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HEAT AND MASS TRANSFER IN THE FLOW OF CONDENSABLE RAREFIED GASES THROUGH POROUS MATERIALS

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Heat and mass transfer in the flow of a condensable vapor through porous materials with substantially different thermophysical parameters is investigated at pressures below the triple point.

In technological processes involving the vacuum distillation and purification of materials, and in vacuum sublimation drying, problems of heat and mass transfer in the condensation of vapors into the solid state become very important. This is particularly true of the problem of the total recovery of the evolved vapors. At the present time, the foremost problem is the development of technological processes and devices for separating a vapor—gas mixture and completely recovering the condensable vapor. The uncondensable component of the mixture must be drawn off with a vacuum pump. This formulation of the problem is not dictated by purely economic considerations in working with vapors of valuable materials, but also involves problems of safety procedures and the prevention of atmospheric contamination in working with corrosive, dangerously explosive, and toxic vapors.

The purpose of the present investigation is to study heat and mass transfer in the flow of condensable vapors through porous materials with various thermophysical parameters at pressures below the triple point and to develop recommendations on the production of permeable porous barriers for vacuum condensers. To do this we devised a research procedure and built an experimental setup.

The experimental setup shown schematically in Fig. 1 was mounted in a temperature and pressure controlled test chamber made of stainless steel and having the necessary thermal lead-ins and a viewing port. A pan vaporizer 3 with an electric heater 4, whose power could be controlled, was mounted on the laboratory balance 1. A flux of vapor was produced by the sublimation of naphthalene. The porous sample 5 was attached to the base of cylinder 6 which was fastened to laboratory balance 2. The pan vaporizer 3 and cylinder 6 were made of Duralumin. Cavity A was filled with VM-4 vacuum oil, forming a hydroseal which ensured independent displacement and recording of the weight of pan 3 and cylinder 6 on balances 1 and 2, respectively.

The pressure in the test chamber was maintained at $5 \cdot 10^{-2}$ mm Hg and recorded by two VT-3 (7) thermocouple vacuum gages; the pressure in space B was determined by the temperature of saturated naphthalene vapor. The temperature of the material being sublimed, the porous sample, the nitrogen plate, the medium, and the walls of the test chamber were monitored with differential copper—Constantan thermocouples. The emfs of the thermocouples were recorded by a type M25 high-sensitivity mirror galvanometer in a circuit with a PMS-48 low-resistance potentiometer.

The porous materials used were single and multilayer felt, stainless steel, porous graphite, and a bulk porous material consisting of glass beads.

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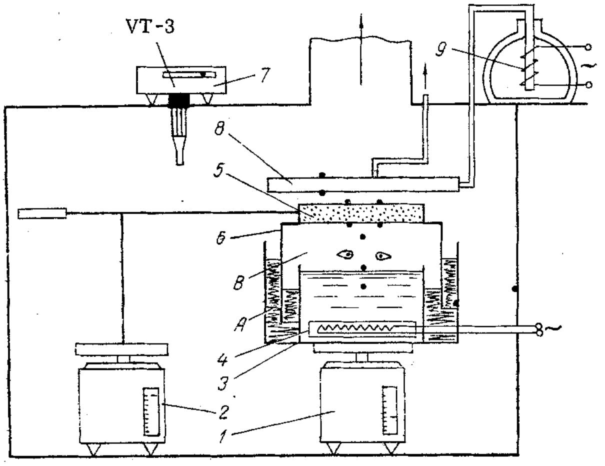

Fig. 1. Schematic diagram of experimental arrangement.

The porous samples were cooled by a thin layer of gas, using a flat nitrogen plate 8 above the sample. The temperature of the nitrogen plate was controlled by the nitrogen flow rate which was varied by adjusting the heater in the Dewar flask 9.

After evacuating the test chamber the electric heater 4 was turned on, and the temperature (and, consequently, the saturated naphthalene vapor pressure) rose in accordance with the phase state diagram. As the pressure in space B increased, the flow rate of the vapor filtering through the porous body increased. After a steady filtration state was established, the cooler was turned on, lowering the temperature of the porous sample. As soon as the temperature in any cross section of the porous sample became lower than or equal to the temperature corresponding to the saturated vapor pressure, vapor began to condense in this cross section. The position of the condensation zone in this case depends on the rate of change of temperature in the porous body. As gas filters through the porous body its rate of change of temperature is determined not only by the thermal diffusivity of the body itself, but also depends on the flow rate of the coolant, its specific heat, and the thickness of the porous sample.

If the porous sample has a "low" thermal diffusivity (felt, bulk porous body) the surface of the porous sample toward the nitrogen plate is rapidly cooled by the supply of liquid nitrogen, while the temperature distribution over the thickness of the porous sample remains close to its original value. Therefore, naphthalene vapor passes through the whole porous body and is condensed only at the outer cooled surface, clogging the pores, and changing the hydrodynamic and thermophysical characteristics of the porous sample and its emissivity. As the porous sample is cooled the condensation front is displaced into the material, causing a gradual filling of the pores by condensed naphthalene. After this, condensation of naphthalene vapor occurs at the inner surface of the porous body facing the pan vaporizer. The energy expended in vaporizing a certain amount of naphthalene from the pan vaporizer is carried off by the vapor and is completely liberated as heat given off in condensing. Heat is transferred through the porous material filled with naphthalene to the outer surface of the sample by conduction, where part of this heat goes into vaporizing naphthalene and the rest is carried away by molecular means and radiation from the outer surface. The temperature distribution over the thickness of the porous sample is established in accordance with the boundary conditions mentioned and the thermophysical parameters of the sample under study. It should be noted that the porous sample can be supercooled in such a way that the partial pressure of the naphthalene vapor corresponding to the temperature of the outer surface of the porous sample facing the vacuum chamber becomes considerably lower than the overall pressure which can be attained in the given vacuum apparatus. In this case the intensity of sublimation of condensed naphthalene from the outer surface of the porous sample is appreciably decreased, and practically the whole amount of sublimed material is condensed and remains on the porous sample.

Let us now consider the special features of mass transfer of condensable vapor through a porous sample having a "high" thermal diffusivity (porous graphite). When such a sample is cooled there is a negligible temperature difference between the outer surface of the porous sample facing the nitrogen plate and the inner surface facing the pan vaporizer. As a result, at a pressure in cavity B corresponding to the saturated vapor pressure of naphthalene the temperature of the inner surface of the porous sample is lower than the saturation temperature, and this leads to condensation of naphthalene vapor on this surface. The amount of vapor filtering through the porous sample is determined by the difference between the pressure corresponding to the

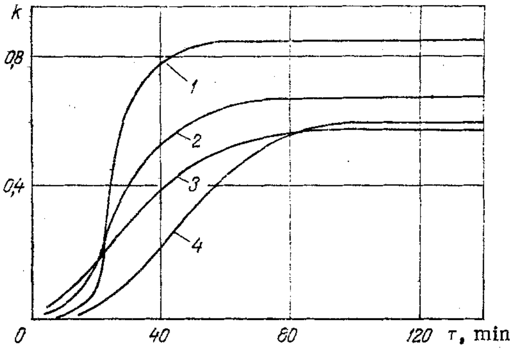

Fig. 2

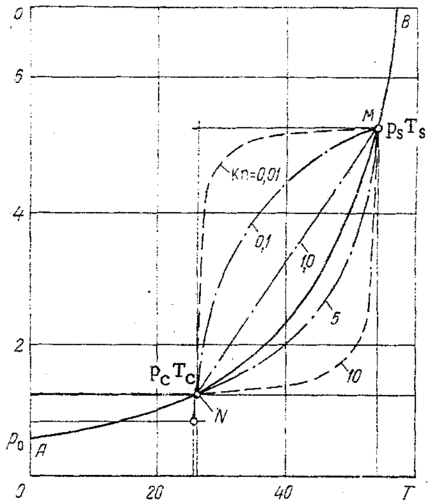

Fig. 3

Fig. 2. The dependence $k = f(\tau)$: 1) bulk porous material, beads 10^{-3} m in diameter; 2) multilayer felt, $\delta = 25 \cdot 10^{-3}$ m; 3) single-layer felt, $\delta = 5 \cdot 10^{-3}$ m; 4) bulk porous material, beads $3 \cdot 10^{-3}$ m in diameter.

Fig. 3. Matching the phase equilibrium curve AB with the dependence $T = f(p)$ for porous materials for various values of the cooling criterion Kn. p, mm Hg; T, °C.

temperature of the saturated vapor of the condensate on the inner surface of the porous sample facing the sublimation zone and the pressure in the vacuum chamber. We considered two limiting cases of the formation of a solid condensate in the filtration of a condensable vapor through porous media.

The experimental arrangement with the hydroseal, shown schematically in Fig. 1, permits a direct measurement of both the amount of naphthalene vaporized G_{vap} (balance 1) and the amount of vapor condensed on the porous sample G_{cond} (balance 2). Knowing G_{vap} and G_{cond} we construct the relations $G_{cond}/G_{vap} = f(\tau)$, shown in Fig. 2 for the porous samples investigated. The figure shows that $k = G_{cond}/G_{vap}$ reaches a certain constant value characterized by a definite ratio of the masses of vaporized and condensed material. The values of k are determined by the saturated vapor pressures in the sublimation and condensation zones and the overall pressure in the vacuum chamber.

By choosing a porous material with specific thermophysical, filtration, and geometric parameters, and varying the value of the mass flow rate of the vapor and the pressure in the vacuum chamber, it is possible to regulate the condensation process and the position of the initial condensation zone according to the requirements of the technological process.

In general, the process of condensation during the filtration of a condensable vapor through porous materials is determined by the temperature distribution in the porous sample, the pressure distribution inside the sample, and the temperature dependence of the saturated vapor pressure for the specific substance being sublimed. Depending on the thermodynamic conditions, the structure of the material, and its thermophysical characteristics, the vapor may condense both inside the porous material and on its surface. Let us consider the conditions for the formation of a solid condensate in the flow of a condensable vapor through porous materials. In a steady state of filtration of vapor the temperature distribution over the thickness of a porous plate has the form [1, 2]

$$\frac{T - T_s}{T_2 - T_s} = \exp\left[-\left(1 - \frac{x}{\delta}\right)\mathrm{Kn}\right], \tag{1}$$

where

$$\mathrm{Kn} = \frac{cG\delta}{\lambda_{eff}}.$$

For viscous flow of vapor the pressure distribution over the thickness of a porous material obeys a parabolic law [3, 4]:

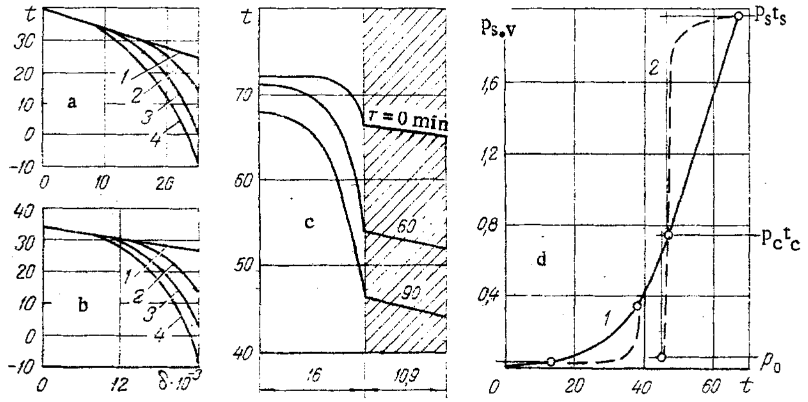

Fig. 4. Graphical solution of dependence $T = f(p)$ for porous samples of graphite and felt and dependence $p_{s.v} = f(T)$ for a sublimable material (naphthalene); a, b, and c show, respectively, the time dependence of the temperature profile over the thickness of the porous samples of multilayer felt, bulk porous material consisting of glass beads 10^{-3} m in diameter, and graphite; d is graphical solution for felt (1) and graphite (2); for a: 1) $\tau = 0$ min; 2) 10; 3) 25; 4) 80, 115; for b: 1) $\tau = 0$ min; 2) 15; 3) 25; 4) 100. t, °C; $\delta \cdot 10^{-3}$, m; $p_{s.v}$, mm Hg.

$$p^2 = p_s^2 - \frac{p_s^2 - p_0^2}{\delta} x. \tag{2}$$

From Eqs. (1) and (2) we obtain

$$\frac{T - T_s}{T_2 - T_s} = \exp\left[-\mathrm{Kn}\,\frac{p^2 - p_0^2}{p_s^2 - p_0^2}\right]. \tag{3}$$

The temperature dependence of the saturated vapor pressure is given by the Clapeyron–Clausius equation. For naphthalene this relation can be written in the form

$$\lg p_{s.v} = A - \frac{B}{C + (T - 273.2)}, \tag{4}$$

where $A = 5.8089$; $B = 978.66$; $C = 118.39$.

The simultaneous solution of Eqs. (3) and (4) determines the temperature and pressure and, consequently, the value of x at which vapor condenses (a simultaneous solution is possible only graphically or numerically on a computer, and it exists only when condensation occurs). The graphical solution of Eqs. (3) and (4) is shown in Fig. 3. The open curves are plots of the dependence $T = f(p)$ from Eq. (3) for various values of Kn. The solid line gives the temperature dependence of the saturated vapor pressure of the material being sublimed. The point M (p_s, T_s) on the phase equilibrium curve AB corresponds to the thermodynamic conditions for the formation of vapor in the sublimation of material at the sublimation surface. If the outer surface of the porous sample is cooled and maintained at a temperature T_c, it can be seen from Fig. 3 that for values of $\mathrm{Kn} \geq 5$ all points on the curve $T = f(p)$ corresponding to the state of the vapor over the thickness of the porous sample lie below the phase equilibrium curve AB; i.e., the conditions for the condensation of vapor are not met. Only for $x = \delta$ can vapor condense into the solid state. As vapor condenses, the condensation front moves, filling all the pores with condensed matter.

For flow conditions such that $\mathrm{Kn} \leq 1$, all points on the curve $T = f(p)$ lie above the phase equilibrium curve, and, consequently, vapor condenses even at $x = 0$. The porous space in this case remains free of condensate and permeable for gases and uncondensable vapors.

Thus, depending on the value of the cooling criterion Kn, vapor can condense either on the inner surface of the porous sample facing the sublimation zone or on the outer surface of the porous sample facing the vacuum chamber, with the solid condensate filling the pores in the process.

The simultaneous graphical solution of the experimental relation $T = f(p)$ for specific porous samples (graphite, $\delta = 10.9 \cdot 10^{-3}$ m, and multilayer felt) and the equation $p_{s.v} = f(T)$ calculated from Eq. (4) for the

TABLE 1

Thickness of condensate layer, mm	Time of filtration of 5 dm3 of air, sec
0	26,3
3,5	29,4
5,9	36,0
18,0	38,3

sublimable material naphthalene is shown in Fig. 4d. The values of the cooling criterion Kn for graphite and felt are, respectively, $0.7 \cdot 10^{-3}$ and 2.16. The experimental data showed that for $Kn = 0.7 \cdot 10^{-3}$ condensation occurs on the outer surface of the porous graphite; for Kn = 2.16 condensation begins on the outside of the porous sample, filling the porous space in the condensation process. The numbers 2.25, 1.47, 0.9, 0.41, and 0.15, measuring the increase of mass (g) of felt layers I-V, respectively, in a special experiment, indicate the direction of the condensation front; layer I faces the nitrogen plate. The data were obtained after cooling the porous sample for 2 h.

The time variations of the temperature profiles over the thickness of porous samples of multilayer felt, bulk porous material, and graphite are shown in Fig. 4a, b, c. The temperature gradient over the thickness of a porous sample of graphite is negligible, which causes an appreciable gradient at the inner side of the porous sample and the condensation of vapor on this surface.

During the experiment the permeability of the condensate with respect to an uncondensable gas was also investigated. We also studied samples having thermal diffusivities $\sim 5 \cdot 10^{-6}$ m^2/sec (stainless steel) and $\sim 60 \cdot 10^{-6}$ m^2/sec (porous graphite). The experiments performed with naphthalene and water vapors showed that the condensate formed has a porous structure, permeable with respect to an uncondensable gas. The permeability of the condensate depends on the conditions of its formation and, in particular, on the temperature difference between the saturated vapor and the condensation surface. The experimental results listed in Table 1 show that a porous sample remains highly permeable even when an appreciable thickness of condensate is formed.

These results are particularly important for technical applications involving the purification of contaminated materials where the final product must be refined and condensed and the contaminants eliminated. The permeability of the condensate permits an uncondensable gas to filter through it and the porous material. Porous samples with a "low" thermal diffusivity become impermeable after condensation has gone on for a certain time, since the condensate formed fills the pores.

We estimated the error in measuring weights. The errors result mainly from the use of the hydroseal and the presence of leads to the electric heater and thermocouples. The errors due to the leads were kept to no more than 0.5-0.8% by attaching springs to them. The errors resulting from the use of the hydroseal involve the influence of the readings of balances 1 and 2 on one another; these errors are about 5%. An estimate of the total error, including the errors of the measuring apparatus, shows that the maximum relative error in measuring the amounts of vaporized and condensed naphthalene is no more than 12%.

On the basis of the result obtained it is possible to formulate the basic requirements for porous permeable barriers of vacuum sublimation condensers: high thermal diffusivity of the porous material of the element ($a > 5 \cdot 10^{-6}$ m^2/sec); uniformly high permeability of the porous element over the surface; minimum possible thickness of the porous element to ensure the necessary mechanical strength. The construction of the condenser must ensure control of the temperature of the porous element according to the requirements of the technological process.

NOTATION

G, mass flow rate of vapor, kg/sec·m^2; δ, thickness of porous sample, m; τ, time, sec; λ_{eff}, effective thermal conductivity of porous material, W/m·deg; c_p, specific heat of vapor of sublimed material, J/kg·deg; T_s, temperature of sublimation surface, °K; T_c, temperature of condensation surface; p, vapor pressure, N/m^2; $p_{s.v}$, saturated vapor pressure, mm Hg; Kn, cooling criterion of porous materials.

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