

Adsorption phenomena at high pressures and temperatures

5.* Heats of excess and total adsorption of krypton on zeolite NaA

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Thermodynamic principles for the calculation of differential heats of excess and absolute adsorption were considered. A set of isosteres of excess adsorption of krypton on zeolite NaA are presented, from which the coverage and temperature dependences of the heats of excess adsorption are calculated and analyzed. The reasons for infinitely high values of the excess heats at finite values of adsorption are discussed. The problems of recalculation of the excess adsorption to absolute adsorption are considered.

Key words: adsorption; differential heats; excess adsorption; absolute adsorption; high pressures and temperatures.

The physical meaning, methods of calculation and measurement, and the character of changes in differential adsorption heats of total content (absolute adsorption) have been considered in detail in the literature and even in textbooks.^{2,3} However, the effect of high equilibrium pressures of adsorptives on a change in the differential adsorption heat has been studied insufficiently.

The situation for isosteric heats of excess adsorption is quite different, while they have been studied in detail for adsorption processes at low gas pressures (see, e.g., Ref. 4), in the case of measurements over a wide pressure range neither their physical meaning nor dependences on adsorption and temperature have been sufficiently explained in the literature. This concerns first of all the problem of infinitely high values of differential heats of excess adsorption.

Thermodynamic aspects of adsorption

As we know, the heat of phase transition is the change in enthalpy of the system upon the reversible transition of unit mass (1 mol) of any component of the system from one coexisting phase to another.

In the general case, the heat of the phase transition is described by the thermodynamic Clausius—Clapeyron equation. For adsorption phenomena in the simplest case, it is reasonable to consider the two-phase, two-component system in which one of the phases is condensed (adsorbent + adsorbate) and another phase is gaseous. In this case, the Clausius—Clapeyron equation has the form (see, e.g., Ref. 5):

$$\left. \frac{\partial p}{\partial T} \right|_{X_2^g} = \frac{X_2^g \Delta h_{g2}^c + (1 - X_2^g) \Delta h_{g1}^c}{T[X_2^g \Delta V_{g2}^c + (1 - X_2^g) \Delta V_{g1}^c]} \quad (1)$$

* For Part 4, see Ref. 1.

Indices "g" and "c" in Eq. (1) indicate the gaseous and condensed phases, respectively, and the transition of the substance occurs in the direction "g" → "c"; indices "1" and "2" denote the numbers of components; and X_{gi} is the molar fraction of the i th component in the gas phase.

$$\Delta h_{gi}^c = h_i^c - h_i^g; \Delta V_{gi}^c = V_i^c - V_i^g, \quad (2)$$

where h_i^c and h_i^g are partial molar enthalpies, and V_i^c and V_i^g are partial molar volumes of the component in the corresponding phases.

Imposing some limitations on the adsorption system considered, one can substantially simplify Eq. (1). It is reasonable to consider the condensed phase to be two-component (adsorbent + adsorbate) and the gas phase to be one-component (adsorptive), i.e., an adsorbent (component No. 1) is considered absolutely nonvolatile at the given temperature, and its molar fraction in the gas phase is equal to zero, while the molar fraction of the second component (adsorptive) is equal to unity in this phase. Since the amount of the adsorbent is constant, the condition $X_2 = \text{const}$, under which the derivative is calculated, is equivalent to the condition that the derivative is calculated along the adsorption isostere. Thus, Eq. (1) takes the form

$$\left(\frac{\partial p}{\partial T} \right)_j = \frac{h_2^c - h_2^g}{T(V_2^c - V_2^g)} \quad (3)$$

As applied to adsorption, two definitions (excess and absolute adsorption) were introduced; therefore, j in Eq. (3) can mean either the value of the excess adsorption Γ_i or the value of the absolute adsorption a_i , i.e., one of the two conditions can be introduced for the calculation of $\partial p / \partial T$: either $\Gamma_i = \text{const}$ or $a_i = \text{const}$.

Thus, the notion about two different isosteric adsorption heats designated as q_{st}^Γ and q_{st}^a is introduced. In the first case, Eq. (3) takes the form

$$\left(\frac{\partial p}{\partial T}\right)_\Gamma = \frac{q_{st}^\Gamma}{T(V_g - \bar{V}_\Gamma)}, \quad (4)$$

and in the second case it takes the form

$$\left(\frac{\partial p}{\partial T}\right)_a = \frac{q_{st}^a}{T(V_g - \bar{V}_a)}. \quad (5)$$

In these equations, indices "g" correspond to molar values in the gas phase. The line above the corresponding symbol \bar{S} or \bar{V} means that partial molar values of the excess and absolute entropy or volume, respectively, are considered:

$$\begin{aligned} \bar{S}_\Gamma &= \left(\frac{\partial S_\Gamma}{\partial m_2}\right)_{m_1}; & \bar{S}_a &= \left(\frac{\partial S_a}{\partial m_2}\right)_{m_1}; \\ \bar{V}_\Gamma &= \left(\frac{\partial V_\Gamma}{\partial m_2}\right)_{m_1}; & \bar{V}_a &= \left(\frac{\partial V_a}{\partial m_2}\right)_{m_1}. \end{aligned}$$

Here S_Γ and S_a are the excess and absolute entropies, respectively, of the whole system; V_Γ and V_a are the corresponding values for the volume; m_2 is the mass of the adsorbate; and m_1 is the mass of the adsorbent.

Since $(S_g - \bar{S}_\Gamma) = (H_g - \bar{H}_\Gamma)/T$; $(S_g - \bar{S}_a) = (H_g - \bar{H}_a)/T$; $V_g = ZRT/p$, factoring in the nonideal character of the gas phase; Z is the compressibility factor, and V_Γ is the excess volume that is equal to zero in the Gibbs thermodynamics, we finally have

$$q_{st}^\Gamma = -RZ(\partial \ln p / \partial T^{-1})_\Gamma \quad (6)$$

and

$$q_{st}^a = -RZ(\partial \ln p / \partial T^{-1})_a \cdot (1 - \bar{V}_a/V_g). \quad (7)$$

Equation (7), obtained on the basis of the thermodynamics of solutions,⁵ differs from Eq. (6) by the factor containing the term \bar{V}_a , which takes into account a change in the adsorption volume as adsorption values vary. However, the equation for isosteric heat, whose form coincides with that of Eq. (6), was derived upon the consideration⁶ of adsorption on the solid surface in terms of the adsorption model, the layer of finite thickness. One of the main disadvantages of this model, as mentioned,⁶ is the fact that it is difficult to draw the adsorbate—adsorptive interface, *i.e.*, to distinguish the adsorption volume. When, as in our case, a microporous adsorbent (zeolite) is used, the adsorption volume can be determined, for example, by the procedure developed previously,¹ and its change at various adsorption values (\bar{V}_a) is experimentally determined by the value of deformation of zeolite crystals. The following equation for the adsorption heat was derived for this adsorption system by the method of substitution of variables⁷:

$$q_{st}^a = -RZ(\partial \ln p / \partial T)_a [1 - (\partial V_0 / \partial a)_T / V_g] - (\partial p / \partial a)_T [V_0 - T(\partial V_0 / \partial T)_a], \quad (8)$$

where V_0 is the adsorption volume in the porous solid. As seen, Eq. (8) differs from Eq. (7) by the fact that it contains the terms that take into account changes in the adsorption volume affected by adsorption and temperature.

Interconversion of q_{st}^Γ and q_{st}^a values

Let us consider the thermodynamic correlation between the excess (4) and absolute (5) isosteric adsorption heats. Let us write the equations of excess and absolute adsorption in the general form:

$$F(\Gamma, p, T) = 0 \text{ and } \Phi(a, p, T) = 0. \quad (9)$$

It follows from these equations that:

$$\left|\frac{\partial \Gamma}{\partial p}\right|_T \left|\frac{\partial p}{\partial T}\right|_\Gamma \left|\frac{\partial T}{\partial \Gamma}\right|_p = -1 \text{ and } \left|\frac{\partial a}{\partial p}\right|_T \left|\frac{\partial p}{\partial T}\right|_a \left|\frac{\partial T}{\partial a}\right|_p = -1. \quad (10)$$

The values a and Γ are related by the universal dependence

$$a = \Gamma + \rho W, \quad (11)$$

where ρ is the density of the equilibrium gas and W is the adsorption volume.

Differentiating the latter equation by pressure at $T = \text{const}$ for the first time and by temperature at $p = \text{const}$ for the second time, we obtain

$$\left|\frac{\partial a}{\partial p}\right|_T = \left|\frac{\partial \Gamma}{\partial p}\right|_T + W \left|\frac{\partial \rho}{\partial p}\right|_T + \rho \left|\frac{\partial W}{\partial p}\right|_T \quad (12)$$

and

$$\left|\frac{\partial a}{\partial T}\right|_p = \left|\frac{\partial \Gamma}{\partial T}\right|_p + W \left|\frac{\partial \rho}{\partial T}\right|_p + \rho \left|\frac{\partial W}{\partial T}\right|_p. \quad (13)$$

Solving Eq. (10) with respect to $(\partial a / \partial p)_T$ and, correspondingly, with respect to $(\partial \Gamma / \partial p)_T$ and inserting the determined values into Eqs. (12) or (13), we obtain the following correlation after simple transformations:

$$q_{st}^\Gamma = q_{st}^a \frac{(\partial a / \partial p)_T}{(1 - \bar{V}_a/V_g)} \left|\frac{\partial p}{\partial \Gamma}\right|_T + TW \left|\frac{\partial p}{\partial \Gamma}\right|_T \left[\left|\frac{\partial \ln \rho}{\partial T}\right|_p + \left|\frac{\partial \ln W}{\partial T}\right|_p \right]. \quad (14)$$

Equation (14) gives the rigorous solutions of the formulated problem, *i.e.*, the relationship between q_{st}^a and q_{st}^Γ . A similar expression also was obtained⁸ using the different approach.

Results and Discussion

Since the set of isotherms of excess adsorption in the temperature range from 334 to 500 K and the pressure range from 0.1 to 160 MPa is available in our previous work,¹ we can plot and analyze the runs of isosteres of both excess $\ln p = f(T^{-1})_{\Gamma}$ and absolute adsorption $\ln p = f(T^{-1})_a$.

Thermodynamics requires that the isotherm of total content is a monotonically ascending function. On the contrary, the isotherms of excess adsorption are functions with extrema (maxima). Therefore, the runs of the excess isosteres (Fig. 1) differ sharply from those of the absolute isosteres, i.e., two values of $\ln p$ correspond to one value of Γ at the given temperature. In the upper part of Fig. 1, the locus of points Γ_g in which the excess adsorption becomes null is shown.

This segment of the curve can be called the null excess isostere. It is quite evident that our experimental data are insufficient to judge the general form of the null isostere over a wide temperature range. Two isosteres $a = \text{const}$ at $a = 0.05 \text{ g g}^{-1}$ and $a = 0.09 \text{ g g}^{-1}$ are presented in Fig. 1 as an example. The lower branch of each of the excess isosteres at rather low values of equilibrium pressure almost coincides with the corresponding isostere of absolute adsorption. This region of the excess isostere is well approximated by a straight line. Two isosteres diverge drastically as equilibrium pressures increase. The absolute isostere remains almost straight and bends only slightly at high pressures under the effect of the factor $Z(1 - P_a/V_g)$. The absolute values of the slope of excess isosteres at first slowly increase as the temperature increases, and this slope brings the derivative to the infinitely high value at the

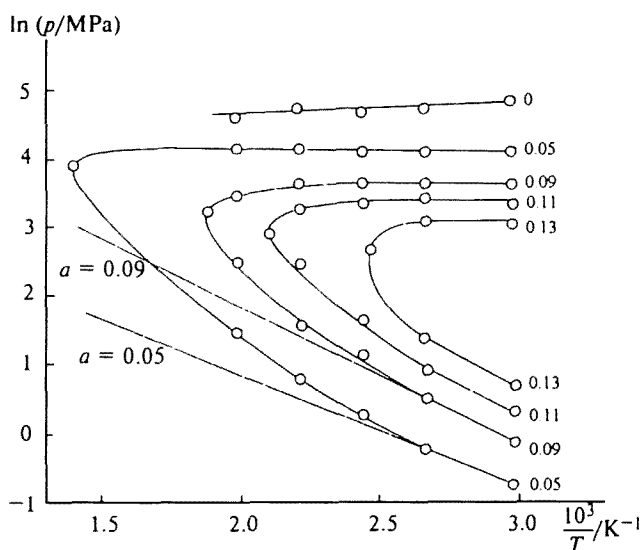


Fig. 1. Isosteres of excess adsorption of krypton on zeolite NaA. Numbers near curves are values of excess adsorption in g g^{-1} ; straight lines are isosteres of absolute adsorption, and numbers near lines are values of absolute adsorption in g g^{-1} .

value of pressure at which Γ becomes equal to Γ_m . When the equilibrium pressure further increases, the derivative $(\partial \ln p / \partial T^{-1})$ changes its sign, i.e., the process gains an explicitly endothermic character. Upon going from positive to negative values, isosteric heats of excess adsorption calculated by Eq. (6) should in fact pass through zero rather than take infinitely high values, i.e., Eq. (6) is not quite adequate to the physical process.

The calculated values of q_{st}^{Γ} and q_{st}^a for some values of Γ and a are presented in Figs. 2 and 3. The dependences of adsorption heats on coverage are presented in Fig. 2, and the temperature dependences of adsorption heats (along the isostere) are presented in Fig. 3. The isosteric adsorption heats obtained from the ascending excess isosteres at $p < p_{\text{max}}$ are positive for both dependences and are close to null values at pressures $p > p_{\text{max}}$. It is likely that in this pressure range the energy of the adsorbate—adsorbent interaction and repulsion energy between adsorbate molecules take such values that the excess adsorption heat is close to zero. As for the coverage and temperature dependences of the excess adsorption heat at pressures close to p_{max} , the curves presented have regions in which the adsorption heat tends to infinity. In this case, the character of the isosteric excess adsorption heats, in particular, division into two branches, is associated with the existence of a maximum on the isotherm of excess adsorption. In this maximum, the tangent slope is null. This is qualitatively confirmed by Eq. (14), which shows that under certain conditions when the heat q_{st}^a is finite (see Figs. 2 and 3) W is a constant temperature-independent value¹ and a change in density of the gas phase as temperature varies is also finite, the sole term (the derivative of the isotherm of excess adsorption) turns the isosteric adsorption heat into infinity. Since the adsorption model corresponding to Eq. (6) inadequately describes the run of

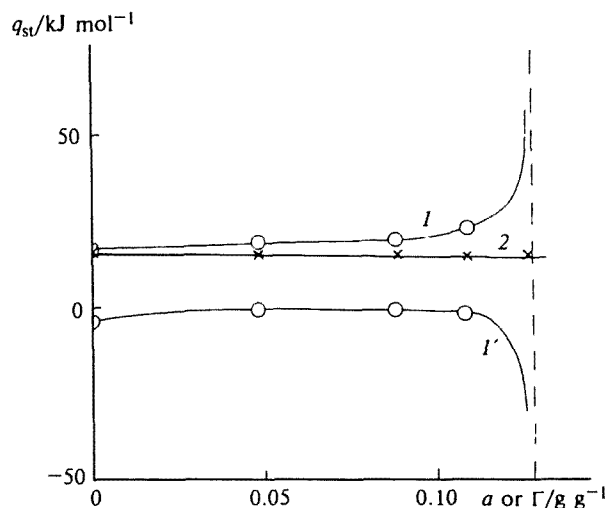


Fig. 2. Dependences of isosteric differential heats of krypton adsorption on zeolite NaA on adsorption at $T = 408 \text{ K}$; 1 and 1' are heats of excess adsorption, and 2 is heat of absolute adsorption.

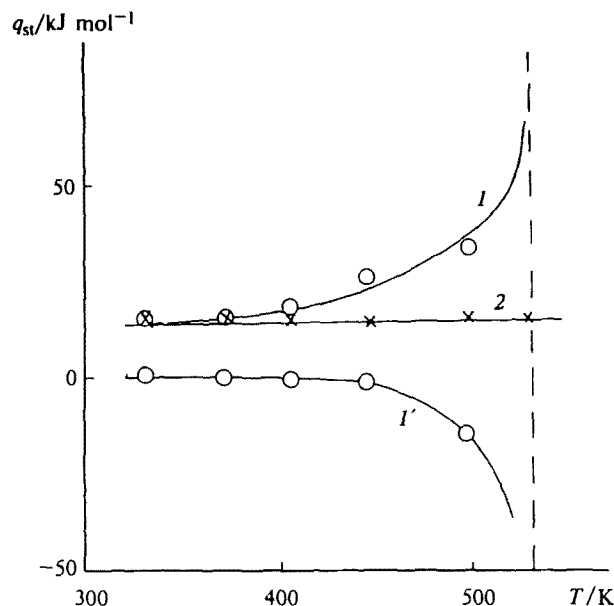


Fig. 3. Temperature dependence of isosteric differential heats of krypton adsorption on zeolite NaA along the adsorption isostere ($a \approx \Gamma = 0.09 \text{ g g}^{-1}$); 1 and 1' are heats of excess adsorption, 2 is heat of absolute adsorption.

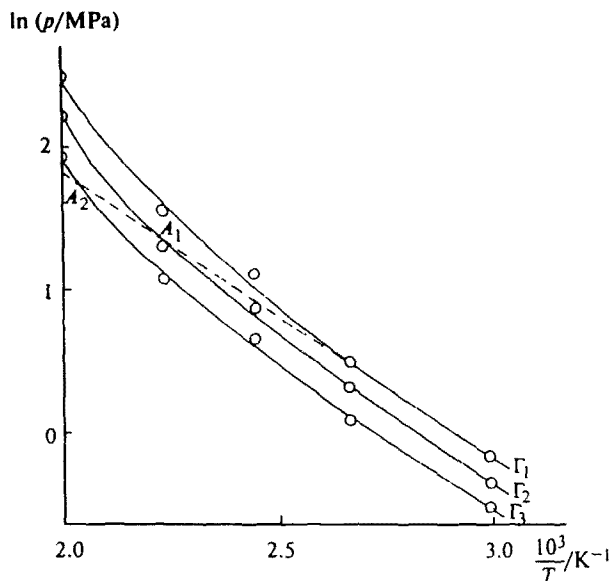


Fig. 4. Isosteres of excess ($\Gamma_1 = 0.09$, $\Gamma_2 = 0.08$, $\Gamma_3 = 0.07 \text{ g g}^{-1}$) and absolute (dotted line) krypton adsorption on zeolite NaA for $a = 0.09 \text{ g g}^{-1}$.

the change in the isosteric heat of excess adsorption as the temperature and coverage vary, it would be desirable to recalculate experimental values of excess adsorption to values of total content, for which values of the adsorption volume W should be determined.

Dubinin's method⁹ is widely used to determine the adsorption volume in microporous carbon adsorbents. The limiting adsorption value is determined and, assuming that the density of the adsorbate in pores is equal to the density of the liquid phase at the given temperature, the adsorption volume of pores is calculated. For crystalline porous adsorbents (zeolites), the calculation of the volume of pores has been described previously.¹ We suggested¹⁰ a method for the determination of the adsorption volume that is applicable for adsorbents with arbitrary porous structure, including nonporous adsorbents. The method is based on the correlation between the adsorption of total content and excess adsorption (Eq. (11)) and on using the experimental isotherm of excess adsorption measured in a wide range of pressures of the equilibrium gas phase (as a rule, up to 100–150 MPa) as well as on the equation of the isotherm of total content adsorption (see, for example, Ref. 11).

The essence of the method is the following: coefficients and the W value for the isotherm equation are selected in such a way that calculated excess values coincide with experimental values.

It can be shown that the existence of at least two isosteres of excess adsorption, including regions of low values of equilibrium pressures where $\Gamma \approx a$ can be accepted with good accuracy, makes it possible to deter-

mine the adsorption volume W at the given p and T taking into account Eq. (11).

Three excess adsorption isosteres $\Gamma_1 = 0.09$, $\Gamma_2 = 0.08$, and $\Gamma_3 = 0.07 \text{ g g}^{-1}$ as well as the absolute adsorption isostere at $a = 0.09 \text{ g g}^{-1}$ are presented in Fig. 4. At low pressures, the latter coincides with the isostere $\Gamma_1 = 0.09 \text{ g g}^{-1}$ within the experimental accuracy, but the excess adsorption isostere bends as the pressure increases, while the absolute adsorption isostere remains linear, which allows one to extrapolate it until the intersection with the isosteres $\Gamma_2 = 0.08 \text{ g g}^{-1}$ and $\Gamma_3 = 0.07 \text{ g g}^{-1}$ in points A_1 and A_2 . The coordinates of points A_1 and A_2 make it possible to determine the values of the equilibrium gas density in these points (ρ_{A_1} and ρ_{A_2}). Since each of the points A_1 and A_2 lies on the intersection of the isostere $a = 0.09 \text{ g g}^{-1}$ with the isosteres $\Gamma_2 = 0.08 \text{ g g}^{-1}$ and $\Gamma_3 = 0.07 \text{ g g}^{-1}$, respectively, the values $\Gamma_{A_1} = \Gamma_2$ and $a_{A_1} = a_1$ and $\Gamma_{A_2} = \Gamma_3$ and $a_{A_2} = a_2$, respectively, are known. Therefore, (see Eq. (11))

$$W = \frac{a_1 - \Gamma_2}{\rho_{A_1}} = \frac{\Gamma_1 - \Gamma_2}{\rho_{A_1}} \quad \text{and} \quad W = \frac{a_2 - \Gamma_3}{\rho_{A_2}} = \frac{\Gamma_1 - \Gamma_3}{\rho_{A_2}}. \quad (15)$$

Two values of the adsorption volume were calculated by Eqs. (15), and the average value is $W = 0.171 \text{ cm}^3 \text{ g}^{-1}$, which agrees well with the results of calibration $W = 0.171 \pm 0.008 \text{ cm}^3 \text{ g}^{-1}$ presented in the previous publication.¹

In conclusion, the authors are obliged to mention that Vladimir Vladimirovich Serpinski, who dies before

his time, should be one of the authors of this publication. This work is devoted to his memory.

References

1. A. A. Pribylov and T. S. Yakubov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1138 [*Russ. Chem. Bull.*, 1996, **45**, 1078 (Engl. Transl.)].
2. V. A. Bakaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 2648 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1971, **20**, 2516 (Engl. Transl.)].
3. Ya. I. Gerasimov, V. P. Dreving, E. N. Eremin, A. V. Kiselev, V. P. Lebedev, G. M. Panchenkov, and A. I. Shalygin, *Kurs fizicheskoi khimii* [The Course of Physical Chemistry], Khimiya, Moscow, 1970, **1**, 582 pp. (in Russian).
4. A. A. Lopatkin, *Teoreticheskie osnovy fizicheskoi adsorbtsii* [Theoretical Fundamentals of Physical Adsorption], Izd. Mosk. Univ., Moscow, 1983, 344 pp. (in Russian).
5. I. Prigozhin and R. Defei, *Khimicheskaya termodinamika* [Chemical Thermodynamics], Nauka, Novosibirsk, 1966, 510 pp. (in Russian).
6. A. A. Lopatkin, *Zh. Fiz. Khim.*, 1993, **67**, 2315 [*Russ. J. Phys. Chem.*, 1993, **67** (Engl. Transl.)].
7. V. A. Bakaev, *Molekulyarnaya teoriya fizicheskoi adsorbtsii* [Molecular Theory of Physical Adsorption], D. Sc. (Phys.-Mat. Sci.) Thesis, Moscow, 1989 (in Russian).
8. A. A. Lopatkin, *Zh. Fiz. Khim.*, 1987, **61**, 33 [*Russ. J. Phys. Chem.*, 1987, **61** (Engl. Transl.)].
9. M. M. Dubinin, *Dokl. Akad. Nauk SSSR*, 1961, **138**, 866 [*Dokl. Chem.*, 1961, **138** (Engl. Transl.)].
10. T. S. Yakubov, L. G. Shekhovtsova, and A. A. Pribylov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2438 [*Russ. Chem. Bull.*, 1995, **44**, 2277 (Engl. Transl.)].
11. V. A. Bakaev, *Dokl. Akad. Nauk SSSR*, 1966, **167**, 369 [*Dokl. Chem.*, 1966, **167** (Engl. Transl.)].

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