Differential heats of adsorption*

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The meaning of the isosteric heat q_{st}, which follows from its definition and the used thermodynamic models, was discussed and the dependences of q_{st} on the occupancy of the adsorbed layer (at $T \leq T_v$) were derived for an adsorbate with both ideal and non-ideal behaviour on an energetically homogeneous adsorbent.

With the assumption that the energetic heterogeneity of the surface can be described by a single distribution curve, the general form of the dependence of the integral and differential adsorption heat on the occupancy of the adsorbed layer was derived both without and with the presence of a lateral interaction between the adsorbed molecules at higher occupancies Θ of the adsorbed layer.

The maximum on the q_{st}—Θ dependence at high values of Θ is shown to be a consequence of the properties of differential quantities in the adsorption systems with either an energetically heterogeneous surface or the presence of a lateral interaction, or with both these properties.

После обсуждения значения изостерической теплоты q_{st}, которое вытекает из её определения и использования термодинамических моделей адсорбционных систем, были выведены зависимости q_{st} от заполнения адсорбированного слоя (при $T \leq T_v$) для идеального и реального адсорбата на энергетически гомогенном адсорбенте.

Предполагая, что энергетическую гетерогенность поверхности можно описать единственной кривой распределения, была выведена общая форма зависимости интегральной и дифференциальной теплоты адсорбции от заполнения адсорбированного слоя в присутствии и без присутствия латерального взаимодействия между адсорбированными молекулами при более высоких величинах заполнения адсорбированного слоя Θ.

Было показанно, что максимум зависимости q_{st} от Θ при больших значениях Θ является следствием свойств дифференциальных величин в адсорбционных системах с энергетически гетерогенной поверхностью или в системах с присутствием латерального взаимодействия, или же в системах обладающих одним и другим свойством.

In the usual thermodynamic models of the adsorption systems, the isosteric adsorption heat q_{st} appears to be the most frequently used differential adsorption heat. It is defined as a partial derivative of the enthalpy change of the system with respect to the adsorbed amount at a certain temperature, pressure, adsorbed amount and surface area.

There is one extensive quantity among the constant parameters in the defining relationship, consequently, q_{st} is a differential quantity. At the given constant parameters, q_{st} is not a linear homogeneous function of masses and, therefore, it does not posses the properties of a partial molar quantity.

Therefore the individual values of the isosteric heat at certain adsorbed amounts do not give a direct information on the properties of the adsorbate in the adsorbed layer at the same adsorbed amount [1—3].

For an inert adsorbent the values of the isosteric heats can be obtained from the isotherms measured at two or more temperatures using the integrated form of the equation

$$\left(\frac{\partial \ln P}{\partial T}\right)_{n_a} = \frac{q_{st}}{RT^2} \tag{1}$$

derived under the assumption of an ideal behaviour of the adsorbate in the gaseous phase.

Introducing another assumption of the state behaviour of the adsorbate in the adsorbed layer (e.g. the state of normal liquid), q_{st} may be calculated from a single isotherm by means of the relationship [11]

$$\frac{q_{st}}{RT^2} = \left(\frac{\partial \ln P}{\partial T}\right)_{n_a} = \left(\frac{\partial \ln P}{\partial W}\right)_T \left(\frac{\partial W}{\partial T}\right)_{n_a} =$$
$$= \left(\frac{\partial \ln P}{\partial n_a}\right)_T \frac{n_a}{v_e} \frac{dv_e}{dT} = \left(\frac{\partial \ln P}{\partial n_a}\right)_T n_a \, \alpha. \tag{2}$$

Or from the potential curve

$$q_{st} = -\frac{\partial \varepsilon}{\partial W} \cdot T \, W \, \alpha, \tag{3}$$

where according to the *Polanyi* potential theory [4, 5]

$$\varepsilon = RT \ln P^0/P$$

is the change in the thermodynamic potential (e.g. of the Gibbs function) which accompanies the adsorption of one mole of adsorbate at the adsorbed amount corresponding to the equilibrium pressure P in the gaseous phase and temperature T, related to a reference state of the liquid adsorbate at the saturated vapour pressure P^0 and temperature T. Furthermore, W is the volume of the adsorption layer occupied by the adsorbate, v_e is the molar volume of the liquid adsorbate at temperature of the isotherm, and α is the coefficient of the thermal expansion of the liquid adsorbate.

The obtained values of q_{st} are generally subject to error owing to the deviation of the real behaviour of the substance in the adsorbed layer from the assumed behaviour.

Values of q_{st} calculated by any of these methods do not include owing to the definition of models of adsorption systems casual changes of the adsorbent in the course of the adsorption process which may be accompanied by a heat exchange with the surroundings, hence they are calculated under the assumption of an inert adsorbent (the constancy of the surface area A at an isothermal adsorption includes the assumption of the adsorbent inertness).

Therefore the integral heats obtained for an non-inert adsorbent by integrating the differential heats q_{st} from zero up to a given adsorbed amount are not identical with the heat really exchanged by the system with its surroundings. However, by means of the relationships derived from the thermodynamic models, they allow to calculate the thermodynamic quantities of substances in the adsorbed layer, in contradistinction to the calorimetrically measured heats which are subject to error up to 5%, owing to the adsorbent non-inertness [8, 11].

The dependence of the isosteric heat q_{st} on the adsorbed amount has a typical course in all the examined systems [7—11], shown in a simplified form in Fig. 1. Generally, the course is not so simple and on the curve there are several insignificant maxima. However, all the systems we examined exhibited a marked maximum in the region of higher adsorbed amounts than those corresponding to a completed monolayer after the B.E.T. theory.

The problem of this maximum was often discussed and some authors regarded it as an experimental error. We have verified the existence of this maximum [6] by the investigation of a series of adsorption systems by means of isothermal measurements with various adsorbents as well as isothermal and adiabatic calorimetric measurements [7—11].

Till now, no satisfactory explanation has been given in literature as to the reason of the cause of this finite maximum on the dependence of the isosteric heats upon the adsorbed amount in the region where the adsorbate is adsorbed under the condition of a weak force effect exerted by the adsorbent, *i.e.* where the adsorption potential is lower than RT.

As probable causes of the maxima on the course of the isosteric heats, the following factors are mostly reported [1, 6, 7]:

— interactions between the adsorbed molecules,
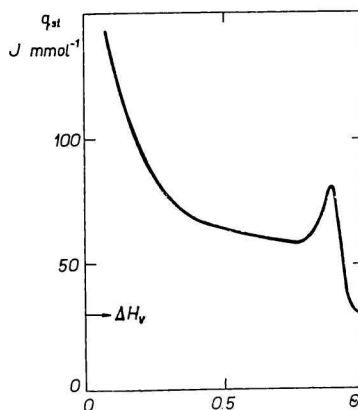— the entropy of congregation,

Fig. 1. General simplified dependence of the isosteric heats q_{st} on the occupancy of the adsorbed layer Θ.

— the transition between the localized and mobile adsorption,
— the change in the hindered rotations of molecules,
— the change in the short-distance and long-distance order,
— the compensation of the negative pressure of liquid condensed in capillaries.

On the basis of thermodynamic considerations of the theoretical course of the dependence of differential heats upon the adsorbed amount we shall discuss other possible origins of the finite maxima.

The derivation of the course of the adsorption on an energetically homogeneous surface begins with the general equilibrium condition

$$\mu^{(g)} = \mu^{(a)}, \tag{4}$$

where $\mu^{(g)}$ and $\mu^{(a)}$ denote the chemical potentials of the adsorbate in the gaseous phase and in the adsorbed layer, respectively.

If we assume an ideal behaviour both in the gaseous phase and in the adsorbed layer, it holds

$$\mu^{(g)} = \mu^{+}(T) + RT \ln P. \tag{5}$$

From the state equation of an ideal gas it follows that

$$d \ln P = d \ln n, \quad \text{at } (T, V). \tag{6}$$

The chemical potential of the adsorbate $\mu^{(g)}$ in the gaseous phase is therefore a linear function of both log P and the logarithm of the number of moles of the adsorbate n in the gaseous phase. In the case of an energetically homogeneous surface, the chemical potential of the adsorbate $\mu^{(a)}$ in the adsorbed layer is also a linear function of the logarithm of the adsorbed amount at constant temperature and the surface area.

The adsorption isotherm on an energetically homogeneous surface in the form of the graphical plot of the logarithm of the adsorbed amount, $\ln n_a$, against $\ln P$ has a linear course if the adsorbate in the adsorbed layer behaves as an ideal two-dimensional gas. From the above discussion and from eqn (2) it follows, that the isosteric heat is then constant in the whole range of the adsorbed amounts.

For the adsorbate with a real behaviour in the gaseous phase, a linear relationship between the logarithm of fugacity, $\ln f$, and $\mu^{(a)}$ holds but the relationship between $\ln n$ and $\ln f$ will not be exactly linear. However, the deviation from linearity in the usually narrow range of the measured pressures may be very small with respect to eqn (7)

$$\ln f = \ln P + \frac{2B}{v}, \tag{7}$$

where B is the second virial coefficient and v the molar volume of the gas. In the adsorbed layer a linear relationship between $\ln f$ and $\mu^{(a)}$ will hold for the adsorbate with the behaviour of a real two-dimensional gas. The relationship between $\ln n_a$ and $\ln f$ will be non-linear; due to the effect of the homogeneous force field it will correspond to the relationship between the fugacity and pressure at increasingly high pressures.

Supposing that the lateral interaction between the adsorbed molecules at higher occupancies does not take place, the dependence of the isosteric heat on the adsorbed amount may be expressed by a curve which starts from the values of q_{st} similar to those for an ideal adsorbate and then it decreases with increasing adsorbed amount. The lateral interaction between the adsorbed molecules, which may occur at higher occupancies of the surface, affects the course of the dependence of q_{st} on Θ. The contribution of the lateral interaction to the adsorption heats will be discussed later.

For the derivation of the course of a dependence of q_{st} upon the adsorbed amount n_a or upon the surface occupancy Θ at the adsorption on a heterogeneous surface, we consider at first such a surface where the relative frequency of the adsorption sites f_i with corresponding adsorption energies U_i can be expressed by a single distribution curve (Fig. 2a)

$$f_i = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(U - U_s)^2}{2\sigma^2(RT)^2} \right] \tag{8}$$

Supposing the validity of the relationship

$$q_i = \psi(U_i) \tag{9}$$

between the adsorption heat and the energy of the corresponding adsorption site, the frequency of the adsorption sites f_i with the adsorption heat q_i is expressed e.g. by the curve q_i in the diagram a (Fig. 2).

Since we may assume that on an energetically heterogeneous surface, the sites with the instantaneously highest adsorption energy are gradually occupied, the
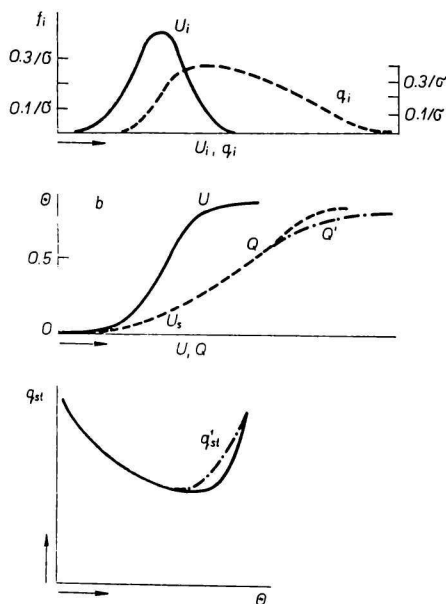

Fig. 2.

a) Distribution curve of the adsorption energies U_i and the adsorption heats q_i.
b) Distribution function of the adsorption energies U, the integral adsorption heats Q, and the integral adsorption heats Q' with the contribution of the interaction heat.
c) Dependence of the isosteric heats q_{st} and q'_{st} (with the contribution of the interaction heat) on the occupancy of the adsorbed layer Θ.

relationship between the integral adsorption heat Q and the surface occupancy Θ can be expressed as

$$\Theta(Q) = \frac{1}{\sigma\sqrt{2\pi}} \int\limits_{U_{\max}}^{U_{\min}} \left\{ \psi(U) \exp\left[-\frac{(U - U_s)^2}{2\sigma^2(RT)^2} \right] \right\} \mathrm{d}U. \qquad (10)$$

A diagram of this dependence (Θ vs. Q) together with the distribution function of the energies (Θ vs. U) is shown in Fig. 2b.

From the dependence of the integral adsorption heat Q on the surface occupancy Θ we can obtain by differentiating $(\partial Q/\partial n_a)_{T,n_a'}$ values for the dependence of the isosteric heat on the surface occupancy. The corresponding curve is shown in Fig. 2c.

During the occupation of the adsorption layer on the surface of a solid adsorbent, a stronger lateral interaction between the adsorbed molecules begins from a certain degree of the occupancy. The rise of this interaction is reflected in a corresponding increase of the adsorption heat in the given region of the isotherm.

The heat effect of the lateral interaction upon the values of the heats of the adsorption on the given adsorption sites cannot be expressed by an arrangement of the shape of the distribution curve $f_i(q_i)$ since it is necessary to suppose that, during the increasing surface occupancy, the adsorption on the energetically equal adsorption sites is also accompanied by an increase of the lateral interaction and the corresponding heat.

The effect of the interaction heat on the values of the integral adsorption heat is outlined by the course of the Q' curve in the diagram b (Fig. 1) and its effect on the course of the q_{st} vs. Θ dependence is expressed by the q_{st}' curve in Fig. 2c. The diagram shows that the lateral interaction moderates the slope of the final part of the q_{st} vs. Θ dependence.

From the foregoing discussion it follows that the course of the dependence of the differential thermodynamic adsorption quantities for the adsorption on an energetically heterogeneous surface upon the surface occupancy is determined, at certain occupancies, mainly by the frequency of the sites with given adsorption energies and by the extent of the lateral interaction between the adsorbed molecules.

In the case of a heterogeneous adsorbent, for which the frequency of the adsorption energy can be expressed by a single distribution curve of the type of eqn (8), the corresponding dependence of q_{st} on Θ is expressed by the diagram c (Fig. 2). This curve gradually decreases, passes through a minimum and rises again. The substantial increase of the values of the isosteric heat at high occupancies of the surface thus appears to be an unavoidable consequence of the properties of the differential quantities corresponding to the adsorption on an energetically heterogeneous surface. These quantities depend here not only on the extent of the interaction with the surface and on the lateral interaction, but also on the frequency of occurrence of the sites with a given adsorption energy.

If the energetical heterogeneity of the surface or the heterogeneity of the interaction energies of the adsorption process cannot be expressed by a single distribution curve and, instead, a combination of several curves is required, this influences accordingly the course of the dependence of the differential heats on the surface occupancy. Such combination of curves with the course outlined in Fig. 2c leads to the dependences with minima and maxima. These minima and maxima correspond to the higher and lower frequency of the sites with the given adsorption energy.

The general form of the dependence of q_{st} on Θ valid for the energetically heterogeneous adsorption systems has been shown above. A quantitative derivation of the course of this dependence (numerical values for the maxima and minima) can be obtained for a particular adsorption system from a discussion of the changes in the molecular behaviour during the adsorption process. This will be reported in the next communications.

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