# Adsorption Equilibria of *n*-Heptane on the Molecular Sieve Calsit 5

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The measured equilibrium data of *n*-heptane adsorption on molecular sieve were tested according to the Dubinin and Langmuir equations of adsorption isotherms. The deviations from Langmuir concept were evaluated by means of equilibrium function. The applicability of Dubinin equations was examined graphically. The cause of deviations from Dubinin equations was investigated by using characteristic curves.

The differential isosteric heats of adsorption as well as entropy of adsorption were calculated. The latter was correlated with the translation contribution to gaseous adsorbate entropy.

## Theoretical

The examination of adsorption isotherms of *n*-heptane on molecular sieve (Fig. 1) reveals an apparent shape similarity between them and the I. type of isotherm classification according to Brunauer. This type characterizes the systems in which the concentration of adsorbate on the surface of adsorbent results in a formation of unimolecular layer. The equilibrium in such a system is described by the *Langmuir* adsorption isotherm [1].

The adsorption of molecules on solid surface may be expressed as follows

$$\mathrm{A} + \mathrm{P} \rightleftarrows \mathrm{AP}.$$

Assuming that all adsorption centres are uniform, the equilibrium constant of adsorption is to be defined by the expression

$$K = \frac{a_{\mathrm{AP}}}{a_{\mathrm{P}}\, a_{\mathrm{A}}}\,. \tag{1}$$

Provided the activity coefficients of all components equal one, it holds

$$K = \frac{\Theta}{(1-\Theta)\, p}\,. \tag{2}$$

This equation is noted as Langmuir adsorption isotherm. On substituting for the adsorbed amount and transforming (*2*) into linear form we get

$$\frac{p}{a} = \frac{1}{a_{\mathrm{m}}}\, p + \frac{1}{K\, a_{\mathrm{m}}}. \tag{3}$$

The deviations from the Langmuir adsorption isotherm may be evaluated by using the equilibrium constant [2]. The equilibrium constant of adsorption is thermodynamically defined by the expression

$$-\Delta G^0 = \boldsymbol{RT} \ln K. \tag{4}$$

The equilibrium constant is independent of the degree of covering of adsorption surface. In case the constant calculated according to the equation (*1*) does change with the degree of covering (*Graham* [2] calls it equilibrium function in this event), it indicates that the adsorption system is not ideal. If the adsorption is affected by the interaction of adsorbed molecules, the value of equilibrium function increases with the degree of covering. On the other hand, the inhomogeneity of adsorption surface effects a decrease in the value of equilibrium function with increasing amount of the adsorbate. Another factor which may induce a dependence of the value of equilibrium function thus defined on the amount of adsorbate is the mobility of adsorbate.

The surface heterogeneity may be appreciated on the basis of distribution of the active centres with respect to their energy. The corresponding partition function is to be calculated according to the equation [1, 3]:

$$h(q) = -\left[\frac{\partial a}{\partial q}\right]_T = \frac{1}{\boldsymbol{RT}}\left[\frac{\partial a}{\partial \ln p}\right]_T. \tag{5}$$

The authors of the papers [4, 5] have proved the applicability of Dubinin equations for the adsorption of *n*-alkanes on molecular sieves. They started from the adsorption isotherms proposed by *Dubinin* [6] for adsorbents of the first structural type, hence for vapour adsorption $T \leq T_k$:

$$a = W_0 \varrho \exp\left[-B\left(\frac{T}{\beta}\right)^2\left(\log\frac{p_s}{p}\right)^2\right] \tag{6}$$

and for gas adsorption $T \geq T_k$:

$$a = W_0 \varrho \exp\left[-B\left(\frac{T}{\beta}\right)^2\left(\log\frac{T_r\, p_k}{p}\right)^2\right]. \tag{7}$$

The suitability of Dubinin equations to express the adsorption isotherm of a system can be judged from the plot of experimentally found equilibrium data treated in a way which permits a corroboration of the equations (*6*) and (*7*). In case the experimental data thus expressed do not show a linear course but the characteristic curves

$$\varepsilon = f(V) \tag{8}$$

have a similar shape (*i.e.* they are shifted with respect to the axis of abscissas) or the characteristic curve is invariant with respect to temperature, it indicates that the mathematical formulation of characteristic curve (*8*) suggested by Dubinin does not comprehend the equilibrium in the system under consideration. The determination of characteristic curve involves some difficulties connected with the calculation of the adsorbed phase density [7].

From the thermodynamical point of view the Dubinin equations are limited by the feasibility to express the adsorption potential according to Polanyi

$$\varepsilon = RT \ln \frac{p_s}{p}. \qquad (9)$$

As stated by *Bering* and *Serpinskij* [8], the adsorption potential may be expressed by the Polanyi formula only if $C_s - C_a < 0$, since none but this case involves $\bar{S}_a - S_g < 0$. The physical sense of $C_s$ and $C_a$ is evident from following equations

$$\ln p_s = -\frac{r}{RT} + C_s, \qquad (10)$$

$$\ln p = -\frac{q_{st}}{RT} + C_a. \qquad (11)$$

## Experimental

The properties of materials used were as follows:

*n*-Heptane — $d_{20\,°C} = 0.6838$ g/cm$^3$, $n_D^{20} = 1.3878$, boiling point 98.3°C.

Chromatographic analysis — 99.7 mole % of *n*-heptane, 0.3 mole % of 3-methylhexane.

Calsit 5 — balls with the diameter of 1—2 mm, binder Passan clay (20 weight % with respect to crystalline phase).

Chemical composition in weight percents — 41.8% $SiO_2$, 37.4% $Al_2O_3$, 1.7% $Fe_2O_3$, 16.3% CaO, 0.5% MgO, 2.2% $Na_2O$.

Density of crystal skeleton 2.858 g/cm$^3$, density of particle (pores included) 1.148 g/cm$^3$, crystallographic density (primary pores included) 1.771 g/cm$^3$, bulk density 0.70 g/cm$^3$.

Volume of voids inside crystals 0.215 cm$^3$/g. Volume of secondary pores ($7.5\ \mu m > d > 0.65$ nm) 0.306 cm$^3$/g. Volume of secondary pores ($d > 4.0$ nm) 0.314 cm$^3$/g.

Amount of water adsorbed from air at 25°C and 60% relative humidity 21.0 g/100 g.

The measurements of adsorption equilibria and equipment used have been described in preceding paper [9]. The results of measurement of the adsorption equilibria are given graphically in Fig. 1.

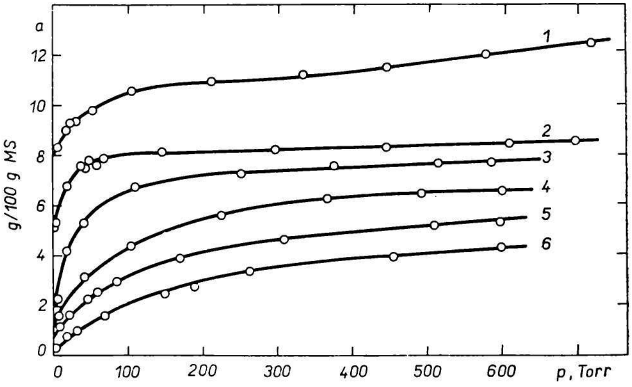

*Fig. 1.* Adsorption isotherms of the system *n*-heptane—Calsit 5.
*1.* 120°C; *2.* 210°C; *3.* 280°C; *4.* 340°C; *5.* 380°C; *6.* 420°C.

## Discussion

The measured equilibrium data treated according to the equation (*3*) are plotted in Fig. 2. It is evident that only the values measured at temperatures between 210—280°C are conform with the Langmuir isotherm for the investigated pressure range. The results of measurements at 340, 380, and 420°C show deviations in the region of low partial pressures of adsorbate ($p < 150$ Torr). On the other hand, the deviations from the Langmuir adsorption isotherm are to be observed only in the region of higher partial pressures ($p > 500$ Torr) at 120°C.

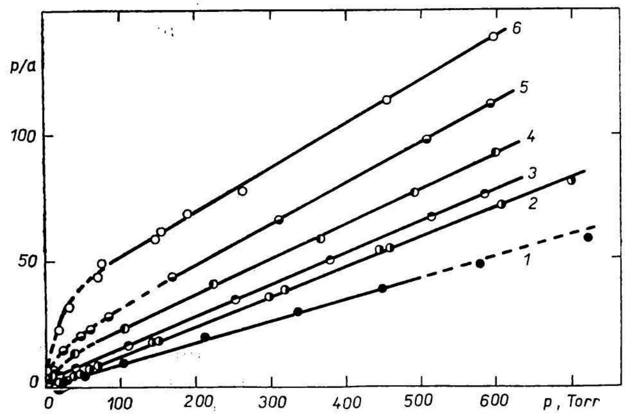

*Fig. 2.* Experimental equilibrium data in coordinates of the Langmuir isotherm transformed into linear form.
*1.* 120°C; *2.* 210°C; *3.* 280°C; *4.* 340°C; *5.* 380°C; *6.* 420°C.

It results from these facts that the equilibrium in the system *n*-heptane—molecular sieve 5 A cannot be expressed by the Langmuir isotherm in a physically justified manner. The cause may be due to the inhomogeneity of the adsorption surface on

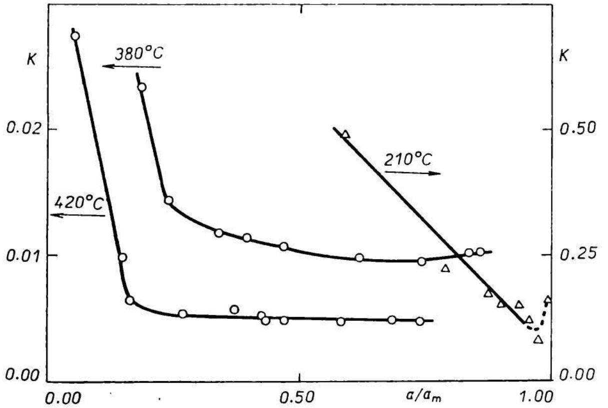

*Fig. 3.* Variation of the equilibrium function with the degree of covering.

molecular sieves, the interactions of molecules adsorbed on sieves or to the simultaneous effect of these factors.

In order to estimate these influences, the values of the equilibrium function defined by the equation (*1*) have been calculated and their dependence on the degree of covering of adsorbent surface has been expressed graphically (Fig. 3). The value of $a_m$ has been determined by using the slope of linear sections of isotherms drawn in Fig. 2.

It is not possible to draw conclusions on the disagreement between the experimental results and Langmuir model from the relationships given in Fig. 3. Without doubt, the heterogeneity of adsorption surface and mobility of adsorbate play an important role in this case.

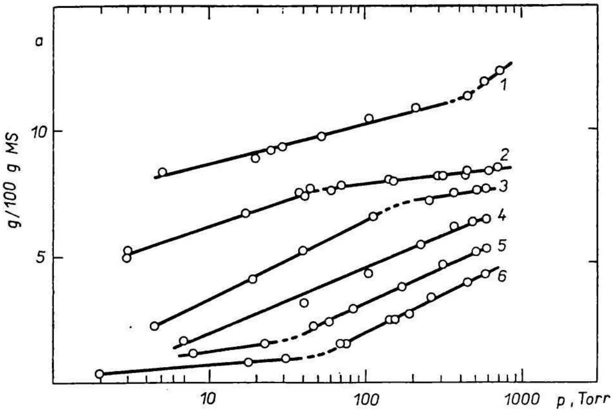

*Fig. 4.* Experimental equilibrium data in semilogarithmic coordinates.
*1.* 120°C; *2.* 210°C; *3.* 280°C; *4.* 340°C; *5.* 380°C; *6.* 420°C.

To appreciate the heterogeneity of adsorption surface, the values found experimentally have been plotted in coordinate system $a = \mathrm{f}(\log p)$ (Fig. 4) and the subsequent relationships have been deduced from the slopes of the linear sections of isotherms

$$h(q) \leq 0.43 \frac{1}{RT}, \tag{12}$$

$$0.70 \frac{1}{RT} \leq h(q) \leq 1.30 \frac{1}{RT}, \tag{13}$$

$$h(q) = 2.04 \frac{1}{RT}. \tag{14}$$

The expression (*12*) has been ascertained for $\Theta < 0.25$ and $\Theta > 0.90$ (except the isotherm at 120°C). The relationship (*13*) holds for $0.25 < \Theta < 0.90$ (for the isotherm at 120°C and $\Theta = 0.95$). The equation (*14*) has been deduced from the isotherm at 120°C for $\Theta > 0.95$.

The relationships (*12—14*) may indicate a discontinuity of partition function which should give evidence for the inhomogeneity of adsorption surface. The isotherm corresponding to 120°C escapes a universal appreciation what is likely to be due to capillary condensation in secondary pores of the adsorbent.

The mobility of adsorbate may be estimated by comparing the entropy change due to adsorption with the translation contribution to the entropy of gaseous adsorbate. This correlation can be expressed quantitatively provided the contribution of internal entropy does not change in the process of adsorption.

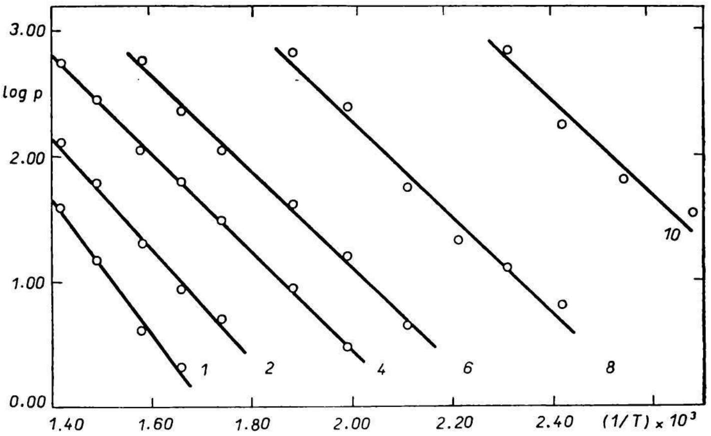

*Fig. 5.* Experimental equilibrium data in coordinates of the isosters transformed into linear form.
*1.* 1 g/100 g; *2.* 2 g/100 g; *4.* 4 g/100 g; *6.* 6 g/100 g; *8.* 8 g/100 g; *10.* 10 g/100 g.

By using the linear isosters (Fig. 5), the differential isosteric heats of adsorption have been calculated. The entropy change due to adsorption has been computed from the equation

$$S_g - \bar{S}_a = \frac{q_{st}}{T}. \qquad (15)$$

The translation contribution to entropy has been calculated according to the Sackur—Tetrode equation [10]:

$$\left(\frac{S_g}{2.3026\,\boldsymbol{R}}\right)_{tr} = \frac{3}{2}\log M + \frac{5}{2}\log T - \log p + 2.37483. \qquad (16)$$

The results of calculation for three temperatures are presented in Table 1.

It follows from Table 1 that the differential isosteric heat of adsorption decreases with increasing amount of the adsorbate. The entropy decrease in adsorption reaches about 2/3 of the translation contribution to the entropy of the gas which is in equilibrium with adsorbate. This corresponds to the loss of two degrees of freedom of translation motion. The molecules adsorbed behave as an one-dimensional gas what may be interpreted as a consequence of the crystalline structure of molecular sieves [11].

The verification of the Dubinin adsorption isotherms for the system *n*-heptane—molecular sieve 5 A has been performed on the basis of the relationships (*6*) and (*7*).

*Table 1*

| $t$ [°C] | $a$ [g/100 g] | $q_\mathrm{st}$ [kcal mole$^{-1}$] | $S_\mathrm{g} - \bar{S}_\mathrm{a}$ [cal mole$^{-1}$] | $(S_\mathrm{g})_\mathrm{tr}$ [cal mole$^{-1}$] | $\dfrac{S_\mathrm{g} - \bar{S}_\mathrm{a}}{(S_\mathrm{g})_\mathrm{tr}}$ |
|---|---|---|---|---|---|
| 300 | 2.0 | 20.5 | 35.8 | 52.7 | 0.68 |
| | 4.0 | 18.1 | 31.6 | 48.9 | 0.65 |
| | 6.0 | 17.6 | 30.7 | 46.0 | 0.67 |
| 350 | 1.0 | 24.1 | 38.7 | 53.5 | 0.72 |
| | 2.0 | 20.5 | 33.0 | 50.3 | 0.66 |
| | 4.0 | 18.1 | 29.1 | 46.9 | 0.62 |
| | 6.0 | 17.6 | 28.3 | 44.0 | 0.64 |
| 400 | 1.0 | 24.1 | 35.8 | 51.1 | 0.70 |
| | 2.0 | 20.5 | 30.5 | 48.3 | 0.63 |
| | 4.0 | 18.1 | 26.9 | 45.2 | 0.60 |

As evident in Fig. 6, there are distinct bends on some isotherms which prevent their expressing by a single equation of the Dubinin form. It is therefore useful to judge the validity of basic conditions from which Dubinin started in deducing his equations.

The values given in Table 2 show that the value of the difference $C_\mathrm{s} - C_\mathrm{a}$ is negative in the region studied. That is a sufficient thermodynamical condition for expressing the adsorption potential by the Polanyi relationship which has been used for the deduction of the Dubinin equation. However, the fulfilment of this condition is still not a sufficient justification for the applicability of the Dubinin adsorption isotherm to the system under investigation.

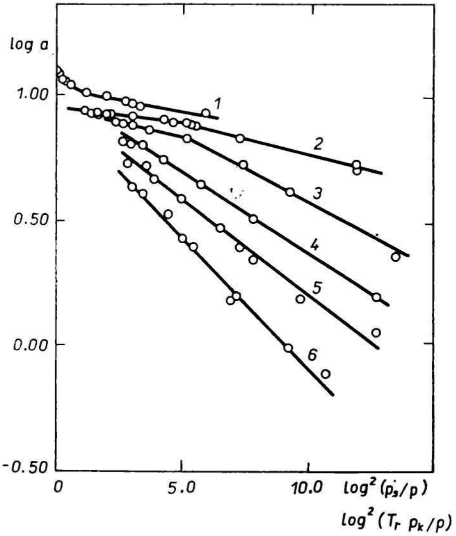

*Fig. 6.* Experimental equilibrium data in coordinates of the Dubinin adsorption isotherms transformed into linear form.
*1.* 120°C; *2.* 210°C; *3.* 280°C; *4.* 340°C; *5.* 380°C; *6.* 420°C.

*Table 2*

| $a$ [g/100 g] | 1.0 | 2.0 | 4.0 | 6.0 | 8.0 | 10.0 | — | — |
|---|---|---|---|---|---|---|---|---|
| $C_a$ | 3.99 | 3.63 | 3.62 | 3.84 | 4.02 | 5.03 | $C_s$ | 3.55 |

By using the equilibrium data, the coordinates of points on the characteristic curves $\varepsilon = f(V)$ have been calculated for observed temperatures. The density of adsorbed phase has been determined by the method described in the paper [6]. The characteristic curves thus obtained are given in Fig. 7. The greatest irregularity is to be observed in the characteristic curves corresponding to 210 and 280°C. The characteristic curves determined for the temperatures exceeding the critical temperature of adsorbate are similar in shape and shifted with respect to the axis of abscissas. The density of adsorbed phase does, therefore, change with temperature provided that $t > t_k$. The points of characteristic curves for $t > t_k$ have been calculated by evaluating the dependence of the density of adsorbed phase on temperature by the method proposed by *Dubinin* [6] for $t\ \varepsilon < t_V, t_k >$. Therefore, the density of adsorbed phase above the boiling point of adsorbate may be calculated according to the Benson equation

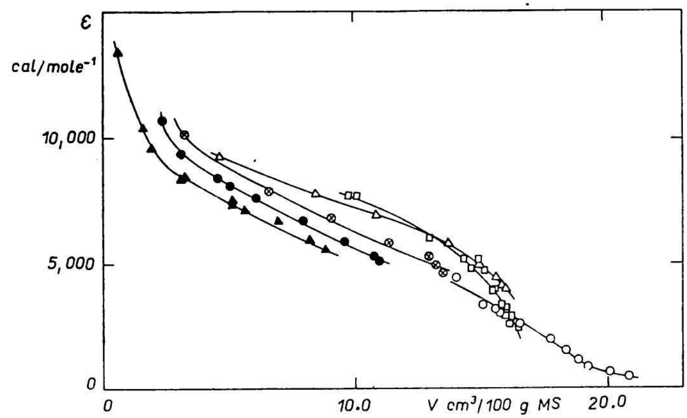

*Fig. 7.* Characteristic curves. The volume of adsorbed phase calculated according to the paper [6].
○ 120°C; □ 210°C; △ 280°C; ⊗ 340°C;
● 380°C; ▲ 420°C.

$$\varrho = \varrho_V - \frac{\varrho_V - \varrho_k}{t_k - t_V}(t - t_V) . \qquad (17)$$

The points of characteristic curves thus calculated for $t > t_k$ are plotted in Fig. 8. The comparison between Fig. 7 and Fig. 8 shows that the characteristic curves for singular temperatures approach together for $t > t_k$ provided the density of adsorbed

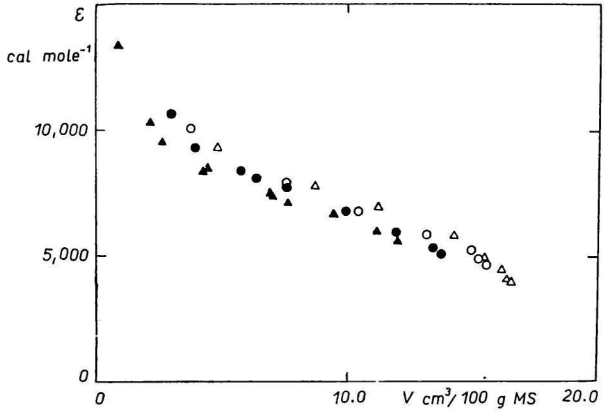

*Fig. 8.* Points of the characteristic curves for $t > t_k$. The volume of adsorbed phase calculated by means of the equation (*17*).
△ 280°C; ○ 340°C; ● 380°C; ▲ 420°C.

phase changes with temperature. It follows from this comparison that the density of adsorbed phase changes with temperature for $t > t_k$ more significantly than the equation (*17*) postulates. The idea of Dubinin assuming that the density of adsorbed phase does not change with temperature for $t > t_k$ is only a rough approximation for the system studied.

Therefore, the equation (*17*) is more convenient if the potential theory is used to convert the equilibrium data corresponding to a definite temperature to the values corresponding to another temperature provided $t > t_k$.

## Symbols

| | |
|---|---|
| $a$ | amount of the substance adsorbed on molecular sieve, g/100 g |
| $a_A$ | activity of the free molecules of adsorbate |
| $a_{AP}$ | activity of the covered adsorption centres |
| $a_P$ | activity of the free adsorption centres |
| $a_m$ | amount of the substance adsorbed in unimolecular layer on molecular sieve, g/100 g |
| $b$ | constant of the van der Waals equation, cm$^3$ g$^{-1}$ |
| A | free molecules of the adsorbate |
| AP | covered adsorption centres |
| $B$ | constant in the Dubinin equations |
| $C_a$ | constant in the equation (*11*) |
| $C_s$ | constant in the equation (*10*) |
| $d$ | diameter of the pores |
| $\Delta G^0$ | change of standard free enthalpy |
| $h(q)$ | partition function of the adsorption centres in the equation (*5*) |
| $\boldsymbol{K}$ | equilibrium constant in the equation (*4*) |
| $K$ | equilibrium function |
| $P$ | free adsorption centres |
| $M$ | molecular weight of the adsorbate |
| $p$ | pressure of the adsorbate, Torr |
| $p_s$ | vapour pressure of adsorbate, Torr |

| | |
|---|---|
| $p_k$ | critical pressure of adsorbate, Torr |
| $q$ | energy of the adsorption centres |
| $q_{st}$ | differential isosteric heat of adsorption, kcal mole$^{-1}$ |
| $r$ | heat of evaporation |
| $\mathbf{R}$ | gas constant, cal deg$^{-1}$ mole$^{-1}$ |
| $S_g$ | molar entropy of the gaseous adsorbate, cal mole$^{-1}$ |
| $\overline{S}_a$ | partial molar entropy of the adsorbate on adsorbens, cal mole$^{-1}$ |
| $(S_g)_{tr}$ | translation contribution to the molar entropy of gas, cal mole$^{-1}$ |
| $t$ | temperature of adsorption, °C |
| $t_v$ | boiling point of the adsorbate, °C |
| $t_k$ | critical temperature of the adsorbate, °C |
| $T$ | temperature of adsorption, °K |
| $T_k$ | critical temperature of adsorbate, °K |
| $T_r = \frac{T}{T_k}$ | reduced temperature |
| $V$ | volume of the adsorbed phase, cm$^3$/1000 g of molecular sieve |
| $W_0$ | constant in the equations (*6*) and (*7*) |
| $\beta$ | constant in the equations (*6*) and (*7*) |
| $\varepsilon$ | adsorption potential, cal mole$^{-1}$ |
| $\Theta = \frac{a}{a_m}$ | degree of the covering of adsorption surface |
| $\varrho$ | density of the adsorbed phase, g cm$^{-3}$ |
| $\varrho_v$ | density of the liquid adsorbate at boiling point, g cm$^{-3}$ |
| $\varrho_k = \frac{1}{b}$ | density of the adsorbed phase at critical temperature, g cm$^{-3}$ |

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