

THE POTENTIAL THEORY OF ADSORPTION OF GASES AND VAPORS FOR ADSORBENTS WITH ENERGETICALLY NONUNIFORM SURFACES

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I. INTRODUCTION

This review surveys the results of experimental and theoretical investigations which have led to the development of the potential theory of adsorption in which the determining role is played by dispersion forces. The views developed are first of all applicable to the physical adsorption of gases and vapors on carbonaceous adsorbents that consist of a nonpolar substance—carbon. These views are also of importance for other adsorbent-adsorbate systems in which dispersion forces are the dominant component of adsorption interaction.

II. ADSORPTION ON ACTIVE CARBON

Active carbons are adsorbents with energetically non-uniform surfaces, which are a consequence of the disordered arrangement of the elementary crystallites of carbon at the surface of the adsorbent, giving the surface a mosaic-like structure. This results in an enhanced adsorption energy (adsorption potentials) in the micropores of the carbon, owing to superposition of the fields of the opposite walls of the pores.

Curve 1 in figure 1 gives the heat of adsorption calculated per mole of adsorbed vapors of hexane as a function of the amount of adsorption for small-pore active carbon. This curve is located considerably higher than the analogous curve 2 for the nonporous carbonaceous adsorbent, carbon black (1). It is precisely this difference that is due to the increase in energy of adsorption in the carbon micropores whose dimensions are comparable to those of the molecules being adsorbed.

The vapor, adsorbed on the surface chiefly of the smallest pores of active carbon, is converted into a liquid, owing to compression. From the conditions of equilibrium it follows that the surface of the condensed adsorption layer is equipotential. As a reasonably good approximation, the volume of liquid expresses the volume of filled adsorption space.

The distribution of volume of the filled adsorption space according to adsorption potentials is the principal

characteristic of the adsorption-force field. Since the adsorption potential expresses the work of temperature-independent dispersion forces, the above-mentioned distribution curve or characteristic curve is independent of the temperature. This basic proposition of the potential theory of adsorption was earlier enunciated and experimentally substantiated by Polanyi (11, 12).

For the vapors of different substances, the forces of attraction of the molecules to the surface of the adsorbent are naturally not the same. According to the theory of dispersion interaction, their relationship is approximately equal to the ratio of polarizability of the molecules of the vapors (α). The ratio is the same for the work done by the adsorption forces or adsorption potentials. Thus, for identical fillings of the volume of adsorption space W for two vapors, the adsorption potentials ϵ have a constant ratio:

$$\frac{\epsilon}{\epsilon_0} = \frac{\alpha}{\alpha_0} = \beta \quad (1)$$

The constant β is called the affinity coefficient (4).

III. ADSORPTION THEORY

The principal task of the theory of adsorption consists in finding the distribution of the volume of adsorption space, W , as a function of adsorption potentials, ϵ :

$$W = f\left(\frac{\epsilon}{\beta}\right) \quad (2)$$

that is, the equation of the characteristic curve. Since the nature of the vapor has already been taken into account and the temperature (for the foregoing reasons) does not produce any effect on the characteristic curve, each adsorbent has its own characteristic curve that describes its adsorption-force field.

Investigations have established that, owing to the effect of increasing the adsorption potentials in the micropores of the carbon, the characteristic curve of the adsorbent is a reflection of its porous structure (5, 7). Radushkevich (13) made an attempt to substan-

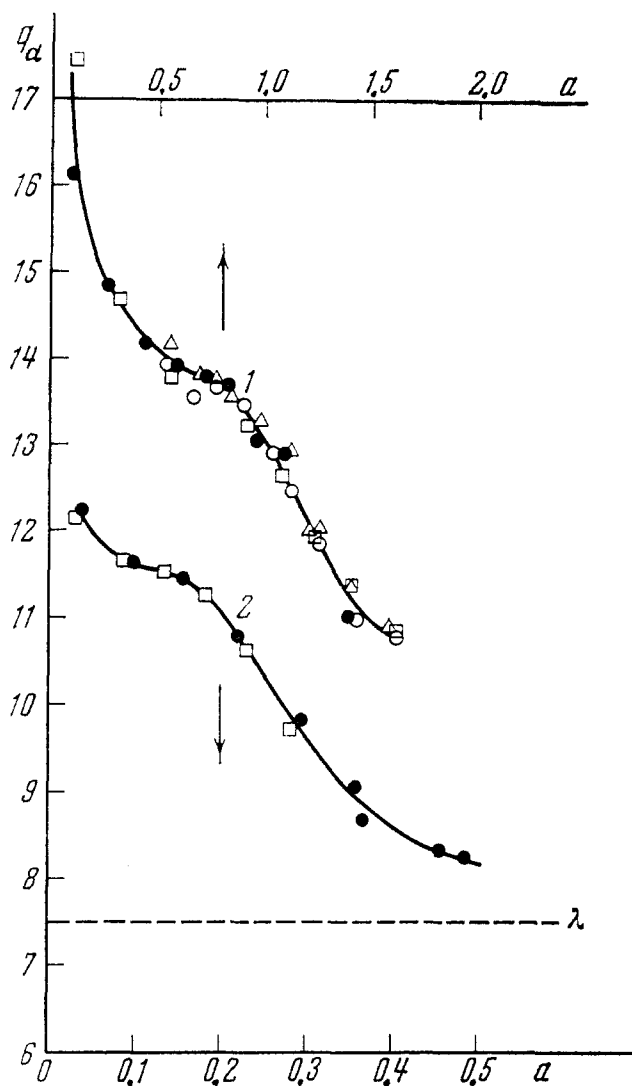


FIG. 1. Differential heat of adsorption of hexane vapor at 20°C. as a function of the amount of adsorption: curve 1, small-pore active carbon; curve 2, nonporous carbon black.

tiate theoretically the characteristic-curve equations for extreme structural types of adsorbents.

Adsorbents of the first structural type include active carbons with extremely small micropores, for which the effect of increasing adsorption potentials as a result of overlapping of the fields of opposite walls of the pores is prominent. For such carbons the equation of the characteristic curve assumes the form (5):

$$W = W_0 e^{-\kappa \frac{\epsilon^2}{\beta^2}} \quad (3)$$

where W_0 is the limiting volume of adsorption space that represents the volume of micropores of the active carbon. The parameter κ reflects the function of the distribution of volume of the pores according to sizes.

In linear form this equation is:

$$\log W = \log W_0 - 0.434 \frac{\kappa}{\beta^2} \epsilon^2 \quad (4)$$

Figure 2 gives the results of experiments by Nikolaev and Dubinin (10) illustrating the applicability of the characteristic-curve equation (equation 3) for the adsorption of nitrogen, krypton, xenon, tetrafluoroethylene, and hexafluoropropylene in the range of fillings of the volume of adsorption space, W/W_0 , from 0.06 to 0.94. The experimental points were calculated from the adsorption isotherms for the temperature range from -195°C . (nitrogen) to 50°C . (tetrafluoroethylene and hexafluoropropylene) on two specimens of active carbons that belong to the extreme members of a series of adsorbents of the first structural type.

For each active carbon, all the straight lines intersect the ordinate axis at practically a single point. This is an indication of the constancy of the limit volumes of the adsorption space for each carbon. On the average there is obtained: for AC-1, $W_0 = 0.32 \pm 0.01 \text{ cm}^3/\text{g}$.; for AC-2, $W_0 = 0.53 \pm 0.01 \text{ cm}^3/\text{g}$.

From the slopes of the straight lines it is easy to calculate the affinity coefficients (β) of the characteristic curves given in table 1. The standard vapor is nitrogen ($\beta = 1$). Judging from the data, the affinity coefficients are practically independent of the specimen of carbon.

Adsorbents of the second structural type include active carbons with appreciably larger pores, in which the fields of the opposite sides of the pores do not over-

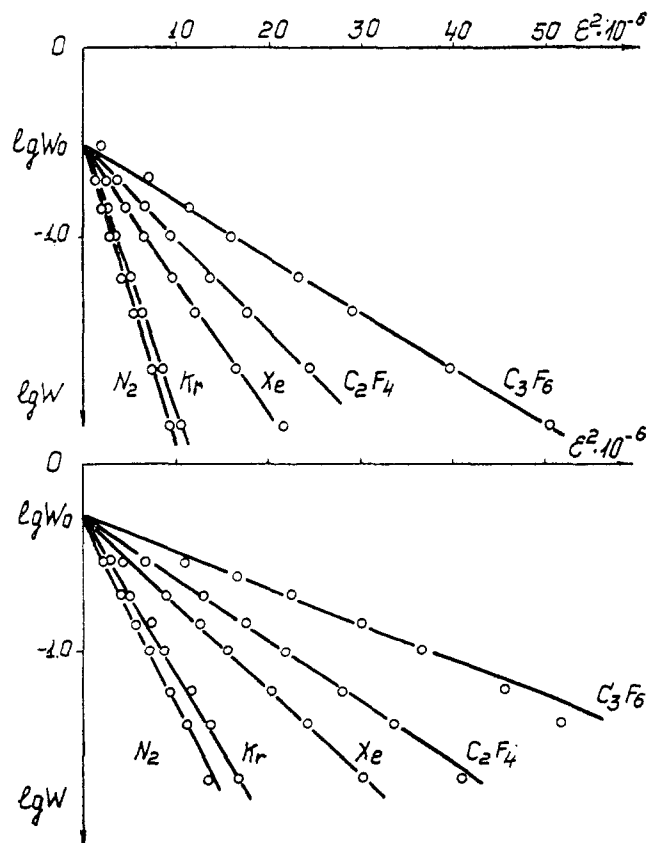


FIG. 2. Characteristic curve of adsorption in the linear form: active carbon 1 (above) and active carbon 2 (below).

TABLE 1
Affinity coefficients of characteristic curves

Substance	Affinity Coefficient β for		Mean β
	AC-1	AC-2	
Nitrogen.....	1.00	1.00	1.00
Krypton.....	1.11	1.10	1.11
Xenon.....	1.50	1.47	1.49
Tetrafluoroethylene.....	1.80	1.75	1.78
Hexafluoropropylene.....	2.31	2.29	2.30

lap, and for this reason there is no increase in the adsorption potentials. Naturally, the adsorbents of the second structural type include also nonporous carbonaceous adsorbents, for example, carbon blacks.

The characteristic equation for adsorbents of the second structural type (5) is of the form:

$$W = W'_0 e^{-\frac{\epsilon}{\beta}} \quad (5)$$

where W'_0 is the limit volume of adsorption space. This equation likewise accords with the experimental data over a broad range.

It is easy, on the basis of the characteristic-curve equation, to obtain the adsorption isotherm equation. The following equations demonstrate this for the case of adsorbents of the first structural type (5, 7).

Substituting in the equation of the characteristic curve (equation 3), the expression for

$$W = a \cdot v \quad (6)$$

where v is the volume of one millimole of condensed vapor, and the expression for the Polanyi adsorption potential:

$$\epsilon = 2.3 RT \log \frac{p_s}{p} \quad (7)$$

one obtains the adsorption isotherm equation:

$$a = \frac{W'_0}{v} \cdot e^{-B \frac{T^2}{\beta^2} \left(\log \frac{p_s}{p} \right)^2} \quad (8)$$

which in linear form is:

$$\log a = C - D \left(\log \frac{p_s}{p} \right)^2 \quad (9)$$

The graph in figure 3 points to the applicability of the equation in a broad interval of equilibrium relative pressures from 1×10^{-5} to 0.1. The adsorption isotherm (equation 8) permits one to calculate the amount of adsorption for different temperatures if use is made of the tabular figures for the saturated vapor, p_s .

Recently, in research by Nikolaev and Dubinin (10), the applicability of the adsorption isotherm equation (equation 8) was substantiated right up to the critical temperature, t_{cr} , of the adsorbate, on the condition that the value of its molar volume near t_{cr} (10) is precisely specified. This specification consisted of the following.

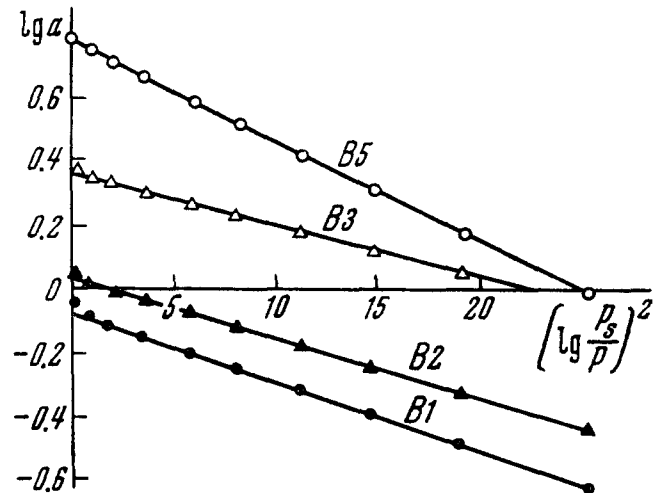


FIG. 3. Isotherm of adsorption of benzene vapor at 20°C. in the linear form according to equation 9.

The density of the liquid in the volume phase falls sharply on approaching the critical temperature. By way of illustration, figure 4 gives the density of liquid tetrafluoroethylene as a function of the temperature. For temperatures below the boiling temperature of the substance at atmospheric pressure (-76.3°C .), that is, on the portion AB , the density of the liquid falls off slowly with the temperature according to an approximately linear law. The considerable fall in density of the liquid which was noted is characteristic of the BC

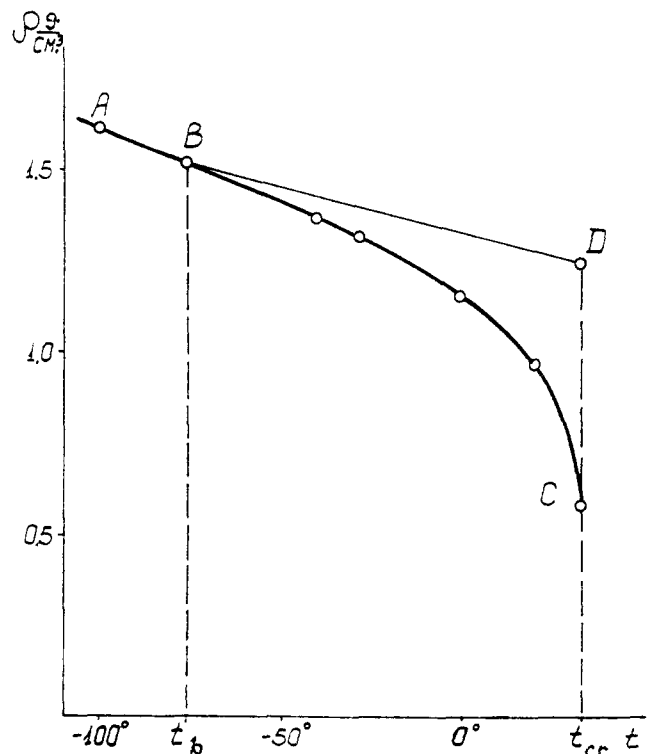


FIG. 4. Density of liquid tetrafluoroethylene as a function of temperature.

portion of the curve, that is to say, for the temperature region close to critical (+33.3°C.).

The adsorbed substance (in the form of a liquid) is in the adsorption-force field in a highly compressed state. And since upon approaching the critical temperature the compressibility of the liquid increases rapidly, the application (for calculating the volume of filled adsorption space) of tabular values of the density of the liquid—permissible for temperatures far from the critical, which is practically below the boiling temperature—ceases to be justified.

We have shown that the temperature dependence of the density of a substance in the adsorbed state may be expressed, in the temperature interval from t_b to t_{cr} , by a linear relationship, that is, by the portion BD , if one takes for the boiling temperature, t_b , the tabular value of the density of the liquid, and for the critical temperature, t_{cr} , the density ζ_m , which corresponds to the quadrupled volume proper of the molecules, that is, to the constant b of the van der Waals equation (equation 8):

$$\zeta_m = \frac{M}{1000b} \quad (10)$$

where M is the molecular weight and b a constant expressed in $\text{cm.}^3/\text{M}$.

In other words, the corrected value of the density of the liquid in the adsorbed state, ζ^* , is expressed as:

$$\zeta^* = \zeta_b - n(t - t_b) \quad (11)$$

where

$$n = \frac{\zeta_b - \zeta_m}{t_{cr} - t_b} \quad (12)$$

Then for a volume of a millimole of liquid in the adsorbed state v^* for $t_b < t < t_{cr}$ one obtains:

$$v^* = \frac{M}{1000\zeta^*} \quad (13)$$

When applying the corrected value of the molar volume for the temperature interval from t_b to t_{cr} for calculating characteristic curves from adsorption isotherms of vapors one obtains one and the same characteristic curve for each specimen of active carbon. To illustrate, figure 5 gives the characteristic curve of adsorption of tetrafluoroethylene on AC-1 calculated from five experimental adsorption isotherms for the temperature interval from $t_b = -76.3^\circ\text{C.}$ to $t_{cr} = 33.3^\circ\text{C.}$ The points designated by different symbols fall on the same curve.

Further, it was shown that for substances at temperatures above critical, that is, for gases, the filled volumes of adsorption space are expressed as:

$$W = a \cdot b \quad (14)$$

where a is the amount of adsorption and b is a constant of the van der Waals equation.

It is possible, for the adsorption potential, to obtain an expression (equation 15) by assuming that at the critical temperature the adsorption potentials for the substance (regarded as a vapor or a gas) should be the same:

$$\epsilon = 2.30 RT \log \left(\tau^2 \frac{p_{cr}}{p} \right) \quad (15)$$

where

$$\tau = \frac{t}{t_{cr}} \quad (16)$$

is the reduced temperature and p_{cr} is the critical pressure (12).

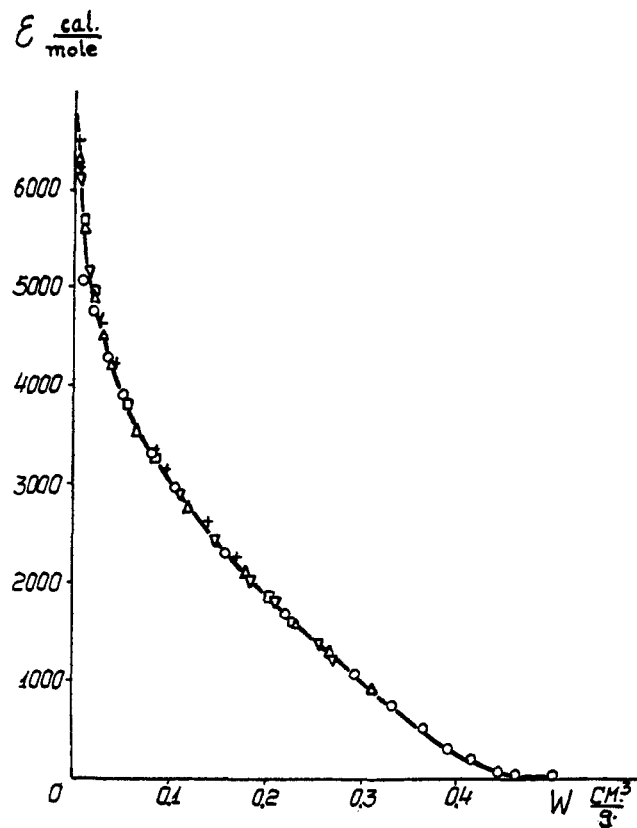


FIG. 5. Characteristic curve of adsorption of tetrafluoroethylene on active carbon 1, calculated from experimental adsorption isotherms for different temperatures: +, 33.3°C. (critical); □, 0°C.; ▽, -28°C.; △, -40°C.; ○, -76.3°C.

Figures 6 and 7 give the characteristic curves of adsorption of different substances calculated from isotherms for broad intervals of temperature, including the critical regions, when applying equations 6, 7, and also 13 for the vapor state of the substances, and equations 14 and 15 for the gaseous state. For each adsorbate-adsorbent system there is a single characteristic curve in a sufficiently good approximation.

If the curve for equation 3 for active carbons of the first structural type is used and the expressions above for the volumes of adsorption space filled, also the adsorption potentials, then the adsorption isotherm equa-

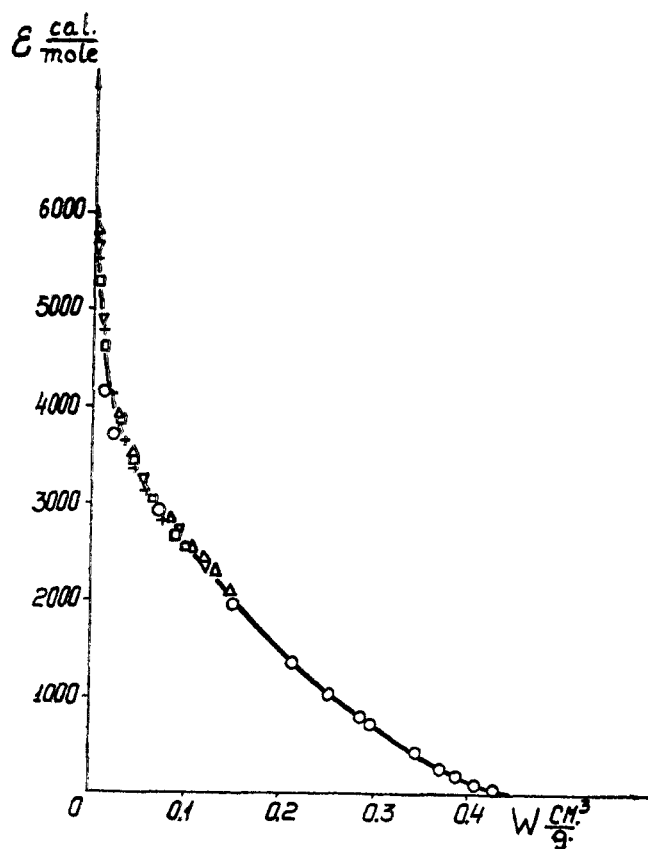


Fig. 6. Characteristic curve of adsorption of xenon on active carbon 1, calculated from experimental adsorption isotherms for different temperatures: +, 50°C.; □, 30°C.; ▽, 16.6°C. (critical); △, 0°C.; ○, -107°C.

tions for substances in the vapor (equation 17) and gaseous (equation 18) states can be derived. The magnitudes of adsorption are expressed in millimoles per gram.

For vapors $t \leq t_{cr}$

$$a = \frac{W_0}{v^*} e^{-B \frac{T^2}{\beta^2} \left(\log \frac{Z_t}{p} \right)^2} \quad (17)$$

and for gases $t \geq t_{cr}$

$$a = \frac{W_0}{b} e^{-B \frac{T^2}{\beta^2} \left(\log r^2 \frac{Z_{cr}}{p} \right)^2} \quad (18)$$

where the volume of one millimole of liquid, v^* , for the temperatures $t < t_b$ is taken from the tables (in this case equation 17 coincides with equation 8). Values for $t_b < t < t_{cr}$ are calculated from equation 13. These equations are applicable for an interval of fillings of the adsorption space, W/W_0 , from 0.06 to 0.94, which, for substances in the vapor state, corresponds to an ordinary interval of equilibrium relative pressures from 1×10^{-5} to 0.1 (10).

Dubin, Bering, Serpinsky, and Vasil'ev (2) have investigated the adsorption isotherms of the vapors of carbon dioxide on silica gel of the second structural type over a broad range of temperatures and pressures

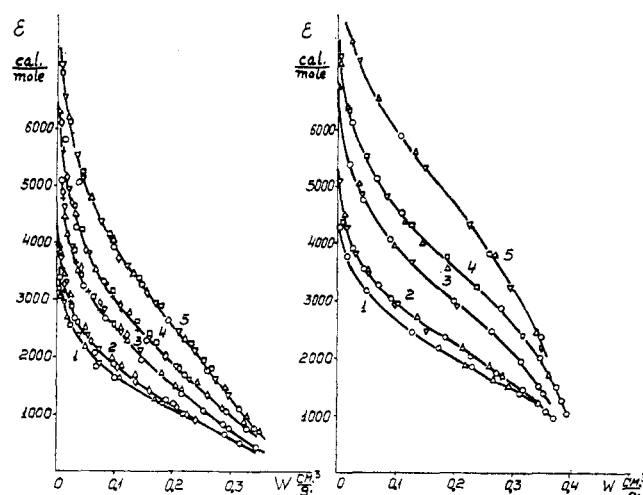


Fig. 7. Characteristic curves of adsorption on active carbon 1 (left) and active carbon 2 (right). Curve 1, nitrogen; curve 2, krypton; curve 3, xenon; curve 4, tetrafluoroethylene; curve 5, hexafluoropropylene.

that included the critical region (9). The adsorption isotherms were used to calculate the characteristic curve of the adsorption of carbon dioxide; the molar volumes were found from equation 13, which takes into account the enhanced density of the substance in the adsorption layer in the region of temperatures approaching critical. As figure 8 shows, the calculated points make good fits with one and the same curve. Summarizing, one may say that these views are of a general nature and embrace adsorbents of two extreme structural types.

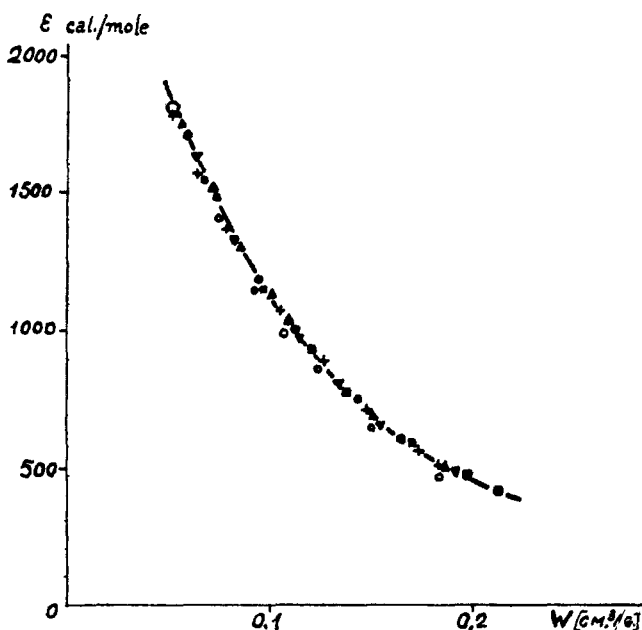


Fig. 8. Characteristic curve of adsorption of carbon dioxide on silica gel, calculated from experimental adsorption isotherms for various temperatures: ○, 25°C.; +, 0°C.; ▲, -20.4°C.; ●, -30°C.; ▼, -41°C.; ■, -51.1°C.

The characteristic-curve equation (equation 5) for adsorbents of the second structural type can also be expressed in a linear form:

$$\log W = \log W'_0 - 0.434 \frac{m}{\beta} \epsilon \quad (19)$$

Figure 9 gives the results of calculations from the experiments of Vasil'ev. These results attest the applicability of the characteristic-curve equation 3 to the

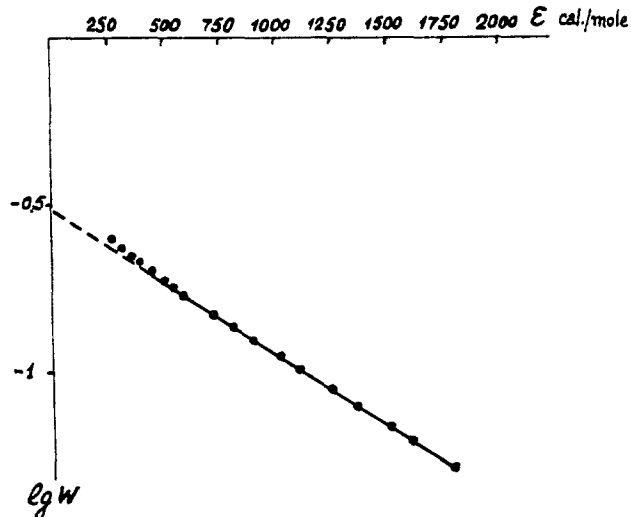


Fig. 9. Characteristic curve of adsorption of carbon dioxide on silica gel in the linear form according to equation 19.

adsorbent-adsorbate system under study within a sufficiently broad interval of fillings of the volume of adsorption space.

Using as a basis the characteristic-curve equation 5 for adsorbents of the second structural type, it is easy (working in a manner similar to that for the adsorbents of the first structural type) to derive an adsorption isotherm equation for substances in the vapor state:

$$a = \frac{W'_0}{v^*} e^{-A \frac{T}{\beta} \log \frac{p_s}{p}} \quad (20)$$

where the volume of one millimole of liquid, v^* , for the temperatures $t < t_b$ is taken from the tables, and for $t_b < t < t_{cr}$ is calculated from equation 13.

Figure 10 gives a correlation of the characteristic curves and isotherms of adsorption for adsorbents of the first and second structural types. The isotherm for active carbons of the first structural type is distinguished by a sharper rise. The lower the constant B , the steeper is the isotherm curve.

Since the polarizability of a molecule of a substance is approximately proportional to the volume of the molecule or the molar volume of the substance in the form of a liquid, the result of investigations by Dubinin and Timofeyev (3) was a substantiation of the proportionality of the affinity coefficients of characteristic curves β and the molar volumes of the substances v .

Then, as an approximation, the adsorption isotherm equation (equation 8) takes on the form:

$$a = \frac{W_0}{v} e^{-\kappa \frac{T^2}{v^2} \left(\log \frac{p_s}{p} \right)^2} \quad (21)$$

and contains only the physical constants of the adsorbates, W_0 and κ , in addition to the constants v and p_s , which are found from the adsorption isotherm of a standard vapor, for instance, benzene. This equation expresses the dependence of adsorbability on the physical properties of the substances, and permits an evaluation of the amount of adsorption for any vapors with satisfactory accuracy.

A similar method for calculating the affinity coefficients was developed by Vaskovsky (14), who showed that in the best approximation, the affinity coefficients are expressed by the ratio of parachors of the substances (P after Sugden):

$$\beta = \frac{P}{P_0} \quad (22)$$

The parachors of substances are known to be equal to their molar volumes in the form of liquid in the state when their surface tensions are close to unity. In these conditions, the intermolecular forces of attraction would bring about identical compression of the liquids, and the proportionality of their molar volumes and volumes of molecules would hold more precisely. A substantiation of expression 22 is given elsewhere (8, 9).

To summarize, the theoretical views given above permit a quantitative description of the physical adsorption of gases and vapors by means of real adsorbents in a broad range of temperatures that include the critical region. These views establish a relationship between

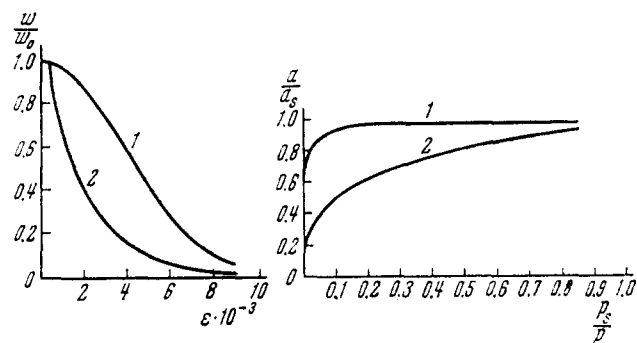


Fig. 10: General shape of characteristic curves (left) and of adsorption isotherms (right) for active carbons of the first and second structural types.

adsorption and the porous structure of the adsorbents and enable one to evaluate the adsorbability of substances on the basis of their physical constants.

IV. SUMMARY

Characteristic adsorption equations were experimentally substantiated for extreme structural types of

carbonaceous adsorbents. The methods of calculation of the filled volumes of adsorption space and of the adsorption potentials for substances in gaseous and vapor states have been considered. Adsorption isotherms for gases and vapors were obtained for broad ranges of temperatures that include the critical region.

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