# State properties of adsorbates*

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The changes of thermodynamic functions of adsorbate caused by changes of its structure in the field of adsorption forces were determined. The analysis of these changes of thermodynamic functions (further denoted as perturbation functions $\Delta G^*$, $\Delta H^*$, and $\Delta S^*$) confirms the validity of two fundamental postulates of the Polanyi—Dubinin theory. It is shown that 1. the Polanyi postulate is valid if the perturbation entropy $\Delta S^*$ is zero; 2. the condition of the validity of Dubinin postulate is the proportionality of perturbation enthalpy $\Delta H^*$ of adsorbate with the perturbation enthalpy of the standard adsorbate $\Delta H_0^{\bullet}$. From the experimental studies of adsorption equilibria the conclusion can be made that in most cases the perturbation entropies and enthalpies are close to zero. The good agreement of the Polanyi—Dubinin theory with the experimental data ensues from a close resemblence of the state properties of most adsorbates ($p$, $v$, $T$ relations) to the state properties of vapours and liquids.

The exceptions are observed in case of substances associating by means of hydrogen bonds (water, alcohols). The explanation of these deviations made the formulation of a general theory of adsorption for nonspecific interactions feasible.

With this general theory it is possible to predict without exception the adsorption equilibria of any gases and vapours on active carbons at any temperature on the basis of three parameters which characterize the structure of micropores ($W_0$, $n$, and $E_0$).

The good agreement of the theory with experimental data is evident from the tables of adsorption isotherms of benzene, argon, ammonia, methanol, ethanol, and water.

Описывается определение изменений термодинамических функций адсорбатов, вызванных изменением их структуры в поле действия адсорбционных сил. Анализ этих изменений термодинамических функций, далее названных возмущенными функциями (обозначенных $\Delta G^*$, $\Delta H^*$ и $\Delta S^*$) объясняет применимость двух фундаментальных постулатов теории Поляни—Дубинина. Из него вытекает, что 1. постулат Поляни действителен, если возмущение энтропии $\Delta S^*$ равно нулю и 2. постулат Дубинина действителен, если возмущенная энтальпия $\Delta H^*$ адсорбата пропорциональна возмущенной энтальпии стандартного адсорбата $\Delta H_0^{\bullet}$. Из экспериментального изучения

адсорбционного равновесия может быть сделан вывод, что в большинстве случаев возмущение энтропии и энтальпии близко нулью. Согласие теории Поляни—Дубинина с экспериментальными данными объясняется тем фактом, что свойства состояния большинства адсорбатов ($p$, $v$, $T$ соотношения) близки свойствам состояния паров и жидкостей.

Исключение из этого факта наблюдается в случае ассоцирующих, посредством водородных связей адсорбатов (вода, спирты). Эти отклонения можно объяснить на основе общей теории адсорбции для неспецифических взаимодействий.

Общая теория позволяет без исключения предсказывать адсорбционное равновесия газов и паров при определенной температуре на основе трех параметров, которые характеризуют структуру микропоров ($W_0$, $n$ и $E_0$).

Согласие теории с экспериментальными данными видно из таблицы адсорбционных изотерм бензола, аргона, аммиака, метанола, этанола и воды.

The study of deviations from the equation of state for gases and vapours in the adsorption forces field is of fundamental importance for the theory of physical adsorption.

The experience shows that the conception of temperature invariance of the characteristic curve is a rational approximation of numerous adsorption systems. The interpretation of this fact offered by Polanyi in principle was based on the assumptions that the so-called potential of adsorption forces, $\varepsilon$ (which has a physical meaning of the potential energy of the intermolecular interactions of molecules of adsorbate with the adsorbent) is temperature invariant, and that the state behaviours of adsorbate are the same as those for bulk liquid. It has been proven theoretically that adsorption forces are temperature invariant for frequent nonspecific interactions [1]. However, a number of authors have pointed out that deviations from the equation of state in the field of adsorption forces may occur [2—5]. Their determination, which is very difficult, would enable us to obtain quantitative relations between the thermodynamic adsorption potential $\Delta G$ (e.g. the Gibbs free energy or differential molar work of adsorption $A = -\Delta G = RT \ln f_0/f$, where $f$ and $f_0$ is the equilibrium and saturated adsorbate vapour fugacity, chosen as a standard state, respectively, at temperature $T$ [6]) and the potential of adsorption forces $\varepsilon$. The knowledge of quantitative relations between potentials $\varepsilon$ and $A$ would allow for an improvement in the adsorption theory, based on the assumption that the potential of intermolecular forces is temperature invariant, similar to the Polanyi potential theory of adsorption. As will be shown below, the results obtained in the experimental study of adsorbent—adsorbate systems render the solution of this problem possible.

### Theoretical

There can be many reasons for the $p$, $v$, $T$ relations of an adsorbate to be different from those of an adsorptive. (The term "adsorptive" denotes an adsorbate located outside the range of adsorption forces.) Thus, e.g. the orientation of molecules in the adsorption forces field may lead to a specific structural arrangement of the adsorption layer. Similarly, limitation of the degree of association of some substances ($H_2O$, alcohols, and Hg) in micropores as well as in the adsorption layer causes deviations from the normal state behaviour of these adsorbates [7]. It can be assumed that such structural perturbations impart the adsorbed layer (film) a molar

free energy higher or lower than that of nonperturbed adsorbate with $p$, $v$, $T$ properties of bulk liquid.

This excess of free energy can be written as $RT \ln \nu$, where

$$\nu = \frac{f_\omega}{f_0}, \tag{1}$$

$f_0$ is the fugacity of saturated vapour at temperature $T$ and $f_\omega$ denotes the saturated vapour fugacity of the modified liquid assumed to be free of the adsorption potential field but not otherwise changed [7]. Than the potential of intermolecular forces $\varepsilon$ can be expressed by the equation

$$\varepsilon = RT \ln \frac{f_\omega}{f} = A + RT \ln \nu, \tag{2}$$

which gives the required relation between $\varepsilon$ and $A$. The eqn (2) is identical with the relation between $\varepsilon$ and $A$ derived by *Kiselev* [2, 3].

There remains a problem of the determination of the function $\nu = \nu(\Theta, T)$, where $\Theta = a/a_0$ is the degree of filling of the adsorption space with microporous substances or of the monolayer with nonporous substances ($a$ and $a_0$ are the adsorbed amount and limiting adsorbed amount values, respectively).

It can be shown that the so-called Polanyi postulate

$$\left( \frac{\partial RT \ln f_0/f}{\partial T} \right)_\Theta = 0 \tag{3}$$

can be fulfilled even for $\nu \neq 1$, if $\nu$ is a suitable function of temperature, provided that the adsorption force potential, $\varepsilon$, is temperature independent, according to the equation

$$\left( \frac{\partial \varepsilon}{\partial T} \right)_\Theta = \left( \frac{\partial RT \ln f_\omega/f}{\partial T} \right)_\Theta = 0. \tag{4}$$

If a simultaneous validity of eqns (3) and (4) is assumed, the following relation is obtained for the function $\nu = \nu(\Theta, T)$

$$\left( \frac{\partial RT \ln \nu}{\partial T} \right)_\Theta = 0. \tag{5}$$

By an integration of relation (5), a form of function $\nu$ satisfying simultaneously the validity of eqns (3) and (4) is obtained

$$\nu = \exp \left[ \frac{k}{T} \right]; \quad \Theta = \text{const.} \tag{6}$$

Relation (6) is basically the same temperature function as the dependence of the relaxation of a structural perturbation on the distance from the surface $x$ proposed by *Adamson* [8]: $RT \ln \nu = \beta \exp [-\alpha x]$. However, relation (6) might not be generally valid.

For a narrow temperature range it can be assumed that the temperature dependence of fugacity $f_\omega$, determining the adsorbate standard state, can be expressed by a relation analogous to the Clausius—Clapeyron formula for the dependence of the saturated vapour pressure, $p_0$, on the temperature

$$\ln f_\omega = -B/RT + C, \tag{7}$$

where the coefficient $B$ is nearly equal to the condensation heat of perturbed adsorbate free of the adsorption potential field. This relation resembles the relation for the temperature dependence of the saturated vapour pressure $p_0$

$$\ln p_0 = -\lambda/RT + C_0, \tag{8}$$

where $\lambda$ is the condensation enthalpy. Let us suppose that for the temperature dependence of the fugacity of saturated vapours of the bulk liquid $f_0$ the relation is valid

$$\ln f_0 = -B'/RT + C'. \tag{9}$$

The change of the free energy of the adsorbate caused by the perturbation of its state properties $\Delta G^*$ can be expressed by the eqns (7) and (9)

$$\Delta G^* = -RT \ln \nu = -RT \ln f_\omega/f_0 = (B-B') - RT(C-C'). \tag{10}$$

From the comparison of eqn (10) with the Gibbs—Helmholtz equation

$$\Delta G^* = \Delta H^* + T\left(\frac{\partial \Delta G^*}{\partial T}\right)_{\hat{a}} = \Delta H^* - T \Delta S^* \tag{11}$$

the physical meaning of the coefficient $B$ and $C$ of the eqn (7) and (9) follows

$$B-B' = \Delta B = \Delta H^*, \tag{12}$$

$$R(C-C') = R \Delta C = \Delta S^*. \tag{13}$$

The difference of the coefficients $B$ is equal to the perturbation enthalpy of the adsorbate $\Delta H^*$ and the difference of the coefficients $C$ is proportional to the perturbation entropy $\Delta S^*$.

These so-called perturbation changes of thermodynamic functions can be understood as differences of free energy, enthalpy, and entropy of a normal and modified adsorbate, free of adsorption potential field but otherwise not changed, at the same temperature.

From a comparison of eqns (7), (9), (12), and (13) it follows that the function $\nu = \nu(\Theta, T)$ can assume the general form

$$\nu = \exp[\Delta C] \exp\left[\frac{k}{T}\right] = \exp\left[\frac{\Delta S^*}{R}\right] \exp\left[-\frac{\Delta H^*}{RT}\right], \tag{14}$$

where

$$\Delta C = \Delta S^*/R \text{ and } k = -\Delta B = -\Delta H^*/R.$$

When $\Delta C = C-C' = \Delta S^*/R \neq 0$, the Polanyi postulate (eqn (3)) cannot be ful-

filled even when the adsorption forces are temperature independent as evident from eqns (14) and (6). Assuming the validity of eqns (4) and (10), it holds

$$\left( \frac{\partial RT \ln f_0/f}{\partial T} \right)_\Theta = R \, \Delta C = \Delta S^*. \tag{15}$$

Thus the condition of the validity of Polanyi postulate (3) is not the zero change of the entropy $\Delta S$ of adsorption (as erroneously supposed by *Barrer* [9]) but merely the zero change of the entropy corresponding to the perturbation of state properties of the adsorbate (perturbation entropy $\Delta S^*$).

The value of constants $C'$ and $B'$ can be calculated from the tabulated values of the saturated vapour pressures and compressibility factors for the adsorptive. At the present stage of development of the adsorption theory, the values of coefficients $C$ and $B$ can be determined only from experimental data on adsorbent—adsorbate systems.

The following procedure has proven to be the most suitable for this purpose. If intermolecular forces are temperature independent, from relation (4) it follows that adsorption force potentials, $\varepsilon$, have equal values at two different temperatures, $T_1$ and $T_2$, if the filling of the adsorption space $\Theta$ is constant

$$\varepsilon(T_1) = \varepsilon(T_2); \quad \Theta = \text{const.} \tag{16}$$

On substituting the expression for $\varepsilon$ from eqn (2) into eqn (16), the equation

$$RT_1 \ln \frac{f_{\omega 1}}{p_1} = RT_2 \ln \frac{f_{\omega 2}}{p_2}; \quad \Theta \text{ const} \tag{17}$$

is obtained. By rearrangement and substitution for the $\ln f_\omega$ the values from eqn (7), the following relation is obtained for differences of the $RT \ln p$ terms, corresponding to temperatures $T_1$ and $T_2$ at a constant $\Theta$ valu e

$$\Delta x = RT_2 \ln p_2 - RT_1 \ln p_1 = R \, C \, \Delta T; \quad \Theta = \text{const}, \tag{18}$$

where $\Delta T = T_2 - T_1$. When the adsorption isotherms measured at various temperatures are plotted in $\Theta$ *vs.* $RT \ln p$ coordinates, they are mutually shifted by a value corresponding to $\Delta x$, which is a linear function of the difference of temperatures at which the adsorption isotherms were measured.

The value of the constant $C$ equals $s/R$, where $s$ is the slope of the $\Delta x$ *vs.* $\Delta T$ dependence and $R$ is the gas constant.

The determination of the coefficient $B$ from adsorption equilibria is rather difficult since the temperature dependence of adsorption isotherms is not affected by the value of constant $\Delta H^*$, as evident from eqn (15).

It has also been shown by *Adamson* [8] that the structural perturbation which may be expressed by an equation of the type (6) changes the shape of the characteristic curve only, its temperature independence, however, remains preserved (*cf.* eqns (6) and (8) in *Adamson*'s paper [8]). Thus it is possible to determine differences in functions $\Delta H^*$ for individual adsorbates employing the deviations from the Dubinin postulate on the affinity of the characteristic curves [10]

$$\left( \frac{A}{A_0} \right)_\Theta = \beta = \text{const.} \tag{19}$$

Postulate (19) is valid if the perturbation enthalpy of adsorbate, $\Delta H^*$, is linearly proportional to the perturbation enthalpy of the standard adsorbate, $\Delta H_0$.

The values of $\Delta S^*$, $\Delta G^*$ and the general significance of $\Delta H^*$ are determined in the experimental part for some typical adsorbent—adsorbate system.

## Experimental

The adsorption isotherms of benzene, argon, methanol, ethanol, ammonia, and water measured on a series of active carbon samples, Nos. 27—33, from the joint stock of adsorbents of the multilaterally cooperating institutes of physical chemistry of the Academies of Sciences of USSR, GDR, and CSSR for the determination of the parameters of function $v = v(\Theta, T)$. The sample numbers correspond to the sample protocol of the J. Heyrovský Institute of Physical Chemistry and Electrochemistry of the Czechoslovak Academy of Sciences. The adsorption isotherms of benzene on a series of carbons, measured in the temperature range from 20 to 350°C have been taken from [11]. The procedure and results have already been published [12]. The isotherms of methanol, ethanol, and water at 20, 40, and 70°C were measured in the weight adsorption apparatus described by *Kadlec* and *Daneš* [13]. The adsorption isotherms of argon and ammonia on active carbons were measured by Kloubek using a volume adsorption apparatus [14]. Before the measurement the samples were evacuated at 400 to 450°C and pressures of approx. $10^{-6}$ Torr for 6—8 hrs.

The nitrogen adsorption isotherms measured on NaA zeolite by *Arkharov et al.* [15] were also used. A table of the experimental data was available to the author through the mentioned cooperation scheme.

*a) The determination of perturbation entropy, $\Delta S^*$, and enthalpy, $\Delta H^*$, of nonassociating adsorbates*

In order to determine the values of constant $C$, the isotherms were plotted in the $a\,v$ vs. $RT \ln p$ coordinates (where $a$ is the amount adsorbed, $v$ is the molar volume of adsorbate; values for benzene were taken from [12] whilst for nitrogen the values determined by the Nikolayev—Dubinin method were used [16]). In Fig. 1, these plots are given for systems benzene—active carbon Nos. 27, 29, and 33 and for nitrogen—NaA zeolites. It is evident that the $\Delta x$ values for these systems are independent on the degree of filling of the adsorption space, $\Theta = a\,v/W_0$. In Fig. 2, the $\Delta x$ vs. $\Delta T$ dependence for the benzene adsorption isotherms on active carbon No. 27 is given (various temperatures were gradually substituted for $T_1$).

Similar to the system benzene—active carbon No. 27, all the studied $\Delta x$ vs. $\Delta T$ dependences were linear. The values of coefficient $C$ and of $C'$ for benzene together with those for nitrogen, methanol, ethanol, and water, calculated from the slopes, are given in Table 1.

It can be seen from Table 1 for the benzene—active carbon and the nitrogen—NaA zeolite systems that the $\Delta C$ coefficient values are very small. For this reason $\Delta S^*$ nearly equals zero within experimental error. This result is in agreement with the temperature invariancy of the benzene characteristic curves on active carbon samples Nos. 27—33, found by *Zukal* [11].

The values of the coefficient $\Delta H^*$ can be assessed on the basis of study of the characteristic curve affinity. For analysis of deviations from the Dubinin postulate (19), with the studied adsorbate—active carbon system, the general Dubinin equation was employed

$$\Theta = \frac{a\,v}{W_0} = \exp\left[-\left(\frac{A}{E}\right)^n\right], \qquad (20)$$

## Table 1

The values of coefficients $C$ and $C'$ for benzene, nitrogen, water, methanol, and ethanol on different adsorbents

| Benzene $C_0 = 17.84$ $C' = 16.27$ | | | Nitrogen $C_0 = 15.37$ $C' = 14.20$ | | |
|---|---|---|---|---|---|
| Active carbon | $C$ | $C-C'$ | Zeolite | $C$ | $C-C'$ |
| 27 | 16.36 | 0.09 | NaA | 14.18 | −0.07 |
| 29 | 16.12 | −0.15 | | | |
| 33 | 16.47 | 0.20 | | | |

| Methanol $C' = 20.00$ | | | Ethanol $C' = 21.25$ | | |
|---|---|---|---|---|---|
| Active carbon | $C$ | $C-C'$ | Active carbon | $C$ | $C-C'$ |
| 27 | 18.63 | −1.37 | 27 | 18.83 | −2.42 |
| 29 | 18.82 | −1.18 | 29 | 18.42 | −2.83 |
| 31 | 18.92 | −1.08 | 31 | 18.32 | −2.93 |
| 33 | 18.52 | −1.48 | 33 | 18.43 | −2.82 |

| Water $C' = 22.2$ | | |
|---|---|---|
| Active carbon | $C$ | $C-C'$ |
| "Supersorbon" | 21.5 | −0.7 |

where $W_0$, $E$, and $n$ are constants. The characteristic energy $E = \beta E_0$, where $E_0$ is the characteristic energy of a standard substance (usually benzene) and $\beta$ is the so-called affinity coefficient of eqn (19).

As shown by the author [17, 18], the empirical constants, $n$ and $E_0$, have unambiguous physical significance for $v \to 1$. $E$ is the adsorption force potential in the most frequently occurring micropores and coefficient $n$ determines the width of the micropore distribution; the latter can take any, including non-integral, value in a certain interval, depending on the type of active carbon. The optimum parameters, $W_0$, $n$, and $E$, were determined by selecting the $W_0$ and $n$ values for which the characteristic energy values, $E$, calculated from eqn (20) in an explicit form

$$E = \exp\left[\ln RT \ln f_0/p - \frac{\ln \ln W_0/a\,v}{n}\right] \qquad (21)$$

exhibited the smallest dependence on the value of the adsorbed amount, $a$. The adsorption isotherms of benzene on active carbons Nos. 27, 29, and 33 at 20, 111.5, and 181.4°C, of argon at −195.25 and 195.65°C, and ammonia at temperatures from −57.9 to −78.7°C, respectively, are given in Tables 2—7 together with the calculated $E$ values for individual adsorption isotherm points calculated from expression (21). From Tables 2—7 it follows that the $E$ values are independent on the temperature within experimental error.

The somewhat higher values of the so-called limiting volume, $W_0$, determined from the measurement of argon and ammonia adsorption isotherms as compared with the values obtained from the benzene isotherms, are apparently caused by the presence of a small

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*Table 2*

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Adsorption isotherms of benzol, argon, and ammonia on active carbons *27, 29,* and *33,* and values of characteristic energies *E* calculated according to eqn (22)
Employed values of fugacities of saturated vapours *f* (or saturated pressures $p_0$) and molar volumes *v* for all adsorbates are those given in Table 1

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*Benzene*
$W_0 = 0.312$ cm³ g⁻¹, $n = 2.2$

</div>

| Temperature 20°C | | | Temperature 111.5°C | | |
|---|---|---|---|---|---|
| $p$ Torr | $a$ mmol g⁻¹ | $E$ kcal mol⁻¹ | $p$ Torr | $a$ mmol g⁻¹ | $E$ kcal mol⁻¹ |
| 0.049 | 2.349 | 6.46 | 0.026 | 0.485 | 6.38 |
| 0.15 | 2.660 | 6.47 | 0.120 | 0.796 | 6.33 |
| 0.55 | 2.925 | 6.20 | 0.460 | 1.164 | 6.31 |
| 1.70 | 3.146 | 6.01 | 1.780 | 1.604 | 6.30 |
| 2.37 | 3.210 | 6.02 | 5.070 | 1.978 | 6.34 |
| 6.75 | 3.360 | 5.80 | 14.290 | 2.340 | 6.41 |
| | Mean value | 6.16 | 40.270 | 2.640 | 6.41 |
| | | | | Mean value | 6.35 |

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Temperature 181.4°C

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| $p$ Torr | $a$ mmol g⁻¹ | $E$ kcal mol⁻¹ |
|---|---|---|
| 0.17 | 0.241 | 6.34 |
| 0.79 | 0.484 | 6.31 |
| 2.95 | 0.794 | 6.26 |
| 9.55 | 1.158 | 6.23 |
| 30.28 | 1.593 | 6.28 |
| 75.86 | 1.944 | 6.33 |
| Mean value | | 6.29 |

amount of very small pores exhibiting molecular sieve properties (the ultraporosity effect). In fact, the parameter *n* determines the form of the so-called reduced characteristic curve *viz.* of the dependence $A/E$ on $\Theta$. From the agreement of the parameter *n* for benzene, argon, and ammonia on given samples of active carbons it is evident that the value of perturbation enthalpies $\Delta H^*$ are identical for these adsorbates. This conclusion is confirmed also by the approximate agreement of values of the affinity coefficient, $\beta$, calculated from a comparison of the characteristic energies, $E/E_0 = \beta$ with the $\beta$ values, calculated from the relation, $\beta = v/v_0$, where $v$ and $v_0$ are the molar volumes at the same reduced temperature of the adsorbate and of the standard substance (benzene), respectively (Table 5).

The similarity of the values of $\Delta S^*$ of nonassociating adsorbates with different molecular weight (argon, ammonia, benzene) indicates that $\Delta H^*$ of these adsorbates is also close to zero. This follows from the fact (as will be shown later) that the absolute values of $\Delta S^*$ and $\Delta H^*$ increase simultaneously with the increasing molecular weight of associating adsorbates perturbed on active carbons (water, methanol, ethanol; Table 14).

On the basis of these results it can be concluded, that $\Delta S^*$ and $\Delta H^*$ are close to zero for all the mentioned adsorbates (benzene, argon, ammonia), and that the $p, v, T$ relations of these adsorbates are nearly the same as for adsorptives.
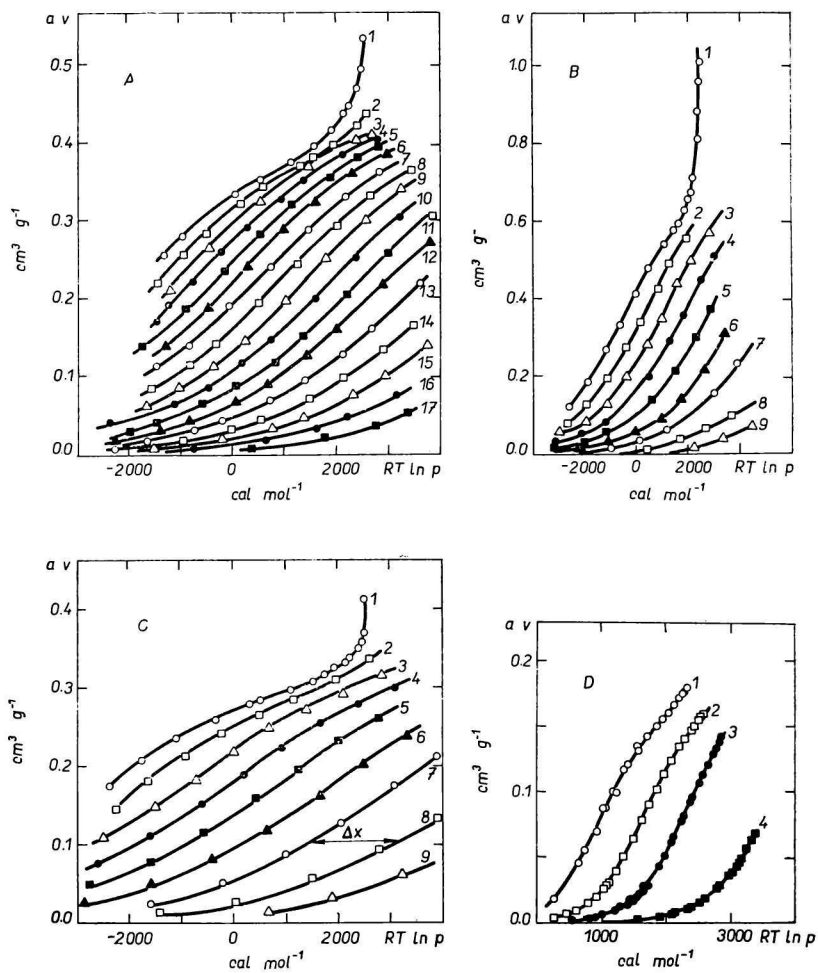
*Fig. 1.* Adsorption isotherms of *benzene* measured on active carbon

$$A - 29, B - 33, C - 27$$

at temperatures

*A*: *1.* 20°C; *2.* 30°C; *3.* 39.4°C; *4.* 49.5°C; *5.* 60.1°C; *6.* 71.7°C; *7.* 84.0°C; *8.* 97.2°C;
*9.* 111.5°C; *10.* 126.8°C; *11.* 143.5°C; *12.* 161.6°C; *13.* 181.4°C; *14.* 203.1°C; *15.* 226.8°C;
*16.* 253.3°C; *17.* 288.5°C;

*B*: *1.* 20°C; *2.* 39.4°C; *3.* 60.1°C; *4.* 84°C; *5.* 111.5°C; *6.* 143.5°C; *7.* 181.4°C; *8.* 226.8°C;
*9.* 282.3°C;

*C*: *1.* 20°C; *2.* 39.4°C; *3.* 60.1°C; *4.* 84°C; *5.* 111.5°C; *6.* 143.5°C; *7.* 181.4°C; *8.* 226.8°C;
*9.* 282.3°C;

and of *nitrogen* on zeolite NaA
*D*: *1.* −98°C; *2.* −78°C; *3.* −58.5°C; *4.* −17°C.

### Table 3

### Active carbon 27

#### Argon
Temperature $-195.25$

$W_0 = 0.345$ cm³ g$^{-1}$, $n = 2.2$

| $p$<br>Torr | $a$<br>mmol g$^-$ | $E$<br>kcal mol$^{-1}$ |
|---|---|---|
| 0.10 | 5.469 | 1.30 |
| 0.35 | 8.793 | 1.61 |
| 4.64 | 10.949 | 1.50 |
| 10.07 | 11.594 | 1.56 |
| | Mean value | 1.49 |

| Ammonia<br>Temperature $-64.0$°C<br>$W_0 = 0.304$ cm³ g$^{-1}$, $n = 2.2$ | | | Ammonia<br>Temperature $-78.7$°C<br>$W_0 = 0.317$, $n = 2.2$ | | |
|---|---|---|---|---|---|
| $p$<br>Torr | $a$<br>mmol g$^{-1}$ | $E$<br>kcal mol$^{-1}$ | $p$<br>Torr | $a$<br>mmol g$^{-1}$ | $E$<br>kcal mol$^{-1}$ |
| 0.90 | 2.883 | 1.71 | 0.17 | 2.291 | 1.63 |
| 1.10 | 3.219 | 1.70 | 0.69 | 4.933 | 1.57 |
| 2.81 | 5.254 | 1.66 | 1.275 | 6.763 | 1.58 |
| 3.91 | 6.291 | 1.68 | 1.42 | 7.242 | 1.61 |
| 5.19 | 7.400 | 1.74 | 2.09 | 8.907 | 1.70 |
| 8.31 | 7.663 | 1.53 | | Mean value | 1.62 |
| 11.92 | 9.105 | 1.60 | | | |
| 17.81 | 10.239 | 1.60 | | | |
| 17.32 | 10.355 | 1.66 | | | |
| | Mean value | 1.65 | | | |

b) *The determination of perturbation entropy, $\Delta S^*$, enthalpy, $\Delta H^*$, and free energy, $\Delta G^*$, of adsorbates associated with hydrogen bonds*

Those adsorbates for which hydrogen-bond association in liquid state is typical (methanol, ethanol, and water) exhibit different behaviour on active carbons. This is manifested by somewhat lower values of coefficients $C$ compared to coefficients $C'$ (related to deviations from the Polanyi postulate (3) which were also observed) and especially by deviations from Dubinin's postulate (19) concerning the characteristic curve affinity.

Since the values of coefficient $\Delta H^*$ cannot be directly determined in a simple manner for nonassociated substances, let us assume (for the calculation of coefficients $\nu$ for associating substances) that $\nu \doteq 1$ for the benzene—active carbon system. The expression for $\ln \nu$ of an associated substance can then be derived using eqns (1), (2), and (20)

$$-\Delta G^* = RT \ln \nu = \exp\left[\frac{\ln \ln W_0/a\,\nu}{n} + \ln \beta E_0\right] + RT \ln p/p_0. \tag{22}$$

Using expression (18) and the values of constants $W_0$, $n$, and $E_0$ determined from the benzene adsorption isotherms and $\beta$ from Table 8, functions $\nu = \nu(\Theta, T)$ can be determined

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*Table 4*

Active carbon *29*

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*Benzene*

$W_0 = 0.400$ cm$^3$ g$^{-1}$, $n = 2.1$

</div>

| Temperature 20°C | | | Temperature 111.5°C | | |
|---|---|---|---|---|---|
| $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ | $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ |
| 0.10 | 2.885 | 5.66 | 0.11 | 0.648 | 5.54 |
| 0.21 | 3.165 | 5.62 | 0.26 | 0.876 | 5.50 |
| 1.01 | 3.778 | 5.74 | 0.61 | 1.192 | 5.53 |
| 2.45 | 3.998 | 5.49 | 1.31 | 1.490 | 5.50 |
| 3.31 | 4.011 | 5.07 | 3.84 | 2.010 | 5.55 |
| 6.92 | 4.226 | 5.17 | 10.52 | 2.553 | 5.68 |
| | Mean value | 5.46 | 29.18 | 3.040 | 5.73 |
| | | | 73.42 | 3.430 | 5.82 |
| | | | | Mean value | 5.61 |

<div align="center">

Temperature 181.4°C

</div>

| $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ |
|---|---|---|
| 0.16 | 0.170 | 5.64 |
| 0.44 | 0.294 | 5.61 |
| 0.80 | 0.410 | 5.63 |
| 2.24 | 0.648 | 5.58 |
| 4.57 | 0.876 | 5.57 |
| 10.62 | 1.190 | 5.53 |
| 20.23 | 1.486 | 5.53 |
| 54.83 | 2.000 | 5.56 |
| Mean value | | 5.58 |

for hydrogen-bond associated substances on the basis of their adsorption isotherms. The $\Delta G^*$ values calculated for methanol and ethanol and water on active carbons Nos. *27*, *29*, and *33* are given in Tables 9—14.

It is surprising that for all these materials the dependence $\nu$ on $\Theta$ and temperature can be expressed by the universal empiric function

$$-\Delta G^* = RT \ln \nu = K(1 - \Theta), \qquad (23)$$

where $K$ is a constant with a value identical to that for methanol and ethanol on active carbons *27* and *29*; $K = 1.0$ kcal mol$^{-1}$. For methanol and ethanol on active carbon *33*, the value of $K$ is lower ($K = 0.5$ kcal mol$^{-1}$). The function $\nu = \nu(\Theta, T)$ for water and active carbon *29*, *27*, and *33* can be expressed by the eqn (23) where $K = 1.25$ kcal mol$^{-1}$ (see Figs. 4 and 5). The formerly obtained dependence of the coefficient $\nu$ on the value of the characteristic energy, $E_0$, was obtained by a less accurate procedure — with the use of an integer coefficient $n = 2$ for all samples of active carbons *27—33* for the calculation of $\nu$ and $E_0$ from adsorption isotherms of benzene and other associated substances [17].

Fig. 2. Dependence of $RT \ln p$ on $T = T_2 - T_1$ for benzene isotherms on active carbon 27. Temperature $T_1 = 111.5°C$.
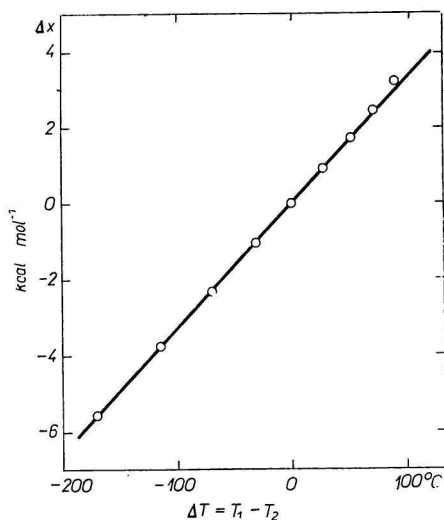
These results enable us to calculate the adsorption isotherms of the mentioned substances associated by hydrogen bonds on the basis of structure parameters of active carbons ($W_0$, $n$, and $E_0$) and can be theoretically very well interpreted.
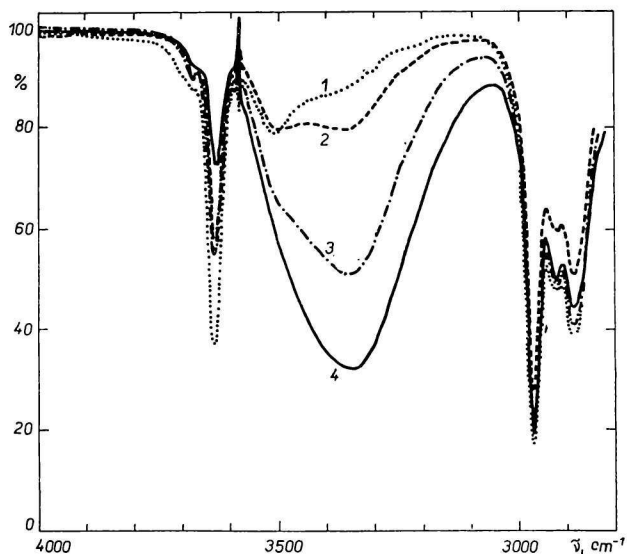


Fig. 3. Infrared spectrum of ethanol solutions in tetrachloromethane.
1. 0.5 vol.%; 2. 1.25 vol.%; 3. 2.5 vol.%; 4. 5 vol.%.
(Measured with spectrometer Perkin—Elmer Type 621.)

## Discussion

Both the presented and the recently published experimental results enable us to determine the state behaviour of gases and vapours in the force field of adsorbents. The deviations of state properties from those of the corresponding liquids are for most adsorbates rather small. If we imply these deviations by the ratio of fugacities of saturated vapours of perturbed and normal liquid $\nu = f_\omega/f_0$, this ratio does not surpass for nonspecific interactions the value 1.6. However, with adsorbates associated by hydrogen and electron gas bonds (water, methanol, ethanol, and mercury) it attains a multiple of this value.

This conclusion is confirmed particularly by the presented results. For non-associated adsorbates, the experimentally obtained values of perturbation entropies $\Delta S^*$ are practically close to zero, and Polanyi postulate (3) is almost fulfilled. The values of the perturbation enthalpies, $\Delta H^*$, must be identical for all these adsorbates since the validity of Dubinin's postulate (19) was proved in these cases (see Tables 2—7). However, this is possible only in the case when the values of $\Delta H^*$ are close to zero.

*Table 5*

Active carbon *29*

*Argon*
Temperature $-195.63°C$
$W_0 = 0.443$ cm³ g⁻¹, $n = 2.1$

| $p$ Torr | $a$ mmol g⁻¹ | $E$ kcal mol⁻¹ |
|---|---|---|
| 0.95 | 11.509 | 1.40 |
| 1.70 | 12.323 | 1.39 |
| 5.10 | 13.702 | 1.37 |
| 8.76 | 14.365 | 1.38 |
| 10.90 | 14.570 | 1.37 |
| 19.51 | 15.086 | 1.35 |
| 29.34 | 15.434 | 1.38 |
| | Mean value | 1.38 |

*Ammonia*
Temperature $-57.9°C$
$W_0 = 0.410$ cm³ g⁻¹, $n = 2.1$

*Ammonia*
Temperature $-77.4°C$
$W_0 = 0.417$ cm³ g⁻¹, $n = 2.1$

| $p$ Torr | $a$ mmol g⁻¹ | $E$ kcal mol⁻¹ | $p$ Torr | $a$ mmol g⁻¹ | $E$ kcal mol⁻¹ |
|---|---|---|---|---|---|
| 1.24 | 1.919 | 1.34 | 0.81 | 3.601 | 1.26 |
| 2.01 | 2.554 | 1.43 | 1.05 | 4.326 | 1.25 |
| 2.64 | 2.976 | 1.40 | 1.41 | 5.671 | 1.27 |
| 4.945 | 4.488 | 1.36 | 1.67 | 6.667 | 1.30 |
| 7.08 | 5.771 | 1.35 | 1.74 | 6.939 | 1.31 |
| 9.495 | 7.191 | 1.37 | 2.097 | 8.223 | 1.36 |
| 11.97 | 8.631 | 1.42 | 2.48 | 9.549 | 1.42 |
| | Mean value | 1.38 | 2.73 | 10.099 | 1.44 |
| | | | | Mean value | 1.33 |

*Table 6*

Active carbon *33*

Benzene

$W_0 = 0.614 \text{ cm}^3 \text{ g}^{-1}$, $n = 1.65$

| | Temperature 20°C | | | Temperature 111.5°C | |
|---|---|---|---|---|---|
| $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ | $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ |
| 0.011 | 1.417 | 3.89 | 0.014 | 0.162 | 4.09 |
| 0.040 | 2.150 | 3.99 | 0.058 | 0.335 | 4.11 |
| 0.14 | 3.060 | 4.14 | 0.2 | 0.6 | 4.14 |
| 0.34 | 3.700 | 4.17 | 0.78 | 0.922 | 3.98 |
| 1.07 | 4.700 | 4.40 | 2.19 | 1.417 | 4.03 |
| 2.46 | 5.390 | 4.62 | 7.08 | 2.15 | 4.06 |
| 7.08 | 6.140 | 5.00 | 19.96 | 3.06 | 4.22 |
| 12.97 | 6.527 | 5.79 | 44.67 | 3.76 | 4.27 |
| 17.42 | 6.683 | 6.68 | | Mean value | 4.21 |
| | Mean value | 4.74 | | | |

Temperature 181.4°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ |
|---|---|---|
| 0.071 | 0.064 | 4.18 |
| 0.32 | 0.162 | 4.18 |
| 1.20 | 0.334 | 4.16 |
| 3.76 | 0.598 | 4.16 |
| 11.61 | 0.917 | 4.02 |
| 29.50 | 1.405 | 4.04 |
| 77.62 | 2.120 | 4.11 |
| Mean value | | 4.12 |

In those cases when it holds simultaneously $\Delta S^* = 0$ and $\Delta H^* = 0$, then $\nu = 1$. On the basis of the study of the relationship between the shape of the adsorption isotherm and the contact angle, it is possible to evaluate the values of $\nu$ for the mentioned nonassociated adsorbates. They do not overpass the value 1.5. The mentioned slight perturbations are effected by the structural changes of the adsorbate in the field of adsorption forces [8].

From the physical meaning of $\Delta H^*$ it follows in most cases that $k \geq 0$ (see Table 14 and eqn *(14)*). It can be supposed that $1 < \exp[\Delta C] < 1.5$. Thus in the case of non-specific interactions which are temperature invariant, the Polanyi postulate will be a good approximation of the temperature dependence of the adsorption isotherms since

$$\left( \frac{\partial RT \ln f_0/f}{\partial T} \right)_\Theta = R \, \Delta C < 0.8 \text{ cal K}^{-1} \text{mol}^{-1}. \tag{24}$$

Hence it follows that at a constant $\Theta$ a temperature increase of 100°C effects an increase of the value $A$ of merely 80 cal mol$^{-1}$, this being in an agreement with the considerable experimental material (see *e.g.* Brunauer monography [19]). Also the

value of the differential molar adsorption work $A$ in these cases is practically identical with the potential of adsorption forces, *e.g.* for 20°C

$$A - \varepsilon = RT \ln v \leq RT \ln 1.5 = 236 \text{ cal mol}^{-1}. \tag{25}$$
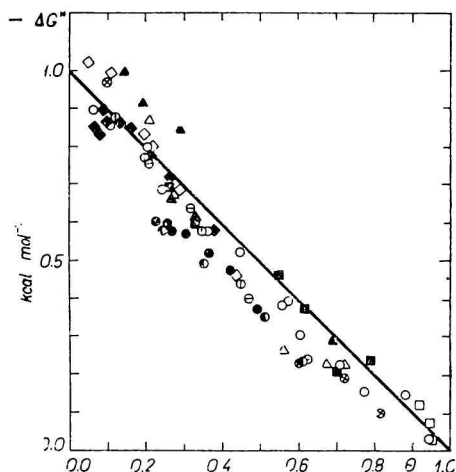


*Fig. 4.* Dependence of perturbation free energy $\Delta G^*$ of methanol and ethanol on the filling degree of micropores $\Theta$, for active carbon

*27:* ○ 20°C; ⊕ 40°C; ● 70°C (methanol);
□ 20°C; ⊗ 40°C; ■ 70°C (ethanol).
*29:* ◊ 20°C; ⊕ 40°C; ♦ 70°C (methanol);
△ 20°C; ⊖ 40°C; ▲ 70°C (ethanol).
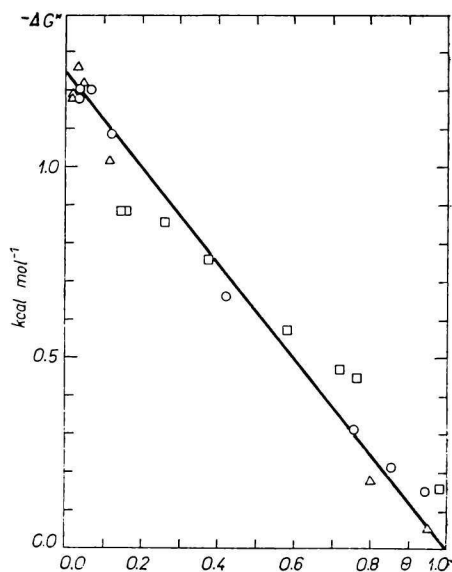
*Fig. 5.* Dependence of perturbation free energy $\Delta G^*$ of water on the filling degree of micropores $\Theta$.
Temperature 20°C, active carbon: □ *27;*
○ *29;* △ *33.*

This conclusion is in agreement with the previously published results [18].

Hence, in most cases there need not be a great discrepancy between the opinions of some authors on the necessity of the deviations of the $p, v, T$ relations of adsorbates from those for adsorptives and the fundamental assumptions of the Polanyi—Dubinin theory.

Greater deviations from the state behaviour of the bulk liquids were found in the case of adsorption of water, methanol, and ethanol on active carbons (see Table 1). The cause of these deviations appears to be the different association degree of these adsorptives in the adsorbed state and in the bulk liquid phase. It is known that water, methanol, and ethanol in liquid phase form linear or even cyclic associates. The energy of the hydrogen bonds depends also on the number of molecules in the associate. This can be illustrated by the results of the study of i.r. spectra of these substances in nonpolar solvents. As example in Fig. 3 the i.r. spectra of differently concentrated solutions of ethanol in the tetrachloromethane are shown. The con-

Table 7

Active carbon 33

Argon
Temperature $-195.25°C$
$W_0 = 0.676$ cm$^3$ g$^{-1}$, $n = 1.65$

| $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ |
|---|---|---|
| 1.25 | 14.949 | 1.24 |
| 4.72 | 17.782 | 1.19 |
| 10.98 | 19.893 | 1.21 |
| 16.81 | 20.884 | 1.22 |
| 17.11 | 20.750 | 1.18 |
| 27.64 | 21.999 | 1.25 |
| 43.28 | 22.401 | 1.10 |
| | Mean value | 1.20 |

| Ammonia Temperature $-64.4°C$ $W_0 = 0.664$ cm$^3$ g$^{-1}$, $n = 1.65$ | | | Ammonia Temperature $-78.4°C$ $W_0 = 0.660$ cm$^3$ g$^{-1}$, $n = 1.65$ | | |
|---|---|---|---|---|---|
| $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ | $p$ Torr | $a$ mmol g$^{-1}$ | $E$ kcal mol$^{-1}$ |
| 6.83 | 9.232 | 1.12 | 0.95 | 5.297 | 1.07 |
| 6.33 | 10.129 | 1.21 | 2.29 | 9.987 | 1.10 |
| 9.73 | 11.990 | 1.16 | 3.54 | 13.788 | 1.17 |
| 12.81 | 14.569 | 1.21 | 4.18 | 15.529 | 1.22 |
| 15.79 | 16.653 | 1.26 | 7.43 | 20.826 | 1.37 |
| 21.20 | 19.679 | 1.36 | 10.48 | 22.557 | 1.32 |
| 32.16 | 22.178 | 1.33 | 14.63 | 24.208 | 1.25 |
| 45.21 | 23.940 | 1.26 | 18.02 | 25.346 | 1.24 |
| | Mean value | 1.24 | | Mean value | 1.22 |

centration of the associates increases with the increasing concentration of ethanol The $\nu$(OH) bond at 3630 cm$^{-1}$ corresponding to the vibration of the hydroxyl groups of nonassociated ethanol vanishes and another very broad band which corresponds to the vibration of the OH groups of associated ethanol appears in the low-frequency region. The low-frequency shift of the $\nu$(OH) vibration caused by association corresponds to an increase in the energy of the hydrogen bond.

If e.g. the possibility of the formation of multiple associates in micropores of active carbons is limited, the state behaviour of the adsorbate differs from that of the bulk liquid.

In such cases, the physical meaning of the fugacity $f_\omega$ can be understood as the saturated fugacity of vapours of liquid bulk phase with the same distribution and structure of the associates as in the case of the adsorbed phase. The energy of the hydrogen bond of low-member perturbed associates is smaller than the energy of the hydrogen bond of the associates corresponding to the bulk liquid. Thus the condensation heat of such a perturbed liquid will also be smaller since the energy of the hydrogen bond determines essentially the values of the evaporating heats of water, methanol, and ethanol.

Table 8

The values of molar volumes $v$, affinity coefficients $\beta$ (determined from the relation $\beta = v/v_0$), saturated tensions $p_0$ of benzene, argon, ammonia, methanol, ethanol, and water vapours and saturated fugacities $f_0$ used in the calculation of values of characteristic energies $E$ and perturbed free energies $-\varDelta G^*$ given in Tables 2 and 4

|  | $v$ cm³ mol⁻¹ | $\beta$ | $p_0$ Torr | $f_0$ Torr |
|---|---|---|---|---|
| *Benzene* |  | 1.0 |  |  |
| 20°C | 88.9 |  | 74.13 | 74.13 |
| 111.5°C | 99.8 |  | 1795 | 1696 |
| 181.4°C | 110.4 |  | 7870 | 6690 |
| *Argon* |  | 0.310 |  |  |
| −195.25°C | 27.61 |  | 222.0 |  |
| −195.63°C | 27.55 |  | 208.0 |  |
| *Ammonia* |  | 0.265 |  |  |
| −78.7°C | 23.21 |  | 41.5 |  |
| −78.4°C | 23.24 |  | 42.5 |  |
| −77.4°C | 23.27 |  | 46.6 |  |
| −64.4°C | 23.72 |  | 121.5 |  |
| −64.0°C | 23.72 |  | 126.0 |  |
| −57.9°C | 23.96 |  | 189.6 |  |
| *Methanol* |  | 0.466 |  |  |
| 20°C | 40.48 |  | 96.0 |  |
| 40°C | 41.40 |  | 260.5 |  |
| 70°C | 42.95 |  | 927.2 |  |
| *Ethanol* |  | 0.672 |  |  |
| 20°C | 58.36 |  | 43.9 |  |
| 40°C | 59.66 |  | 135.3 |  |
| 70°C | 61.95 |  | 542.5 |  |
| *Water* |  | 0.203 |  |  |
| 20°C | 20.02 |  | 17.54 |  |

This conception explains also qualitatively the dependence of the coefficient $v$ on the filling degree of the adsorption space $\Theta$. At small values of $\Theta$, the average number of molecules in the associates is smaller than at higher values of $\Theta$. For this reason also the values of $v$ are the highest (maximal deviations from the $p$, $v$, $T$ relations of the bulk liquid). With $\Theta \to 1$ also $v \to 1$, since the pores of rather large dimensions, where perturbations (steric hindrances) are minimal, are filled up. In the first approximation the dependence $RT \ln v$ on $\Theta$, or $(1 - \Theta)$ can be approximated by a linear dependence.

The independence of the function $v(\Theta, T)$ of water, methanol, and ethanol on the value of $E_0$ of active carbon *27* and *29* can be also explained. On the basis of the De Boer relation between the adsorption potential and the radius of the pores a relation was derived between the characteristic energy $E_0$ and the most probable radii of micropores $\bar r$ of active carbons, $E_0 = b \, r^{-3}$, where $b = 2.142 \times 10^3$ kcal A³

*Table 9*

Free energy change caused by perturbation $-\Delta C^*$ of methanol and ethanol on active
carbon 27, calculated from eqn (23) for $W_0 = 0.312$, $n = 2.2$, and $E_0 = 6.27$ kcal mol$^{-1}$
The values of saturated pressure $p_0$, molar volume $v$,
and affinity coefficients are in Table 8

Active carbon 27

*Methanol* 20°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 0.16 | 0.497 | 0.064 | 0.895 |
| 0.30 | 0.821 | 0.107 | 0.855 |
| 0.796 | 1.600 | 0.208 | 0.797 |
| 0.90 | 1.898 | 0.246 | 0.686 |
| 1.68 | 2.810 | 0.365 | 0.577 |
| 2.57 | 3.483 | 0.452 | 0.523 |
| 3.70 | 4.316 | 0.560 | 0.384 |
| 4.11 | 4.440 | 0.576 | 0.394 |
| 4.14 | 4.666 | 0.605 | 0.305 |
| 6.46 | 5.477 | 0.711 | 0.221 |
| 8.32 | 5.955 | 0.773 | 0.154 |
| 17.29 | 6.788 | 0.881 | 0.145 |
| 26.5 | 7.297 | 0.947 | 0.030 |

*Methanol* 40°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 2.84 | 1.884 | 0.250 | 0.578 |
| 4.89 | 2.681 | 0.356 | 0.492 |
| 9.33 | 3.882 | 0.515 | 0.353 |
| 12.79 | 4.622 | 0.613 | 0.235 |

*Methanol* 70°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 13.50 | 1.662 | 0.229 | 0.603 |
| 16.10 | 1.869 | 0.257 | 0.594 |
| 16.78 | 1.951 | 0.269 | 0.573 |
| 21.36 | 2.252 | 0.310 | 0.568 |
| 27.66 | 2.684 | 0.369 | 0.521 |
| 34.47 | 3.099 | 0.427 | 0.472 |
| 42.0 | 3.608 | 0.497 | 0.374 |

*Ethanol* 20°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 5.10 | 4.911 | 0.919 | 0.119 |
| 7.04 | 5.055 | 0.946 | 0.070 |
| 7.05 | 5.079 | 0.950 | 0.027 |

*Table 9* (Continued)

### Ethanol 40°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 0.032 | 0.520 | 0.099 | 0.967 |
| 1.37 | 3.158 | 0.604 | 0.229 |
| 3.16 | 3.773 | 0.721 | 0.195 |
| 6.05 | 4.278 | 0.818 | 0.098 |

### Ethanol 70°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 1.30 | 1.324 | 0.263 | 0.692 |
| 2.01 | 1.658 | 0.329 | 0.603 |
| 8.01 | 2.768 | 0.550 | 0.462 |
| 11.05 | 3.106 | 0.617 | 0.373 |
| 16.12 | 3.558 | 0.706 | 0.209 |
| 27.19 | 3.985 | 0.791 | 0.237 |

*Table 10*

Free energy change caused by perturbation $-\Delta G^*$ of ethanol and ethanol on active carbon *29*, calculated from eqn (*23*) for $W_0 = 0.400$, $n = 2.1$, and $E_0 = 5.55$ kcal mol$^{-1}$
The values of saturated pressure $p_0$, molar volume $v$,
and affinity coefficients are in Table 8

### Active carbon 29

#### Methanol 20°C

| $p$ Torr | $a$ mmol l g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 0.30 | 0.480 | 0.0486 | 1.021 |
| 0.796 | 1.069 | 0.108 | 0.993 |
| 1.525 | 1.974 | 0.1997 | 0.832 |
| 1.68 | 2.174 | 0.220 | 0.795 |
| 2.3 | 2.871 | 0.291 | 0.687 |
| 3.7 | 4.335 | 0.439 | 0.462 |

#### Methanol 40°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 2.84 | 1.175 | 0.122 | 0.876 |
| 4.89 | 1.937 | 0.200 | 0.768 |
| 9.33 | 3.370 | 0.349 | 0.579 |
| 12.79 | 4.376 | 0.453 | 0.439 |

*Table 10* (Continued)

Active carbon *29*

*Methanol* 70°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 7.35 | 0.627 | 0.0673 | 0.851 |
| 8.63 | 0.742 | 0.0797 | 0.835 |
| 10.61 | 0.825 | 0.0886 | 0.894 |
| 11.42 | 0.915 | 0.098 | 0.863 |
| 16.10 | 1.211 | 0.130 | 0.868 |
| 21.14 | 1.534 | 0.165 | 0.847 |
| 27.66 | 2.011 | 0.216 | 0.775 |
| 34.47 | 2.455 | 0.264 | 0.721 |
| 42.00 | 3.050 | 0.327 | 0.615 |
| 52.61 | 3.557 | 0.382 | 0.583 |

*Ethanol* 20°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 0.07 | 1.428 | 0.208 | 0.869 |
| 0.10 | 1.880 | 0.274 | 0.672 |
| 0.17 | 2.399 | 0.350 | 0.582 |
| 0.30 | 3.072 | 0.448 | 0.454 |
| 0.50 | 3.849 | 0.562 | 0.264 |
| 1.08 | 4.630 | 0.676 | 0.230 |
| 1.51 | 4.947 | 0.722 | 0.224 |

*Ethanol* 40°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 0.27 | 1.391 | 0.207 | 0.759 |
| 0.42 | 1.784 | 0.266 | 0.669 |
| 0.65 | 2.159 | 0.322 | 0.637 |
| 1.37 | 3.162 | 0.472 | 0.398 |
| 3.01 | 4.183 | 0.624 | 0.240 |

*Ethanol* 70°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 1.30 | 0.931 | 0.144 | 0.995 |
| 2.01 | 1.242 | 0.192 | 0.915 |
| 4.34 | 1.864 | 0.289 | 0.844 |
| 8.01 | 2.529 | 0.392 | 0.742 |
| 27.19 | 4.450 | 0.689 | 0.289 |

mol$^{-1}$. This relation was found to be in a good agreement with the experimental data [18]. On its basis the values of the most probable radii of active carbons *27—33* could be evaluated. From the Table 13 it follows that the values of radii $\bar{r}$ of active carbons *27—33* are in the range from 6.7 to 7.7 A. If the adsorbates form linear

## Table 11

Free energy change caused by perturbation $-\Delta G^*$ of methanol and ethanol on active carbon *33*, calculated from eqn (*23*) for $W_0 = 0.614$, $n = 1.65$, and $E_0 = 4.36$ kcal mol$^{-1}$

The values of saturated pressure $p_0$, molar volume $v$,

and affinity coefficients are in Table 8

### Active carbon *33*

*Methanol* 20°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 0.25 | 0.718 | 0.047 | 0.528 |
| 0.80 | 1.080 | 0.071 | 0.872 |
| 1.40 | 1.530 | 0.101 | 0.898 |
| 3.07 | 3.282 | 0.216 | 0.625 |
| 4.11 | 3.809 | 0.251 | 0.636 |
| 4.12 | 3.889 | 0.256 | 0.615 |
| 5.06 | 4.672 | 0.308 | 0.529 |
| 6.00 | 5.307 | 0.350 | 0.478 |
| 6.46 | 5.745 | 0.379 | 0.424 |
| 7.30 | 6.975 | 0.460 | 0.243 |
| 7.65 | 6.953 | 0.458 | 0.274 |
| 9.62 | 8.142 | 0.537 | 0.184 |

*Methanol* 40°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 1.92 | 1.111 | 0.075 | 0.563 |
| 2.84 | 1.330 | 0.090 | 0.652 |
| 4.89 | 1.917 | 0.129 | 0.662 |
| 9.33 | 3.046 | 0.205 | 0.612 |
| 12.79 | 4.010 | 0.270 | 0.515 |

*Methanol* 70°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 17.64 | 1.584 | 0.111 | 0.575 |
| 18.20 | 1.647 | 0.115 | 0.561 |
| 25.86 | 2.098 | 0.147 | 0.575 |
| 34.34 | 2.515 | 0.176 | 0.593 |
| 46.71 | 3.275 | 0.229 | 0.532 |
| 83.70 | 5.281 | 0.369 | 0.387 |
| 103.45 | 6.614 | 0.463 | 0.240 |

*Ethanol* 20°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 0.07 | 1.480 | 0.141 | 0.655 |
| 0.13 | 1.902 | 0.181 | 0.665 |
| 0.20 | 2.522 | 0.240 | 0.496 |
| 0.50 | 3.593 | 0.342 | 0.453 |
| 0.70 | 4.189 | 0.398 | 0.377 |
| 1.17 | 5.043 | 0.479 | 0.320 |
| 1.77 | 6.078 | 0.578 | 0.166 |

*Ethanol* 40°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 0.42 | 1.715 | 0.167 | 0.579 |
| 0.65 | 2.102 | 0.204 | 0.557 |
| 1.37 | 2.854 | 0.277 | 0.549 |
| 3.01 | 4.350 | 0.424 | 0.304 |

## Table 11 (Continued)

### Active carbon 33

#### Ethanol 70°C

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 4.34 | 1.789 | 0.181 | 0.766 |
| 8.01 | 2.485 | 0.251 | 0.693 |
| 11.06 | 2.985 | 0.301 | 0.618 |
| 16.12 | 4.048 | 0.408 | 0.343 |

## Table 12

Free energy change caused by perturbation $-\Delta G^*$ of water, calculated from isotherms measured at 20°C on active carbon 27, 29, and 33 by means of eqn (23)

### Active carbon 27

$W_0 = 0.312$ cm$^3$ g$^{-1}$, $n = 2.2$    $E_0 = 6.27$ kcal mol$^{-1}$

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 4.192 | 2.248 | 0.144 | 0.885 |
| 4.560 | 2.526 | 0.162 | 0.886 |
| 6.192 | 4.008 | 0.257 | 0.856 |
| 7.226 | 5.806 | 0.373 | 0.759 |
| 8.963 | 9.075 | 0.582 | 0.571 |
| 10.471 | 11.185 | 0.718 | 0.470 |
| 11.383 | 11.923 | 0.765 | 0.447 |
| 16.084 | 15.309 | 0.982 | 0.157 |

### Active carbon 29

$W_0 = 0.400$ cm$^3$ g$^{-1}$, $n = 2.1$    $E_0 = 5.55$ kcal mol$^{-1}$

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 4.192 | 0.683 | 0.034 | 1.177 |
| 4.560 | 0.738 | 0.037 | 1.204 |
| 6.192 | 1.343 | 0.067 | 1.201 |
| 7.226 | 2.453 | 0.123 | 1.087 |
| 8.963 | 8.431 | 0.422 | 0.659 |
| 10.471 | 15.125 | 0.757 | 0.312 |
| 11.383 | 17.085 | 0.855 | 0.214 |
| 13.699 | 18.817 | 0.942 | 0.151 |

### Active carbon 33

$W_0 = 0.614$,    $n = 1.65$    $E_0 = 4.36$

| $p$ Torr | $a$ mmol g$^{-1}$ | $\Theta$ | $-\Delta G^*$ kcal mol$^{-1}$ |
|---|---|---|---|
| 4.192 | 0.611 | 0.020 | 1.191 |
| 4.560 | 0.725 | 0.024 | 1.186 |
| 6.192 | 0.992 | 0.032 | 1.262 |
| 7.226 | 1.460 | 0.048 | 1.221 |
| 8.963 | 3.569 | 0.116 | 1.017 |
| 10.471 | 12.755 | 0.416 | 0.517 |
| 11.383 | 19.305 | 0.629 | 0.303 |
| 12.892 | 24.534 | 0.800 | 0.177 |
| 15.084 | 29.085 | 0.948 | 0.061 |

## Table 13

Structural parameters $W_0$, $n$, and $E$ of active carbon *27*, *29*, and *33* obtained from adsorption isotherms of benzene, argon, and ammonia, and mean radii of pores $\bar{r}$ calculated from the relation $E_0(\bar{r})^3 = 2.142 \times 10^3$ kcal A mol$^{-1}$

Maximal numbers of molecules with hydrogen bonds $N$ linearly associated in micropores of radii $\bar{r}$

Experimental values of affinity coefficients $\beta_{\mathrm{exp}}$ of argon and ammonia calculated from $\beta = E/E_0$ where $E_0$ is the characteristic energy determined by means of benzene isotherm (standard adsorbate)

| Active carbon | Constants calculated from *benzene* adsorption isotherms | | | | |
|---|---|---|---|---|---|
| | $W_0$ cm$^3$ g$^{-1}$ | $n$ | $E_0$ kcal mol$^{-1}$ | $\bar{r}$ A | $N$ |
| 27 | 0.312 | 2.20 | 6.27 | 6.99 | 4.66 |
| 29 | 0.400 | 2.10 | 5.55 | 7.28 | 4.85 |
| 33 | 0.614 | 1.65 | 4.36 | 7.89 | 5.26 |

| Active carbon | Constants calculated from *argon* adsorption isotherms | | | |
|---|---|---|---|---|
| | $W_0$ cm$^3$ g$^{-1}$ | $n$ | $E$ kcal mol$^{-1}$ | $\beta_{\mathrm{exp}}$ |
| 27 | 0.345 | 2.2 | 1.49 | 0.238 |
| 29 | 0.443 | 2.1 | 1.38 | 0.249 |
| 33 | 0.676 | 1.65 | 1.20 | 0.275 |

| Active carbon | Constants calculated from *ammonia* adsorption isotherms | | | |
|---|---|---|---|---|
| | $W_0$ cm$^3$ g$^{-1}$ | $n$ | $E$ kcal mol$^{-1}$ | $\beta_{\mathrm{exp}}$ |
| 27 | 0.311 | 2.2 | 1.64 | 0.262 |
| 29 | 0.414 | 2.1 | 1.36 | 0.245 |
| 33 | 0.662 | 1.65 | 1.23 | 0.282 |

associates of the type $H-O\cdots H-O\cdots H-O\cdots$ it can be assumed that the number

of members of these associates in a given micropore does not depend essentially on the fact whether the radical R denotes H·, $CH_3$ or $C_2H_5$. Under the assumption that the $O-O$ distance in the hydrogen bond is 3 A it is possible to calculate the maximum number of molecules of water, methanol, and ethanol which form a linear associate in micropores, $N$. As evident from Table 13, the values of $N$ for active carbons *27* and *29* are about 4.9. The smaller value of $K$ for methanol and ethanol on active carbon *33* is probably caused by a slightly higher value of $N$. On the other hand, liquid water behaves at 20°C as if it was associated in clusters on the average of about six water molecules [20]. The energy of the hydrogen bond depends equally on its geometry. The changes in the geometry of hydrogen bonds are probable in micropores, and they can grow with the increasing dimensions of molecules. This is confirmed by absolute values of perturbation entropies, $\Delta S^*$, and enthalpies, $\Delta H^*$, which increase from water to ethanol (see Table 14). As evident from eqn (*14*), the influence

*Table 14*

Perturbation thermodynamic values of water, methanol, and ethanol at the adsorption on active carbon (micropores filling degree $\Theta = 0.5$, temperature 20°C), determined under the assumption that the perturbation enthalpy of standard substance (benzene) $\Delta H_0^* = 0$

| | *Water* | | | |
|---|---|---|---|---|
| Active carbon | $\Delta G^*$ kcal mol$^{-1}$ | $\Delta C$ | $\Delta S^*$ cal mol$^{-1}$ K | $\Delta H^*$ kcal mol$^{-1}$ |
| "Supersorbon" | $-0.59$ | $-0.7$ | $-1.39$ | $-0.998$ |
| | *Methanol* | | | |
| Active carbon | $\Delta G^*$ kcal mol$^{-1}$ | $\Delta C$ | $\Delta S^*$ cal mol$^{-1}$ K | $\Delta H^*$ kcal mol$^{-1}$ |
| 27 | $-0.49$ | $-1.37$ | $-2.72$ | $-1.29$ |
| 29 | $-0.49$ | $-1.18$ | $-2.35$ | $-1.18$ |
| 33 | $-0.20$ | $-1.48$ | $-2.94$ | $-1.06$ |
| | *Ethanol* | | | |
| Active carbon | $\Delta G^*$ kcal mol$^{-1}$ | $\Delta C$ | $\Delta S^*$ cal mol$^{-1}$ K | $\Delta H^*$ kcal mol$^{-1}$ |
| 27 | $-0.49$ | $-2.42$ | $-4.81$ | $-1.89$ |
| 29 | $-0.49$ | $-2.83$ | $-5.62$ | $-2.14$ |
| 33 | $-0.20$ | $-2.82$ | $-5.60$ | $-1.84$ |

of the increasing values from water to ethanol of $-\Delta S^*$ and $-\Delta H^*$ is mutually compensated. For this reason the function $\nu(\Theta, T)$ is essentially universal for the substances studied.

The study of adsorption of mixtures of water and dimethylformamide also indicates the correctness of the accepted conception. This system can be described with a sufficient accuracy on the basis of structure parameters of active carbons obtained from individual isotherms of benzene and by choosing the standard state of water vapours $p_\omega = p_0 \nu$, where $\nu = 1.8$ (see *Zukal* and *Kadlec* [21]).

The Polanyi—Dubinin theory is considered by many authors as empirical because in their opinion the thermodynamic values of adsorbates are loosing physical sense in micropores. The result of the present paper proves that for most adsorbates the Polanyi's conception represents a good approximation to reality since the perturbation entropies and enthalpies are rather small. Thus it proves that $p$, $v$, $T$ relations for these substances in adsorbed state are almost equal to $p$, $v$, $T$ relations in the gas phase.

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