

DETERMINATION OF THE CHEMICAL POTENTIAL OF MASS- AND HEAT-TRANSFER PROCESSES IN POROUS BODIES

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UDC 536.423

The problem of determining the chemical potential of mass- and heat-transfer processes for porous bodies of a classical shape (an infinite plate, a sphere, etc.) is considered; the solution obtained is illustrated with examples of the nonisothermal extraction and nonisothermal adsorption purification of vegetable oils.

Mass and heat transfer in porous bodies acquires new characteristics in considering the transfer of energy (change in the chemical potential) with account taken of the actual porosity of solids (extracted materials and adsorbents) [1–5] and the propositions of the kinetic theory of liquids [6]. Introduction of the coefficient of potential conductivity of the energy L_{en} [4, 5] allows one by analogy with heat conduction and diffusion to write the equation

$$\frac{\partial \mu(r, \tau)}{\partial \tau} = L_{en} \left(\frac{\partial^2 \mu(r, \tau)}{\partial r^2} + \frac{v}{r} \frac{\partial \mu(r, \tau)}{\partial r} \right), \quad (1)$$

in which μ is a function of two potentials at a minimum (usually the temperature and the concentration) in conformity with the commonly accepted expression

$$\mu = \rho (\mu_{st} + R_g T \ln C). \quad (2)$$

In the case of a unipotential process (only heat conduction, only diffusion, etc.), Eq. (1) becomes the corresponding equation of this process (the equation of heat conduction, diffusion, etc.). For a polypotential process (two potentials or more) the situation is different.

The polypotential (four-potential [2]) system of equations is quite useful in studying the mechanism of the process; however its analytical solution is impracticable; therefore, investigation of the kinetics of a complex process is difficult. By introducing a base potential [2], it is possible to obtain a system of uncoupled equations. In the present work, we suggest another way of solving the problem, which is based on consideration of the flux balance in a certain cross section of a body.

For simplicity we consider the one-dimensional problem for an infinite plate (the same is also true for any other classical shape of a particle, i.e., a sphere and a cylinder):

$$\frac{\partial \mu(x, \tau)}{\partial \tau} = L_{en} \frac{\partial^2 \mu(x, \tau)}{\partial x^2}. \quad (3)$$

The flux balance in the cross section of the plate which is in parallel to its surface is

$$\mp L_{en} \frac{\partial \mu(x, \tau)}{\partial x} \pm \lambda \frac{\partial T(x, \tau)}{\partial x} \pm Di \frac{\partial C(x, \tau)}{\partial x} = 0. \quad (4)$$

In analysis of the specific processes, the signs in Eq. (4) must reflect the directions of the corresponding fluxes of heat and substance mass.

Equation (4) can be written in generalized form as follows:

$$\mp L_{\text{en}} \frac{\partial \mu(x, \tau)}{\partial x} \pm K_m \frac{\partial P_m(x, \tau)}{\partial x} = 0. \quad (5)$$

For the second derivatives, which is reflected in Eq. (3), we write

$$\mp L_{\text{en}} \frac{\partial^2 \mu(x, \tau)}{\partial x^2} \pm K_m \frac{\partial^2 P_m(x, \tau)}{\partial x^2} = 0 \quad (6)$$

or with account for Eq. (3)

$$\frac{\partial \mu(x, \tau)}{\partial \tau} = \mp K_m \frac{\partial^2 P_m(x, \tau)}{\partial x^2}. \quad (7)$$

Integration leads to

$$\mu(x, \tau) = \mp K_m \int \frac{\partial^2 P_m(x, \tau)}{\partial x^2} \partial \tau + C_{\text{in}}. \quad (8)$$

The integrand in Eq. (8) reflects only one mechanism of all the fluxes, for example, the molecular one. The boundary conditions can be different.

For two mechanisms of the fluxes we have

$$\mu(x, \tau) = \mp K_{m1} \int \frac{\partial^2 P_{m1}(x, \tau)}{\partial x^2} \partial \tau \mp K_{m2} \int \frac{\partial^2 P_{m2}(x, \tau)}{\partial x^2} \partial \tau + C_{\text{in}}. \quad (9)$$

The general representation is

$$\mu(x, \tau) = \mp K_{mn} \int \frac{\partial^2 P_{mn}(x, \tau)}{\partial x^2} \partial \tau + C_{\text{in}}. \quad (10)$$

Let us solve certain problems using the method proposed.

Nonisothermal Extraction of Vegetable Oils. The internal transfer of mass and heat occurs by way of molecules [5]. As the boundary conditions we choose boundary conditions of the third kind (the most widespread in actual practice), i.e., the convective supply of heat and removal of a substance in conformity with the Newton law. An infinite plate (lobe) of thickness $2R$ is considered.

The initial condition is

$$\mu(x, 0) = \frac{\lambda}{a} T_0 + iC_0, \quad (11)$$

the symmetry condition is

$$\frac{\partial \mu(0, \tau)}{\partial x} = 0. \quad (12)$$

We are unaware of theoretical investigations into nonisothermal extraction. The experimental study of this process was carried out by A. G. Neshchadim (see, in particular, [7]) and it was shown that the possibility exists of considerably accelerating the extraction of oil.

The considered case involves two fluxes — of heat and a substance — with one molecular mechanism, i.e., to determine the chemical potential we can use Eq. (8).

The problems are solved for the temperature and the concentration (heat conduction and diffusion) individually, in particular, in [8].

The energy-flux balance for any cross section inside the plate ($0 < x < R$) which is in parallel to its surface can be written in the following manner:

$$-L_{\text{en}} \frac{\partial \mu(x, \tau)}{\partial x} + \lambda \frac{\partial T(x, \tau)}{\partial x} - Di \frac{\partial C(x, \tau)}{\partial x} = 0, \quad (13)$$

where $\lambda = K_1$ and $Di = K_2$.

Having taken the second derivatives of the solutions for $T(x, \tau)$ and $C(x, \tau)$ presented in [8] and substituted them into Eq. (8), after integration with account for Eq. (13) we obtain

$$\mu(x, \tau) = -\frac{\lambda}{a} (T_{\text{med}} - T_0) \sum_{n=1}^{\infty} A_n \cos \mu_n \frac{x}{R} \exp\left(-\frac{\mu_n^2 a \tau}{R^2}\right) + i(C_0 - C_{\text{med}}) \sum_{n1=1}^{\infty} A_{n1} \cos \mu_{n1} \frac{x}{R} \exp\left(-\frac{\mu_{n1}^2 D \tau}{R^2}\right) + C_{\text{in}}. \quad (14)$$

The coefficients A_n and A_{n1} and the roots of the characteristic equations μ_n and μ_{n1} are given in [8].

For $\tau \rightarrow 0$ the constant of integration over the conditions of the problem will be equal to

$$C_{\text{in}} = \frac{\lambda}{a} T_0 + iC_0 + \frac{\lambda}{a} (T_{\text{med}} - T_0) \sum_{n=1}^{\infty} A_n \cos \mu_n \frac{x}{R} - i(C_0 - C_{\text{med}}) \sum_{n1=1}^{\infty} A_{n1} \cos \mu_{n1} \frac{x}{R}. \quad (15)$$

Then finally we obtain

$$\begin{aligned} \mu(x, \tau) = & \frac{\lambda}{a} T_0 + iC_0 + \frac{\lambda}{a} (T_{\text{med}} - T_0) \sum_{n=1}^{\infty} A_n \cos \mu_n \frac{x}{R} - i(C_0 - C_{\text{med}}) \sum_{n1=1}^{\infty} A_{n1} \cos \mu_{n1} \frac{x}{R} - \\ & - \frac{\lambda}{a} (T_{\text{med}} - T_0) \sum_{n=1}^{\infty} A_n \cos \mu_n \frac{x}{R} \exp\left(-\frac{\mu_n^2 a \tau}{R^2}\right) + i(C_0 - C_{\text{med}}) \sum_{n1=1}^{\infty} A_{n1} \cos \mu_{n1} \frac{x}{R} \exp\left(-\frac{\mu_{n1}^2 D \tau}{R^2}\right). \end{aligned} \quad (16)$$

Averaging of Eq. (16) gives

$$\begin{aligned} \bar{\mu}(\tau) = & \frac{\lambda}{a} T_{\text{med}} + iC_{\text{med}} - \frac{\lambda}{a} (T_{\text{med}} - T_0) \sum_{n=1}^{\infty} A_n \frac{1}{\mu_n} \sin \mu_n \exp\left(-\frac{\mu_n^2 a \tau}{R^2}\right) + \\ & + i(C_0 - C_{\text{med}}) \sum_{n1=1}^{\infty} A_{n1} \frac{1}{\mu_{n1}} \sin \mu_{n1} \exp\left(-\frac{\mu_{n1}^2 D \tau}{R^2}\right). \end{aligned} \quad (17)$$

Equation (16) or (17) reflects physically the following law: in the course of the nonisothermal extraction, the chemical potential (heat content) as the algebraic sum of the heat supplied due to heat exchange and the heat with a substance removed due to mass exchange is added to the initial chemical potential (initial heat content). With time this sum decreases rapidly, and for $\tau \rightarrow \infty$ the finite value of the chemical potential will be equal to

$$\bar{\mu}(\infty) = \frac{\lambda}{a} T_{\text{med}} + iC_{\text{med}}, \quad (18)$$

whereas during the extraction with a pure solvent ($C_m = 0$), it is equal to

TABLE 1. Change in the Chemical Potential under Nonisothermal Extraction, $\bar{\mu} \cdot 10^{-8} \text{ J/m}^3$

τ , sec	$C = 40\%$	$C = 100\%$
0	15.03	16.60
10	14.87	14.87
10^2	14.87	14.87
10^3	14.87	14.87
10^4	14.87	14.87
10^5	14.88	14.88

$$\bar{\mu}(\infty) = \frac{\lambda}{a} T_{\text{med}}. \quad (19)$$

Then we perform calculations by Eq. (17).

The extracted material is a preliminary pressed lobe of sunflower seeds. From the data of [7] and using the formula given in [2], we obtain $D = 1.325 \cdot 10^{-11} \text{ m}^2/\text{sec}$ for $R = 0.47 \cdot 10^{-3} \text{ m}$ and a mean extraction temperature of 330.7 K. The concentration of the micella inside the particles is 40% (310 kg/m^3) and 100% (900 kg/m^3) (two variants) at $\tau = 0$. The enthalpy of the oil at 330.7 K is $i = 269 \cdot 10^3 \text{ J/kg}$ [9]. The extraction is carried out using a pure solvent ($C_m = 0$) in intense mixing, so that it can be assumed that $Bi \rightarrow \infty$. For this value of Bi the coefficients A_n are equal to A_{n1} and the roots of the characteristic equation μ_n are equal to μ_{n1} ; their numerical values are given in [8]: $T_m = 388 \text{ K}$ and $T_0 = 323 \text{ K}$. The values of $\lambda = 0.147 \text{ J/(m}\cdot\text{sec}\cdot\text{K)}$ and $a = 3.34 \cdot 10^{-8} \text{ m}^2/\text{sec}$ are calculated from the formulas of [10]. The results of the calculations are presented in Table 1.

It is evident from Table 1 that at first the chemical potential decreases rapidly (when $C_0 = 100\%$, the extraction is real), since at this period a large amount of oil is extracted; the amount of the extracted oil decreases and the chemical potential becomes constant with time, i.e., there comes a balance when the energy is supplied due to heating and is removed due to the extraction of oil. Since a is three orders of magnitude larger than D , already after a short period of time the particles are heated to T_m , and at $\tau = 10^2 - 10^5 \text{ sec}$ we can disregard the terms of Eq. (17) which reflect the change in the chemical potential because of the decrease in the concentration of the internal solution (by this time, the concentration is already so low that it cannot substantially affect the chemical potential). Therefore, the quantity $\bar{\mu}(\tau)$ at $\tau = 10^5 \text{ sec}$ was determined from Eq. (19). This is the chemical potential of the waste material ("shot") saturated with the solvent.

Adsorption Purification of Vegetable Oils. As has been shown previously [2, 5], adsorption and extraction can be considered as processes with the opposite directions of the mass-flux vectors (during the extraction the mass flux is directed from within the particles to the environment, while in the case of adsorption, conversely). Moreover, the adsorption of vegetable oils is a nonisothermal process in character (sorption of substances occurs simultaneously with heating); therefore, it is quite logical to compare the energy fluxes due to the change in the chemical potential and correspondingly in the temperature and the concentration inside the particles.

Let us consider the equation of energy transfer for spherical particles, assuming that the rate of the process is controlled by the diffusion of sorbed substances in a porous particle (the rate of the sorption proper on the active centers of the sorbent is taken to be equal to infinity) and by the heat conduction of the particles proper saturated with oil, i.e., we again use Eq. (8). For simplicity we take boundary conditions of the first kind, i.e., the environment temperature and the concentration of the sorbed substances in the environment will be considered to be constant. The diffusion saturation of particles with a sorbed substance simultaneously with heating of them is observed.

The initial system of equations is as follows:

the equation of internal energy transfer for spherical particles is

$$\frac{\partial \mu(r, \tau)}{\partial \tau} = L_{\text{en}} \left(\frac{\partial^2 \mu(r, \tau)}{\partial r^2} + \frac{2}{r} \frac{\partial \mu(r, \tau)}{\partial r} \right), \quad -R < r < R, \quad \tau > 0, \quad (20)$$

the initial condition is

$$\mu(r, 0) = \frac{\lambda}{a} T_0. \quad (21)$$

At the initial instant of time, the sorbent is saturated (impregnated) with oil at T_0 .

The symmetry condition is

$$\frac{\partial \mu(0, \tau)}{\partial r} = 0. \quad (22)$$

The energy-flux balance for any spherical cross section inside a sphere ($0 < r < R$) can be written in the following manner:

$$-L_{\text{en}} \frac{\partial \mu(r, \tau)}{\partial r} - \lambda \frac{\partial T(r, \tau)}{\partial r} - Di \frac{\partial C(r, \tau)}{\partial r} = 0. \quad (23)$$

Equation (23) reflects the heating of the body and its diffusion saturation with the substance: from the body surface ($R = r$) to the boundary r we have the inflow of energy by heat conduction and the inflow of energy with the mass of the sorbed substance. Here it is allowed that the impregnation of the material with the solution from the environment occurs instantly; this is reflected by Eq. (21).

By analogy with the problem of extraction we obtain

$$\mu(r, \tau) = -\frac{\lambda}{a} (T_{\text{med}} - T_0) \sum_{n=1}^{\infty} A_n \frac{R}{\mu_n r} \sin \mu_n \frac{r}{R} \exp\left(-\frac{\mu_n^2 a \tau}{R^2}\right) - iC_0 \sum_{n1=1}^{\infty} A_{n1} \frac{R}{\mu_{n1} r} \sin \mu_{n1} \frac{r}{R} \exp\left(-\frac{\mu_{n1}^2 D \tau}{R^2}\right) + C_{\text{in}}. \quad (24)$$

The integration constant C_{in} is found from Eq. (24) at $\tau = 0$:

$$C_{\text{in}} = \frac{\lambda}{a} T_{\text{med}} + iC_{\text{med}}. \quad (25)$$

The form of Eq. (25) has been determined by the fact that, according to the formulation of the problem, the initial value of the chemical potential is determined from Eq. (21). Finally we have

$$\begin{aligned} \mu(r, \tau) = & \frac{\lambda}{a} T_{\text{med}} + iC_{\text{med}} - \frac{\lambda}{a} (T_{\text{med}} - T_0) \sum_{n=1}^{\infty} A_n \frac{R}{\mu_n r} \sin \mu_n \frac{r}{R} \exp\left(-\frac{\mu_n^2 a \tau}{R^2}\right) - \\ & - iC_{\text{med}} \sum_{n1=1}^{\infty} A_{n1} \frac{R}{\mu_{n1} r} \sin \mu_{n1} \frac{r}{R} \exp\left(-\frac{\mu_{n1}^2 D \tau}{R^2}\right). \end{aligned} \quad (26)$$

The averaging of Eq. (25) over the radius yields

$$\bar{\mu}(\tau) = \frac{\lambda}{a} T_{\text{med}} + iC_{\text{med}} + \frac{\lambda}{a} (T_{\text{med}} - T_0) \sum_{n=1}^{\infty} \frac{6}{\mu_n} (-1)^{2n+1} \exp\left(-\frac{\mu_n^2 a \tau}{R^2}\right) + iC_{\text{med}} \sum_{n1=1}^{\infty} \frac{6}{\mu_{n1}} (-1)^{2n1+1} \exp\left(-\frac{\mu_{n1}^2 D \tau}{R^2}\right). \quad (27)$$

Let us analyze Eq. (27). When the process is very long ($\tau \rightarrow \infty$) we obtain the maximum value of the chemical potential (of the energy contained in the spent sorbent):

$$\bar{\mu}(\infty) = \frac{\lambda}{a} T_{\text{med}} + iC_{\text{med}}. \quad (28)$$

The evaluational calculations from Eq. (28) indicate that its first term is two orders of magnitude larger than the second term, i.e., during the adsorption purification of vegetable oils, the energy of the spent sorbent is mainly formed due to its heating. This is natural, since the amount of the sorbed substances is small compared to the absorbed oil and the mass of the sorbent itself and is of decisive importance for the quality of refined oil.

In the course of the adsorption purification, the energy components of the sorbent are comparable since D is several orders of magnitude smaller than a [1]. The relationship between the energy components of the sorbent depends in this case on the time of the process and can be determined from Eq. (27).

The energy of the spent sorbent represents the energy loss in production, and no methods to decrease this loss have been suggested until recently. The present work allows one to determine the energy loss at any stage of the process (at any time and any parameters).

NOTATION

μ , chemical potential; μ_{st} , chemical potential in the standard state; τ , time; x, r , coordinates; R , one-half thickness of an infinite plate, sphere radius; R_g , gas constant; L_{en} , coefficient of potential conductivity of the energy; ν , form factor: $\nu=0$, unlimited plate, $\nu=1$, unlimited cylinder, $\nu=2$, sphere; T , temperature; C , concentration; ρ , density; λ , thermal-conductivity coefficient; D , diffusion coefficient; i , enthalpy of the diffusing substance; C_{in} , integration constant; P , potential (temperature, concentration, etc.); a , thermal-diffusivity coefficient; K , kinetic coefficient; A_n and A_{n1} , coefficients; μ_n and μ_{n1} , roots of the characteristic equations; Bi , Biot number. Subscripts: 0, initial state; m, number of the flux (mass flux, heat flux, etc.); n, number of the mechanism of the flux (molecular, convective, etc.); med, medium; st, standard state; en, energy; in, integration; g, gas.

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