TEMPERATURE DEPENDENCE OF THE ADSORPTION HEATS FOR KSM-5 AND KSK-2 SILICA GELS

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A study is made of the temperature dependence of the heats of adsorption for water vapor on KSM-5 and KSK-2 silica gels.

Lykov and others have shown that mass transfer in a dispersed medium is substantially dependent on heat transfer, which is largely determined by the heats of the phase transformations occurring when water is bound in open-pore bodies.

The available data do not fully reflect the temperature dependence of the heats of sorption in heat and mass transfer [1-4]. To allow for the temperature factor, which determines the performance in air drying, we examined commercial specimens of KSM-5 and KSK-2 silica gels at various air temperatures, which provided information on the effects of temperature on the heat of adsorption and thus on the water adsorption.

The heats of adsorption were deduced from those of desorption given by thermogravimetric data under nearly isothermal conditions by the use of desiccator data on the sorption isotherms.

A difference of this method from the usual one of determinine phase-transformation heats Q_{ph}, which involves using a linearly increasing temperature and recording data on nonisothermal derivative charts [5, 6], is that we measured Q_{ph} at a set temperature in the derivative-recorder oven [7], this temperature being close to constant, which was checked on recording the thermogravimetric (TG) and differential thermal analysis (DTA) curves from the linearity in the thermoanalytical curve (TA), which should be parallel to the time axis and isothermal in the given parameter, as well as from the derivative recordings. This method enables one to determine Q_{ph} quantitatively at a given constant temperature as the specimen mass changes virtually throughout the drying from the area under the DTA isothermal curve on the basis of standard thermal conductivity coefficients for KSM-5 and KSK-2 silica gels as given by Dushchenko [8].

Figure 1 shows the DTA and TG curves at various constant desorption temperatures for use in calculating the phase-transformation heats. To obtain the necessary data volume, we supplemented the existing adsorption isotherms [8] with ones for these silica gels at reduced temperatures by placing the desiccator and sorbent in a cold chamber. Figure 2 gives the sorption isotherm data.

Then with Q_{ph} corrected for the corresponding latent heat of evaporation we found the integral values of Q_{des}, which were used with the isotherm data and the corresponding Q_{ads} on the basis that the energy consumed in evaporation or produced in absorption of a given amount of water will be much the same and closely so for engineering pruposes. On this basis, Q_{ads} was taken as close to Q_{des}, and the temperatures of the corresponding Q_{ads} were found from the sorption isotherms (Fig. 2). The integral Q_{des} as measured was used to determine the amount of evaporating water from the TG curves (Fig. 1) and then the desorption ordinate was found from the isotherms (Fig. 2).

Then the amount of evaporated water, and consequently the same amount of absorbed water, was used to mark off on the abscissa the value corresponding to the adsorption ordinate from the desorption ordinate to the isotherm, from which we found the temperature for the given integral Q_{ads}.

As the areas under the isotherms in Fig. 2 are equal to the work of adsorption (desorption), which represents the energy consumed in absorption or evaporation at the sorbent, we

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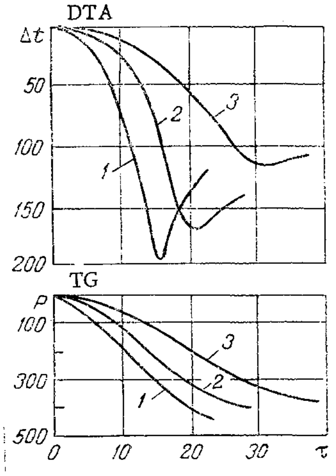

Fig. 1

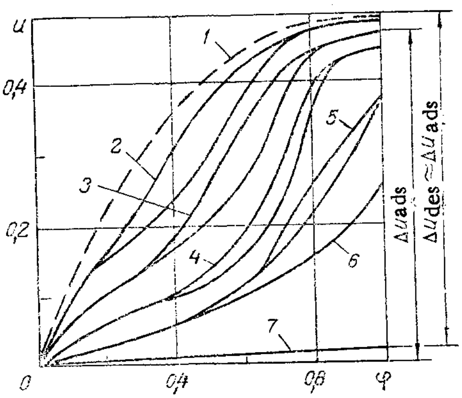

Fig. 2

Fig. 1. Differential thermal analysis (DTA) curves and thermogravimetric (TG) curves for KSM-5 silica gel at the following desorption temperatures: 1) 200°C; 2) 170; 3) 120; Δt in °C, P in mg, and τ in min.

Fig. 2. Water-vapor sorption isotherms for KSM-5 silica gel at the following temperatures: 1) 0; 2) 10; 3) 20; 4) 28; 5) 35; 6) 40; 7) 170°C; u in kg/kg and φ as a fraction.

made allowance for the changes in the individual parts of the isotherm branches in accordance with the form of the process (adsorption or desorption) at the same temperature.

The Q_{ads} on these parts were refined by taking them as somewhat lower than the Q_{des} used in the conversion, which to a first approximation was proportional to the reduction in the area under the adsorption isotherm relative to the area under the desorption isotherm at the same temperature, and correspondingly from the deviation in the isotherm branches we reduced the specific water content of the sorbent u.

To improve the accuracy and reliability, the Q_{ads} were compared with the available data on adsorption heats for the same sorbents measured by a reasonably accurate calorimetric method [1, 8], and we also used the characteristic isotherm data for the largest u at various temperatures. This enabled us to establish and refine the adsorption heats in the temperature range on the sorption isotherms on which our results for 20-30°C were close to those given by others [1, 9, 10] for the same temperatures.

This method of deriving Q_{ads} from Q_{des} by means of isotherms eliminated the need for lengthy and laborious experiments to determine the heat losses that reduce the accuracy and reliability of measurements during adsorption.

The integral heats of adsorption as functions of temperature $Q_{ads} = f(t)$ were differentiated graphically for u = const. The differential heats of adsorption $Q_{dif} = f(t)_u$ are shown in Fig. 3.

The Q_{dif} were additionally checked from the available calorimetric data. The Q_{dif} from Fig. 3 were plotted in $Q_{dif} = f(u)_t$ coordinates and compared with Dushchenko's data for 30°C as regards the dependence on the specific water content [8]. Figure 4 shows that the results from the different methods agree.

The $Q_{dif} = f(t)_u$ data (Fig. 3) show that the differential heats of adsorption decrease as the temperature rises for any u and tend to zero, which agrees with the monimal energy consumption under conditions of stable equilibrium and corresponds to general physical concepts on the reduction in the intermolecular forces occurring as the distances between molecules increase because of temperature rise.

The results show that the differential adsorption heats for the silica gels decrease as the temperature rises, which agrees with the data of [2, 11, 12]. Figure 3 also shows that the adsorption heats for commercial silica gels increase as the temperature is reduced and approach those for commercial zeolites at about 50 kJ/mole (about 2.8 mJ/kg) [5]. Therefore, it is necessary to consider the temperature dependence of the adsorption heat in designing

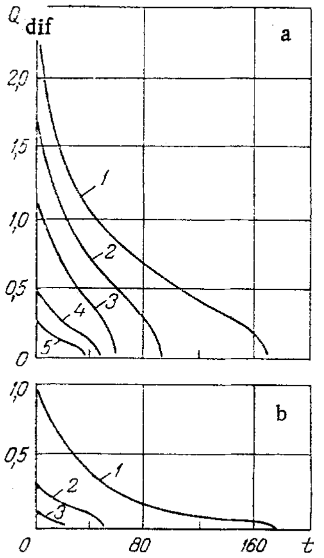

Fig. 3

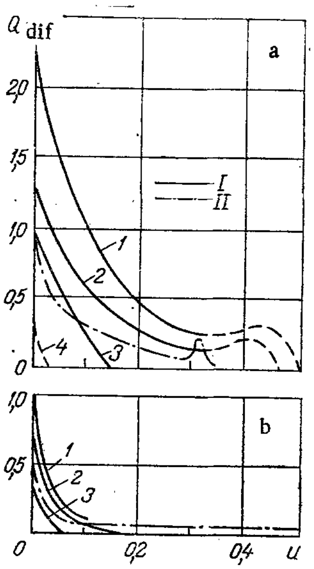

Fig. 4

Fig. 3. Differential adsorption heats (a, KSM-5 silica gel; b, KSK-2 silica gel) as functions of temperature for various specific water contents: 1) 0; 2) 0.05; 3) 0.1; 4) 0.2; 5) 0.3 kg/kg. Q_{dif} in mJ/kg and t in °C.

Fig. 4. Differential adsorption heats (a, KSM-5 silica gel; b, KSK-2 silica gel) as functions of specific water content at various temperatures, °C: 1) 0; 2) 20; 3) 50; 4) 170; I) from derivative and isotherm data; II) from Dushchenko's data for t = 30°C.

equipment for drying air at various temperatures, since this affects the specific water content and the extent of the drying.

The analysis shows that silica gels have elevated performance at low temperatures, and it is desirable to use them under these conditions.

Least-squares fitting [13] was used to derive formulas for the differential adsorption heats as functions of temperature and specific water content. For KSM-5 silica gel, $Q_{dif} = 2.3 \exp(-0.02t) \exp(-10u)$; for KSK-2 silica gel, $Q_{dif} = 1.1 \exp(-0.017t) \exp(-20u)$.

The errors in determining the differential adsorption heats from the formulas are on average 10-15%, which is acceptable, since the heats of adsorption for KSM-5 and KSK-2 silica gels are small fractions of the phase-transformation heats.

These results reflect the direct dependence of the heat and mass transfer on temperature in the physical adsorption of water vapor on KSM-5 and KSK-2 silica gels, and they can be used in calculating dynamic adsorption in equipment for drying air working at various temperatures.

NOTATION

Q, water binding heat in sorbent pores, mJ/kg; u, specific water content, kg/kg; t, temperature, °C; Δt, temperature drop between center of sample and furnace, °C; P, decrease in mass of sample, mg; Δu, amount of absorbed or evaporated water, kg/kg; φ, relative humidity, fraction; τ, time. Subscripts: dif, differential; des, desorption; ads, adsorption; ph, phase conversion.

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ALGORITHMS AND RESULTS OF SOLVING THE INVERSE HEAT-CONDUCTION BOUNDARY PROBLEM IN A TWO-DIMENSIONAL FORMULATION

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The effectiveness of gradient algorithms for solving the inverse problem which are regulated in terms of the number of iterations is investigated.

The need to solve inverse heat-conduction boundary problems (IHBP) most often arises in analyzing the results of thermal experiments when a quantity characterizing the heat transfer at the boundary surface of the body (heat-flux density, heat-transfer coefficient, surface temperature of body) must be determined from the results of temperature measurements at a series of fixed points of a solid.

In view of the incorrectness of the initial formulation of IHBP associated with violation of the stability conditions, regularizing algorithms are used for their solution [1, 2]. Effective algorithms have now been developed for the inverse problem in the one-dimensional formulation. The region of practical use of methods of identifying and diagnosing heat-transfer processes on the basis of solving one-dimensional IHBP is sufficiently large but nevertheless limited. In a series of cases, it is necessary to resort to IHBP in a two-dimensional formulation. However, in terms of algorithm development, such problems have been inadequately studied.

As shown in [3], efficient algorithms for solving two-dimensional IHBP may be obtained by means of iterative regularization using a different approximation of the heat-conduction boundary problem. This approach is developed below for the integral form of the two-dimensional problem with constant thermophysical characteristics. This formulation covers cases of practical application in which the change in properties of the body in the given tempera-

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