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ABOUT DIFFUSIVE TRANSFER OF THERMAL ENERGY AND MASS OF COMPONENTS IN THERMODYNAMICS HEAT-RESISTANT SYSTEMS

Thermodynamics of irretrievable processes of transfer of energy and mass of matter is the special scientific direction, which examines equalization of the second principle of thermodynamics as starting mathematical model for balance of energy and mass of matter in the elementary volume of the thermodynamics system during it co-operating with an environment. In accordance with positions of thermodynamics of irretrievable processes motive forces of processes of transfer of warmth and mass of matter are by vectors and according to principle Curie their fully possible combination, id est force which predetermines stream of thermal energy can to entail a mass stream and back to front. The closed thermodynamics heat-resistant system which interchanges thermal energy and mass of components with an environment is examined. The noted process is limited by absence of convective constituent of process of transfer in the system. The volume of the system does not change during a diffusive transfer and by treason of enthalpy in the system, as by the result of treason of thermal energy and concentration of mass, it is possible to neglect. The mathematical design of diffusive transfer of thermal energy and mass of components in the thermodynamics heat-resistant system at presence of and to absence of cross effects is executed.

Keywords: heat-resistant systems, physic-mathematical models, diffusive transfer, thermodynamics of irretrievable processes

Introduction. Thermodynamics of irreversible processes is the special scientific direction examines the processes of energy and mass transfer of, being based on the substantive theoretical provisions of thermodynamics of convertible processes. Thus its examine equation of the second beginning of thermodynamics as starting mathematical model of balance of energy and mass of matter in the elementary volume of the thermodynamics system at it co-operating with an environment.

A thermodynamics process is characterized by the change of parameters for the state of the system in space-time co-ordinates. Consequently, a task consists in transformation of equation

$$dS = \frac{1}{T} dU + \frac{1}{T} P dV - \frac{1}{T} \cdot \sum_{k=1}^n \mu_k dM_k, \quad (1)$$

where dS is a complete differential of the thermal state of the thermodynamics system; dU , dV are a change of internal energy and volume of the system respectively; P , T are pressure and temperature in the system respectively; μ_k is chemical potential of k -th component of the system; dM_k is an increase of mass of k -th component of the system, – in substantive interpretation, id est to pass from the complete derivative functions of the state to substantive function.

We will take the functions of the state in equation (1) to unit of its mass (M):

$$dS_m = \frac{1}{T} dU_m + \frac{1}{T} P dV_m - \frac{1}{T} \cdot \sum_{k=1}^n \mu_k d\rho_{k_0}, \quad (2)$$

where $U_m = u/M$; $V_m = V/M$; $\rho_{k_0} = M_{k_0}/M = \rho_k/\rho$ – relative concentration of k -th component in unit of mass of the system, kg/kg; V_m is a specific volume of the system, m³/kg.

Multiplying both parts of equation (2) by the density of the system ρ , get

$$dS_V = \frac{1}{T} dU_V + \frac{\rho \cdot P}{T} dV_m - \frac{1}{T} \cdot \sum_{k=1}^n \mu_k d\rho_k. \quad (3)$$

In substantive interpretation equation (3) for irreversible processes looks like:

$$\frac{dS_V}{d\tau} = \frac{1}{T} \frac{dU_V}{d\tau} + \frac{\rho \cdot P}{T} \frac{dV_m}{d\tau} - \frac{1}{T} \cdot \sum_{k=1}^n \mu_k \frac{d\rho_k}{d\tau}, \quad (4)$$

where τ is time.

Diffusive transfer of thermal energy We examine the closed thermodynamics heat resistant system which interchanges thermal energy absents with an environment. The convective constituent of transfer of thermal energy to the system absents. As the noted system is a solid treasons of its volume V can to scorn.

Then, taking it into account $dS_V/d\tau \approx \partial S_V/\partial\tau$, equation of transfer have a kind

$$\frac{dS_V}{d\tau} = -\frac{1}{T} \frac{dU_V}{d\tau}, \quad (5)$$

where S_V , U_V are enthalpy and internal energy of system in equation respectively; which characterizes treason of parameters of state of system at space-time co-ordinates for irretrievable processes.

It is well known that

$$\frac{dU_V}{d\tau} = -\text{div } J_U. \quad (6)$$

Equation (5) may to rewrite as:

$$\frac{\partial S_V}{\partial\tau} = -\frac{1}{T} \cdot \text{div } J_U. \quad (7)$$

Using known correlation $\text{div}(y \cdot \vec{x}) = y \cdot \text{div } \vec{x} + \vec{x} \cdot \nabla y$ and considering, that $y = -\frac{1}{T^2} \cdot \text{grad } T$ nad $\vec{x} = \vec{J}_U$, we get

$$\frac{\partial S_V}{\partial\tau} = -\text{div} \left(\frac{\vec{J}_U}{T} \right) + \frac{J_U}{T^2} \cdot \text{grad } T. \quad (8)$$

According to Umov equation we can be written down

$$\frac{\partial S_V}{\partial\tau} = -\text{div } J_S + \theta. \quad (9)$$

Comparison of equation (6) i (7) allows to get correlation

$$J_S = \frac{J_U}{T}, \quad \theta = -\frac{J_U}{T^2} \cdot \text{grad } T. \quad (10)$$

Coming from a theorem about the production of energy

$$\theta \cdot T = \sum J_i \cdot X_i, \quad (11)$$

where $\partial S_V/\partial\tau$ is speed of production of energy into the system due to the dissipative effect irretrievable processes of transfer of thermal energy; J_i is a special thermal stream of diffusive

transfer of thermal energy, which is caused by the action of X_i -th force, – it is possible to write down:

$$\theta \cdot T = -\dot{J}_U \cdot \frac{1}{T} \cdot \text{grad } T = J_U \cdot X_U. \quad (12)$$

Whence

$$X_U = -\frac{1}{T} \cdot \text{grad } T. \quad (13)$$

On the basis principle of linearity stream of internal energy at the system, in equation determined by correlation

$$\dot{J}_U = L_U \left(-\frac{1}{T} \cdot \text{grad } T \right) = -\frac{L_U}{T} \cdot \text{grad } T, \quad (14)$$

where L_U is a kinetic coefficient of transfer of internal energy which represents physical properties of system.

Enter denotation $-L_U/T = \lambda$, we write down

$$\dot{J}_U = -\lambda \cdot \text{grad } T. \quad (15)$$

Putting correlation (15) to question (3), we get

$$\frac{\partial U_V}{\partial \tau} = -\text{div } \dot{J}_U = \lambda \cdot \text{div grad } T = \lambda \cdot \nabla^2 T. \quad (16)$$

As enthalpy $h_V = U_V + P \cdot V$ then at $dV \approx 0$ $h_V = U_V$ and question (10) looks like:

$$\frac{\partial h_V}{\partial \tau} = \lambda \cdot \text{div grad } T. \quad (17)$$

Equation (17) is differential equation of transfer of specific enthalpy during co-operating of the closed system with an environment.

It is known that, where C_V is a specific mass heat capacity of the system, then we get

$$\rho \cdot C_V \cdot \frac{\partial T}{\partial \tau} = \lambda \cdot \nabla^2 T \quad (18)$$

or

$$\frac{\partial T}{\partial \tau} = \frac{\lambda}{C_V \cdot \rho} \cdot \nabla^2 T. \quad (19)$$

Taking to account that $\lambda/C_V \cdot \rho = a$ it is possible to write down

$$\frac{\partial T}{\partial \tau} = a \cdot \nabla^2 T. \quad (20)$$

Thus, the thermodynamics analysis of co-operation of the system with an environment allows to get differential equation of heat-conducting for diffusive transfer of thermal energy.

$$\frac{\partial U_V}{\partial \tau} = \lambda \cdot \text{div } \nabla T, \quad (21)$$

where $U_V = C_V \cdot T \cdot \rho$, C_V is special mass thermal capacity of system.

At $\rho, C_V \neq f(\tau)$ we can to write

$$\frac{\partial T}{\partial \tau} = \frac{\lambda}{C_V \cdot \rho} \cdot \nabla^2 T. \quad (22)$$

As far as $\lambda/C_V \cdot \rho = a$, differential equation of thermal capacity at diffusive transfer for closed energy for a closed refractory system can be given as [4]

$$\frac{\partial T}{\partial \tau} = a \cdot \nabla^2 T. \quad (23)$$

Diffusive transfer of mass. We examine the open thermodynamics system which interchanges with an environment mass of matter. Such process is limited to absence of convective constituent of process of transfer of mass in the system. The volume of the system V does not change during diffusive transfer of mass, and by treason of enthalpy in the system it is possible to scorn as a result of treason of concentration of mass.

At that rate equation of the second law of thermodynamics acquires a kind:

$$\frac{dS_V}{d\tau} = -\frac{1}{T} \cdot \sum_{k=1}^n \mu_k \cdot \frac{d\rho_k}{d\tau}, \quad (24)$$

where μ_k is chemical potential of k -th component.

Process, that is examined, limit to transfer of one component at $\mu_k = 0$. Then from equation (21) we get

$$\frac{\partial S_m}{\partial \tau} = -\frac{\mu}{T} \cdot \frac{\partial \rho}{\partial \tau}. \quad (25)$$

Taking it into account, that $\frac{\partial \rho}{\partial \tau} = -\text{div } \dot{J}_D$, it is possible to write down

$$\rho \cdot \frac{dS_m}{d\tau} = -\frac{\mu}{T} \cdot \text{div } J_D, \quad (26)$$

where J_D is a specific stream of mass.

Using the known correlation from a vectorial analysis, have

$$\rho \cdot \frac{dS_m}{d\tau} = \text{div} \left[\frac{\mu}{T} \cdot J_D \right] - J_D \cdot \text{grad } \frac{\mu}{T}. \quad (27)$$

In equation (20) distinguish dissipative member which represents the quantitative measure of irreversibility of process:

$$\theta = -J_D \cdot \text{grad } \frac{\mu}{T}. \quad (28)$$

From a theorem about the production of entropy

$$\theta \cdot T = J_D \cdot X_D, \quad (29)$$

where X_D is speed of production of entropy into the system due to the dissipative effects of irretrievable processes of transfer of matter mass

$$X_D = -T \cdot \text{grad } \frac{\mu}{T}. \quad (30)$$

Taking into account that $\nabla \left(\frac{\mu}{T} \right) = \frac{1}{T} \cdot \nabla \mu - \frac{\mu}{T^2} \cdot \nabla T$, at $\nabla T \cong 0$ we get

$$X_D = -\text{grad } \mu. \quad (31)$$

On the basis of phenomenological principle of linearness the stream of mass of matter in the system is given to correlations

$$J_D = L_D \cdot X_D = -L_D \cdot \text{grad } \mu. \quad (32)$$

where L_D is a kinetic coefficient of transfer of matter mass, $L_D = D$, D is a coefficient of diffusion.

Thus, differential equation of mass capacity at diffusive transfer of one component in the system looks like:

$$\frac{\partial \rho}{\partial \tau} = D \cdot \nabla^2 \mu. \quad (33)$$

During consideration of the double-base system potential of transfer of mass of one of components determine the difference of chemical potentials of transfer ($\mu_1 - \mu_2$), id est. relative size of energy, that it is necessary for transfer of mass of one component to the spatial area, which is busy at other component which has the chemical potential.

We bring corresponding treasons to the formula (26)

$$\theta = -\sum_{k=1}^2 J_D \cdot \text{grad} \frac{\mu_1 - \mu_2}{T}. \quad (34)$$

As according to Gibbs-Dugan equation of at $P = \text{const}$ and $T = \text{const}$

$$\rho_{10} d\mu_1 = \rho_{20} d\mu_2, \quad (35)$$

where ρ_{10} , ρ_{20} are relative concentrations of first and second components in the system with a average density ρ , $\rho_{10} = \rho_1/\rho$; $\rho_{20} = \rho_2/\rho$, – at presence of one chemical reaction the gradient of potential of transfer mass is evened:

$$\left[\nabla (\mu_1 - \mu_2) \right]_{T,P} = \left(1 + \frac{\rho_{10}}{\rho_{20}} \right) \cdot (\nabla \mu_1)_{T,P} = \frac{1}{\rho_{20}} \cdot \left(\frac{\partial \mu}{\partial \rho_{10}} \right)_{T,P} \cdot \nabla \rho_{10}. \quad (36)$$

Keeping in mind that, we get

$$X_{D_{12}} = -\frac{1}{\rho_{20}} \cdot \left(\frac{\partial \mu}{\partial \rho_{10}} \right)_{T,P} \cdot \text{grad} \rho_{10}. \quad (37)$$

Then

$$\dot{J}_{D_{12}} = L_{D_{12}} \cdot X_{D_{12}} = -\frac{L_{D_{12}}}{\rho_{20}} \cdot \left(\frac{\partial \mu}{\partial \rho_{10}} \right) \cdot \text{grad} \rho_{10}. \quad (38)$$

Enter denotation we write down

$$J_{D_{12}} = -D_{12} \cdot \rho \cdot \text{grad} \rho_{10}. \quad (39)$$

Then equation of mss capacity during diffusion of the first component to space area which is busy at the second component, acquires a kind:

$$\frac{\partial \rho_1}{\partial \tau} = D_{12} \cdot \rho \cdot \nabla^2 \rho_{10} = D_{12} \cdot \nabla^2 \rho_1. \quad (40)$$

Diffusive transference during cross effects. In accordance with positions of thermodynamics of irreversible processes motive forces of processes of transfer of warmth and mass of matter it is been accordingly:

$$X_q = \frac{\nabla T}{T}, \quad X_D = T \cdot \nabla \left(\frac{\mu_2 - \mu_1}{T} \right). \quad (41)$$

These thermodynamics forces are vectors (by the tensors of the first grade) and their combination fully it admits according to principle of Curie, when force, stipulating the stream of thermal energy, can cause a mass stream and back to front.

Thus, the streams of thermal energy and mass of matter at cross effects are determined respectively by correlations:

$$\dot{j}_q = -L_{qq} \cdot \frac{\text{grad} T}{T} - \sum_{k=1}^{n-1} L_{qk} \cdot T \cdot \text{grad} \left(\frac{\mu_k - \mu_n}{T} \right); \quad (42)$$

$$\dot{j}_m = -L_{iu} \cdot \frac{\text{grad} T}{T} - \sum_{k=1}^{n-1} L_{mk} \cdot T \cdot \text{grad} \left(\frac{\mu_k - \mu_n}{T} \right), \quad (43)$$

where L_{qi} , L_{qk} , L_{mi} , L_{mk} are kinetic coefficients of transfer.

Having because of, that for the double-base system potential of mass transfer is described by correlation

$$[\nabla(\mu_1 - \mu_2)]_{T,P} = \left(1 + \frac{\rho_{10}}{\rho_{20}}\right) \cdot (\nabla\mu_1)_{T,P} = \frac{1}{\rho_{20}} \cdot \left(\frac{\partial\mu}{\partial\rho_{10}}\right)_{T,P} \cdot \nabla\rho_{10}. \quad (44)$$

Enter denotations: $\partial\mu_1/\partial\rho_{10} = \mu'_1$; $L_{qq}/T = \lambda_1$; $L_{11} \cdot \mu'_1/\rho_{20} = D$; $L_{q1} \cdot \mu'_1/\rho_{20} = \lambda_{q1}$; $L_{iq}/T = D_{1q}$, we get:

$$\dot{J}_q = -\lambda \cdot \frac{\text{grad}T}{T} - (\lambda_{q1} \cdot \nabla\rho_1)^*; \quad (45)$$

$$\dot{J}_D = \left(D_{iiq} \cdot \frac{\text{grad}T}{T}\right)^{**} - D \cdot \nabla\rho_1, \quad (46)$$

where * is an effect of diffusive heat conductivity; ** is an effect of thermodiffusion.

Respective to Umov equation, it is possible to write down:

$$\frac{\partial h}{\partial\tau} = -\text{div} \dot{J}_q; \quad (47)$$

$$\rho \cdot \frac{\partial\rho_{10}}{\partial\tau} = -\text{div} \dot{J}_D. \quad (48)$$

Taking into account that $\lambda/c_{qm} = D_{1q}$ from equation (45) we get:

$$-\text{div} \dot{J}_{D1} = D_{1q} \cdot \nabla^2 T, \quad (49)$$

where D_{1q} is a coefficient of diffusivity of the system at the transfer of thermal energy in her due to the gradient of temperature.

For zonal calculations, id est. at $\lambda = \text{const}$ and $\lambda_{q1} = \text{const}$ equation (46) assumes at a kind:

$$\frac{\partial T}{\partial\tau} = \frac{\lambda}{c \cdot \rho} \cdot \text{div} \text{grad} T + \frac{\lambda_{q1}}{c \cdot \rho} \cdot \text{div} \text{grad} \rho_1. \quad (50)$$

Thus, equation of heat conductivity at presence of transfer of mass (47) it is possible to write down as

$$\frac{\partial T}{\partial\tau} = a \cdot \nabla^2 T + \frac{a}{C_{mq}} \cdot \nabla^2 \rho_1. \quad (51)$$

There is like examined the process of mass transfer at a cross effect.

From equation (41) taking into account the accepted denotations we get

$$\rho \cdot \frac{\partial\rho_{10}}{\partial\tau} = -\text{div} (-D_{1q} \cdot \text{grad} T - D \cdot \text{grad} \rho_1) = D_{1q} \cdot \nabla^2 T + D \cdot \nabla^2 \rho_1. \quad (52)$$

Thermodynamics interpretation of this coefficient follows from the next reasoning. Distinguish part of diffusive stream of mass in equation (43), obliged by the origin to the gradient of temperatures

$$\dot{J}_{D1} = -D_{1q} \cdot \nabla T. \quad (53)$$

This stream can be presented as

$$\dot{J}_{D1} = \frac{1}{C_{qm}} \cdot \dot{J}_q, \quad (54)$$

where C_{qm} is a coefficient of specific power-hungriness of the system on the mass transfer.

Then

$$-\text{div} \dot{J}_{D1} = \frac{1}{C_{qm}} \cdot \text{div} \dot{J}_q = \frac{\lambda}{C_{qm}} \cdot \nabla^2 T, \quad (55)$$

or taking to account that $\lambda/C_{qm} = D_{1q}$, it is possible to write down.

$$-\text{div} \dot{J}_{D1} = D_{1q} \cdot \nabla^2 T. \quad (56)$$

Thus, the analysis of features of diffusive processes of transfer of thermal energy and mass of matter in the heat-resistant system from positions of phenomenological thermodynamics allows to get the system of differential equations of transfer of warmth and mass at presence of cross effects.

$$\frac{\partial T}{\partial \tau} = a \cdot \nabla^2 T + \frac{a}{C_{mq}} \cdot \nabla^2 \rho_1; \quad (57)$$

$$\frac{\partial \rho_1}{\partial \tau} = D_{iq} \cdot \nabla^2 T + D \cdot \nabla^2 \rho_1. \quad (58)$$

Conclusions. There are considered physical-mathematical models of diffusive transfer of thermal energy and mass of components, and also their cross effects for the heat-resistant system from positions of thermodynamics of irreversible processes. The higher brought going over near the analysis of processes of transfer allows to get fundamentally new decisions in relation to the package of problem questions of modern technique, in particular transfer of energy and mass of matter at treatment of dispersible powders pressure [8].

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