# HEAT AND MASS TRANSFER UNDER THE CONDITIONS <br> OF THE EXTERNAL PROBLEM FOR PROCESSES OCCURRING WITH A DECREASE IN THE PRESSURE OF THE MEDIUM 

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A mathematical model of the heat and mass transfer in a multicomponent vapor-gas phase is developed for the case of ideal mixing of components with a decrease in the total pressure of the medium above the surface of a wet material or solution.

In many industries, the obtaining of a product at a certain stage of the technological process is accompanied by the removal of a part of a liquid in the form of vapor from the material or solution, when the device is evacuated. This entails a change in its concentration and technological properties (structure) or cooling. Cases in point are the processes of vacuum crystallization and evaporation of solutions [1], desorption of solvents from porous sorbents [2] and drying of capillary-porous materials by decreasing the pressure [3], selffreezing of products prior to sublimation drying [4], manufacture of wood fibers by the "explosion" method in the production of wood-fiber plates [5], etc.

The motive force of all processes, which occur at a reduced pressure of the medium, is the difference of the partial pressures of the vapor of the removed moisture above the material (solution) surface and in the surrounding medium [6]:

$$
\begin{equation*}
j_{i}=\frac{\beta_{i} \mu_{i}}{R^{*} T_{\mathrm{m} . \mathrm{s}}}\left(p_{i \mathrm{~s}}-p_{i}\right) \tag{1}
\end{equation*}
$$

The partial pressure of the $i$ th component in the surrounding medium $p_{i}$ is determined by solving the system of differential equations of flow continuity and energy transfer [7] with volume sources (sinks) of heat and mass.

In Eq. (1), the coefficient of mass transfer $\beta_{i}$ is a function of the thickness of the diffusion boundary layer $\delta$ and is found from the relation

$$
\begin{equation*}
\beta_{i}=\frac{D_{i}}{\delta} \tag{2}
\end{equation*}
$$

For multicomponent gas systems, the coefficient of molecular diffusion can be determined from the equation

$$
\begin{equation*}
D_{i}=\frac{1-y_{i}}{\frac{y_{1}}{D_{i 1}}+\frac{y_{2}}{D_{i 2}}+\frac{y_{3}}{D_{i 3}}+\ldots+\frac{y_{n}}{D_{i n}}} \tag{3}
\end{equation*}
$$

in which, for the vapor diffusion of the $i$ th component, for example, in a gas, Jilliland's semiempirical relation [8]

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$$
\begin{equation*}
D_{i \mathrm{~g}}=\frac{0.0435 T^{3 / 2}}{P\left(v_{i}^{1 / 3}+v_{\mathrm{g}}^{1 / 3}\right)^{2}} \sqrt{ }\left(\frac{1}{\mu_{i}}+\frac{1}{\mu_{\mathrm{g}}}\right) \tag{4}
\end{equation*}
$$

is used.
The devices for moisture removal from a solid phase are fitted with distributing elements that provide identical conditions for the process over the entire volume [3], and a liquid-solid system is characterized by a volume boiling of the solution [1]. Moreover, the coefficient of mass transfer $\beta_{i}$ in Eq. (2) is inversely proportional to the total pressure [6]; therefore, during the system evacuation, the liquid evaporation from the material (solution) surface to the surrounding medium occurs at a high rate $(\delta \rightarrow 0)$ and does not limit the total rate of the process [9]. On these grounds, to describe the heat and mass transfer, the model of ideal mixing of components [10] in a vapor-gas medium that suggests a constant composition of the vapor-gas mixture at all points of the working volume of the device is adopted. Then, in the absence of the velocity, temperature, and density fields of a vapor and a gas in the surrounding medium, and also of the recording of the sources (sinks) of heat and mass in expanded form, the differential equations take the form

$$
\begin{gather*}
\frac{d \rho_{i}}{d \tau}=\rho_{i}\left(\frac{d \bar{y}_{i \mathrm{in}}}{d \tau}-\frac{d \bar{y}_{i}}{d \tau}\right)  \tag{5}\\
\frac{d \rho_{\mathrm{g}}}{d \tau}=-\rho_{\mathrm{g}} \frac{d \bar{y}_{\mathrm{g}}}{d \tau}  \tag{6}\\
c_{\mu, \text { mix }} \rho_{\mathrm{mix}} \frac{d T}{d \tau}=\left[\alpha\left(T_{\mathrm{m} . \mathrm{s}}-T\right)+T_{\mathrm{m} . \mathrm{s}} \sum_{i=1}^{n} j_{i} c_{i}\right] \frac{\mu_{\mathrm{mix}}}{R_{v}}-c_{\mu . \operatorname{mix}} \rho_{\operatorname{mix}} T\left(\frac{d \bar{y}_{\mathrm{g}}}{d \tau}+\sum_{i=1}^{n} \frac{d \bar{y}_{i}}{d \tau}\right) \tag{7}
\end{gather*}
$$

The left-hand side of Eq. (5) characterizes the rate of change in the mass of the $i$ th component of a vapor-gas phase in the unit of free volume of the device; the first term on the right-hand side is the rate of feed of the mass of the ith component into a vapor-gas phase, and the second term is the rate of its discharge into the vacuum line.

Relation (6) differs from Eq. (5) by the absence of a term which defines the feed of the air mass into the unit of free volume, because the device is hermetic.

In the energy transfer equation (7), the left-hand side is the rate of change in the heat content of a multicomponent vapor-gas mixture, and the right-hand side characterizes the heat transfer of the vapor-gas mixture with the surface of a coexistent phase, the heat inflow with a vapor of the evaporated moisture to the unit of free volume of the device, and the heat removal with the vapor-gas mixture to the vacuum line (Fig. 1).

In Eq. (7), the density of a vapor-gas mixture is defined by the relation [11]

$$
\begin{equation*}
\rho_{\operatorname{mix}}=\rho_{\mathrm{g}}+\sum_{i=1}^{n} \rho_{i} \tag{8}
\end{equation*}
$$

or, using the relationship between the partial pressure and the density of the component of an ideal vapor-gas mixture in the form of the Mendeleev-Clapeyron equation [11]

$$
\begin{equation*}
\rho_{i(\mathrm{~g})}=\frac{\mu_{i(\mathrm{~g})} p_{i(\mathrm{~g})}}{R^{*} T} \tag{9}
\end{equation*}
$$

by the expression


Fig. 1. Diagram of material and heat fluxes for a vapor-gas phase.

$$
\begin{equation*}
\rho_{\operatorname{mix}}=\frac{1}{R^{*} T}\left(\mu_{\mathrm{e}} p_{\mathrm{g}}+\sum_{i=1}^{n} \mu_{i} p_{i}\right) . \tag{10}
\end{equation*}
$$

The molar specific heat is defined as the sum of the products of the specific heats of the vapor and the gas which make up the mixture by their mole fractions:

$$
\begin{equation*}
c_{\mu \text { mix }}=\mu_{\mathrm{g}} c_{\underline{e}} v_{\mathrm{g}}+\sum_{i=1}^{n} \mu_{i} c_{i} v_{i} \tag{11}
\end{equation*}
$$

Taking into account that $y_{\mathrm{g}}=p_{\mathrm{g}} / P$ and $y_{i}=p_{i} / P$, where $P$ is the total pressure defined as $P=$ $p_{\mathrm{g}}+\sum_{i=1}^{\prime \prime} p_{i}$ by the Dalton law [12], we can represent Eq. (11) in the form

$$
c_{\mu, \text { mix }}=\frac{c_{\mu, \mathrm{g}} p_{\mathrm{g}}+\sum_{i=1}^{n} c_{\mu i} p_{i}}{p_{\mathrm{g}}+\sum_{i=1}^{n} p_{i}} .
$$

The molecular mass of a vapor-gas mixture is determined similarly to Eqs. (10) and (12) by the rule of additivity [11]:

$$
\begin{equation*}
\mu_{\text {nix }}=\frac{\mu_{\mathrm{g}} p_{\mathrm{g}}+\sum_{i=1}^{n} \mu_{i} p_{i}}{p_{\mathrm{g}}+\sum_{i=1}^{n} p_{i}} . \tag{13}
\end{equation*}
$$

When reduced to the free volume $V_{\mathrm{fr}}$, in which the vapor-gas mixture resides, Eqs. (5) assume the form

$$
\begin{equation*}
V_{\mathrm{fr}} \frac{d \rho_{i}}{d \tau}=V_{\mathrm{fr}} \rho_{i}\left(\frac{d \bar{y}_{\mathrm{inn}}}{d \tau}-\frac{d \bar{y}_{i}}{d \tau}\right) . \tag{14}
\end{equation*}
$$

For liquid-vapor or solid-vapor systems with an interface, the mass flux is represented by the expression

$$
\begin{equation*}
V_{\mathrm{fr}} \mathrm{\rho}_{i} \frac{d \bar{y}_{\mathrm{in}}}{d \tau}=j_{i} F . \tag{15}
\end{equation*}
$$

The discharge of the mass of the $i$ th component from the free volume of the device into a vacuum system is characterized by the volume rate of the vapor-removal system $V_{\mathrm{v} .}$ :

$$
\begin{equation*}
V_{\mathrm{fr}} \frac{d \bar{y}_{i}}{d \tau}=V_{\mathrm{v}, \mathrm{~s}} . \tag{16}
\end{equation*}
$$

Likewise, the discharge of the gas mass from the free volume of the device is defined by the relation

$$
\begin{equation*}
V_{\mathrm{fr}} \frac{d \bar{y}_{\mathrm{g}}}{d \tau}=V_{\mathrm{g} . \mathrm{s}} . \tag{17}
\end{equation*}
$$

Equations (5) and (6) with account for expressions (15)-(17) can be represented as

$$
\begin{gather*}
V_{\mathrm{fr}} \frac{d \rho_{i}}{d \tau}=j_{i} F-V_{\mathrm{v} . \mathrm{s}} \rho_{i}  \tag{18}\\
V_{\mathrm{fr}} \frac{d \rho_{\mathrm{g}}}{d \tau}=-V_{\mathrm{g} . \mathrm{s}} \rho_{\mathrm{g}} \tag{19}
\end{gather*}
$$

On substitution of the densities in the form of relations (9) into expressions (18) and (19) and on differentiation, we obtain equations for the rates of change in the partial pressures of the vapor and gas components:

$$
\begin{gather*}
\frac{d p_{i}}{d \tau}=\frac{F R^{*} T}{V_{\mathrm{fr}} \mu_{i}} j_{i}-p_{i}\left(\frac{V_{\mathrm{v} . \mathrm{s}}}{V_{\mathrm{fr}}}-\frac{1}{T} \frac{d T}{d \tau}\right),  \tag{20}\\
\frac{d p_{\mathrm{g}}}{d \tau}=p_{\mathrm{g}}\left(\frac{1}{T} \frac{d T}{d \tau}-\frac{V_{\mathrm{g} . \mathrm{s}}}{V_{\mathrm{fr}}}\right) . \tag{21}
\end{gather*}
$$

Equation (7) with account for expressions (13), (15), and (16), and for the fact that

$$
\begin{equation*}
V_{\mathrm{vg} . \mathrm{s}}=V_{\mathrm{fr}}\left(\frac{d \bar{y}_{\mathrm{g}}}{d \tau}+\sum_{i=1}^{n} \frac{d \bar{y}_{i}}{d \tau}\right)=V_{\mathrm{g} . \mathrm{s}}+V_{\mathrm{v.s}}, \tag{22}
\end{equation*}
$$

on rearrangement takes the form

$$
\begin{equation*}
\frac{d T}{d \tau}=\left\{\frac{\left[\alpha\left(T_{\mathrm{m} . \mathrm{s}}-T\right)+T_{\mathrm{m} . \mathrm{s}} \sum_{i=1}^{n} j_{i} c_{i}\right] F R^{*}}{\left(c_{\mu . \mathrm{g}} p_{\mathrm{g}}+\sum_{i=1}^{n} c_{\mu i} p_{i}\right)}-V_{\mathrm{vg} . \mathrm{s}}\right\} \frac{T}{V_{\mathrm{fr}}} . \tag{23}
\end{equation*}
$$

The volumetric efficiency of the gas-removal system $V_{\mathrm{g} . \mathrm{s}}=V_{\mathrm{v} . \mathrm{p}}$ depends on the structure of the vacuum pump and is determined by its performance.

The volumetric efficiency of the condenser $V_{\mathrm{c}}=V_{\mathrm{v} . \mathrm{s}}$ can be obtained from the heat-balance equation

$$
\begin{equation*}
V_{\text {v.s }} \sum_{i=1}^{n} \rho_{i}\left[c_{i \text { sup }}\left(T-T_{\text {isat }}\right)+c_{i} T_{i \text { sat }}+r_{0 i}\right]=k \Delta T_{\text {av }} S_{\mathrm{c}}, \tag{24}
\end{equation*}
$$

where the left-hand side takes account of the thermal effect of the cooling of a multicomponent vapor mixture to a saturation state and its condensation, and the right-hand side takes account of the heat quantity that is transferred in unit time from the coolant of a vapor mixture. Then,

$$
\begin{equation*}
V_{\mathrm{c}}=\frac{k \Delta T_{\text {av }} S_{\mathrm{c}}}{\sum_{i=1}^{n} \rho_{i}\left[c_{\text {isup }}\left(T-T_{\text {isat }}\right)+c_{i} T_{\text {isat }}+r_{\text {oii }}\right]} . \tag{25}
\end{equation*}
$$

In Eq. (25), the coefficient of heat transfer $k$ for the condensation of a multicomponent vapor-gas mixture is calculated based on the coolant parameters using the Colburn-Howgen procedure or the Ward model [14].

The saturation temperature for the $i$ th component can be determined from the Antoine equation [15]

$$
\begin{equation*}
T_{i \text { sat }}=\frac{B_{i}}{A_{i}-\ln p_{i \text { sat }}} . \tag{26}
\end{equation*}
$$

The system of equations (20), (21), and (23), which describes a variation in the basic parameters of a vapor-gas mixture during the process, was solved by the numerical method of [16] under boundary conditions of the following form:
boundary conditions

$$
\begin{gather*}
\left.j_{i \mathrm{~m}}\right|_{x=0}=j_{i},  \tag{28}\\
\left.y_{i}\right|_{x=0}=y_{i \mathrm{in}},  \tag{29}\\
\left.\frac{\partial y_{i}}{\partial x}\right|_{\left.R_{v} \geq r x\right)}=\frac{\partial y_{i}}{\partial x}=0 ;
\end{gather*}
$$

initial conditions

$$
\begin{equation*}
T(0)=T_{\mathrm{m}}(0)=T_{\text {m.init }} ; \quad p_{\text {isat }}(0)=\exp \left(A_{i}-B_{i} / T_{\text {m.init }}\right) ; \quad p_{\mathrm{g}}(0)=P_{\text {atm }} . \tag{31}
\end{equation*}
$$

According to boundary condition (28), the moisture flux of the $i$ th component on the surface of a wet material (solution) is determined from the solution of the equations of the internal problem [ $2,3,17,18]$.


Fig. 2. Experimental data and calculated curves for the temperature variation in the vapor-gas phase and the material surface as a function of the pressure in the processes of: 1) drying in the first period for AR-V activated carbon from a three-component liquid of ethyl alcohol, diethyl ether, and water; 2) drying in the second period; 3) evaporation of a $25 \%$ aqueous solution of $\mathrm{CaCl}_{2}$ : a) temperature of the vapor-gas phase; b) temperature of the material surface. $T, T_{\mathrm{m}}, \mathrm{K} ; P, \mathrm{kPa}$.

The adequacy of the mathematical model was tested on a setup that included a vacuum chamber with a built-in balance, a vacuum pump, a condenser, and instruments for recording the temperatures of the material (solution) and the vapor-gas mixture and the absolute pressure in the chamber.

Figure 2 presents calculated results and experimental data for a variation in the temperature of the vapor-gas phase and the surface temperature of AR-V activated carbon in its drying in the first period by decreasing the pressure from a three-component mixture of ethyl alcohol, diethyl ether, and water. The structures of the devices for moisture removal from a solid phase suggest a complete filling of the free volume with the dried material, which is broken up by the distributive elements into a number of thin layers [3]. If the volume of the intergranular space is disregarded, the calculation by Eq. (23) becomes unfeasible. In this case, the temperature of the vapor-gas phase is determined based on boundary condition (27) and decreases from 293 to 240 K with a pressure reduction to $1.0-0.5 \mathrm{kPa}$.

In the drying of the activated carbon in the second period, the regularity of the temperature variation of the vapor-gas phase is affected by the mechanism of deepening of the evaporation zone in the material [3]. The heat flux from the inner layers of carbon particles increases the temperature of the medium by 3-4 K at a residual pressure of 2 kPa .

In the liquid evaporation from a $25 \%$ aqueous solution of $\mathrm{CaCl}_{2}$, the free space above the solution surface causes a discrepancy between the temperature of the vapor-gas phase and the temperature of the solution surface. The maximum difference between the data for the volume of the free space $V_{\mathrm{fr}}=0.0014 \mathrm{~m}^{3}$ and the volumetric efficiencies of the systems of gas $V_{\mathrm{g} . \mathrm{s}}=0.001 \mathrm{~m}^{3} / \mathrm{sec}$ and vapor $V_{\mathrm{r} . \mathrm{s}}=0.008 \mathrm{~m}^{3} / \mathrm{sec}$ was $8-10$ K . The solution temperature was calculated from the heat-balanced equation [17] written for a one=component liquid

$$
c_{\operatorname{mix}} d T_{\mathrm{liq}}=r d U
$$

and the specific heat as a function of the number of solution components was determined from the equation [19]

$$
c_{\operatorname{mix}}=\sum_{i=1}^{n} c_{i} \bar{x}_{i}
$$

The test of the mathematical model for adequacy to an actual process revealed that the maximum discrepancy between the calculated results and the experimental data is no greater than 19\% [3].

## NOTATION

$P$ and $p$, total pressure of mixture and partial pressure of component, $\mathrm{Pa} ; \tau$, time, sec; $F$, heat- and mass- transfer surface, $\mathrm{m}^{2} ; R^{*}$, universal gas constant, $\mathrm{J} /(\mathrm{kmole} \cdot \mathrm{K}) ; T$ and $T_{\mathrm{m}}$, temperature of vapor mixture and material, K ; $j$, mass flux, $\mathrm{kg} /\left(\mathrm{m}^{2} \cdot \mathrm{sec}\right) ; V_{\mathrm{v.s}}, V_{\mathrm{g} . \mathrm{s}}$, and $V_{\mathrm{vg} . \mathrm{s}}$, volumetric efficiencies of systems of removal of vapor, gas, and vapor-gas mixture, respectively, $\mathrm{m}^{3} / \mathrm{sec} ; V_{\mathrm{fr}}$, free volume of device, $\mathrm{m}^{3} ; \mu$, molecular weight of component, $\mathrm{kg} / \mathrm{kmole}$; $c$, mass specific heat, $\mathrm{J} /(\mathrm{kg} \cdot \mathrm{K}) ; c_{\mu}$, molar specific heat, $\mathrm{J} /(\mathrm{kmole} \cdot \mathrm{K}) ; R_{\mathrm{v}}$, reduced dimension, $\mathrm{m} ; \delta$, thickness of diffusion boundary layer, $\mathrm{m} ; \beta$, coefficient of mass transfer, $\mathrm{m} / \mathrm{sec} ; \rho$, density, $\mathrm{kg} / \mathrm{m}^{3}$; $D$, coefficient of molecular diffusion, $\mathrm{m}^{2} / \mathrm{sec} ; y$, mole fraction of component in vapor, kmole $/ \mathrm{kmole}$; $\bar{y}$, mass fraction of component in vapor, $\mathrm{kg} / \mathrm{kg} ; \bar{x}$, mass fraction of component in liquid, $\mathrm{kg} / \mathrm{kg} ; v$, partial molar volume, $\mathrm{m}^{3} / \mathrm{kmole} ; \alpha$, coefficient of heat transfer, $\mathrm{W} /\left(\mathrm{m}^{2} \cdot \mathrm{~K}\right) ; V_{\mathrm{c}}, V_{\mathrm{v} . \mathrm{p}}$, volumetric efficiencies of condenser and vacuum pump, respectively, $\mathrm{m}^{3} / \mathrm{sec} ; S_{\mathrm{c}}$, condensation surface, $\mathrm{m}^{2} ; \Delta T_{\mathrm{av}}$, average temperature difference, $\mathrm{K} ; r, r_{0}$, latent heat of evaporation at running temperature and $0^{\circ} \mathrm{C}$, respectively, $\mathrm{J} / \mathrm{kg} ; A, B$, empirical coefficients in the Antoine equation; $x$, running coordinate, $\mathrm{m} ; k$, coefficient of heat transfer, $\mathrm{W} /\left(\mathrm{m}^{2} \cdot \mathrm{~K}\right) ; U$, moisture content, $\mathrm{kg} / \mathrm{kg}$; $q$, heat flux, $\mathrm{W} / \mathrm{m}^{2}$; n, number of mixture components. Subscripts: m, material; liq, liquid; $i$, vapor or liquid component; s, material surface; fr, free; v.s, vapor system; g.s, gas system; vg.s, system of vapor-gas mixture; sat, saturated; init, initial; c, condenser, atm, atmospheric; $\mu$, molar; in, inlet; mix, mixture; g, gas; v.p., vacuum pump; sup, superheated; 0 , zero temperature.

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