A POSSIBLE UNIFIED DESCRIPTION OF AD- AND ABSORPTION PHENOMENA. THE DUBININ–RADUSHKEVICH EQUATION AND ITS PHYSICAL JUSTIFICATION

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Based on the earlier obtained equation representing the interphase equilibrium condition, it is shown that the known Dubinin–Radushkevich (DR) equation, which is widely used in engineering calculations of different technological processes and, in particular, in the field of chemical protection, follows from it at certain model prerequisites. Physical justification of the DR equation and its refinement are presented.

In [1] the equation has been derived which allows the description of ad- and absorption equilibria from the unified point of view. It is shown at least that the well known equations of Henry, Langmuir, Fowler–Huggengeim, Temkin, BET, and Hill [1, 2] are its particular cases. In [3], this equation has been rather successfully used for thermodynamic analysis of sorption processes in swelling systems.

The obtained equation for an arbitrary magnitude of adsorption has the form

$$p = z\frac{RT}{(V_{\text{ads}} - b)}\exp\left[-\left(\frac{q_{st} - p\Delta V}{RT}\right)\right]. \tag{1}$$

Prescribing a definite ad- or absorption model and using Eq. (1), one may obtain a particular, for the given model, equation relating a pressure p with adsorption *a*.

We will show that at some model prerequisites the known Dubinin–Radushkevich (DR) equation also follows from Eq. (1).

Among reversible adsorption processes there is physical adsorption caused by dispersion interactions. For carbon adsorbents, a determining component of adsorption interactions is just the dispersion forces. An increase of the adsorption energy in micropores is one of the main reasons of increasing the adsorptivity for microporous adsorbents as compared to relatively large-porous or nonporous adsorbents of the same chemical nature [4].

Micropores of the carbon adsorbents are commensurable in size with adsorbed molecules. From high-resolution electron microscopy patterns, the carbon adsorbents micropores have a slit-like form with limited side dimensions, therefore a size of each micrpore is expressed as a halfwidth x. A variety of micropores are slitlike pores with $x < 0.6\text{-}0.7$ nm and larger pores, the so-called supermicropores, with $0.6\text{-}0.7 < x < 1.5\text{-}1.6$ nm [5].

It is assumed that as a result of vapor adsorption in micro- and supermicropores, the pores volumes become filled with adsorbed molecules in accordance with the adsorption force fields in them and the interactions between the adsorbed molecules. This kind of adsorption has been named the micropores volume filling [4]. As is known, one of the adsorption equations in the theory of the micropore volume filling (TMVF) is the DR equation [6, 7]:

$$W = W_0 \exp\left[-\left(\frac{A}{E}\right)^2\right], \quad A = -\Delta\bar{G}_a = RT\ln(p_s/p). \tag{2}$$

Equation (2) for some considered adsorption system has two parameters: micropore volume W_0 and characteristic energy E. Usually the DR equation is valid in the range of relative vapor pressures $p/p_s = 10^{-4}$ to 0.4-0.5.

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Thus, in order to go from Eq. (1), representing the interphase equilibrium condition, to some specific ad- or absorption equation, one must know two functional dependences, i.e., entropy and energy factors as a function of adsorption. These dependences are rigorously connected with a chosen adsorption model. And if in the simplest models, such as those of Henry, Langmuir, Fowler–Huggengeim, Temkin, BET, and Hill, the required information may be found in their original postulates, the DR equation, called the empirical one, is to be somehow transformed to get this information.

Application of the DR equation for different temperature range (up to $T_{boil} \leq T \leq T_{cr}$; after T_{cr}) has its own specific features. Thus, for instance, at the temperature ranged up to T_{boil} a molar volume of the adsorbed substance is usually assumed to be equal to that of a liquid at an experimental temperature. Proceeding just from this principle in the given temperature range, we build the so-called characteristic dependence (or a curve) of W on A.

What does the equality condition of molar volumes mean? From the point of view of phenomenological thermodynamics a change in entropy is determined as

$$\Delta S = S(V,\ T) - S(V_0,\ T_0) = \int\limits_{V_0, T_0}^{V_0, T} \frac{C_V dT}{T} + \int\limits_{T, V_0}^{T, V} \left(\frac{\partial S}{\partial V}\right) dV$$

where V_0 and V are the molar volumes of two different states; C_v is the molar heat capacity at a constant volume. At T = const and V = const, $\Delta S = 0$. Thus, invariance of the characteristic curve with the molar volumes of the adsorbed substance and the liquid being equal at the experimental temperature $(\partial A/\partial T)_w = 0$ [4] is no different from

$$(\partial(-\Delta \bar{H}_a)/\partial T)_W = (\partial Q/\partial T)_W = 0, \tag{3}$$

where $Q = q_{st} - L_s$ is the pure heat of adsorption. Here, it is naturally implied that in the temperature range up to T_{boil} an equilibrium gas phase is ideal.

Consequently, if the model prerequisites, underlying the DR equation, are possible to speak about, then one is concerned with a liquid or a liquidlike adsorbed substance being in an adsorbent field. A liquidlike state is not, obviously, a liquid, but by its one criterion, i.e., a molecule concentration, it corresponds to the latter.

Do any analogies exist in the adsorption theory? Of course they exist. The known polymolecular Hill adsorption model may serve as an example [8]. It considers an adsorption film in the field of a solid nonporous nonpolar adsorbent with a flat interface. The model implies that the adsorbed film has a density equal everywhere to that of a three-dimensional liquid.

It is worth noting that the temperature invariance of the characteristic curve has been discussed in a number of works in terms of the phenomenological theory of adsorption on inhomogeneous surfaces [9-14]. As regards the physical point of view, the assumptions to be made to deduce a rule of the temperature invariance of the characteristic curve [11] seem to be more reasonable. As for the modern viewpoint, the essence of this work is as follows. The temperature invariance rule of the characteristic curve means that the partial molar entropy of the adsorbed substance is equal to the molar entropy of a liquid:

$$\Delta \bar{S}_a = 0.$$

In [15], the author has reached, in essence, a similar conclusion but in terms of the molecular theory.

Thus, from to the above considerations, the quantities Q and adsorption *a*, are related as follows:

$$a = a_0 \exp\left[-\left(\frac{-\Delta \bar{H}_a}{E}\right)^2\right], \tag{4}$$

or

$$a = a_0 \exp\left[-\left(\frac{Q}{E}\right)^2\right]. \tag{5}$$

Now, with this information at hand, we may formulate the model prerequisites of the DR equation in the temperature range up to T_{boil}, namely, 1) concerning a liquidlike state of a substance being in an adsorbent field, at $\Delta \bar{S}_a = 0$; 2) an adsorbed substance is distributed in an adsorbent field with respect to the pure heat of adsorption according to formula (5), i.e., the normal distribution law.

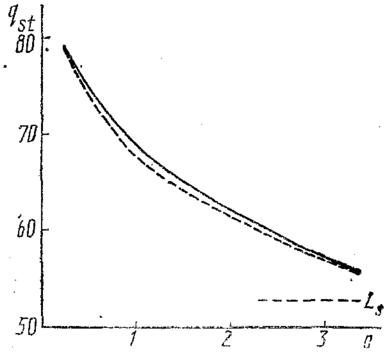

Fig. 1. Isosteric heat q_{st} (kJ/mole) vs benzene adsorption a (mmole/g) by activated carbon CA at T = 303 K: solid line) data [18]; dashed line) calculation by Eq. (5).

Such a model may be compared with Eq. (1), representing the interphase equilibrium condition, to obtain the appropriate adsorption equation. For this, we write (1) in the form:

$$p_s = \frac{RT}{(V_{\text{liq}} - b)} \exp\left[-\left(\frac{L_s}{RT} - 1\right)\right], \tag{6}$$

assuming a gas phase above an adsorbed substance to be ideal. Formula (6) represents the equilibrium condition of a pure liquid with its saturated vapor. If we divide the expression (6) by (1), take the logarithms of the left- and right-hand sides of the quotient and transform the obtained equation, then taking into account (5) and the condition $V_{\text{ads}} = V_{\text{liq}}$, we arrive at the DR equation:

$$a = a_0 \exp\left[-\left(\frac{A}{E}\right)^2\right],$$

or

$$a = a_0 \exp\left[-\left(\frac{Q}{E}\right)^2\right].$$

Is the expression (3), i.e., $(\partial Q/\partial T)_W = 0$, obvious? From the physical point of view it is quite clear. For the given systems, the question is about a liquid or liquidlike state of an adsorbed substance, i.e. a model (we already spoke about some model) does not consider the Henry region inherent to all real systems. An adsorbed substance occupies an adsorption space strictly following the law characteristic for the systems under consideration. This law may be any one of wide diversity, e.g., a linear one as in the Temkin model [16]. In the given case, independently of temperature, the law of filling does not change since the adsorbed substance interacts with the adsorbent field at the expense of dispersion forces which do not depend on T. With the T-independent distribution law, the well-defined quantities Q_1, Q_2, ... correspond to the filled volumes W_1, W_2, ... Thus, when the equal volumes $W_i(T_1)$ and $W_i(T_2)$ are considered at different temperatures, then the equal pure heats at different values of adsorption a will, obviously, correspond to them. Strictly speaking, such an approach is valid only when the density of an adsorbed substance is assumed at any point of an adsorption space at a given a to be the same (in the given case $\rho_{\text{ads}} = \rho_{\text{liq}}$ at any a) and, besides, the temperature coefficient of expansion is everywhere the same.

Now a question naturally arises concerning the co-existence of phases in pores sized to 6-7 Å and up. A clear-cut answer is given by L. D. Landau [17]: the co-existence of phases in the systems of a linear type is impossible, i.e., the phases having only one point of contact cannot co-exist. The considered systems have, at least, not less than two-three points of contact, i.e., from the physical point of view these systems may co-exist.

Obviously, the expression (5) is sufficiently easy to check. Indeed, if we take the plot of isosteric heat q_{st} versus adsorption a calculated from experiment for any system, then taking any two points from it, we determine two parameters of Eq. (5), i.e., a_0 and E. Next, using them, we may restore the entire dependence $q_{st} = f(a)$, starting from p/p_s, at which the DR equation is already fulfilled. In Fig. 1, one can see a good correlation of these two curves for the system activated carbon CA–benzene (T = 303 K) studied in [18].

The detailed thermodynamic analysis of the main propositions of the TVMF is made in [19-21]. Of interest in this case is the possibility of some refinement of the DR equation. If we apply the general thermodynamic approach to calculation of the isosteric heat of adsorption in the assumption of an ideal equilibrium gas phase:

$$q_{st} = -R\left(\frac{\partial \ln p}{\partial T^{-1}}\right)_a, \tag{7}$$

then from the DR equation (2) we obtain

$$Q = q_{st} - L_s = E\sqrt{\ln(a_0/a)} + \frac{E}{2T}\left[\ln\left(\frac{a_0}{a}\right)\right]^{-1/2}\left(\frac{\partial \ln a_0}{\partial T^{-1}}\right), \tag{8}$$

$$\Delta\bar{S}_a = -\frac{E}{2T^2}\left[\ln\left(\frac{a_0}{a}\right)\right]^{-1/2}\left(\frac{\partial \ln a_0}{\partial T^{-1}}\right). \tag{9}$$

From these formulas it follows that at small and large p/p_s, $Q \to \infty$ while $\Delta\bar{S}_a$ at elevated p/p_s tends to $-\infty$. The fact that the DR equation is not valid at small magnitudes of adsorption, i.e., does not extend to the Henry region, is evident. This has been the model of a liquidlike adsorbed substance. Thus, this model ignores the adsorption region with small a, in which an entropy factor is responsible for random scatter of separate molecules throughout the pore space. Counting is started from some adsorption value specified for the considered systems. A question arises why (8) and (9) yield incorrect results at $a \to a_0$. Most likely, this is connected with some incorrectness of the DR equation itself. In what follows, we shall try to modify it further to a greater extent.

Thus, we introduce an assumption that at the temperature range from T to T_{cr} the density of the adsorbed substance is $\rho_{ads} \geq \rho_q$ (let this difference be insignificant). As far as a increases, ρ_{ads} drastically decreases. Obviously, $\Delta\rho = \rho_{ads} - \rho_{liq}$ will be more significant at elevated temperatures because of the increasing compressibility of the adsorbed substance. As mentioned above, ρ_{ads} is a function of the adsorption value a as well as of temperature. In [22], for instance, within the domain $T_{boil} \leq T \leq T_{cr}$, ρ_{ads} is approximated by a linear dependence on T. Then we may write the adsorption equation (5) as

$$a/\rho_{ads} = W_0 \exp\left[-\left(\frac{Q}{E}\right)^2\right],$$

or

$$a = \frac{W_0\rho_{liq}}{\rho_{liq}}\rho_{ads}\exp\left[-\left(\frac{Q}{E}\right)^2\right] = a_0\gamma\exp\left[-\left(\frac{Q}{E}\right)^2\right].$$

In the latter expression, ρ_{liq} is the density of a liquid state corresponding to a_0 at which $Q = 0$; $\gamma = \rho_{ads}/\rho_{liq} > 1$. Now we may write (4) or (5), being quite justified at the temperatures from T to T_{boil}, in the following form

$$a = a_0\gamma\exp\left[-\left(\frac{-\Delta\bar{G}_a - T\Delta\bar{S}_a}{E}\right)^2\right]. \tag{10}$$

Using (7) and (10), we arrive at

$$Q = q_{st} - L_s = E\sqrt{\ln\left(\frac{\gamma a_0}{a}\right)}, \tag{11}$$

$$\Delta\bar{S}_a = -\frac{E}{2T^2}\left[\ln\left(\frac{\gamma a_0}{a}\right)\right]^{-1/2}\left[\left(\frac{\partial \ln\gamma}{\partial T^{-1}}\right)_a + \frac{\partial \ln a_0}{\partial T^{-1}}\right] - \frac{1}{T^2}\left[\frac{\partial(T\Delta\bar{S}_a)}{\partial T^{-1}}\right]_a. \tag{12}$$

From (11), (12) it follows that Q and $\Delta\bar{S}_a$ become correct as $a \to a_0$ which is attributed to two factors: 1) obviously, with filling of micropores, the size of which is about several diameters of adsorbate molecules ($x \approx$ 6-7 Å), Q does not attain a zeroth value; thus, from (5) it follows that a_0 is always larger than a; 2) in connection with the first factor, $\gamma = \rho_{ads}/\rho_{liq}$ is always also larger than unity. Despite this, due to the compensation effect of $\Delta\bar{H}_a$ and $T\Delta\bar{S}_a$ the value of $\Delta\bar{G}_a$ tends to zero or $p/p_s \to 1$ ($\Delta\bar{G}_a = \Delta\bar{H}_a - T\Delta\bar{S}_a$).

If it is possible to apply (10) to the temperature range $T_{boil} \leq T \leq T_{cr}$, then γ and $T\Delta\bar{S}_a$ will be rather significant due to the high compressibility of the adsorbed substance. The fact that the DR equation in the form

$$a = a_0 \exp\left[-\left(\frac{-\Delta\bar{G}_a}{E}\right)^2\right],$$

finds successful application in practice, only emphasizes the mutual compensation (one more) of the characteristics γ and $T\Delta\bar{S}_a$ in Eq. (10). Nevertheless, use of this equation in the range $T_{boil} \leq T \leq T_{cr}$ yields approximate results and may be physically justified only at $\gamma \approx 1$ because of the reasons mentioned above.

As for a transition from one adsorbate to another, from the physical point of view everything remains absolutely the same. Only different heats and thus different E will correspond to the equal occupied volumes (since the dispersion interaction constants change).

Finally, it is worth noting that in order to apply Eq. (10), it is necessary to calculate changes in entropy $\Delta\bar{S}_a$. In [1], based on (1), the following expression is given for it:

$$\Delta\bar{S}_a = \frac{V_{ads} - b}{V_{liq} - b}.$$

The characteristic b, as mentioned above, is a function of the temperature and is calculated from (6) using tabular data, i.e., thermophysical properties of liquids.

Conclusions. Thermodynamical analysis of the empirical Dubinin–Radushkevich equation has allowed model prerequisites to be made for derivation of this equation. Necessary corrections are introduced into it making the thermodynamical characteristics of an adsorbed substance correct in the filling interval, for which the adsorption model is intended. It is shown that the DR equation directly stems from a more general equation, being the interphase equilibrium condition.

NOTATION

p, equilibrium pressure of a gas phase; z, compressibility factor of a gas phase; R, universal gas constant; T, temperature; q_{st}, isosteric heat of adsorption; $p\Delta V = p(V_{gas} - V_{ads})$, work against external pressure p done by one mole of adsorbed substance at an equilibrium transition into a gas phase; V_{ads}, molar volume of the adsorbed substance corresponding at a given value of adsorption a to equilibrium characteristics T, p, and q_{st}; V_{gas}, molar volume of the equilibrium gas phase; b, correction for the occupied volume of one mole of the adsorbed substance molecules, some function of the temperature; W and W_0, current and limiting values of vapor adsorption in volume units; $A = -\Delta\bar{G}_a$, difference between the chemical potentials of the saturated vapor and the current value of the chemical potential of the adsorbed substance at a given temperature (for an ideal gas $A = RT\ln(p_s/p)$); p/p_s, relative pressure of the equilibrium gas phase; E, characteristic energy of adsorption in the DR equation; S, entropy; $\Delta\bar{H}_a$ and $\Delta\bar{S}_a$, changes of partial molar enthalpy and entropy of the adsorbed substance relative to a liquid state, respectively; L_s, heat of evaporation; a, a_0, current and limiting values of adsorption in mass units; V_{liq}, molar volume of the liquid.

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