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MASS TRANSFER IN EVACUATION OF MATERIALS WITH LARGE OUTGASSING

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Non-steady-state mass transfer in materials with large outgassing, used for the heat insulation of cryogenic vessels, was investigated experimentally and theoretically.

Materials used for vacuum-multilayered insulation (VMI) of cryogenic vessels have an extended surface and, consequently, large outgassing in vacuum. The required vacuum in the insulation cavity of the vessels is maintained with the aid of adsorbents which also liberate a large amount of gases during the initial evacuation. All this leads to a substantial extension of the time of evacuation, which sometimes attains more than 100 h.

The outgassing of various materials for VMI was measured by the authors of [1-4]. The experimental data obtained by different authors for the same materials differ, sometimes one being a multiple of the other. The object of the present work is to find the causes of these discrepancies and to work out a method of calculating the process of evacuation on the basis of its theoretical and experimental investigation.

The equation of non-steady-state mass transfer in the diffusion of a sorbed gas with a linear adsorption isotherm in a plane layer of porous material has the form [5]

$$\frac{\partial c}{\partial \tau} = D_e \frac{\partial^2 c}{\partial x^2}. \tag{1}$$

The effective diffusion coefficient $D_e = D/(1 + H)$, when H is the Henry law constant characterizing the slope of the adsorption isotherm, is

$$da = H\, dc. \tag{2}$$

The absorption per unit mass of the sorbent is

$$da = \frac{H}{\rho} dc. \tag{2'}$$

Since the gas pressure is proportional to the concentration, Eq. (1) may be replaced by

$$\frac{\partial p}{\partial \tau} = D_e \frac{\partial^2 p}{\partial x^2}. \tag{3}$$

Some authors (e.g., Mikhal'chenko and Pershin [6]) veiw the process of evacuation of the insulation as a diffusion process with distributed sources of outgassing, with the

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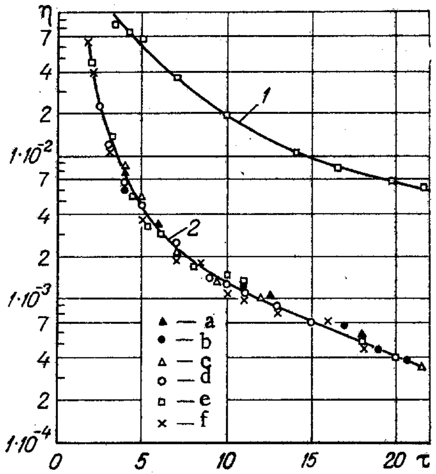

Fig. 1. Specific outgassing rate of adsorbent η, $m^3 \cdot Pa/sec \cdot kg$, in dependence on the evacuation time τ, h: 1) zeolite SaEN-4V, C/G = 0.05 $m^3/sec \cdot kg$; 2) charcoal SKT, C/G: a) 0.0059; b) 0.013; c) 0.025; d) 0.2; e) 0.33; f) 0.69.

outgassing rate being constant or changing with time according to a specified regularity. In that case there is D on the right-hand side of Eq. (3) instead of D_e, and another term is added, viz., the outgassing rate, whose magnitude has to be specified. Below it is shown that the outgassing rate is not an independent magnitude and that it is found from the solution of Eq. (3).

The boundary conditions in the evacuation of a simple medium can be written as follows:

$$p(x,\ 0) = p_0;\quad \frac{\partial p(\pm l)}{\partial x} - \frac{C}{C_1 l}\,[p(\pm l) - p_1] = 0,$$

where p_1 is the pressure at the entrance into the vacuum pump. Here and below we mean by pressure the pressure of the desorbed gases. The pressure of air filling the pores is taken equal to zero because this air is relatively easily removed from the heat-insulation cavity, and evacuation consists essentially in removing the adsorbed gases. With these boundary conditions, the solution of Eq. (3) is analogous to the solution of the equation of heat conductivity with the boundary conditions of the third kind [7]. For the mean integral pressure p_{av} in the pores we obtain the relationship

$$\frac{p_{av} - p_1}{p_0 - p_1} = \sum_{n=1}^{\infty} A_n \exp(-\mu_n^2\,\mathrm{Fo_d}), \tag{4}$$

where $A_n = 2\sin^2\mu_n/\mu_n(\mu_n + \sin\mu_n\cos\mu_n)$; μ_n are the roots of the characteristic equation cot $\mu = \mu/\mathrm{Bi_d}$; C/C_1 is Biot's diffusion numbers; and $\mathrm{Fo_d} = D_e\tau/l^2$ is Fourier's diffusion number.

Maximum evacuation rate is ensured on condition that $\mathrm{Bi_d} \to \infty$ ($C \gg C_1$). In that case, $\mu_n = (2n-1)\pi/2$ and $A_n = 8/(2n-1)^2\pi^2$. When $\mathrm{Fo_d} > 0.1$, all terms in (4), except the first, may be neglected:

$$\frac{p_{av} - p_1}{p_0 - p_1} = \frac{8}{\pi^2}\exp\left(-\frac{\pi^2}{4}\cdot\frac{D_e\tau}{l^2}\right). \tag{5}$$

The above solution is correct when the adsorption isotherm is linear, so that $a/a_0 = p_{av}/p_0$, where a_0 is the adsorbed amount at the initial instant of time. If we differentiate (5), we obtain, using the last relationship,

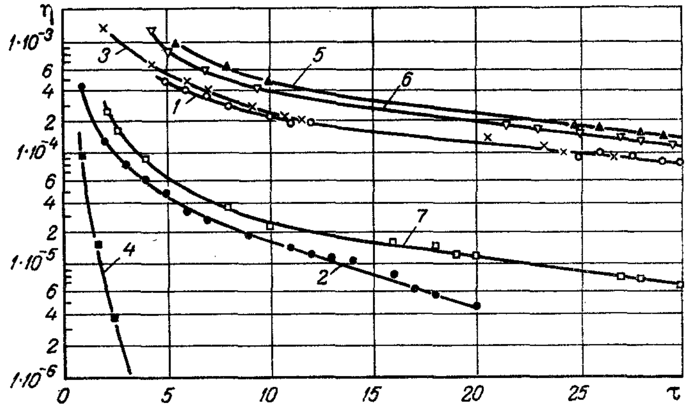

Fig. 2. Specific outgassing rate of materials η in dependence on the evacuation time τ: 1-4) glass-fiber mat ÉVTI-7; 5-7) glass-fiber mat ÉVTI-7 and aluminum foil; ratio C/G, m^3/sec·kg: 1) $7.3\cdot10^{-3}$; 2) $1.7\cdot10^{-1}$; 3) $4.8\cdot10^{-2}$; 4) 2.7; 5) $7.3\cdot10^{-3}$; 6) $6.6\cdot10^{-3}$; 7) $1\cdot10^{-1}$.

$$\frac{\partial a}{\partial \tau} = -\frac{2D_e a_0}{l^2}\cdot\frac{p_0-p_1}{p_0}\exp\left(-\frac{\pi^2}{2}\cdot\frac{D_e\tau}{l^2}\right). \tag{6}$$

With low conductivity of the evacuation line ($C \ll C_1$), all $A_n \to 0$ except the first amplitude which is equal to $A_1 = 1$. The corresponding value of the root is $\mu_1 = \sqrt{Bi_d}$. As a result, Eq. (4) assumes the form

$$\frac{p_{av}-p_1}{p_0-p_1} = \exp(-Bi_d\, Fo_d) = \exp\left(-\frac{C\tau}{HlF}\right). \tag{7}$$

From this we find

$$\frac{\partial a}{\partial \tau} = -\frac{Ca_0}{HlF}\exp\left(-\frac{C\tau}{HlF}\right). \tag{8}$$

In the case of gas desorption from nonporous surfaces, the outgassing rate in evacuation can be found on the basis of the equation of material balance

$$Gda = -Ccd\tau. \tag{9}$$

If adsorption obeys the linear regularity of (2), then integration of Eq. (9) yields a formula that is analogous to (8):

$$\frac{da}{d\tau} = -\frac{C\rho a_0}{GH}\exp\left(-\frac{C\rho\tau}{GH}\right). \tag{10}$$

We measured the outgassing rate of materials used for the heat insulation of cryogenic vessels with different conductances of the evacuation line. The conductance was changed by inserting diaphragms containing holes with different diameters. The outgassing rate was determined by two methods: by the pressure gradient on the diaphragm and by the initial rate of pressure increment when the vacuum pump was switched off. The methods of measurement are described in greater detail in [3].

Figure 1 presents experimental data for the zeolite SaEN-4V and charcoal SKT used as adsorbents for cryogenic vessels with VMI. The ratio of conductance to the mass of adsorbent, proportional to Bi_d, changed in experiments with charcoal by a factor of more than 100. It can be seen from the graph that all the experimental points lie on one line; this is due to the low rate of internal diffusion in the pores of the adsorbent, as a result of which mass transfer is determined completely by diffusion in the pores in accordance with Eq. (6).

The charcoal granules are small cylinders whose length slightly exceeds the diameter. For simplifying the calculation, we assume that they are of spherical shape. In that case, Eq. (6) for an unbounded plate changes to

$$\frac{p_{av}-p_1}{p_0-p_1}=0.6079\exp\left(-\pi^2\frac{D_e\tau}{r_0^2}\right). \quad (11)$$

From the slope of the straight segment in Fig. 1 and with the aid of Eq. (11) we find the diffusion coefficient $D_e = 3.2\cdot10^{-12}$ m²/sec. This value agrees with the values of D_e found by the adsorption kinetics of nitrogen on charcoal SKT [8] and lying within the limits $5\cdot10^{-13}$–$5\cdot10^{-12}$ m²/sec.

The measurement results for heat-insulating materials used in VMI are presented in Fig. 2. The outgassing rate and the rate of its decrease with time depend on the ratio C/G, as also follows from Eq. (10). The investigated materials were wound onto a hollow cylinder; the number of wound layers was 60 on an average. In view of the thinned-out structure of glass-fiber mat, its resistance in the direction parallel to the layers is relatively low. Nevertheless, when the number of layers is large and evacuation is carried out at a high rate, the resistance of the mat may exert a substantial influence on the evacuation process. The experimental data on the conductance of glass-fiber mat in the direction perpendicular to the layers may be represented by the formula

$$\frac{C}{F}=\frac{47}{N}\ \text{m/sec}. \quad (12)$$

When a composite of aluminum foil and glass-fiber mat is evacuated, the removed gases pass through annular channels formed by layers of the foil. The conductance of these channels, which has to be taken into account in the calculations, was determined by a formula obtained in [9].

From the slope of the straight segment of the experimental dependence in semilogarithmic coordinates (Fig. 2) we find the value of H with the aid of (10). It follows from experimental data of [3, 4] that the amount of gases liberated in vacuum by 1 m² of aluminum foil is 3-5 times smaller than the amount liberated by 1 m² of glass-fiber mat. The effect of the foil in an insulating composite of foil and mat expresses itself chiefly in reducing the rate of removal of gases in consequence of lowered conductance. In the calculations of the values of H for glass-fiber mat using data for the above-mentioned composite, a correction for outgassing of the foil was introduced.

The values of H calculated from experimental data are presented in Fig. 3 in dependence on the mean pressure in the evacuated volume during the calculated period of time. In the calculations, the mean value ρ = 100 kg/m³ was adopted for glass-fiber mat. The constant H decreases when the pressure increases, and the dependence is expressed to a sufficient approximation in the logarithmic coordinates of a straight line with a slope of 45°. Such a dependence corresponds to the equation of Temkin's absorption isotherm

$$a=b_1\ln p+b_2,$$

which, as is known, describes very well many experimental data on adsorption at low pressures.

The good agreement of the values of H obtained from data for experiments with different conductances of the insulation and the external vacuum system confirm the possibility of describing the processes of evacuation of VMI by Eq. (10). In this case, the rate of outgassing of the material depends not only on the duration of the evacuation, but, to a decisive extent, also on the conductance upon evacuation.

Things are more complicated in the evacuation of a heat-insulating cavity of a cryogenic vessel which contains simultaneously the insulation and the adsorbent. As an example we present the experimental data on the evacuation of the insulation cavity of a tank with a capacity of 0.5 m³ of liquid oxygen or nitrogen (Fig. 4). The VMI of the cistern contained 2.4 kg glass-fiber mat, and in the adsorption chamber there was 0.4 kg zeolite SaEN-4V. It follows from the data presented in Figs. 1 and 2 that the overall amount of gases liberated by the zeolite is much larger than the amount of gases liberated by the insulation. Nevertheless, in distinction to the data of Fig. 1, the outgassing rate in this case depends strongly on the conductance of the vacuum system, i.e., on the specific evacuation rate. The reason is the low values of the specific evacuation rate which, even with maximum con-

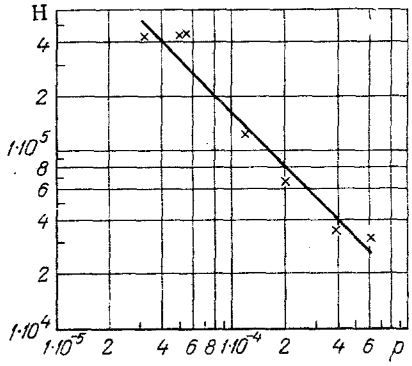

Fig. 3

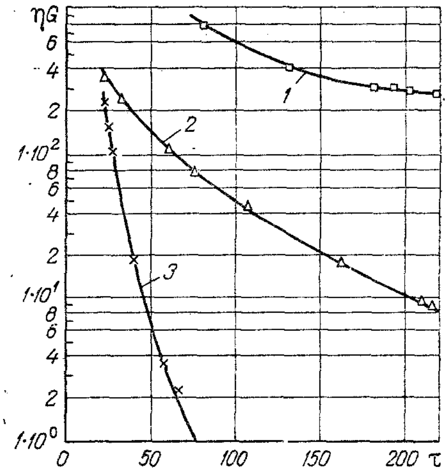

Fig. 4

Fig. 3. Dependence of the Henry law constant H on the pressure p, Pa, for glass-fiber mat ÉVTI-7.

Fig. 4. Rate of outgassing ηG, m^3·Pa/sec, in dependence on the time of evacuation τ, h, of the materials of the heat-insulating cavity of a tank with a capacity of 0.5 m^3 at 473°K. Conductance of the vacuum system: 1) C = 0.0008 m^3/sec; 2) 0.0031; 3) 0.015.

ductance in the evacuation of the tank, was lower than the specific evacuation rate upon evacuation of charcoal SKT. This case corresponds to Eq. (8), according to which the rate of decrease of the outgassing rate is proportional to the conductance. The experimental data of Fig. 4 obey this regularity.

Thus the results obtained in the present work help reveal the regularities characterizing the outgassing rate in the evacuation of different materials, and they make it possible to select the optimum parameters of the vacuum system ensuring fairly rapid evacuation when there are materials with large outgassing.

NOTATION

a, adsorbed amount of gas; c, gas concentration above the adsorbent; C, conductance of the vacuum system; C_1, conductance of the pores of the adsorbent; D, diffusion coefficient of the gas in the pores of the adsorbent; F, surface area of the layer of adsorbent; G, mass of the adsorbent; l, length of the pores; N, number of layers of the material; p, gas pressure above the adsorbent; ρ, apparent density of the adsorbent; τ, time.

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