PHYSICAL CHEMISTRY

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1957

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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CALCULATION OF THE HEAT AND ENTROPY OF ADSORPTION FROM A SINGLE ADSORPTION ISOTHERM

(Presented by Academician M. M. Dubinin on 10 I 1957)

To determine the magnitude of the heat and entropy of sorption as a function of the amount of sorbed substance, either direct calorimetric measurements or thermodynamic calculations are used, based on the experimental determination of the temperature coefficient of sorption. The fundamental principles of each of these methods are clear and do not raise doubts. However, both of them (especially the first) are very laborious and impose very high requirements on the quality of the experiment. Below we shall show under what conditions it is possible to calculate these important thermodynamic characteristics of the sorption process from a single adsorption isotherm.

Extensive experimental material accumulated over several decades shows that, in a very large number of cases, the basic postulate of the potential theory of adsorption, stated by Polanyi as early as 40 years ago, is well fulfilled. According to this postulate, the so-called adsorption potential $\varepsilon = -RT \ln h$ (where h is the relative pressure), at a constant value of the filled adsorption volume $\varphi = aV$ (a is adsorption, V is the molar volume of the adsorbate), does not depend on temperature, i.e.

$$(\partial\varepsilon/\partial T)_{\varphi} = -R(\partial T \ln h/\partial T)_{aV} = 0. \qquad (1)$$

It is easy to see that a single adsorption isotherm uniquely determines the form of the curve $\varphi = f(\varepsilon)$, called the characteristic curve, and, in accordance with (1), the characteristic curve, in turn, uniquely determines the adsorption isotherm at another, nearby temperature, i.e., the temperature coefficient of adsorption. Thus, fulfillment of condition (1) should make it possible to calculate the heat and entropy of sorption from a single isotherm.

Indeed, choosing aV, T, and $\ln h$ as variables, we can write the thermal equation of adsorption in the form $F(aV, T, \ln h) = 0$. Hence:

$$-\left(\frac{\partial aV}{\partial T}\right)_{\ln h} = \left(\frac{\partial aV}{\partial \ln h}\right)_T \left(\frac{\partial \ln h}{\partial T}\right)_{aV} = V\left(\frac{\partial a}{\partial \ln h}\right)_T \left(\frac{\partial \ln h}{\partial T}\right)_{aV}. \qquad (2)$$

From condition (1) it follows that

$$(\partial \ln h/\partial T)_{aV} = -\ln h/T. \tag{3}$$

Moreover:

$$\left(\frac{\partial aV}{\partial T}\right)_{\ln h} = a\left(\frac{\partial V}{\partial T}\right)_{\ln h} + V\left(\frac{\partial a}{\partial T}\right)_{\ln h} = \alpha aV + V\left(\frac{\partial a}{\partial T}\right)_{\ln h}, \tag{4}$$

where α is the thermal coefficient of volume expansion of the adsorbate.

Combining (2), (3), and (4), we obtain

$$(\partial a/\partial T)_{\ln h} = (\partial a/\partial \ln h)_T \ln h/T - \alpha a. \tag{5}$$

The thermal equation of adsorption, with another choice of variables, can also be written in the form $\Psi(a, T, \ln h) = 0$, whence it follows that

$$(\partial a/\partial T)_{\ln h} = -(\partial a/\partial \ln h)_T (\partial \ln h/\partial T)_a. \tag{6}$$

Comparing (5) and (6), and noting that, according to the Clapeyron–Clausius equation, $(\partial \ln h/\partial T)_a = q/RT^2$ (where q is the net heat of adsorption), we finally obtain

$$q = Q - \lambda = \alpha RT^2 (\partial \ln h/\partial \ln a)_T - RT \ln h. \tag{7}$$

In this equation Q is the sought differential heat of adsorption, and λ is the heat of condensation of the adsorbate.*

Taking, as usual, as the standard state of the adsorbate the liquid at the same temperature under the pressure of its saturated vapor, and comparing expression (7) with the Gibbs–Helmholtz equation

$$q = \varepsilon - T(\partial \varepsilon/\partial T)_a =$$

$$= RT(\partial \ln h/\partial T)_a - RT \ln h, \tag{8}$$

we directly obtain an expression for the differential entropy of adsorption:

$$\Delta S = (\partial \varepsilon/\partial T)_a =$$

$$= -\alpha RT(\partial \ln a/\partial \ln h)_T. \tag{9}$$

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

At present we have considerable material showing that the results of calculations of heats of adsorption from a single adsorption isotherm by equation (7) are in very good agreement with direct calorimetric measurements or with the results of reliable calculations from adsorption isosteres. The size of this article compels us to restrict ourselves to only a few examples illustrating this agreement.

Fig. 1

In Fig. 1, curve 1 represents the dependence of the differential heat of adsorption Q of ammonia on activated carbon on the amount of adsorption, calculated by equation (7) from the adsorption isotherm at 0° according to Titov' s data (1). The circles denote the values of Q calculated from Titov' s calorimetric measurements. In the same figure, curve 2 represents the result of analogous calculations of Q by equation (7) from the adsorption isotherm of n-hexane on activated carbon at 20°, obtained by N. N. Avgul' , A. V. Kiselev, and others (2). The black circles correspond to calorimetric measurements by the same authors.

Figure 2 shows an analogous comparison of calculations by equation (7) (curve) with direct calorimetric measurements (circles) according to the data of Beebe, Kington, Polley, and Smith [3] for the adsorption of n-butane on graphitized Spheron-6 carbon black at 0°. Because of the absence of tabulated data in the paper by these authors, the initial part of the curve could not be calculated by us with sufficient certainty, and therefore it is drawn as a dotted line. Finally, curve 3 in Fig. 1 represents an example of comparing calculations by equation (7) (solid curve) with the results of calculating isosteric heats by the Clapeyron–Clausius equation. These data refer to the adsorption of furan on silica gel at 25° [4]. The circles in this figure denote the values of Q given in paper [4].

Fig. 2

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[*] It can be shown that, in the general case, if $\xi = (1/aV)(\partial aV/\partial T)_{\ln h} \neq 0$, which is equivalent to nonfulfillment of Polanyi' s condition (1), then instead of equation (7) the following equation is valid:

$$q = (a - \xi)RT^2(\partial \ln h/\partial \ln a)_T - RT \ln h. \tag{7a}$$

It should be noted that equations (7a) and (7) can be obtained directly from the Gibbs–Helmholtz equation.

As follows from the course of the reasoning in the derivation of equation (7), it is strictly valid only when condition (1) is fulfilled. Nevertheless, it may be expected that equation (7) will in many cases give good agreement with experiment even when condition (1) is not fulfilled. Indeed,

$$Q = -T\Delta S + \varepsilon + \lambda, \tag{10}$$

and from equation (7a) it follows that any deviation from condition (1) affects only the term $T\Delta S$. Therefore, if the relative weight of this term in equation (10) is small, then even appreciable values of ξ will introduce only a small error into the value of Q. The magnitude of the term $T\Delta S$ can be judged directly from the form of the adsorption isotherm, since it is proportional to the derivative $(\partial \ln h/\partial \ln a)_T$. It may be expected (and calculation confirms this) that, for example, for the region of capillary condensation or for the region of the steep rise of the adsorption isotherm of water vapor on carbon adsorbents, the differential heats of adsorption calculated by equation (7) will always be close to the experimental values.

It should be emphasized, however, that theoretically neglecting the term $T\Delta S$ is entirely inadmissible. Equating q to ε, as is done, for example, by Halasz, Schay, and Szényi [4], is obviously equivalent to confusing the change in internal energy with the change in free energy. In many cases, when calculating Q, the term $T\Delta S$ plays a decisive role.

In conclusion, we note that if an analytical expression for the equation of the adsorption isotherm is known, then, by combining it with equation (7), one can obtain the corresponding analytical form of the dependence of the differential heat of adsorption on a or on h. There is reason to believe that the method of analyzing adsorption problems that follows from this may prove very promising.

The authors express their sincere gratitude to M. M. Dubinin for interesting and valuable discussions.

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Received
7 I 1957

CITED LITERATURE

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