Comparison of measured and calculated isosteric heats and integral heats of adsorption*

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The measured and calculated adsorption heats in the system n-hexane— —active carbon Supersorbon were compared. The differential adiabatic and integral isothermal heats were measured directly while the isosteric heats were calculated from the isotherms by different proceedings (classical method of two isotherms and potential theory). On the basis of the correlation of these values the applicability of individual methods as well as the effect of the non-inertness of adsorbent on the calculated data was tested by using the relationships of classical thermodynamics and the course of isosteric heats in the region of low pressures was appraised.

Сравниваются измеренные и рассчитанные теплоты адсорбции системы *n*-гексан—активный уголь Суперсорбон. Прямо были измерены дифференциальные адпабатические и интегральные изотермические теплоты и на основе измеренных изотерм, используя различные методики (классический метод из двух изотерм и потенциальная теория), были рассчитаны изостерические теплоты. Их сравнением, применяя соотношения классической адсорбционной термодинамики, была проверена применимость отдельных рассчетных методик, влияние неинертности адсорбента на рассчитанные данные и обсуждалось поведение изостерических теплот в области низких давлений.

An exact knowledge of the course of isosteric adsorption heats as a function of the amount adsorbed is very important for the explanation of the mechanism of adsorption. For non-porous and wide-porous adsorbents with energetically homogeneous surface it was feasible to calculate these heats on the basis of pure model conceptions and the results are in a good agreement with experiments. An essentially more complicated problem is represented by energetically heterogeneous adsorbents which are, however, of practical importance for industrial use. The most difficult problem from this aspect is to master microporous adsorbents because in addition to the difficulties in proposing adequate models also complications

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accompanying the measurements of adsorption data appear. The steep starts of isotherms are connected with a rather low reproducibility of measurements (the possible causes of this irreproducibility have been discussed in detail by *Juliš* [1, 2]). The inaccuracy of the measurements in this region calls forth a considerable error in the calculation of isosteric heats by the classical method according to equation

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

where T is temperature, P is equilibrium pressure in gaseous phase, $q_{\rm st}$ is isosteric heat, $n_{\rm S}$ is the amount adsorbed, and A is the surface area of adsorbent. Therefore an accurate determination of integral heat is also impossible because the course of the function $q_{\rm st} = f(n_{\rm S})$ at the origin is not known. The calculation of molar integral heat at constant temperature, constant volume of the gaseous and adsorbed phase, and constant surface of adsorbent $U_{\rm S}$ according to eqn (2) may be then subject to a large error

$$U_{\rm S} = -\frac{1}{0} \int_{0}^{n_{\rm S}} q_{\rm st} \, \mathrm{d}n_{\rm S} - RT.$$
 (2)

The most frequently used method which gives the best results in the calculation of thermodynamic quantities from the isotherms obtained for systems with microporous adsorbent is the Polanyi potential theory elaborated by Dubinin and his school. According to this method, the isosteric heats may be calculated in two ways:

1. For the graphical representation of the characteristic curve in the coordinates ε (adsorption potential) vs. W (volume packing of pores) it is always possible to calculate two volume packings W_1 and W_2 for two fixed temperatures T_1 and T_2 for stepwise chosen values of $n_{\rm S}$ and to read the corresponding values of ε_1 and ε_2 from the characteristic curve. Then the isosteric heat is to be calculated from eqn (3) where P_1^{γ} and P_2^{γ} denote the saturated tensions of the liquid adsorbate at temperatures T_1 and T_2

$$q_{\rm st} = RT_1 T_2 \ln \frac{P_0^2}{P_1^0} \frac{1}{T_2 - T_1} - \frac{T_2 \varepsilon_1}{T_2 - T_1} - \frac{T_1 \varepsilon_2}{T_2 - T_1}.$$
(3)

Thus it is possible to obtain the relationship $q_{st} = f(n_s)$ for the whole range of the isotherms measured.

2. From the known analytical form of the equation of characteristic curve [3] Bering and Serpinskii [4, 5] derived a relationship for the calculation of isosteric heat. For the microporous adsorbents with a small share of mesopores it is convenient to extend the Dubinin—Radushkevich equation [3] describing the characteristic curve by one constant and to derive an equation for the calculation of isosteric heat [6] in a way similar to that used by Bering and Serpinskii. This procedure is especially suited for the use of a computer which ensures a rapid calculation of the isosteric heats as a function of the amount adsorbed in the whole region where the characteristic curve is to be described by the equation [6]

$$W = W_0'' \exp[-k'(\varepsilon - \mu)^2].$$
 (4)

The symbols W''_0 , k', and μ denote constants.

In most cases, during adsorption some changes in adsorbents can be observed. Most thermodynamic models, however, assume the inertness of adsorbent during the adsorption process. Hitherto, there is no evidence whether this assumption is correct or it involves an error of an unknown magnitude. Provided this effect manifests itself, it ought to appear most conspicuously in case of microporous adsorbents and it should be possible to estimate it from the difference between the heats measured and calculated by means of the model assuming inert adsorbent.

Experimental

Active carbon Supersorbon (Hrušov SSHR) which is microporous with a small share of mesopores was used as an adsorbent. As an adsorbate n-hexane prepared and purified by the method described earlier [6] was used.

The adsorption isotherms measured at 20 and 28°C as well as the description of the weighting apparatus used were also presented in a previous paper [6].

$n_{ m S}$ mmol/g	$U_{ m s}$ Calculated J/mmol	$U_{ m S}'$ Experimental J/mmol	$\delta_r U_s * \%$
2.681	61.63	60.42	1.89
2.804	59.95	58.72	2.09
3.035	59.26	58.12	1.97
3.450	57.99	56.89	1.93
3.818	57.98	56.76	2.15
3.980	58.15	56.97	2.08
4.031	57.88	56,50	2.44

Table 1

Comparison of calculated and measured integral heats of adsorption

* $\delta_{\rm r} U_{\rm S} = (U_{\rm S} - U_{\rm S}') \, 100/U_{\rm S}'$.

The integral isothermal heat was determined by means of a diphenyl ether calorimeter [7] working at 26.89°C with the sensitivity of 79.61 ± 0.12 J/g Hg. Altogether, the integral heats were measured for seven amounts adsorbed (Table 1) and two of them were published in the previous paper [6]. The reproducibility of measurements was better than 0.4%.

The differential adiabatic heat was measured by means of an adiabatic calorimeter of the *Morrison* type [8, 9] of original construction with an adiabatic shield with a supplementary electrical heating which was fixed around the calorimetric copper vessel in an evacuated container. The temperature was measured using a platinum resistance thermometer placed inside the vessel and the temperature differences between the environs and calorimetric vessel were determined by means of differential thermocouples. The calorimeter worked at the temperature of about 27°C. The dosing of adsorbate was performed by means of a greaseless volume apparatus with a microburette. The temperature regime of calorimeter before or after measurement was 0.001° C in 30 min at maximum. The calculated maximum relative error of the measurement of adiabatic heat in the range of relative packing from 0.2 to 0.95 was 0.7% while the reproducibility of measurements was about 0.3%. By using the corrected Kington-Aston equation [10] the adiabatic heats measured were transformed into the isosteric heats

$$q_{\mathbf{a}} = q_{\mathrm{st}} + V_{\mathrm{g}} \left[\left(\frac{\partial P}{\partial^{n}_{\mathrm{s}}} \right)_{T,A} + \left(\frac{\partial P}{\partial T} \right)_{n_{\mathrm{s}},A} \left(\frac{\partial T}{\partial n_{\mathrm{s}}} \right)_{S} \right], \qquad (5)$$

where q_a stands for adiabatic heat, V_g is the volume of gaseous phase in calorimeter, and S is entropy. For most points this calculation was not necessary since the value of the correction terms in eqn (5) was much less than the experimental error.

Results and discussion

The dependences of isosteric heats on the amount adsorbed obtained by all methods including the direct measurements are presented in Fig. 1. The plot obtained from the measurements with the adiabatic calorimeter marked by B is represented by empty points (measurements 1) and crossed points (measurements 2). The plot marked by A and represented by halved points was obtained by the classical method from two isotherms using the integrated form of eqn (1). The curve marked by C



Fig. 1. Dependence of isosteric heats on adsorbed amount. $q_{\rm st}$ denotes isosteric heat in J/mmol, $n_{\rm s}$ adsorbed amount in mmol/g. Other symbols are explained in the text.

(dashed line without points) was calculated by the method 2 described in the first part of this paper. The constants of eqn (4) were calculated by the least-square method and for the calculation of heats the characteristic curve was extrapolated to the region of low adsorption. The full points were obtained by method 1 from the graphical representation of the characteristic curve which is presented in Fig. 4a of the previous paper [6].

From a comparison of these curves it follows that the curve obtained by means of the potential theory by the method 2 is in a very good agreement with the plot of the heats measured. The full points calculated by the method I are in agreement with experimental values. Curve A is initially somewhat deviated from the others, but in the region of minimum of the isosteric heat it coincides with other curves. This difference in the course of the curve A may be due to the non-inertness of adsorbent and perhaps also to a lower accuracy of the measurements in the initial steeply growing part of the isotherm.

The reason why this deviation does not appear in the case when the heats have been calculated by means of the potential theory may be explained by a detailed examination of the course and character of the characteristic curve. It is obvious that the points obtained from the isotherms measured at different temperatures are not situated ideally on a single characteristic curve. The deviations of whole groups of points on the one or the other side from the ideal curve are only small and might be explained by the assumption of an ideal behaviour of a liquid under normal conditions by which in the potential theory the behaviour of the gas adsorbed (at temperatures sufficiently under the critical temperature) is replaced. The excellent agreement of the calculated curve of isosteric heats with the values measured may be assumed to be the result of a compensation of the deviations due to the inertness of adsorbent and deviations from the state behaviour of a liquid adsorbate. Both the effects must, however, be small enough, otherwise their good compensation could be hardly explained. It is also not possible to evaluate these effects quantitatively because the accuracy of calorimetric measurements is not sufficient in this respect.

Moreover, the measured isothermal integral heat was compared with the heat calculated according to eqn (2). The value of the integral occurring in this equation was obtained by graphical integration of the area under the curve expressing the directly measured isosteric heat B. The starting part of the curve as far as the first measured point was extrapolated by means of curve C up to the axis of heats. We did not succeed in measuring the heats in that region directly since the conduction of heat in calorimeter is based mainly on the gas which is, however, present in a very small amount at low pressures. Another process which could cause this trouble at the beginning of adsorption is an instantaneous adsorption on nearest places with a subsequent desorption and diffusion to more active sites. These phenomena manifest themselves by a very slow establishment of equilibrium as wel as by the fact that no observable increase in temperature appears after the dosing of gas has started. Only after a long period of time (approx. 3 to 4 hrs) it is possible to observe a very small temperature rise which is, however, shaded by the proper temperature regime of calorimeter.

The calculated and measured integral heats of adsorption are presented in Table 1. The value of the deviation $\delta_r U_S$ is almost equal for all adsorptions and amounts to about 2% in the whole range of measurements. This fact indicates another course of the curve expressing q_{st} . (The possibility of a systematic error in the measurements by means of the diphenyl ether calorimeter is not considered because of good results with the electrical calibration of calorimeter as well as the reproducibility of measurements achieved.) Since a greater part of this curve is verified both by experiments and calculation, only the extrapolated beginning is not certain.

From the above confrontation it follows that one or even several extremes are to be expected between the first measured point of curve B and the axis of heats. An explanation may be given on the assumption of several partition functions of energies [11]. As far as known, similar extremes have not been directly observed before, however, for the present the number of papers in which accurate measurements with energetically and superficially rather heterogeneous materials in the region of low pressures have been presented is very limited.

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