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Abstract

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A THERMODYNAMIC CRITERION FOR THE APPLICABILITY OF THE POTENTIAL THEORY OF ADSORPTION

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Usually, in expounding the potential theory of adsorption of vapors on solid adsorbents, one follows the scheme of reasoning of Polanyi, proposed by him as early as 1916. In particular, the adsorption phase is considered as a normal liquid with the normal pressure p_s of saturated vapor directly above its surface. However, in recent decades our ideas about the properties of the adsorbed substance have broadened and deepened to such an extent that such a point of view can no longer be regarded as valid. The basic assertion of the potential theory concerning the existence of a characteristic curve invariant with respect to temperature does not require identifying the adsorption phase with a normal liquid.

As is known, the characteristic curve is the dependence of ε on av, where a is the amount of adsorption, v is the molar volume of the adsorbed substance, and $\varepsilon = RT \ln p_s/p$ is the change in free energy upon isothermal transfer of a mole of substance from the normal liquid to an adsorbent in equilibrium with the gas phase at pressure p. The condition for the existence of a single temperature-independent characteristic curve may be written in the form

$$(\partial\varepsilon/\partial T)_{av} = 0. \tag{1}$$

Let us consider the derivative $(\partial\varepsilon/\partial T)_a$. Along the characteristic curve, ε in all cases decreases with increasing av, i.e. $d\varepsilon/dav < 0$; therefore it can be shown that $(\partial\varepsilon/\partial T)_a < 0$. Indeed, at $a = \text{const}$

$$d\varepsilon/dav = 1/a \cdot (d\varepsilon/dv)_a = (\partial\varepsilon/\partial T)_a/a\,(\partial v/\partial T)_a < 0.$$

Assuming that, with increasing temperature, the molar volume of the adsorption phase increases and, consequently, $(\partial v/\partial T)_a > 0$, we obtain

$$(\partial\varepsilon/\partial T)_a < 0. \tag{2}$$

Fig. 1

Figure 1: Fig. 1

The derivative entering this inequality represents the change in the differential entropy of adsorption ΔS relative to the chosen standard state—the normal liquid. Consequently, fulfillment of the fundamental equation of the potential theory (1), regardless of the particular form of the equation of the characteristic curve, requires fulfillment of inequality (2), equivalent to the condition

$$\Delta S < 0. \tag{3}$$

For the particular form of the equation of the characteristic curve corresponding to the equation of the first type of Dubinin, Zaverina, and Radushkevich ([1]), this purely thermodynamic criterion (3) for the applicability of the potential theory was noted by us earlier ([2]). It is necessary to emphasize that satisfaction of inequality (3) is a necessary, but not sufficient, condition for the applicability of the potential theory.

Let us note that recently objections have been raised against

potential theory ([3]), based on the fact that it allegedly requires the differential entropy of adsorption to be equal to zero. This objection is based on the erroneous assumption that the partial derivative in equation (1) represents the entropy. From inequality (3) it is evident that the potential theory not only does not assume the entropy to be zero, but requires that it be negative.

Condition (3) can be represented in other forms, more convenient in the analysis of experimental data. It is well known that in the coordinates $\ln p, 1/T$, the dependence of the saturated-vapor pressure p_s on temperature, as well as the dependence on temperature of the equilibrium vapor pressure of this substance over the adsorbent at a constant amount of adsorption (the so-called adsorption isostere), are well approximated by straight lines. In Fig. 1, straight line 1 corresponds to the dependence of $\ln p_s$ on $1/T$, while straight lines 2, 3, and 4 represent isosteres at different values of adsorption. If these dependences deviate from linearity, then, without loss of generality, these straight lines may be regarded as tangents to the corresponding curves drawn at a specified value of T. The equations of straight lines 1 and 2–4 may be written as follows:

Fig. 1

$$\begin{aligned} \ln p_s &= -(\lambda/RT) + C_s, \\ \ln p &= -(Q/RT) + C_a, \end{aligned} \tag{4}$$

where λ is the latent heat of vaporization of the pure adsorbate, Q is the isosteric heat of adsorption, and C_s and C_a are the intercepts cut off by these straight lines on the ordinate axis. It follows that

Fig. 2

Figure 2: Fig. 2

$$\varepsilon = RT\ln(p_s/p) = q + (C_s - C_a)RT, \tag{5}$$

where $q = Q - \lambda$ is the so-called net heat of adsorption. Comparing equation (5) with the Gibbs-Helmholtz equation

$$\varepsilon = q + T(\partial\varepsilon/\partial T)_a = q + T\Delta S, \tag{6}$$

we obtain

$$\Delta S = (C_s - C_a)R. \tag{7}$$

Fig. 2

As is seen from Fig. 1, the adsorption isosteres (or tangents to the isosteres), when extended, may intersect the ordinate axis above or below the point C_s. In accordance with condition (3), the difference $C_s - C_a$ must be negative and, consequently, the potential theory can be fulfilled only under the condition

$$C_a > C_s. \tag{8}$$

The adsorption isostere that intersects the ordinate axis at the point C_s (straight line 3 in Fig. 1) determines the limiting value of adsorption a_{gr}, above which lies the region of applicability of the potential theory.

From equation (6) it is clear that for $\Delta S < 0$ the inequality $q > \varepsilon$ is valid, and for $\Delta S > 0$, correspondingly, $q < \varepsilon$. On this basis one may conclu-

consider that the isostere $a = a_{\text{gr}}$ (curve 3 in Fig. 1), for which $C_a = C_s$, i.e. $q = \varepsilon$ or $\Delta S = 0$, divides the entire region of existence of adsorption isosteres into two parts: one (above curve 3), where $a > a_{\text{gr}}$ and, consequently, $C_a > C_s$, $q > \varepsilon$, $\Delta S < 0$, and for which the potential theory may be valid, and another (below curve 3), where $a < a_{\text{gr}}$ and, consequently, $C_a < C_s$, $q < \varepsilon$, and $\Delta S > 0$, for which the potential theory is in principle inapplicable. For the temperature region in which the adsorption isosteres and the curve $\ln p_s = f(1/T)$ remain linear, the lower limit of applicability of the potential theory, a_{gr}, does not depend on temperature.

The considerations set out above can be illustrated by many examples, one of which we shall examine in more detail. Figure 2 shows curves of the dependence of the net differential heat of adsorption q and of the change in free energy ε (at $T = 77.4^{\circ}\text{K}$) on the amount of adsorption a, calculated by us for the case of

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

nitrogen adsorption on activated carbon from the data of work ([4]). In the region of small values of a, the curve ε lies above the curve q. At $a_{gr} = 3.7$ mmol/g, the two curves intersect, and with a further increase in adsorption the curve ε goes below the curve q. The lower curve in Fig. 2 gives the dependence of the differential entropy ΔS on the amount a. At $a < a_{gr}$ the differential entropy is positive (i.e., higher than the entropy of liquid nitrogen), while at $a > a_{gr}$ it is negative (i.e., lower than the entropy of liquid nitrogen). In accordance with what was said above, the potential theory can be satisfied in this case only at $a > 3.7$ mmol/g.

Fig. 3

In Fig. 3, in the coordinates $\lg p$, $1/T$, adsorption isosteres are shown for this system, together with the curve $\lg p_s = f(1/T)$ for nitrogen. This figure clearly shows the linearity of the isosteres over a wide temperature interval,* including the critical temperature T_{cr}, and the isostere $a_{gr} = 3.7$ mmol/g, when linearly extrapolated, actually passes through the point C_s.

Fig. 4

Figure 4 shows the application of the equation of the first type of Dubinin, Zaverina, and Radushkevich ([1]) (in coordinates corresponding to the linear form of this equation) to the experimental data under consideration at the three temperatures indicated in the figure. Straight lines 1, 2, and 3 were drawn using the independently determined ([4]) constants of this equation, and their slopes correspond to the theoretical temperature dependence. The dotted line in the figure shows the temperature-independent lower limit of applicability of the potential theory for this system, $a_{gr} = 3.7$ mmol/g.

* The fact that the adsorption isosteres remain linear even when passing through the critical temperature makes it possible, as it seems to us, to find the parameters of adsorption equilibrium for the region of the gaseous state on the basis of the parameters of adsorption equilibrium for the region of the vapor-like state. This question will be considered elsewhere.

For temperatures of 77.4 (curve 1) and 126.1° K (curve 3), it is directly evident that in the region $a < 3.7$ mmol/g the experimental points deviate noticeably from the theoretical straight lines. At $T = 101°$ K (curve 2), the linear dependence is preserved also at values of a smaller than a_{gr}; however, in the present case this circumstance proves to be entirely accidental and in no way indicates the applicability of the potential theory at $a < a_{gr}$, since below a_{gr} the theo-

retical temperature dependence of adsorption predicted by the potential theory evidently ceases to hold.

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Note: Figure translations are in progress. See original paper for figures.