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Abstract

Full Text

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INVESTIGATION OF ADSORPTION AT HIGH PRESSURES

To elucidate a number of fundamental questions in the theory of physical adsorption, it is essential to carry out adsorption studies over a wide range of temperatures and pressures. In the overwhelming majority of cases, measurements of physical adsorption are performed only at a single temperature or within a very narrow temperature region. Therefore, the experimental results of such investigations do not make it possible to judge how correctly a given theory describes the temperature dependence of adsorption. Broadening the temperature interval of adsorption measurements inevitably entails the need for a corresponding broadening of the pressure interval. Because of the considerable experimental difficulties associated with conducting experiments at high pressures, very little has been done in this field up to the present time. The most systematic investigations of gas adsorption at high pressures are set forth in papers (1-4). Individual cases are described in works (5-6), etc. However, because of the low accuracy of the measurements or because of an unsuccessful choice of research objects, the experimental data obtained in most of these works have not led to an unambiguous solution of the questions posed.

Seeking to fill this gap to some extent, we undertook a systematic study of the physical adsorption of carbon dioxide on silica gel over a wide temperature interval from -85 to 40° , including the critical temperature ($t_{cr} = 31^\circ$), at pressures from 0 to 85 atm. To carry out this investigation we constructed a special apparatus, described in detail in paper (7), characterized by the absence of compressors and manometers for high pressures. The adsorption measurements were carried out by the volumetric method, with the volume of the dead space determined using helium. All necessary calculations were made on the basis of empirical data obtained in the study of the P, V, T -diagram of CO_2 in a precision metrological work (8). Since CO_2 is characterized in the region studied by very large deviations from ideality, in all subsequent thermodynamic calculations the pressure P was replaced by the fugacity f . For this purpose, by means of a known thermodynamic method (see, for example, (9)), the fugacity of CO_2 was calculated in the interval from 0 to 100 atm according to the empirical equation of state of Beattie-Bridgeman (10), which for CO_2 is at present regarded as the best.

Two silica-gel samples obtained from the laboratory of A. V. Kiselev were taken as adsorbents: the fine-pored C-340 with specific surface $S_{\text{BET}} = 573 \text{ m}^2/\text{g}$ and

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

limiting volume of adsorption space $V_a = 0.47 \text{ cm}^3/\text{g}$, and the wide-pored E-II ($S_{\text{BET}} = 325 \text{ m}^2/\text{g}$ and $V_a = 1.61 \text{ cm}^3/\text{g}$). For C-340, adsorption isotherms were obtained at 25; 0; -20 ; -30 ; -40 ; -50 ; -60 ; -70 ; -78 , and -85° over the interval of relative fugacities f/f_s from 0 to 1 (at temperatures below t_{cr}) and over the interval of f from 0 to 60 atm for 32 and 40° . For E-II, only three isotherms were obtained: at 0; -40 , and -50° up to $f/f_s = 1$. In all cases, excellent reproducibility of the measurements was established.

In Fig. 1 the adsorption isotherms obtained for silica gel S-340 are plotted in the coordinates $\lg f, a$. As the temperature is raised from -85° , the curve $a(\lg f)$ shifts to the right, and at -60° a sorption hysteresis loop appears on it. This loop becomes most distinct at -50° , then gradually decreases and, on approaching t_{cr} , disappears, becoming practically imperceptible already at -20° . According to the theory of capillary condensation, sorption hysteresis can appear only in the region where the liquid phase of the sorbed substance exists. In the present case, the normal liquid phase of CO_2 can exist in the interval from t_{tr} (-56.6°) to t_{cr} (31°). In this sense the experiment agrees with this theory. However, as will be shown below, there are strong grounds for considering that at temperatures below -56.6° the adsorption phase is in the state of a supercooled liquid. If this is so, then the disappearance of the hysteresis loop below -60° cannot be explained within the framework of these concepts and requires further study.

Fig. 1

Our measurements make it possible to calculate the distribution curves $dv/dr = \varphi(r)$ of pore volumes according to their radii r for a number of temperatures. It is obvious that, for adsorbents with a rigid skeleton, the curve $\varphi(r)$ should not depend on temperature. Figure 2 shows the curves $\varphi(r)$ calculated for temperatures -30° (curve 1) and -50° (curve 2) for S-340, with allowance for corrections for the thickness of the adsorption layer⁽¹²⁾, calculated on the basis of adsorption isotherms on wide-pore silica gel E-II.

Fig. 2

It should be noted that curves 1 and 2 differ greatly in their form. The maximum of curve 1 is shifted along the abscissa by approximately 25% relative to the maximum of curve 2, while curve 2 indicates a much greater monodispersity of the pore volumes of the silica gel than follows from curve 1. Thus, in the present case the position of the maximum and the form of the distribution curve depend on temperature. It is possible that this fact indicates the inapplicability of the

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Kelvin equation in describing liquid menisci with a radius of curvature $r \approx 20 \text{ \AA}$. Obviously, we cannot a priori establish the lower limit of r below which this equation loses its force; it can be found only experimentally. However, on the basis

of this single experiment it would be premature to assert where exactly this boundary lies. Further investigations are necessary in order to resolve this question.

In the curves of Fig. 1, the adsorption a was in all cases calculated as the Gibbs excess. It is known that at high pressures a quantity a determined in this way may differ appreciably from the total content of substance in the adsorption volume. Since at $f/f_s = 1$ the whole volume V_a is filled with substance, $a = a_s + V_a \delta$, where a_s is the limiting value of sorption and δ is the density of the gas under these conditions. If the value of V_a obtained from the limiting sorption of N_2 vapors is taken as the true value of the adsorption volume, then it is easy to find the mean density

$$\rho_a = a/V_a$$

of the adsorbed substance in the volume V_a .

Fig. 3

Figure 3 gives a plot of the dependence of ρ_a on the density ρ of normal liquid CO_2 at the same temperatures. The values of ρ_a at $-20, -30, -40,$ and -50° are on average 6% higher than the corresponding values of ρ . However, as t_{cr} is approached, the mean density ρ_a becomes 14% higher than ρ (at 25°). This anomalously large value of ρ_a is most naturally explained by the high compressibility β near t_{cr} (at $t_{cr}, \beta = \infty$). As a result, even a very weak adsorption field acting beyond the limits of the first layer can cause a considerable increase in the density in polymolecular layers.

Fig. 4

Analysis of the isotherms in Fig. 1 showed that the experimental data obtained are well described by the Dubinin and Zaverina equation ⁽¹¹⁾ for carbons of the second structural type. However, near t_{cr} the characteristic curves of the Polanyi theory

$$\varepsilon = -RT \ln h = \psi(av),$$

where $h = f/f_s$ and v is the molar volume of CO_2 , proved to depend somewhat on T . The curves $\psi(av)$ calculated for 0 and 25° lie above the single characteristic curve obtained for the other temperatures. This position of the curves $\psi(av)$ is probably due to the above-mentioned anomaly of the density ρ_a near t_{cr} (see Fig. 3). If the curves $\psi(av)$ are calculated for the total content a and the effective density ρ_a , a single curve is obtained for all temperatures, including 0 and 25°.

In Fig. 4, in coordinates $\lg f, 1/T$, adsorption isosteres are shown, constructed from the isotherms of Fig. 1 for values of a equal to 1, 2, ..., up to 10 mmol/g. Each of these isosteres consists of two linear segments intersecting in a narrow temperature interval in the region of -60° . In the upper part of Fig. 4, the corresponding line is shown by a dashed line.

the curve $\lg f = \varphi\left(\frac{1}{T}\right)$ for ordinary CO_2 , the break in this curve, lying at -56.6° , corresponds to the melting of solid CO_2 . The difference between the slopes of the linear segments of this curve at the phase-transition point A approximately determines the thermal effect of the transition, $-\Delta H^0$, equal to 2.0 kcal/mole. It is natural to regard breaks in adsorption isotherms as an indication of the existence of a phase transition also in the adsorbed substance. However, it follows from Fig. 4 that this phase transition occurs only in some part of the adsorbed substance. Indeed, if a phase transition of the crystallization type took place throughout the entire mass of the adsorbed substance, then the thermal effect, $-\Delta H$, of this process, approximately equal to the difference of the tangents of the angles of inclination of the isotherms at the transition point (for example, at point B), should increase with increasing adsorption a and approach the value $-\Delta H^0$ at point A for the ordinary condensed phase of CO_2 . In contrast to this, the value $-\Delta H$ does not increase, but decreases with increasing a , as is directly evident from Fig. 4. At $a = 10$ mmol/g the break on the isotherm becomes almost imperceptible.

The character of the isotherms in Fig. 4 can be readily explained if one assumes that the phase transition occurs only in the first adsorption layer, while all the remaining adsorbed substance at temperatures below the transition point is in the state of a supercooled liquid.

The phase transition found by us is probably a two-dimensional analogue of crystallization and is caused by the "freezing out" of the translational degrees of freedom of the adsorbed molecules. We note that in the well-known work of Coolidge (3) a break in the adsorption isotherms of CO_2 under analogous conditions was not observed, probably owing to the lower accuracy of the measurements.

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