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Abstract

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ADSORPTION ISOSTERES IN POTENTIAL THEORY

It is well known that adsorption isosteres, i.e., curves expressing the dependence of the equilibrium pressure on temperature at a constant value of adsorption, in the coordinates $1/T$, $\lg p$ are usually satisfactorily approximated by straight lines over a more or less broad temperature range. As an example it is sufficient to point to at least several works ($^{1-3}$), in which families of linear adsorption isosteres are given for a number of substances on various adsorbents. In all cases in which, over some temperature interval, the state of the adsorbed substance does not change, the adsorption isosteres remain practically linear in this interval. A break in an isostere, or a smoother change in its slope in a comparatively narrow temperature region, characterizes the appearance of a phase transformation in the adsorbed substance. Thus, the approximate linearity of adsorption isosteres in the region of existence of a homogeneous adsorption phase may be regarded as an experimental fact of very general significance. In studying adsorption equilibrium, one usually measures the dependence of adsorption on pressure at constant temperature, i.e., the adsorption isotherm. Direct experimental measurement of adsorption isosteres has begun to be carried out in individual cases only recently (^{4,5}). In some respects the adsorption isostere is a more important characteristic of adsorption equilibrium than the traditional isotherm, since it makes it possible to determine the differential heats and entropies of adsorption. The approximate linearity of isosteres observed experimentally is not an obvious consequence of the basic concepts of the theories of physical adsorption. The best-known equations of adsorption isotherms either do not contain explicitly the dependence of the equation parameters on T, or else lead to a complex temperature dependence of the pressure p on T at $a = \text{const}$, from which, in the general case, the linearity of isosteres does not follow. An exception is potential theory, which in principle makes it possible, from the characteristic curve, to find the dependence of adsorption on temperature and to construct adsorption isosteres. However, up to now the question of the form of these isosteres has not been considered. Below we shall clarify the conditions under which the linearity of isosteres is a consequence of potential theory.

As is known, the development of potential theory in works (^{6,7}) made it possible to obtain thermal equations of vapor sorption for two structural types of sorbents, giving an explicit dependence of adsorption on temperature. Let us first consider the equation for adsorbents of the first structural type:

$$a = (W_0/v)\exp[-(BT^2/\beta^2)\lg^2(p_s/p)], \tag{1}$$

in which W_0 and B are constants characterizing the adsorbent, and v, p_s, and β are, respectively, the molar volume of the adsorbate, the pressure of its saturated vapor, and the affinity coefficient of the characteristic curve, approximately expressed by the ratio of the parachors of the adsorbate and of the standard substance (7). Equation (1) can be given the following form:

$$\ln p = \ln p_s - 2.30\,\beta B^{-1/2}[\ln(W_0/av)]^{1/2}\cdot 1/T, \tag{2}$$

which, for $a = \text{const}$, is the equation of the adsorption isostere in the coordinates $1/T$, $\ln p$, where v is regarded as a function of T. In accordance with extensive factual material, we shall proceed from the assumption that, over a more or less broad temperature interval, the latent heat of vaporization λ may always be regarded as constant, i.e.,

$$\lambda = Rd\ln p_s/d(1/T) = \text{const}, \tag{3}$$

and, consequently,

$$\ln p = -(\lambda/R)\cdot 1/T + C_s. \tag{4}$$

Differentiating equation (2) with respect to $1/T$ at $a = \text{const}$, we obtain:

$$Q = -R\left(\frac{\partial\ln p}{\partial(1/T)}\right)_a = \lambda + 2{,}30\beta RB^{-1/2}\frac{\partial}{\partial(1/T)}\left[\left(\ln\frac{W_0}{av}\right)^{1/2}\frac{1}{T}\right]_a, \tag{5}$$

where Q denotes the differential isosteric heat of adsorption. Let us find the form of the function $v(T)$ for which $Q = \text{const}$ and, consequently, isostere (2) is linear, i.e., is expressed by an equation of type (4). From equation (5) it is evident that, under condition (3), Q will be constant if, at $a = \text{const}$,

$$[\ln(W_0/av)]^{1/2}\cdot 1/T = K/T + D$$

or

$$F_1(T) = [\ln(W_0/av)]^{1/2} = [\ln(v_m/v)]^{1/2} = K + DT. \tag{6}$$

As a result,

$$\ln v = \ln v_m - (K + DT)^2, \tag{7}$$

where K and D do not depend on T, and $v_m = W_0/a$. The quantity v_m is the largest value of the molar volume v of the adsorbed substance at which, for the given isostere, the entire volume of the adsorption space is filled at some temperature T_m. It is obvious that substitution of this expression for $\ln v$ into equation (2) gives a linear form of the isostere of the type of equation (4). It follows from equation (7) that, for exact fulfillment of the condition of linearity of the isostere (6), the molar volume of the substance in the adsorbed state must be a function of temperature of the form

$$\ln v = m + \alpha T + cT^2, \tag{8}$$

where $\alpha > 0$ and $c < 0$.

Usually, for the normal bulk phase of a substance, the molar volume is satisfactorily approximated by expression (8), but not with a negative, rather with a positive value of the coefficient c. It follows from this that, upon substitution of the values of $\ln v$ from equation (8) for the normal bulk phase (with $c > 0$) into equation (2), the isosteres will deviate somewhat from linearity (especially near T_{cr}). However, calculations carried out by us, for example, for the adsorption isosteres of benzene on activated carbon according to equation (2), showed that these deviations, even in the interval 0–170°, are still small and the isosteres remain practically linear. It should be noted that the linear dependence of the volume of the adsorbed substance v^* on T between T_{boil} and T_{cr}, introduced in work (^{8}), can be approximated by equation (8) with coefficient $c < 0$, and therefore substitution of $\ln v^*$ into equation (2) should, to a good approximation, lead to linear isosteres even at temperatures close to T_{cr}.

In a narrower interval of T (not very close to T_{cr}), for many substances the quadratic term in expression (8) is small (especially in the region of existence of the solid phase), and it may be neglected. Under this condition

$$\ln v = m + \alpha T, \tag{9}$$

and, consequently, the true coefficient of expansion α is constant:

$$\alpha = \frac{1}{v}\frac{dv}{dT} = \text{const}. \tag{10}$$

Calculations we have carried out for a number of special cases (for example, for the adsorption of alkanes from C_4 to C_8 on zeolites, according to the data of work (^{2})) show that, when $\ln v$ from equation (9) is substituted into expression (6) and the resulting function $F_1(T)$ is subsequently expanded in a series in powers of T, one may, with a good degree of accuracy, retain only the term containing T

to the first power. Therefore, if in the specified temperature interval $\ln v$ can be represented by equation (9), then F_1 is satisfactorily approximated by a linear function of T, and, consequently, isostere (2) will be approximately linear.

Let us now consider the thermal equation of the potential theory of adsorption for adsorbents of the 2nd structural type (^{7}):

$$a = (W_0'/v)\exp\left[-(AT/\beta)\lg(p_s/p)\right], \tag{11}$$

where W_0' and A are temperature-independent constants characterizing the adsorbent, while v, β, and p_s have the same meaning as in equation (1). As before, in order to obtain the equation of the adsorption isostere it is sufficient to solve equation (11) with respect to $\ln p$ at $a = \text{const}$:

$$\ln p = \ln p_s - \frac{2.30\beta}{A}\frac{1}{T}\ln\frac{W_0'}{av}. \tag{12}$$

We shall continue to assume that, in the specified temperature interval, condition (3) is observed, i.e. $\lambda = \text{const}$. Under this condition, the isostere equation (12) will be linear and, consequently, the heat of adsorption $Q = \text{const}$, if $F_2(T) = \ln(W_0'/av)$ is a linear function of temperature. If equation (9) is used for the dependence of v on T, we obtain:

$$F_2(T) = \ln\frac{W_0'}{av} = \ln\frac{W_0'}{a} - m - \alpha T = l - \alpha T. \tag{13}$$

Substituting F_2 into equation (12), we obviously obtain a strictly linear equation of the isostere, of the type of expression (4).

Thus, if in the given temperature interval the conditions

$$\lambda = \text{const}, \qquad \alpha = d\ln v/dT = \text{const}, \tag{14}$$

are fulfilled, i.e. the latent heat of vaporization and the true expansion coefficient of the adsorbate are constant, then, in this approximation, both for adsorbents of the 1st structural type (equation (1)) and for adsorbents of the 2nd structural type (equation (11)), the adsorption isosteres are linear and the isosteric heats of adsorption are constant. Deviations from linearity of $\ln v$ in equation (8) at $c > 0$ must in both cases lead to some curvature of the isosteres over a wide temperature interval.

If in the temperature region under consideration the conditions

$$\lambda = \text{const}, \qquad Q = \text{const}, \tag{15}$$

are satisfied, then it is easy to show that, along the isostere a = const, the differential entropy of adsorption is constant. Indeed, let us write for adsorption equilibrium the Gibbs-Helmholtz equation

$$q = Q - \lambda = \varepsilon - T\Delta S = \varepsilon - T(\partial\varepsilon/\partial T)_a, \tag{16}$$

where ε is the free energy of adsorption, and ΔS is the differential entropy of adsorption. If the liquid at temperature T is chosen as the standard state, then

$$\varepsilon = RT\ln(p_s/p). \tag{17}$$

At the same time

$$\Delta S = (\partial\varepsilon/\partial T)_a. \tag{18}$$

Differentiating equation (16) with respect to T under condition (15) and taking (18) into account, we obtain:

$$(\partial^2\varepsilon/\partial T^2)_a = (\partial\Delta S/\partial T)_a = 0,$$

whence it follows that, at a = const, the differential entropy ΔS = const. Let us note that an analogous result was obtained in work [2] when the gas phase at a pressure of 1 atm was chosen as the standard state. In that work, in studying the adsorption of hydrocarbons on synthetic zeolite—faujasite, constant values of ΔS were found for all the substances studied along linear isosteres. Similarly, constant values of ΔS along linear isosteres of adsorption of CO_2 on silica gel were obtained by us in treating the experimental data of work [3].

Thus, if in some temperature interval simultaneously λ = const and Q = const, or if $q = Q - \lambda$ = const, then along the adsorption isostere the differential entropy of adsorption remains constant, irrespective of the particular form of the adsorption-isostere equation. Consequently, linear adsorption isosteres are characterized by the simultaneous constancy of the differential heat and the differential entropy of adsorption. On the basis of the foregoing, it may be asserted that, in the indicated approximation, the linearity of isosteres and the constancy of the quantities Q and ΔS along isosteres are consequences of the fundamental equations (1) and (11) of the potential theory of adsorption.

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