Thermodynamic behavior of adsorption systems with porous adsorbents along the curves describing equilibrium between bulk phases of an adsorptive

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The thermodynamic aspects of adsorption equilibrium in systems with crystalline, liquid, and dense gas phases have been considered. The heats of phase transition and corresponding directions of mass transfer from the adsorbed phase into crystalline and liquid phases at different temperatures have been determined. The general equilibrium diagram in the coordinates $\ln p - T^{-1}$ has been given with indication of the equilibrium lines of three-phase systems and characteristic points on the isosteres of adsorption, *viz.*, the Gurvitsch and quasicritical points.

Key words: thermodynamics of three-phase equilibrium of adsorption systems; differential heats of adsorption; isosteres; quasicritical temperature.

Despite recent advances in the study of adsorption of gases and vapors, there is a need to properly define some fundamental problems such as: the limiting temperature of positive physical adsorption at high temperatures, as well as the state of an adsorbate and phase transitions near absolute zero. The concept of adsorption systems at saturation (ASS), which allows one to reveal specific behavior of an adsorbate near curves describing equilibrium and near points characterizing the bulk phases, is therefore a convenient subject of investigation.

An ASS is formed if the equilibrium vapor pressure over the adsorbate is equal to that of vapor over the individual bulk liquid or bulk solid at the same temperature. The concept of ASS implies that three phases can coexist, an adsorbed substance, a pure bulk phase as liquid or solid, and a gas (vapor). In this system, temperature is the only thermodynamic degree of freedom. When a temperature is chosen, a definite state and definite physical properties of the adsorbate are established that are thermodynamically related to the properties of the corresponding bulk phases. By exploring the points along the "saturation curve" at various temperatures, it is possible to estimate the interaction between the coexisting phases. In most cases a strong thermodynamic treatment of this interaction can be offered, one that relies on the information on the properties of the adsorbate obtained from isotherms and heats of adsorption as well as from the thermodynamic properties of the equilibrated bulk phases. To examine calculations experimentally, isotherms of adsorption along the saturation curves can be measured. In addition, the heat capacities of the ASS can be determined, because transition of the compound between the phases is accompanied by the additional changes in the heat capacity of the system.

In this work, an attempt is made to describe the properties of the ASS for porous sorbents at high and low temperatures. The possibility is demonstrated to construct a unified phase diagram for a substance adsorbed on a surface or in pores of adsorbents over a wide range of temperatures and pressures.

Experimental

The experimental data used in this work are taken from earlier measurements of the isotherm of adsorption along the saturation curves vapor—liquid[1] and vapor—solid[2] and from reported values of the heats of adsorption[3] and heat capacity of ASS.[4–6] Results illustrating adsorption at zero excess values[7,8] and adsorption of compressed liquids[9] are also included.

Results and Discussion

Thermodynamics of adsorption systems at saturation. Consider an adsorption system containing one nonvolatile solid adsorbent and a one-component volatile adsorptive. Since the amount of gas adsorbed (*a*) is a function of pressure (*p*) and temperature (*T*), one finds that

$$\frac{dp}{dT} = \left(\frac{\partial p}{\partial a}\right)_T \cdot \frac{da}{dT} + \left(\frac{\partial p}{\partial T}\right)_a . \qquad (1)$$

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† Deceased.

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For the adsorption system lying on the line describing equilibrium between bulk phases of the adsorptive, one degree of freedom vanishes, because in this case $p_s = f(T)$. Throughout the work, subscript "s" indicates that the variables refer to the equilibrium lines which describe the state of saturation.

$$\frac{da_s}{dT} = \left[\frac{dp_s}{dT} - \left(\frac{\partial p_s}{\partial T}\right)_a\right] \Big/ \left(\frac{\partial p}{\partial a_s}\right)_T \qquad (2)$$

This equation serves to analyze the values of adsorption as a function of temperature along the equilibrium line.[10] The denominator in Eq. (2) represents a reciprocal slope of the isotherm describing the absolute rather than the excessive adsorption at $a = a_s$. Since the denominator is positive, the sign of the derivative da_s/dT is determined by the sign of the numerator in Eq. (2). Consider, first, transition of an adsorptive from phase *1* to phase *2* and adsorption from phase *1*. From general considerations, it follows that

$$\begin{aligned} \frac{dp_s}{dT} &= \frac{H^{(1)} - H^{(2)}}{T(V^{(1)} - V^{(2)})} = \frac{Q^{ph}}{T(V^{(1)} - V^{(2)})}, \\ \left(\frac{\partial p}{\partial T}\right)_a &= \frac{H^{(1)} - \bar{H}^a}{T(V^{(1)} - \bar{V}^a)} = \frac{Q^a}{T(V^{(1)} - \bar{V}^a)}, \end{aligned} \qquad (3)$$

where $H^{(i)}$ is the molar enthalpy for phase *i*; Q^{ph} is the heat of the phase change 1→2; $V^{(i)}$ is the molar volume of phase *i*; Q^a is the isosteric heat of adsorption from phase *1*; $\bar{H}^a$ and $\bar{V}^a$ are the partial molar enthalpy and the volume of the adsorbate, respectively. Substituting Eq. (3) into Eq. (2) gives

$$\frac{da_s}{dT} = \left[\frac{Q^{ph}}{T(V^{(1)} - V^{(2)})} - \frac{Q^a}{T(V^{(1)} - \bar{V}^a)}\right]\left(\frac{\partial a_s}{\partial p}\right)_T. \qquad (4)$$

Specify equilibrium conditions. Let phase *1* be vapor, phase *2* — bulk crystalline adsorptive, whereas the adsorbed phase is an adsorbate penetrating into the hole pore volume. Therefore, $T < T^{tr}$ and $p_s < p_s^{tr}$ where superscript "tr" is used to denote the triple point of the adsorptive. Correspondingly,

$$\frac{da_s}{dT} = \frac{Q^{cr} - Q^a}{TV^{(1)}} \cdot \left(\frac{\partial a_s}{\partial p}\right)_T. \qquad (5)$$

By analyzing typical plots of heats of adsorption Q^a against values of relative pressure p/p_s it can be easily recognized that the value of Q^a near $p/p_s = 1$ is ordinarily greater than the heat of condensation of liquid Q^{lq}, but lower than that of crystal Q^{cr}. Eq. (5) also predicts that as the temperature increases the amount of substance adsorbed along the vapor—crystal equilibrium line increases, and it decreases with decreasing temperature. Hence, as the temperature decreases the adsorbed substance tends to "leave" the adsorption field and form the bulk crystalline phase outside the field.[10] The onset of this transition is associated with $T \le T^{tr}$. Formation of the bulk crystalline phase induced by reduction in temperature is supported by X-ray investigations.[2]

The transition of a substance from the adsorbed phase to the condensed bulk phase *2*, which can be either liquid or crystalline, requires a change in the heat capacity (c) of the adsorbate[10] by an amount

$$\Delta c_s = \left(Q^{ph} - Q^a\right) \cdot \frac{da_s}{dT}, \qquad (6)$$

where $(Q^{ph} - Q^a)$ is the heat of the transition of the substance from phase *2* into the adsorbed phase. If Eqs. (5) and (6) are combined, it follows that

$$\Delta c_s = \frac{(Q^{ph} - Q^a)^2}{TV^{(1)}} \cdot \left(\frac{\partial a_s}{\partial p}\right)_T. \qquad (7)$$

Eq. (7) indicates that the contribution to the heat capacity of the adsorbate is always positive and independent of the sign of the heat of the phase transition $(Q^{ph} - Q^a)$.

The extent to which migration of the adsorbate from the adsorption field and crystallization outside the field in response to the decrease in temperature is possible, remains to be further explored. Indeed, neither theoretical nor experimental studies describe the pattern of influence of temperature on the heats of adsorption and the heats of crystallization at $T \ll T^{tr}$. It appears that these two types of heats approach one another with the decreasing temperature while the derivative da_s/dT from Eq. (5) decreases. Whether this derivative attains the zero value under these conditions, is yet to be explained.

The behavior of porous ASS along the equilibrium line liquid—vapor is clearly quite different from that shown by these systems along the equilibrium line crystal—vapor on the interface between the condensed phases. When a porous ASS is cooled, a highly dispersed crystalline phase can ultimately leave the adsorbent pores to form large crystals in the wide pores or on the external surface of the adsorbent. Accordingly, no "interface" between the crystals and the remaining adsorbed phase could be distinguished. In this case, the excessive liquid phase completely wets the surface of the porous adsorbent, and a continuous transition from the adsorbed phase to the bulk liquid occurs for mesoporous and macroporous adsorbents. By contrast, sharp discontinuities in the physical and thermodynamic properties on the interface between adsorbate and liquid phase were observed for zeolites.

In the region near saturation, the dependence of the heats of adsorption on the amounts adsorbed is described by the curves with maxima for macro- and mesoporous adsorbents,[3] whereas for zeolites the values of Q^a fall rapidly with the filling of cavities. Based on the experimental data,[11] the differences in the shape of the curves describing the dependence of a_s on tempera-

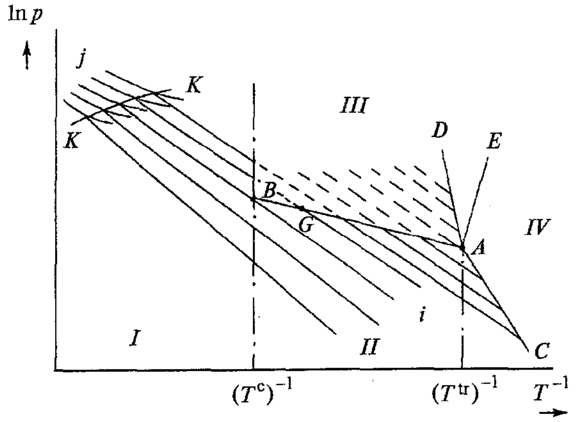

Fig. 1. Schematic representation of the diagram expressing the equilibrium relations between the adsorbed phase and bulk phases of the adsorptive:
I — gas; *II* — vapor; *III* — liquid; *IV* — crystal. Equilibrium lines: *AB*, liquid—vapor; *AC*, crystal—vapor; *AD*, crystal—liquid; *AE*, ice—water. *KK* is the line describing a quasicritical state of the adsorbate; *i* — family of isosteres, and *j* — family of isochores.

ture, can be primerily accounted for by variations in the mean density of adsorbate ($\bar{\rho}_s^a$):

$$\bar{\rho}_s^a = \frac{a_s}{W}, \tag{8}$$

where W is the pore volume of the adsorbent. Assuming that W is nearly independent of temperature, it is found that

$$\frac{da_s}{d_T} = a_s\frac{d\ln\bar{\rho}_s^a}{dT}. \tag{9}$$

At the same time, examination of the plots of ln*p* *vs.* T^{-1} (Fig. 1) shows an isostere corresponding to a lower adsorption cuts the line of equilibrium, liquid—vapor, at a higher temperature. Hence, the value a_s decreases with an increase in temperature. Assuming that Eq. (5) is valid under these conditions, it is found that at $V^{(1)} \gg V^{(2)}$ and $V^{(1)} \gg V^a$

$$\frac{da_s}{dT} = \frac{Q^{lq} - Q^a_{eff}}{TV^{(1)}}\cdot\left(\frac{\partial a_s}{\partial p}\right)_T, \tag{10}$$

where $Q^a{}_{eff}$ is the effective isosteric heat of adsorption that can be significantly different from the heat of condensation of liquid Q^{lq}.

Comparison of theoretical and experimental data. Adsorption isotherms of benzene vapor (T^{tr} = 281 K) were measured at various temperatures over the region $T < T^{tr}$ on a KSK-2 silica gel sample (S_{BET} = 340 m^2 g^{-1}, v = 0.93 mL g^{-1}, d = 10 nm). On the basis of the data collected in Fig. 2, *a* one may consider how strongly a reduction in the temperature of adsorption can influence the shape of isotherms and the amount of limiting adsorption. For adsorbents with a uniform pore size distribution, the latter quantity can be read off with an adequate accuracy from the intercept of the smooth line portion of the isotherm with the axis of ordinates at p/p_s = 1 (Fig. 2, *b*).

By comparing the isotherms depicted in Fig. 2, *b* it is evident that at temperatures 240—260 K, the loop of hysteresis disappears and an S-type isotherm transforms to give a Langmuir-type curve. The amount of the limiting adsorption decreases more than twofold. A sharp downward turn of the curve, which represents a_s values plotted *vs.* *T*, is followed by a gradual decline of adsorption that approaches apparently some limiting value, close to the volume of the unimolecular layer.

Separation of the bulk crystalline phase on cooling the system silica—benzene was supported by the direct

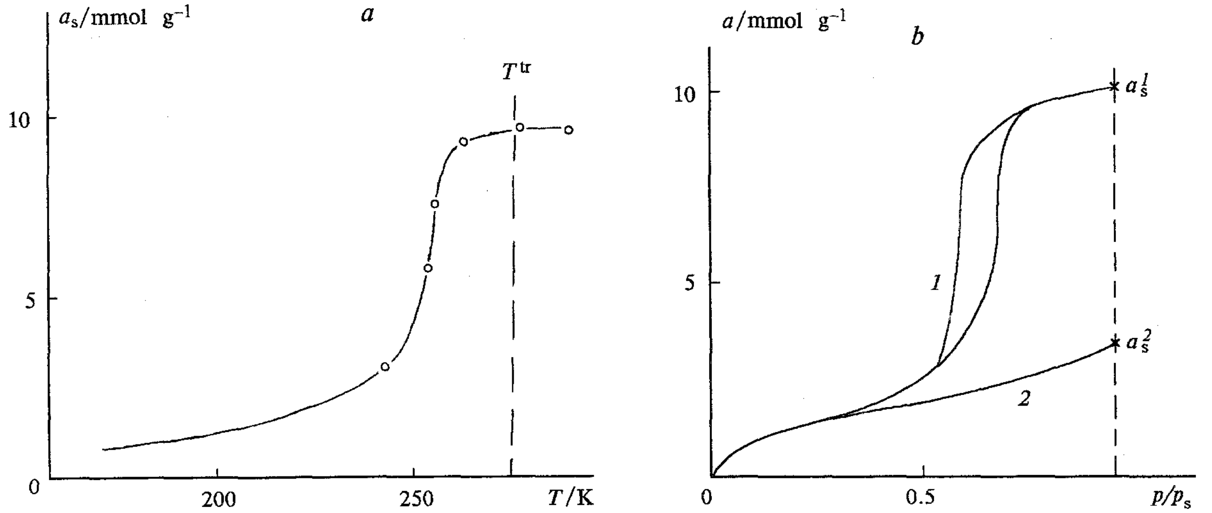

Fig. 2. *a*. Limiting amount of adsorption a_s of benzene on KSK-2 silica gel as a function of temperature. Points — experimental data. The curve is calculated from the adsorption isotherms measured at different temperatures by intersecting the relevant adsorption isosteres with the equilibrium line crystal—vapor. *b*. Adsorption isotherms of benzene on KSK-2 silica gel at 293.3 (*1*) and 242.7 K (*2*).

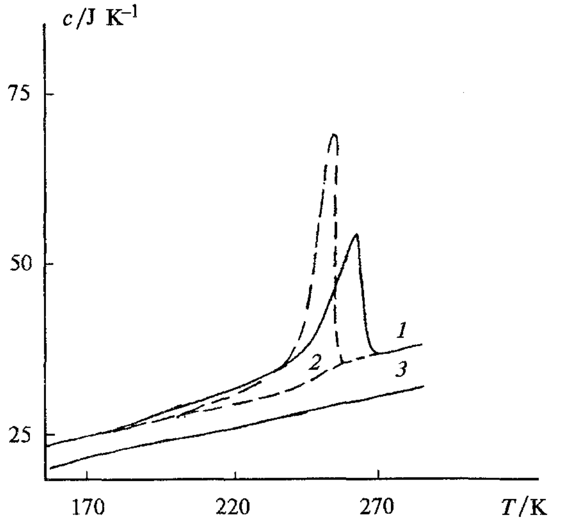

Fig. 3. Experimentally measured heat capacity (c) of benzene adsorbed on KSK-2 silica gel as a function of temperature (*1*) and the dependence on temperature of the contribution to the heat capacity calculated from the heat of transition of benzene from the crystalline into the adsorbed state (*2*). Curve *3* refers to the heat capacity of the calorimetric ampule with pure silica gel in the absence of adsorbed benzene.

calorimetric measurements of the heat capacity of this system.[4] Figure 3 demonstrates experimentally measured heat capacity of the calorimetric ampule with silica gel and adsorbed benzene as a function of temperature (curve *3*). Figure 3 indicates that adsorption of benzene leads to the appearance of the maximum on the plot of c *vs.* T. The same figure shows additional contributions to the heat capacity of the adsorbed benzene (curve *2*) calculated from Eq. (6). The calculations were based on the dependence of a_s on temperature found by graphically differentiating the curve in Fig. 2, *b* and on the reported[3] heat of adsorption of benzene on KSK-2 silica gel. The calculated and experimentally determined curves are different both in the shape of the peak and in the position of the peak. It is likely that these differences stem from an irregular distribution of temperatures inside the sample, caused by the use of an adiabatic calorimeter with constant heating.[5] In addition, phase changes can be retarded by the transfer of the material through the gaseous phase containing the inert gas. At the same time, the values on the calculated curve refer to the strong equilibrium conditions. However, the areas under the maxima, characteristic of the integral change of a_s over the wide range of temperatures, are independent of the heating rate and of the rate of the mass-transfer processes. A comparison of the areas shows that they are equal within the experimental errors. Similar results are obtained for the systems silica gel—water, silica gel—dioxane, silica gel—n-hexane.[5,6]

In the region $T > T^{tr}$, the system silica gel—carbon dioxide is explored in the most extensive way. Earlier,[11] isotherms of CO_2 adsorption on silica gel with a uniform pore-size distribution (S_{BET} = 540 m^2 g^{-1}, v = 0.5 mL g^{-1}, d = 2 nm) were reported for the temperature range 188—313 K, including T^{tr} (216.6 K) and the critical (T^c) point (304.2 K). The isotherm measured near the critical point is depicted in Fig. 4, *b*, while Fig. 4, *a* shows the limiting value of adsorption a_s as a function of temperature. For the region $T < T^{tr}$ rapidly falling values of a_s were observed, implying formation of a bulk crystalline phase of CO_2, analogous to that found in the system benzene—silica gel. As temperature increases above T^{tr} a decreasing value of a_s was also recorded, associated with variations in the density of the adsorbate. Figure 4, *a* shows the curve calculated from Eq. (8) with the assumption that the pore volume is completely filled by the adsorbate and that the density

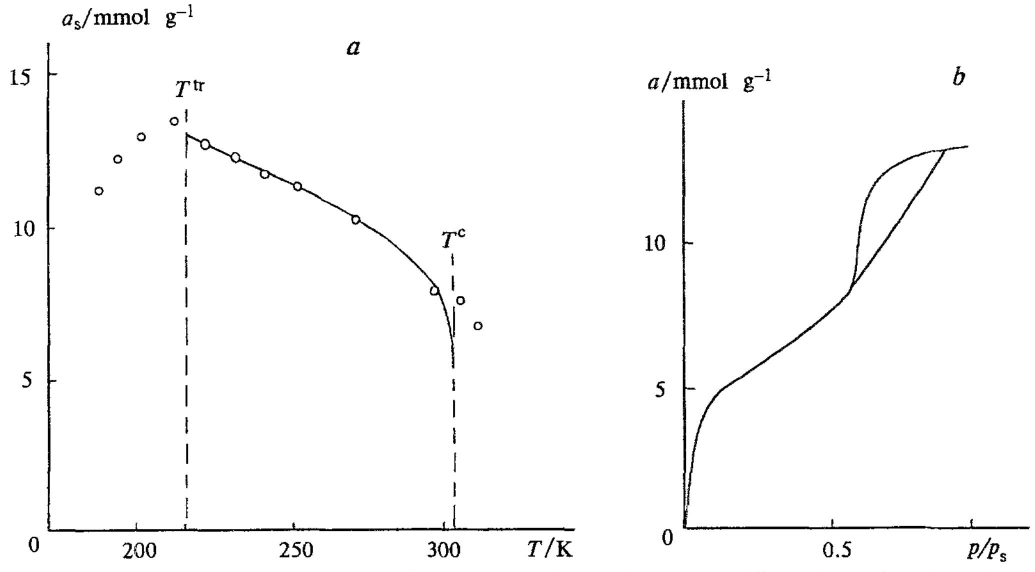

Fig. 4. *a*. Limiting amount of adsorption a_s of carbon dioxide on microporous silica gel as a function of temperature. *b*. Adsorption isotherm of CO_2 on microporous silica gel at T = 211.8 K.

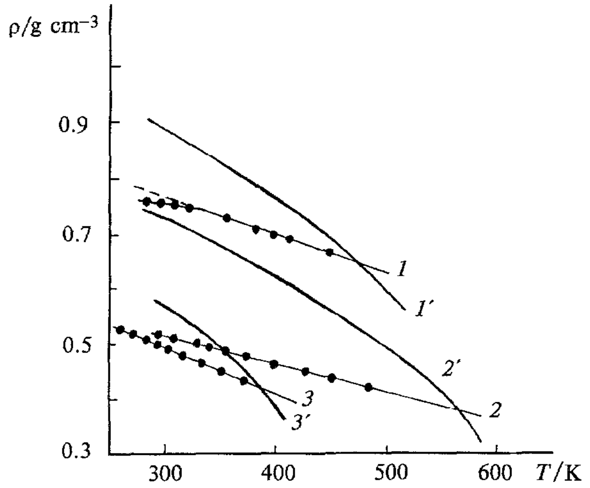

Fig. 5. Effect of temperature on the mean density of adsorbate in the cavities of NaX zeolite (curves *1—3*) and density of liquids (curves *1′—3′*) along the equilibrium line liquid—vapor; *1,1′* — benzene; *2,2′* — *n*-nonane; *3,3′* — *n*-butane.

of the adsorbate is equal to that of the bulk liquid phase along the equilibrium line at the appropriate temperature. The agreement between the theoretical curve and the experimental data is evident. Typically, in the vicinity of the critical point, a_s decreases less rapidly with T than in the case of bulk liquid CO_2.

Temperature dependence of the limiting value of adsorption on the NaX zeolite is linear over a wide range of temperatures for a number of adsorbates, while the values of a_s show little variations in the neighborhood of T^{tr} and T^c (see Fig. 4, *a*). The reason is that the heat of adsorption always exceeds not only the heat of vaporization of the liquid adsorptive but also the heat of sublimation. As a result, unlike the situation in the systems with silica gels, the limiting value of adsorption in the systems zeolite—adsorbate decreases gradually over the entire temperature range studied.

It was shown that at temperatures far from the critical points, the density of the adsorbate ρ_s^a (see Eq. (8)) is typically lower than that of the bulk liquid suggesting negative values for excessive adsorption of the liquid. The curves describing the densities of the adsorbate and liqiud as the function of temperature intersect in the region of the normalized temperature $\tau = T/T^c = 0.88$ (Fig. 5). For this point one has $\rho^{lq} = \bar{\rho}^a$, and the value of the excessive adsorption of the liquid is equal to zero, while it attains positive values at higher temperatures. This implies that the frequently used Gurvitsch rule ($\rho^{lq} = \bar{\rho}^a$) is obeyed, strictly speaking, only at the single temperature (Gurvitsch point). It appears that the excessive adsorption of vapor along the line describing equilibrium vapor—liquid is positive at any temperature.

The state and the forms of the adsorbed substance. The data discussed above serve to qualitatively characterize a common state of the adsorbate in porous sorbents and phase changes in the adsorbed substance. The adsorbed material can form condensed capillary liquid or an adsorbed layer that covers the surface of the adsorbent or fills the cavities of zeolite.

Condensed capillary liquid undergoes the phase changes analogous to those found in bulk liquid. In particular, it forms crystalline phase, but contrary to bulk liquid this transition can occur over a wide temperature range. The critical point in the neighborhood of T^c of the pure bulk liquid can be expected for the condensed capillary adsorbate.

Thermodynamic properties of the adsorbate that covers the surface of the sorbent or fills the cavities of zeolites should be substantially different from those of the bulk liquid. Under these conditions, the heat of adsorption as a rule exceeds the heat of sublimation and on cooling the adsorbate does not form a conventional bulk crystalline phase and accordingly cannot be characterized by the "normal" critical point. Following accurately the definition of the critical point above which differences in the properties of the coexisting phases disappear, we have to admit that, strictly speaking, the critical point for the adsorbed substance cannot exist at all. Indeed, the presence of the adsorption field modifies in any case structural and other properties of the adsorbate. We may, however, introduce a more narrow definition of the critical point as the value of the parameter of state describing the system in which the densities of the coexisting phases coincide. The existence of the "quasicritical points" for adsorbate has already been reported.[7]

The quasicritical points of the adsorbate are defined as intersections of the isosteres of adsorption with the corresponding isochores (or isopycnes) of a real gas. Each isochore is therefore characterized by its own quasicritical point. This does not mean, however, that

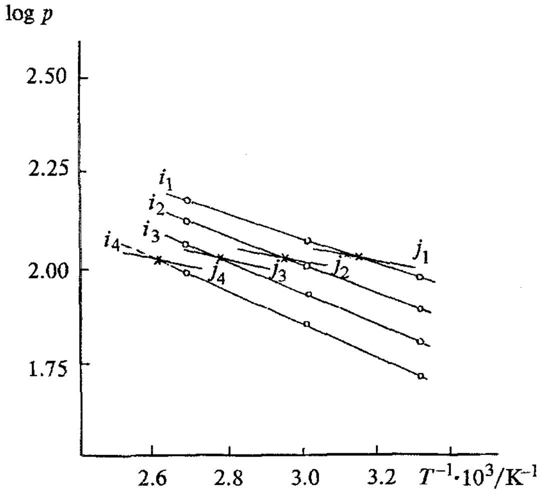

Fig. 6. Intersection of adsorption isosteres (*i*, a = const) and isochores of adsorptive (*j*, ρ = const) for the system nitrogen—NaA zeolite: i_1 = 4.80, i_2 = 4.60, i_3 = 4.40, i_4 = 4.20 mmole g^{-1}; j_1 = 0.585, j_2 = 0.560, j_3 = 0.536, j_4 = 0.512 g cm^{-3}.

each quasicritical point is actually attainable. Since the densities of adsorbate and gas coincide, excessive adsorption at the quasicritical point is equal to zero. A series of quasicritical points form a zero isotherm of excessive adsorption ($\Gamma^a = 0$). The position of quasicritical points was evaluated experimentally for a number of systems, including nitrogen—NaA zeolite (Fig. 6).[8]

When there are only isosteres of adsorption measured in the field of lower pressures, a combined solution of the linear equation of isostere and the equation of state for real gas with multiple parameters can be found to evaluate coordinates for the relevant quasicritical points.

Since the experimentally determined isosteres and isopycnes intercept at the parameters corresponding to the "supercritical states" rather than approach each other, the excessive adsorption is negative.

Although the adsorption phenomena occurring along the equilibrium lines liquid—crystals have not so far been investigated, some features characterizing adsorption under these conditions can nevertheless be predicted currently.

A two-component system with three phases in which adsorbate, liquid adsorptive and crystalline adsorptive coexist can be at equilibrium at any temperature provided that an equilibrium pressure exceeds the pressure of vapor saturated at this temperature. When, however, compressibility factors for the vapor and liquid are known, one can use the Pointing relation, $\mathrm{d}p_s = (V^{lq}/V^{vp})\mathrm{d}p$, to find readily the pressure of the saturated vapor corresponding to that of the compressed liquid. Such a system can be represented as liquid under the hydrostatic pressure exerted by a semipermeable piston chosen to be "transparent" to vapor. Vapor above the piston is expected to be saturated in this system.

Adsorption of the compressed liquids such as water and benzene was investigated experimentally in the presence of NaX zeolite at temperatures ranging from 20 to 100 °C under hydrostatic pressures p, varying from p_s to 100 MPa.[9] The experiments indicated that on the isosteres of adsorption measured for the compressed liquid and for unsaturated vapor at $T > T^c$ one can distinguish the portions corresponding to the same amounts of adsorption, and in a plot, $\ln p - T^{-1}$, these portions form single lines.

Figure 1 gives a schematic representation of the adsorbent—adsorbate phase diagram, the most important fragments of which were discussed above. Dashed portions of isosteres denote the results obtained from the data on adsorption of the compressed liquids calculated according to the Pointing equation. The intersections of isosteres and isochores occur at points at which the differences in density between adsorptive and adsorbate disappear. These points are the quasicritical points of the adsorbate. The line KK describes a quasicritical state of the adsorbate at zero ($\Gamma^a = 0$) excessive adsorption. The excessive adsorption is negative in the region above the line KK. A family of isosteres of adsorption intersecting the equilibrium line liquid—crystal is denoted by the dashed lines. Inspection of Fig. 1 shows that for a "normal" liquid, adsorption a_s increases in this region with temperature, then $\mathrm{d}a_s/\mathrm{d}T > 0$. For water, adsorption a_s decreases with temperature, and thus $a_s/\mathrm{d}T < 0$. It can, therefore, be inferred that the effect of "migration" of material from the adsorption field followed by crystallization outside the field can be encountered in adsorption from the liquid phase only in the case of "normal" liquids.

In conclusion, it is worth noting that the phase diagram in the coordinates $\ln p - T^{-1}$ seems to be very suitable for describing behavior of the adsorption systems over a wide range of temperatures and pressures. The adsorption processes on porous solids discussed above constitute but a part of the extensive class of the adsorption systems. It appears that such concepts as quasicritical temperatures and phase changes can be extended to other adsorption systems including those with the nonporous solids. The usefulness of this approach can be illustrated by numerous works on wetting transition, the effect caused by the bulk-film mismatch at a temperature below T^{tr} of the adsorptive. The transition is accompanied by a dramatic change in the value of limiting adsorption that can be attributed to segregation of the bulk crystalline phase of the adsorbate.

References

1. I. I. Seliverstova, A. A. Fomkin, V. V. Serpinsky, and M. M. Dubinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 493 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 444 (Engl. Transl.)].
2. M. Bienfait, *Surf. Sci.*, 1985, **162**, 411.
3. A. A. Isirikyan and A. V. Kiselev, *Dokl. Akad. Nauk SSSR,* 1956, **110,** 1009 [*Dokl. Chem.*, 1956, **110** (Engl. Transl.)].
4. G. I. Berezin, A. V. Kiselev, and A. A. Kozlov, *J. Colloid Interface Sci.*, 1973, **45**, 190.
5. G. I. Berezin, A. V. Kiselev, and A. A. Kozlov, *Zh. Fiz. Khim.*, 1964, **38**, 2106; 1967, **41**, 1426 [*Sov. J. Phys. Chem.*, 1964, **38**; 1967, **41** (Engl. Transl.)].
6. G. I. Berezin, A. V. Kiselev, A. A. Kozlov, and L. V. Kuznetsova, *Zh. Fiz. Khim.*, 1970, **44**, 1959 [*Sov. J. Phys. Chem.*, 1970, **44** (Engl. Transl.)].
7. B. P. Bering, E. G. Zhukovskaya, B. Kh. Rakhmukov, V. V. Serpinsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, **16**, 1656 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967, **16** (Engl. Transl.)].
8. A. A. Pribylov, V. V. Serpinsky, and S. M. Kalashnikov, *Zeolites*, 1991, **11**, 846.
9. A. A. Fomkin, V. A. Avramenko, I. I. Seliverstova, and V. V. Serpinsky, *Dokl. Akad. Nauk SSSR*, 1986, **288,** 678 [*Dokl. Chem.*, 1986, **288** (Engl. Transl.)].
10. G. I. Berezin, *Zh. Fiz. Khim.*, 1968, **42,** 563 [*Sov. J. Phys. Chem.*, 1968, **42** (Engl. Transl.)].
11. B. N. Vasil'ev, B. P. Bering, M. M. Dubinin, and V. V. Serpinsky, *Dokl. Akad. Nauk SSSR*, 1957, **117**, 131 [*Dokl. Chem.*, 1957, **117** (Engl. Transl.)].

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