

# THE METHOD OF DISSIPATIVE FUNCTION AS THE FUNDAMENTAL PRINCIPLE OF CALCULATING IRREVERSIBLE PROCESSES

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The quantitative description of the principle of irreversibility is expressed by the second law of thermodynamics by introducing entropy as a measure of dissipation.

The value of dissipation  $\dot{\Psi}$  for a thermodynamic system overall can be defined through distribution of the local dissipative function  $\dot{\Psi}^V$  over the whole considered volume  $V$  (1):

$$\dot{\Psi} = \int_0^V \dot{\Psi}^V dV = \int_0^V T \cdot J_S^V dV = \bar{T}_{\tau/\mu} \cdot in\dot{S}, \quad (1)$$

where  $\bar{T}_{\tau/\mu}$  is the average thermodynamic temperature, K;  $in\dot{S}$  is the speed of entropy increase in the whole system under consideration as a result of inner irreversible processes, W/K; local production of entropy  $J_S^V$ , W/m<sup>3</sup>·K;  $\dot{\Psi}^V$  is the dissipative function of the elementary volume of a system, W/m<sup>3</sup>;  $T$  is the absolute temperature for a heterogeneous system, K [1]. The method of dissipative functions, as an analytical tool for estimating the actual energy costs, allows us to combine the fundamental structural and descriptive concepts of classical thermodynamics with the kinetic laws of the mechanism of energy and matter transfer phenomena [2].

Differential equations of the balance of mass, energy, entropy and kinetic relations of local speeds in heat-transfer processes, substance components and the impulse near the equilibrium, as well as the Gibbs equation, give us an analytical expression of the dissipative function in a generalized form (2):

$$\dot{\Psi}^V = \sum_{i=1}^n J_i \cdot X_i, \quad (2)$$

where  $J_i$  is the local speed of a process,  $X_i$  is the moving force.

As follows from the equation (2), the dissipative function  $\dot{\Psi}^V$  equals the sum of the products of local speeds of the processes  $J_i$  and their moving forces  $X_i$ , expressed in the form that allows to receive the dimension of the dissipation ( $\text{W}/\text{m}^3$ ). In an equilibrium system intensive parameters are spread evenly, and as a result, relaxation processes and forces identical to these processes arise, i.e.  $J_i = 0$  and  $X_i = 0$ .

In a generalized way the local speed near the equilibrium can be presented as a linear relation (3):

$$J_i = \sum_{k=1}^n L_{ik} \cdot X_k, \quad (3)$$

where  $J_i$  is the local speed of the  $i$ -process, generally depending on all moving forces;  $X_k$ ,  $L_{ik}$  are phenomenological proportionality coefficients that can be functions of state of an object, but do not depend on moving forces  $X_k$ .

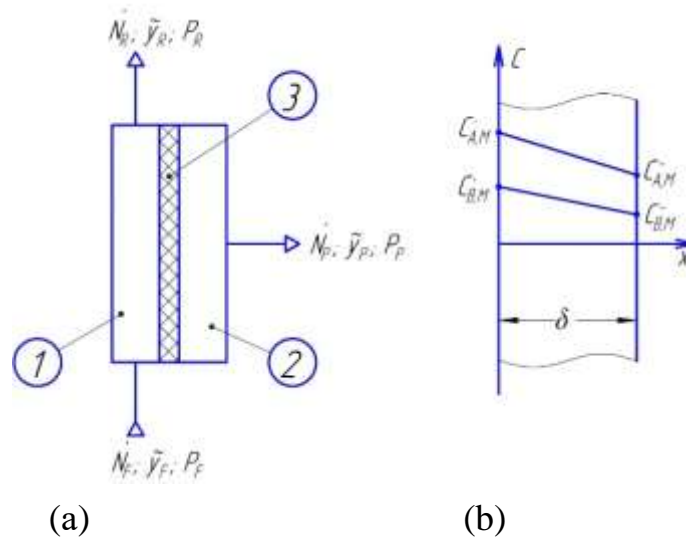
For non-conjugated processes the speed depends on its own moving force  $X_i$  (4):

$$J_i = L_{ii} \cdot X_i, \quad (4)$$

where  $L_{ii}$  are phenomenological proportionality coefficients connected with the coefficients of thermal conductivity  $\lambda$  and diffusion  $D_j$  of the  $j$ -component, the viscosity of a medium  $\mu$  and constants of the forward and backward reactions  $k^+$  и  $k^-$ .

To obtain the analytical relation and find the numerical values of dissipation, two methods can be used. The first method is based on the integration of the local dissipative function over the whole volume of the considered system. The second method lies in using integral balance equations of mass, energy, entropy, exergy for a fixed controlled volume of a non-equilibrium thermodynamic system. Let us analyze both ways on a specific example of dissipation of convertible energy in the diffusive membrane process: to obtain an analytical and a numerical solution for the value of the local and integral dissipation of energy in the diffusive layer of the membrane that divides the ideal mixture of carbohydrates of propane (component  $A$ ) and methane (component  $B$ ) at a temperature  $T_f = 279 \text{ K}$  and pres-

pressure  $P_f = 4,6$  bar in the pressure channel of the apparatus. The composition of gas mixture in the pressure channel  $\widetilde{y}_A' = 0,59 \frac{\text{kmolA}}{\text{kmol of mixture}}$ , in the draincavity  $\widetilde{y}_A'' = \widetilde{y}_P = 0,95 \frac{\text{kmolA}}{\text{kmol of mixture}}$ . The thickness of the diffusive layer of the polymer membrane  $\delta = 0,2 \mu\text{m}$ ; working area  $A = 117 \text{ m}^2$ ; the pressure in the pressure channel  $P'' = 1 \text{ bar}$ . The performance of the initial mixture is  $\dot{N}_F = 0,023 \frac{\text{kmol}}{\text{c}}$ . The gas mixture of initial composition  $\widetilde{y}_F$  is injected into the pressure channel 1 of the membrane apparatus at  $P = P_F$  and  $T_F$ , the flow  $\dot{N}_p$  that goes through the membrane 3 with the concentration  $\widetilde{y}_A'' = \widetilde{y}_P$  is let out through the drain cavity 2; the discharge flow  $\dot{N}_R$  is let out of the pressure channel with the concentration  $\widetilde{y}_R = \widetilde{y}_{A0}'$ .



**Figure 1.**a) The distribution and characteristics of the flows in the apparatus: 1 – pressure channel; 2 – drain channel; 3 – silicone membrane. b) The concentration profile in the membrane layer of the apparatus.

The process is stationary and isothermal, the gas mixture is ideal. The hydraulic resistance in the pressure and drain channels is negligible. The external diffusive resistance in the pressure and drain channels is excluded. The structure of the gas flow in the cavity of the pressure channel 1

corresponds with the model of ideal mixing (MIM). Proceeding from these presuppositions:

$$P' = P_f = P_R = 4,6 \text{ bar, where } P' \text{ is the pressure in the cavity 1;}$$

$$P'' = P_p = 1 \text{ bar, where } P'' \text{ is the pressure in the cavity 2;}$$

$$\widetilde{y}_A' = \widetilde{y}_R = 0,59 \frac{\text{kmol A}}{\text{kmol of mixture}}; \quad \widetilde{y}_A'' = \widetilde{y}_R = 0,95 \frac{\text{kmol A}}{\text{kmol of mixture}}, \text{ where}$$

$\widetilde{y}_A', \widetilde{y}_A''$  are compositions of the gas phase near the membrane surface on the side of the pressure and drain channels. The resistance to the mass transfer is focused on the diffusive layer of the silicone membrane  $\delta$  exclusively. Let us take that on the border between the gas and the membrane there is a local equilibrium.

The concentration of the components A ( $C_{A,M}'$ ) and B ( $C_{B,M}'$ ) in the membrane on the border with the pressure channel equals the following values:

$$C_{A,M}' = \sigma_{A,M} \cdot P' \cdot \widetilde{y}_A', \frac{\text{kmol A}}{\text{m}^3}$$

$$C_{B,M}' = \sigma_{B,M} \cdot P' \cdot \widetilde{y}_B', \frac{\text{kmol B}}{\text{m}^3},$$

where  $\sigma_{A,M} = 8,825 \cdot 10^{-5} \frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}$  and  $\sigma_{B,M} = 1,683 \cdot 10^{-6} \frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}$  are values of the solubility coefficients of the membrane (made of polydimethylsiloxane  $[(CH_3)_2SiO]_x$ ) for both components at a temperature  $T = 279 \text{ K}$ .

We obtain the following values of the concentrations of components on the border with the membrane:

$$C_{A,M}' = 8,825 \cdot 10^{-8} \cdot 4,6 \cdot 10^5 \cdot 0,59 = 23,951 \cdot 10^{-3} \frac{\text{kmol}}{\text{m}^3}$$

$$C_{A,M}'' = 8,825 \cdot 10^{-8} \cdot 1 \cdot 10^5 \cdot 0,95 = 8,3837 \cdot 10^{-3} \frac{\text{kmol}}{\text{m}^3}$$

$$C_{B,M}' = 1,683 \cdot 10^{-9} \cdot 4,6 \cdot 10^5 \cdot 0,41 = 0,3174 \cdot 10^{-3} \frac{\text{kmol}}{\text{m}^3}$$

$$C_{B,M}'' = 1,683 \cdot 10^{-9} \cdot 1 \cdot 10^5 \cdot 0,05 = 0,00841 \cdot 10^{-3} \frac{\text{kmol}}{\text{m}^3}$$

The values of the diffusion flows  $J_A, J_B$  in the membrane are defined based on the condition of the constant diffusion coefficients of components in the membrane layer. For a flat and one-dimensional task, the concentration distribution of the substance in the membrane is linear, and the concentration gradients are constant.

$$\frac{\partial C_{A,M}}{\partial x} = \frac{C_{A,M}'' - C_{A,M}'}{\delta} = \frac{(8,3837 - 23,951) \cdot 10^{-3}}{2 \cdot 10^{-7}}$$

$$\frac{\partial C_{A,M}}{\partial x} = -7,784 \cdot 10^4 \frac{\text{kmol}}{\text{m}^4}$$

$$\frac{\partial C_{B,M}}{\partial x} = \frac{C_{B,M}'' - C_{B,M}'}{\delta} = \frac{(0,00841 - 0,3174) \cdot 10^{-3}}{2 \cdot 10^{-7}}$$

$$\frac{\partial C_{B,M}}{\partial x} = -0,1545 \cdot 10^4 \frac{\text{kmol}}{\text{m}^4}$$

The density values of the diffusive flows of the components:

$$J_A = -D_{A,M} \frac{\partial C_{A,M}}{\partial x} = -5,558 \cdot 10^{-10} \cdot (-7,784 \cdot 10^4)$$

$$J_A = 4,326 \cdot 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$$

$$J_B = -D_{B,M} \frac{\partial C_{B,M}}{\partial x} = -1,433 \cdot 10^{-9} \cdot (-0,1545 \cdot 10^4)$$

$$J_B = 0,2214 \cdot 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$$

The total specific flow (general density of the substance) that went through the separating membrane has the value:

$$J = J_A + J_B = 4,326 \cdot 10^{-5} + 0,2214 \cdot 10^{-5}$$

$$J = 4,5474 \cdot 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$$

The general flow, taking into account the active surface of the membrane, equals the value:

$$\dot{N}_p = \int_0^A J dA = J \cdot A = 4,5474 \cdot 10^{-5} \cdot 117 = 0,532 \cdot 10^{-2} \frac{\text{kmol}}{\text{s}}$$

The discharge flow according to the material balance equation:

$$\dot{N}_R = \dot{N}_F - \dot{N}_p = 0,023 - 0,00532 = 0,01768 \frac{\text{kmol}}{\text{s}}$$

Let us check the composition of the flow that went through the diffusive membrane layer:

$$\widetilde{y}_A'' = \frac{J_A}{J} = 0,95 \frac{\text{kmol A}}{\text{kmol of mixture}}$$

Initial composition:

$$\begin{aligned} \widetilde{y}_F &= \frac{\dot{N}_R}{\dot{N}_F} \widetilde{y}_R + \frac{\dot{N}_p}{\dot{N}_F} \widetilde{y}_P = \frac{0,01768}{0,023} \cdot 0,59 + \frac{0,00523}{0,023} \cdot 0,95 \\ &= 0,673 \frac{\text{kmol A}}{\text{kmol of mixture}} \end{aligned}$$

The local dissipative function in the isothermal membrane diffusion process is defined on the basis of the relation (5):

$$\dot{\Psi}^V = \vec{J}_A \cdot (-\Delta \overline{\mu}_{A,M}) + \vec{J}_B \cdot (-\Delta \overline{\mu}_{B,M}) \quad (5)$$

For ideal solutions of the component in the membrane (the activity coefficient equals one) under the condition of planar geometry of the membrane we get:

$$\frac{\partial \mu_A}{\partial x} = \frac{\partial \mu_A}{\partial c_{A,M}} \cdot \frac{\partial c_{A,M}}{\partial x},$$

where taking into account the suppositions:  $\frac{\partial \mu_A}{\partial c_{A,M}} = \frac{\partial \ln(\gamma \cdot c_{A,M})}{\partial c_{A,M}} = \frac{RT}{c_{A,M}}$ .

Let us present the estimated relation for the local dissipation and calculate its value for given boundary conditions ( $x = 0, x = \delta$ ):

$$\dot{\Psi}^V = RT \left[ D_{A,M} \left( \frac{\partial c_{A,M}}{\partial x} \right)^2 \frac{1}{c_{A,M}} + D_{B,M} \left( \frac{\partial c_{B,M}}{\partial x} \right)^2 \frac{1}{c_{B,M}} \right]$$

$$\begin{aligned} \dot{\Psi}_{x=0}^V &= 8,314 \cdot 279 \cdot [5,558 \cdot 10^{-10} \cdot (-7,784 \cdot 10^4)^2 \cdot \frac{1}{23,951 \cdot 10^{-3}} + \\ &+ 1,433 \cdot 10^{-9} \cdot (-0,1545 \cdot 10^4)^2 \cdot \frac{1}{0,3174 \cdot 10^{-3}}] = 3,51 \cdot 10^5 \frac{\text{kW}}{\text{m}^3} \end{aligned}$$

$$\begin{aligned} \dot{\Psi}_{x=\delta}^V &= 8,314 \cdot 279 \cdot [5,558 \cdot 10^{-10} \cdot (-7,784 \cdot 10^4)^2 \cdot \frac{1}{8,3837 \cdot 10^{-3}} + \\ &+ 1,433 \cdot 10^{-9} \cdot (-0,1545 \cdot 10^4)^2 \cdot \frac{1}{0,00841 \cdot 10^{-3}}] = 18,7525 \cdot 10^5 \frac{\text{kW}}{\text{m}^3} \end{aligned}$$

The local dissipation of the convertible Gibbs energy is proportional to the square of the moving force and inversely proportional to the local concentration of components; so, the maximum value  $\dot{\Psi}^V$  corresponds to the membrane areas that border the drain cavity.

The integral value of the dissipative function per unit of the membrane area is defined by integrating its local value over  $x$  coordinate:

$$\dot{\Psi}_{\delta=1m^2} = \int_0^{\delta} \dot{\Psi}^V dx$$

For planar geometry the linear distribution of the concentration of components in the membrane obeys the expression:

$$C_{j,M} = C_{j,M}(x = 0) + bx_j, \text{ where } b = \frac{\partial C_j}{\partial x} = \text{const.}$$

The diffusion membrane is used to separate components that are similar in nature and structure, but differ in the shape and size of the molecules [3].

The integral value of the convertible energy dissipation while going through the membrane with the contact area  $A = 117 \text{ m}^2$  is defined by integrating  $\dot{\Psi}_{\delta=1m^2}$  over all working area:

$$\dot{\Psi}^V = \int_0^A \dot{\Psi}_{\delta=1m^2} dA = 0,1239 \cdot 117 = 14,5 \text{ kW}$$

The article is devoted to the diffusion in a binary gas system that obeys Fick's law: the intensity of mass transfer of a separate component is proportional to its concentration gradient and does not depend on potentials of other intensive system properties. Often such limitations in terms of application are justified, despite the fact that engineering applications of diffusion phenomena, particularly in gas systems, are quite diverse, so they need to be considered in connection with the convection mechanisms of heat and mass transfer on a case-by-case basis.

### **Список литературы**

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