_1 n_1}{\nu_2 n_2} \right) \frac{\partial \mu_1}{\partial n_1} \nabla n_1 . \qquad (30)$$

Now we determine the coefficients of diffusion and thermal conductivity

$$D_1 = L_{11} \frac{1}{T} \left(1 + \frac{\nu_1 n_1}{\nu_2 n_2} \right) \frac{\partial \mu_1}{\partial n_1} ; \qquad k = \frac{L_{qq}}{T^2} .$$

and get reciprocity relations

$$L_{q1} = L_{1q} . \qquad (31)$$

Cross flow $-(L_{1q} / T^2) \nabla T$ usually presented as $-n_1 D_T \nabla T$, wherein D_T – thermal diffusion coefficient, so that the flow of matter is proportional to n_1. The ratio of the thermal diffusion coefficient to the ordinary diffusion coefficient is called the Soret coefficient.

$$s_T = \frac{D_T}{D_1} = \frac{L_{1q}}{D_1 T^2 n_1} . \qquad (32)$$

In a closed system with a temperature gradient (Fig. 3), concentration gradients are established due to heat flows. Assuming $J_1 = 0$, one can obtain the stationary value of the concentration gradient

$$J_1 = -\frac{L_{1q}}{T^2} \nabla T - D_1 \nabla n_1 = 0 . \qquad (33)$$

Insofar as $L_{1q}/T^2 = n_1 D_T$, we write the gradient ratio as follows:

$$\frac{\nabla n_1}{\nabla T} = -\frac{n_1 D_T}{D_1} = -n_1 s_T\,. \tag{34}$$

The Soret coefficient has units of T^{-1}. In the general case, it is small and ranges from 10^{-2} to 10^{-3} for electrolytes and gases [6-12], but in polymer solutions it can take larger values. The heat flux caused by the flow of matter is determined by the Dufour coefficient D_d. Since heat accompanies the flow of matter and is proportional to the concentration n_1, the Dufour coefficient is defined as

$$n_1 D_d = L_{q1}\frac{1}{T}\left(1+\frac{\nu_1 n_1}{\nu_2 n_2}\right)\frac{\partial \mu_1}{\partial n_1}\,. \tag{35}$$

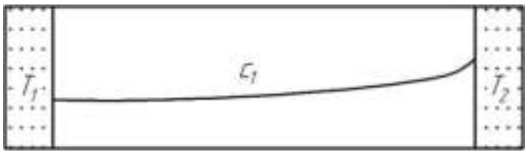

Figure 3 – Thermal diffusion. The temperature gradient and the resulting heat flux causes a concentration gradient in the incoming (T_2) and escaping (T_1) surfaces of the lining

Since, $L_{1q}/T^2 = n_1 D_T$ the Onsager reciprocity relation $L_{1q} = L_{q1}$ determines the ratio of the Dufour coefficient and to the thermal diffusion coefficient:

$$\frac{D_d}{D_T} = T\left(1+\frac{\nu_1 n_1}{\nu_2 n_2}\right)\frac{\partial \mu_1}{\partial n_1}\,. \tag{36}$$

This ratio has been confirmed experimentally. Thus, nonequilibrium thermodynamics is a generalized theory of irreversible processes. Onsager's reciprocity relations are general and valid for all systems in which linear relations hold.

Conclusion

The study of non-equilibrium thermodynamics with linear regimes in tribocouplers of brake devices using the laws of thermal conductivity of Fourier and Fick, as well as the Sor and Dufour effects in relation to the flow of equilibrium processes of diffusion and thermal diffusion in the surface layers of friction linings, made it possible to establish the following: the factors in the tribosystem are the potentials (T - the potential of thermal energy; p - the potential of the specific load; μ - the potential of chemical energy, etc.), i.e. the voltages of the acting type of energy, each time when two tribosystems with different potentials enter into interaction, there is an equalization of potentials due to a change in the corresponding capacitance factors. So, the pressure of gases is leveled off due to a change in volume, temperature - due to a change in entropy, etc.; 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; the change in the Gibbs energy of the surface layer of the polymer lining is associated with its temperature and heat content, which affect the direction of shifting the equilibrium of the chemical reaction; application of the Onsager reciprocity relation allowed to determine the quantitative dependences between the parameters of diffusion and thermal diffusion and their coefficients by calculation and experiment.

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