6. S. S. Kutateladze, Heat Transfer in Condensation and Boiling [in Russian], Mashgiz (1952).
7. S. S. Kutateladze, Basic Heat-Transfer Theory [in Russian], Nauka, Novosibirsk (1970).
8. V. M. Borishanskii, Tr. TsKTI, No. 57, 3 (1965).
9. I. I. Novikov, in: Heat Transfer and Hydraulics of Two-Phase Media [in Russian], Gosénergoizdat (1961).
10. M. D. Kirpichev, Theory of Similarity [in Russian], Izd. Akad. Nauk SSSR (1953).
11. A. A. Gukhman, Introduction to the Theory of Similarity [in Russian], Vysshaya Shkola, Moscow (1963).
12. M. P. Vukalovich and I. I. Novikov, Thermodynamics [in Russian], Mashinostroenie (1972).
13. I. P. Vishnev, Khim. Neft. Mash., No. 5 (1973).
14. V. I. Tolubinskii, Author's Abstract of Doctoral Dissertation, Kiev (1950).
15. N. Yu. Tobilevich, Author's Abstract of Candidate's Dissertation, Kiev (1948).
16. V. A. Grigor'ev, A. G. Illarionov, et al., in: Papers of a Science and Engineering Conference [in Russian], MÉI, Moscow (1967), pp. 108-116 and 146-151.

THEORY OF DEEP DRYING OF FINELY POROUS BODIES AND EXPERIMENTAL VERIFICATION OF THEORY

P. P. Zolotarev, Ya. I. Rabinovich, and N. V. Churaev

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Approximate formulas for calculating the initial phase of the deep drying of finely porous bodies are obtained for the case of random adsorption isotherms. Examples of calculations using these formulas showing a satisfactory agreement with experimental data are given.

Formulas for the coefficients of internal mass transfer accompanying the deep drying of finely porous bodies under isothermal conditions are derived in [1] on the basis of the kinetics of desorption processes. The next problem is that of calculating the rates and duration of isothermal deep drying up to a given final mass content u_F. In order to simplify the calculations it is convenient to approximate the actual continuous adsorption isotherms by broken isotherms comprising n links [2-4]. The initial section of the isotherm, corresponding to the deep-drying region, can be replaced with adequate accuracy [5] by a broken line in two links (n = 2). The equation for the isotherm is written in this case as follows:

$$a = a_1 = \beta_1 c, \quad 0 \leqslant c \leqslant c_*; \quad a = a_2 = \beta_1 c_* + \beta_2 (c - c_*), \quad c \geqslant c_*. \tag{1}$$

Here β_1 and β_2 are the isotherm parameters: when $\beta_1 > \beta_2$, the isotherm is convex, and when $\beta_1 < \beta_2$, it is concave.

In [2, 4], in particular, the problem of the kinetics of desorption from a porous half-space is examined for an isotherm of type (1). When the coefficient of internal diffusion D_i = const, it is formulated as follows:

$$\begin{aligned} (1+\beta_1)\frac{\partial c_1}{\partial \tau} &= D_i \frac{\partial^2 c_1}{\partial x^2}, \quad 0 \leqslant x \leqslant l(\tau); \\ (1+\beta_2)\frac{\partial c_2}{\partial \tau} &= D_i \frac{\partial^2 c_2}{\partial x^2}, \quad l(\tau) \leqslant x < \infty; \end{aligned} \tag{2}$$

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$$c_1(0,\tau)=0;\quad c_2(x,0)=c_0;\quad a_2(x,0)=a_0;\quad c_1(l,\tau)=c_2(l,\tau)=c_*;$$
$$(\partial c_1/\partial x)_{l(\tau)}=(\partial c_2/\partial x)_{l(\tau)};\quad l(0)=0. \tag{3}$$

Here the indices 1 and 2 refer to the concentrations c and a in the $0 \le c_1 \le c_*$ and $c_* < c_2 \le c_0$ regions, respectively; $l(\tau)$ is the mobile boundary separating regions 1 and 2 at which $c = c_*$.

Using the results of [2, 4], it is easy to find that the initial phase of the deep drying for isotherms of all types and for a random porous particle shape is described by the equation

$$u(\tau)/u_0 = 1 - B\sqrt{\tau}. \tag{4}$$

This corresponds to a rate of drying in the initial phase equal to

$$W = du/d\tau = -u_0 B/2\sqrt{\tau}. \tag{5}$$

The constant B is dependent on D_i, the adsorption isotherm parameters, and the size and shape of the particles. For isotherm (1), specifically, it turns out to be equal to

$$B = \frac{2h}{\sqrt{\pi}}\left(\frac{c_*}{a_0}\right)\frac{\sqrt{D_i(1+\beta_1)}}{\operatorname{erf}(\xi_0\sqrt{1+\beta_1})}. \tag{6}$$

Here h is a geometrical factor; for spherical particles $h = 3/R_0$. The constant $\xi_0 = l(\tau)/2\sqrt{D_i\tau}$ [where $l(\tau) \sim \sqrt{\tau}$] is determined [2, 4] from the transcendental equation

$$\sqrt{1+\beta_2}\,\operatorname{erf}(\xi_0\sqrt{1+\beta_1})\,[(c_0/c_*)-1]\exp[-(1+\beta_2)\xi_0^2]$$
$$=\sqrt{1+\beta_1}\,\operatorname{erfc}(\xi_0\sqrt{1+\beta_2})\exp[-(1+\beta_1)\xi_0^2], \tag{7}$$

which is solved graphically or by the method of successive approximations.

It follows from [2-4, 6] that the initial phase of drying, described by Eqs. (4)-(7), occurs for the concave and linear isotherms when $u/u_0 \ge 0.5$. For the convex isotherms the limits of applicability of the equations should be determined in each specific case.

In a number of cases a further simplification of the deep drying formulas is possible; for example, when a linear ($n = 1$) isotherm is used $a = \beta c$. Then, for spherical particles,

$$D_i = m(D + \beta\bar{D}_s); \tag{8}$$
$$B = 6\sqrt{D_i(1+\beta)}/R_0\beta\sqrt{\pi}. \tag{9}$$

Here $\bar{D}_s$ is the mean value of the coefficient of surface diffusion over a range of mass contents from u_0 to u_F.

For the linear isotherm complete (right up to $u_F = 0$) solutions to these types of problems, which are identical to the corresponding thermal conductivity problems [7], are known. Thus, for a spherical grain the drying time from u_0 to $u_F = 0.1u_0$ and to $u_F = 0.05u_0$, respectively, is

$$\tau_0 \approx 0.182R_0^2 a_0/c_0 D_i;\quad \tau_0 \approx 0.253R_0^2 a_0/c_0 D_i. \tag{10}$$

The drying time can be assessed also for concave isotherms close to the maximum concavity ($a = 0$, $c < c_0$; $a = a_0$, $c = c_0$), for which a complete solution to the desorption problem is also known [2-4].

All the results presented refer to the case in which the ambient does not contain the vapor of the substance being eliminated and in which the limiting phase of the process is the internal mass transfer. For the linear and limiting concave isotherm, however, the corresponding solutions can also be obtained for the final rate of external mass exchange [4, 7, 8].

An analysis of the formulas obtained shows that the basic influence on the kinetics of deep drying is exerted by three parameters: 1) the size of the particles being dried R_0; 2) the strength of the bonding of the adsorbed molecules as characterized by the parameter β; 3) the coefficient of internal diffusion D_i which is dependent on the porosity, the pore size, the temperature, and the contribution of surface diffusion [1]. The possibilities of intensifying the deep drying lie primarily in raising the values of D_i, since there is, as a rule, a technological limit to the refinement of the particles. There is also a possibility of a certain reduction in β, for example, as a result of the modification of the surface of the porous body by means of physical or chemical methods.

Unfortunatly, there are little experimental data which would enable us to verify the theory devised. Deep drying covers the region of low initial mass contents, when the porous body contains only the adsorbed substance (region of mono- and polymolecular adsorption). Moreover, investigations in which the adsorption isotherms and information on pore sizes, to say nothing of the surface mobility of the adsorbed molecules, are given simultaneously with the graphs of the drying rate are rare. In the first place, this kind of verification must be made on systems with a rigid framework, i.e., with a structure which does not vary during the drying and with a sufficiently narrow distribution of pores by radius. A convenient model is that of spherical granules of silica gel with different specific surfaces. Observations on moisture desorption from such systems combined with the sorption-desorption isotherms are given in [9-13].

The deep-drying theory examined above is compared with experimental results as follows. The values of the constant B are determined from data on the rate of adsorption or desorption [in the region of mass contents in which the dependences (4) and (5) are satisfied]. Then in the case of desorption the D_i values are found from (6) and in the case of adsorption the D_i values are obtained from the formula [6]

$$D_i = \frac{\pi}{36(1+\beta_2)} \left\{ \frac{BR_0 \operatorname{erf}(\xi_0 \sqrt{1+\beta_2})}{[1-(c_*/c_0)]\,(c_0/a_0)} \right\}^2. \tag{11}$$

For the linear adsorption isotherm this expression is simplified and takes the form

$$D_i = \pi B^2 R_0^2 \beta/36. \tag{11'}$$

With desorption the values of a_0 and c_0 refer to the initial state of the system and are calculated from the initial moisture content of the specimen u_0 and from the relative pressure of the vapor p/p_s corresponding (according to the isotherm) to this u_0 value.

Further, assuming that the pores are small ($r \leq 10^{-5}$ cm) and that the mass transfer in the gas phase is achieved through Knudsen diffusion, the mean radius of the cylindrical pores is determined:

$$r = (3/8)\, D_i \sqrt{2\pi M/RT}. \tag{12}$$

The surface diffusion is neglected in these calculations. It follows from [1] that it must be taken into account only in very fine pores.

The pore dimensions r obtained in this way are compared with the values of r_F found by independent methods for these specimens from the Kelvin equation in [9-13] and with the values for the mean hydraulic pore radius $r_0 = 2m/S$.

Two specimens of silica gel are used in the experiments [9-13]: KSK-2 with a mean pore radius $r_F = 40$ Å and $r_0 = 50$-60 Å and KSM-5 with $r_F = 13$ Å and $r_0 = 11$-12 Å. The processing of the data in [9] on the kinetics of the adsorption of water from an atmosphere of saturated vapor for KSK-2 gives $B = 4 \cdot 10^{-3}$ sec$^{-1/2}$ for T = 293°K and $R_0 = 0.2$ cm. On the basis of the adsorption isotherm taken from the same paper (approximating it by a broken line with two linear sections), we find $\beta_1 = 9.8 \cdot 10^3$, $\beta_2 = 5.6 \cdot 10^5$, $c_*/c_0 = 0.9$. The solution to Eq. (7) gives $\operatorname{erf}^2(\xi_0\sqrt{1+\beta_2}) = 0.35$. Then from (11) we find $D_i = 0.0145$ cm^2/sec. A mean pore radius magnitude of r = 37 Å, close to the values of r_F and r_0 for KSK-2 given above, corresponds to this value of D_i according to (12).

Table 1 gives data calculated by the same method for KSM-5. Water adsorption isotherms taken at different temperatures [11] are used for the calculations. It should be noted here that the different methods of approximating the experimental isotherms by two linear sections of a broken line do not produce marked differences in the values obtained for D_i and r. As can be seen from Table 1, a fairly good coincidence between the r values and the magnitudes of r_F and r_0 is also obtained for the KSM-5.

TABLE 1. Results of Calculations of Parameters Governing Kinetics of Adsorption of Water Vapor for KSM-5 Silica Gel

T, °K	β_1	β_2	$\frac{c_*}{c_0}$	B, $\mathrm{sec}^{-1/2}$	D_i, $\mathrm{cm}^2/\mathrm{sec}$	r, Å	$\mathrm{erf}(\xi_0\sqrt{1+\beta_2})$
293	$4{,}2\cdot10^4$	$6{,}9\cdot10^4$	0,25	$4{,}5\cdot10^{-3}$	0,0046	12	0,81
313	$8{,}3\cdot10^3$	$1{,}8\cdot10^4$	0,6	$1{,}03\cdot10^{-2}$	0,051	13	0,56
313	$5{,}9\cdot10^3$	$1{,}7\cdot10^4$	0,5	$1{,}03\cdot10^{-2}$	0,051	13	0,69

TABLE 2. Results of Calculation of Parameters Governing Kinetics of Desorption and Adsorption of Water Vapor for KSK-2 Silica Gel

Experimental conditions	$\frac{p}{p_s}$	u_E, %	u_0, %	β	$B\cdot10^2$, $\mathrm{sec}^{-1/2}$	D_i, $\mathrm{cm}^2/\mathrm{sec}$	r, Å
Water adsorption T=298 °K	0 1	2,02	0	$7{,}2\cdot10^3$	3,3	0,033	83
	0,32	4,3	2,88	"	3,0	0,028	70
	0,4	5,84	4,3	"	2,9	0,027	68
Water desorption T=298 °K	0,24	4,7	7,0	$7{,}2\cdot10^3$	3,2	0,0315	78
	0,16	2,5	4,7	"	3,1	0,03	74
	0	0	1,1	"	3,3	0,028	70
Water adsorption T=313 °K	0,073	2,0	0	$4{,}5\cdot10^3$	4,2	0,033	82
	0,18	3,9	2,33	"	3,4	0,022	54
	0,27	5,36	3,9	"	4,1	0,031	78
Water desorption T=313 °K	0,198	8,1	9,1	$4{,}5\cdot10^3$	4,35	0,036	90
	0,07	5,7	6,6	"	3,8	0,028	70
Water adsorption T=323 °K	0,049	2,02	0	$3{,}3\cdot10^3$	4,5	0,028	68
	0,098	3,5	2,02	"	3,2	0,0142	35
	0,14	4,7	3,5	"	3,5	0,017	41
	0,196	5,9	4,7	$3{,}3\cdot10^3$	4,05	0,023	56
	0,238	6,6	5,9	"	4,5	0,0285	69
	0,28	7,8	6,6	"	4,05	0,023	56
	0,322	8,8	7,8	"	4,05	0,023	56
	0,385	10	8,8	"	3,5	0,017	41

In the other series of calculations, V. P. Dushchenko's data on the kinetics of water adsorption and desorption with a gradual progressive increase or reduction in the p/p_s values in the ambient around the KSM-2 silica gel granule are used. Since the kinetic curves are plotted for narrow ranges of variation in p/p_s, each isotherm section corresponding to this range can, with a good degree of approximation, be considered linear. It is thus possible to use the simpler equation (11') for calculating D_i. The values of the constant B accompanying desorption are found from the equation

$$B = (u_0 - u)/(u_0 - u_E)\sqrt{\tau}, \tag{13}$$

and those accompanying adsorption, from

$$B = (u - u_0)/(u_E - u_0)\sqrt{\tau}, \tag{14}$$

where u_E is the equilibrium mass content corresponding to a given value of p/p_s in the ambient.

The B values are found from the linear section of drying graphs plotted in $u(\sqrt{\tau})$ coordinates. Values for D_i are obtained from (11') using the angular coefficient of the isotherm for a given region of p/p_s values as β. The granule radius is R_0 = 2 mm. Then, assuming that $D_i = mD_F$, the radius of the pores is found from Eq. (12). The results of the calculations made are given in Table 2, which shows that, although there is a series of falling points, the majority of the data obtained have r values close to r_0 and r_F for KSK-2. Thus, the mean pore radius for all the points is found to be 60 ± 17 Å, which is close to r_0 = 50-60 Å and r_F = 40 Å.

Thus the theory devised for the deep drying of porous particles using the adsorption isotherm as the basis for calculations is in fairly good agreement with known experimental data. It is therefore possible to have confidence in the possibility of using it to calculate the drying rate and clarify the mechanism of internal mass transfer accompanying the deep drying of various finely porous materials.

NOTATION

u_0, u, u_F, u_E, initial, current, final, and equilibrium mass contents, g/g solid phase; a, mass of adsorbed substance per unit volume of porous body, g/cm³; $\beta = da/dc$, adsorption isotherm parameter; c, mass of vapor in pore space per unit volume of porous body, g/cm³; D_i, effective coefficient of internal diffusion, cm²/sec; R_0, radius of spherical grain, cm; D_s, coefficient of surface diffusion, cm²/sec; S, specific surface, 1/cm; r, pore radius, cm; τ, time, sec; p, adsorbate vapor pressure, g/mole; R, universal gas constant, erg/mole; T, absolute temperature, °K; m, porosity.

LITERATURE CITED

1. P. P. Zolotarev, Ya. I. Rabinovich, and N. V. Churaev, Inzh.-Fiz. Zh., 32, No. 4 (1977).
2. P. P. Zolotarev, Izv. Akad. Nauk SSSR, Ser. Fiz., No. 10, 2403 (1968); No. 3, 711 (1969); No. 5, 1174 (1969).
3. P. P. Zolotarev, Teor. Osn. Khim. Tekhnol., 3, 854 (1969).
4. P. P. Zolotarev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 1882 (1971).
5. P. P. Zolotarev, Zh. Fiz. Khim., 48, 1778 (1974).
6. P. P. Zolotarev and M. M. Dubinin, Dokl. Akad. Nauk SSSR, 203, 1347 (1972).
7. A. V. Lykov, Theory of Heat Conduction [in Russian], Vysshaya Shkola, Moscow (1967).
8. P. P. Zolotarev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 526 (1972).
9. M. S. Panchenko, V.P. Dushchenko, et al., in: Heat and Mass Transfer [in Russian], Vol. 6, ITMO, Akad. Nauk BelorusSSR (1972), p. 118.
10. V. P. Dushchenko, M. S. Panchenko, I. A. Romanovskii, and I. B. Slinyakova, Inzh.-Fiz. Zh., 15, No. 4 (1968).
11. V. P. Dushchenko, M. S. Panchenko, and S. F. D'yachenko, Inzh.-Fiz. Zh., 16, No. 1, 67 (1969).
12. M. S. Panchenko, V. P. Dushchenko, A. L. Panasyuk, and A. S. Mosievich, Inzh.-Fiz. Zh., 22, No. 5 (1972).
13. M. S. Panchenko, V. P. Dushchenko, A. L. Panasyuk, and A. S. Mosievich, in: Physics of Solids [in Russian], KGPI, Kiev (1972), p. 107.

NONSTATIONARY PROBLEM OF HEAT TRANSFER IN LAMINAR-VACUUM INSULATION

I. S. Zhitomirskii, A. M. Kislov, and V. G. Romanenko

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A mathematical model for nonstationary heat and mass transfer in multilayered insulation for the case of transverse evacuation of the packet is proposed. Results of numerical computations of the gas pressure, the shield temperature, and the heat flux in the packet for certain insulation variants are presented.

Experimental [1-4] and theoretical [4-6] investigations of the heat transfer in laminar-vacuum insulation have shown that one of the fundamental interrelated and simultaneously operating heat-transfer mechanisms therein (radiation, thermal conduction by the gas and by the solid) is thermal conduction by the residual gas. Hence, stationary processes of evacuation of the insulation packet and the heat transfer therein for a steady temperature distribution and molecular gas flow mode are considered in almost all the papers. Theoretical results for the stationary gas pressure distribution in an insulation packet with perforated radiation shields and an estimate of its influence on the heat transfer are obtained for a temperature distribution given in the form of a constant [6] or power-law [4, 7] function of the number of shields. The nonstationary equation of the process of transverse evacuation of the packet was solved

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