

## Relation between characteristic adsorption energy and internal pressure in the theory of volume filling of micropores

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An equation for the internal pressure acting on an adsorbate in micropores was obtained on the basis of the assumption that the chemical potential of an adsorbate in micropores is equal to that in an equilibrium gas phase and using the Dubinin—Radushkevich equation. The empirical relation between the characteristic adsorption energy and the half width of pores was expressed in terms of internal pressure and diameter of adsorbate molecules. The two-dimensional pressure was calculated for micropores with plane-parallel walls, where the width of a micropore coincides with the diameter of an adsorbate molecule. The results obtained were compared with the two-dimensional pressure of a monolayer on a free planar surface for an adsorbate and adsorbent of the same nature.

**Key words:** thermodynamics of adsorption, internal pressure of adsorbate, theory of the volume filling of micropores.

Previously,<sup>1</sup> an empirical relation between the characteristic energy  $E_0$  in the Dubinin—Radushkevich (DR) equation and the half width of a micropore  $x$  (nm) was found:

$$E_0 x = k, \quad (1)$$

where  $k$  is a constant equal to  $\sim 12$  kJ nm mol<sup>-1</sup>. Later, an attempt at theoretical calculation of this dependence,<sup>2</sup> taking into account the potential energy of interaction of nitrogen and benzene molecules with carbon molecules in crevice micropores with different widths, was made, and (in the same work) an exponential dependence of the potential energy on the micropore width was obtained.

The present work deals with the relation between  $E_0$  and the internal pressure acting on an adsorbate in a micropore.

First of all, it is necessary to determine the generalized pressure  $p_a$  using the equality of isobaric-isothermic potentials in an adsorption phase ("a" index) and a gas phase:

$$V_a dp_a = V dp. \quad (2)$$

Here  $p_a$  is the internal pressure which results from intermolecular interactions in the adsorption field of an adsorbent. Integration of Eq. (2), provided that the gas phase is ideal, gives:

$$p_a = RT \int \frac{d(\ln p)}{V_a}. \quad (3)$$

The molar volume of adsorbate  $V_a$  is equal to the ratio of the total volume of micropores to the value of adsorption  $a$ :

$$V_a = W_0/a. \quad (4)$$

The value of  $a$  at pressure  $p$  in the gas phase is related to the limiting value of adsorption  $a_0$  at the pressure of saturated vapor of a liquid adsorbate  $p_s$  by the DR equation:

$$a = a_0 \exp \left[ - \left( \frac{RT \ln(p_s/p)}{\beta E_0} \right)^2 \right], \quad (5)$$

where  $\beta$  is affinity coefficient.

It follows from Eq. (4) that:

$$V_0 = W_0/a_0. \quad (6)$$

$V_0$  is usually considered to be equal to the molar volume of the liquid ( $V_{liq}$ ). Substitution of Eqs. (4) and (5) into Eq. (3) followed by rearrangements gives:

$$p_a = \frac{RT}{V_{liq}} \int_0^y \exp \left[ - \left( \frac{RTy}{\beta E_0} \right)^2 \right] dy, \quad (7)$$

where  $y = \ln p_s/p$ , and  $dy = -d(\ln p)$ .

The expression obtained is the probability integral, whose maximum value within the limits from zero

( $p_s/p = 1$ ) to  $\infty$  ( $p_s/p \rightarrow \infty$ ) may be calculated using the equation:

$$p_a = \frac{RT}{V_{\text{liq}}} \int_0^\infty \exp \left[ - \left( \frac{RTy}{\beta E_0} \right)^2 \right] dy = \frac{\sqrt{\pi}}{2} \frac{E_0 \beta}{V_{\text{liq}}} \quad (8)$$

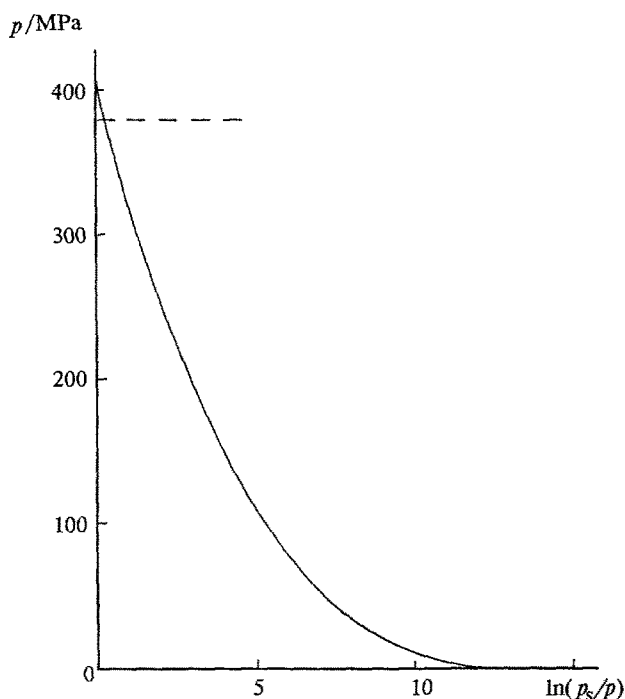
For the standard compound, benzene,  $\beta = 1$ , and the internal pressure  $p_{a,0}$  can be calculated by the formula:

$$p_{a,0} = 0.886 \frac{E_0}{V_{\text{liq}}} \quad (9)$$

Figure 1 shows the dependence of  $p_{a,0}$  on  $\ln(p_s/p)$  for benzene ( $\beta = 1$ ) at  $E_0 = 40 \text{ kJ mol}^{-1}$  calculated using the tabulated values of the probability integral. In the region of low relative pressures,  $p_{a,0}$  is close to zero, it increases monotonically when  $p/p_s$  increases, and becomes equal to 407 MPa at  $p/p_s = 1$ , which practically coincides with the internal pressure of benzene in the liquid phase determined from the ratio of evaporation enthalpy  $\Delta H$  to the molar volume:

$$V_{\text{liq}}/p_{\text{int}} = \Delta H/V_{\text{liq}} = 380 \text{ MPa}.$$

The half width of the micropore determined from Eq. (1) for  $E_0 = 40 \div 38 \text{ kJ mol}^{-1}$  is within 0.3–0.35 nm. These values are close to the value of the "external radius" of a benzene molecule (0.378 nm).<sup>4</sup>



**Fig 1.** Dependence of generalized pressure  $p_a$  of benzene calculated using Eq. (7) at  $\beta = 1$ ,  $E_0 = 40 \text{ kJ mol}^{-1}$ ,  $T = 293 \text{ K}$ , on the relative pressure in the gas phase. The dashed line is the internal pressure of liquid benzene at the same temperature.

Let us consider the "surface pressure" in a micropore. The surface pressure for the pore, whose half width corresponds to the radius of the adsorbed molecule, may be determined similarly to that for monolayer adsorption on a homogeneous solid surface. This pressure is related to the work of formation  $W^s$  of surface  $A$ . Surface  $A$  is new but its nature is identical to the starting one.<sup>4</sup> For example, the equation for pushing of an ideal piston into a micropore is as follows:

$$\pi = (\partial W^s / \partial A)_T = \sigma_0 - \sigma, \quad (10)$$

where  $\pi$  is the surface pressure,  $\sigma_0$  is the surface tension of micropore walls at a boundary with vacuum, and  $\sigma$  is the surface tension of micropore walls at a boundary with the adsorbate.

By definition, surface pressure  $\pi$  is a force acting at a unit length. Pressures  $p_a$  and  $\pi$  are connected by the relation:

$$\pi = p_a \tau, \quad (11)$$

where  $\tau$  is the thickness of the layer.

It follows from Eqs. (9) and (11) that:

$$\pi = 0.886 \frac{E_0 \tau}{V_{\text{liq}}} \quad (12)$$

Substituting the numerical values from Eq. (1) into Eq. (12) and taking into account that  $\tau = 2x$  and  $V_{\text{liq}} = 88 \text{ cm}^3 \text{ mol}^{-1}$ , we obtain:  $\pi_0 = 0.240 \text{ J m}^{-2}$ .

The micropores in active carbons are formed mainly by micro crystallites of graphite<sup>5</sup> and have crevice-like structures. Therefore, it is interesting to compare the values of  $\pi_0$  obtained for micropores with the surface pressure of benzene on graphitized carbon black (GCB) or cleaved graphite, whose pore surface is composed mainly of the base faces of graphite. Benzene adsorption on GCB at room temperature is complicated by poly-molecular adsorption. Therefore, using the Brunauer—Emmett—Teller (BET) model, one can calculate only approximately the surface pressure in the first adsorption layer on the adsorbate-graphite boundary. First, let us determine the molar volume of the adsorbate. According to the BET model, the volume of the first layer is  $W_0 = a_0 V_{\text{liq}}$ , where  $a_0/\text{mol g}^{-1}$  is the amount of the substance in the dense monolayer. The adsorption in the first layer is expressed by the equation:

$$a_1 = a_0 \frac{C p/p_s}{1 + (C - 1)p/p_s}, \quad (13)$$

where  $C$  is a constant. The value of adsorption in the first layer,  $a_1$ , and the total value of adsorption,  $a$ , are connected by the equation  $a_1/a = (1 - p/p_s)$  (see Ref. 6). The molar volume of the first layer is determined from Eqs. (3) and (13):

$$V_a = V_{\text{liq}} \frac{1 + (C - 1)p/p_s}{C p/p_s} \quad (14)$$

Equation (2) is valid for any part of the adsorbate volume, including the first layer. Therefore, substitution of Eq. (14) into (2), integration, and rearrangement taking Eq. (11) into account gives:

$$\pi = \frac{RT\tau}{V_{\text{liq}}} \frac{C}{C-1} \ln [(C-1)p/p_s + 1]. \quad (15)$$

In the case of saturation ( $p/p_s = 1$ ), Eq. (15) transforms into:

$$\pi_0 = \frac{RT\tau}{V_{\text{liq}}} \frac{C}{C-1} \ln C. \quad (16)$$

Substituting the accepted numerical value  $\tau = 0.756$  nm and the constants of the BET equation for benzene on GCB ( $C = 108$ ) (see Ref. 7), we obtain  $\pi_0 = 0.0975$  J m<sup>-2</sup>. This value is approximately 2.5 times smaller than the  $\pi_0$  value for microporous carbon adsorbents. Expression (1) is an averaged equation, and the calculation of pressure in a monolayer according to the

BET model is rather approximate. Therefore, the result obtained suggests that the internal pressure in carbon adsorbents is approximately doubled when passing from a nonporous surface to micropores.

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