THERMODYNAMIC RATIOS IN ADSORPTION SYSTEM: KRYPTON – ZEOLITE NaX

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A study of the adsorption of krypton on zeolite NaX [1] at temperatures ranging from 120 to 600°K, and pressures ranging from 0.1 Pa to 14 MPa, on the equipment described in [2], disclosed that the adsorption isosteres, when plotted in the coordinates log P vs T^{-1}, are approximated well by straight lines in the entire range of change in the equilibrium adsorption parameters, in which connection the linearity of the isostere is not disturbed when passing through the normal critical temperature of krypton.

The Henry region, extending up to ~ 0.6 mmole/g, was observed on the initial sections of the adsorption isotherms. As is known, the logarithm of the Henry constant should be a linear function of the reciprocal temperature in harmony with the equation

$$\lg K = \frac{Q_0}{2{,}303RT} + C_0 \qquad (1)$$

where K is the Henry constant, Q_0 is the initial adsorption heat, and C_0 is a constant. As can be seen from Fig. 1, the experimental values of log K, plotted as a function of the reciprocal temperature, give a very good linear relation, in which connection the initial adsorption heat, determined from the slope of the obtained straight line, is $Q_0 = 15.3$ kJ/mole.

As was mentioned in [3], the isosteric adsorption heat Q depends both on the properties of the adsorption system itself and the properties of the gas phase, and in the general case is expressed by the equation

$$Q = -\left(1 - \frac{\bar{V}_{ad}}{V_g}\right) ZR \left(\frac{d\ln P}{dT^{-1}}\right)_a \qquad (2)$$

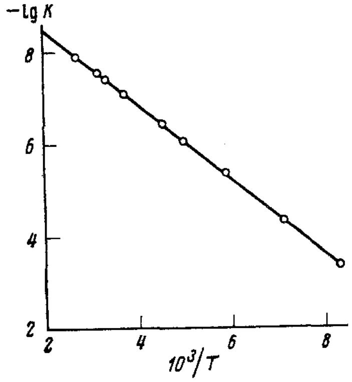

Fig. 1

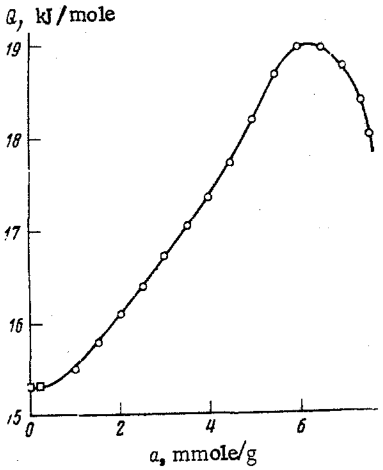

Fig. 2

Fig. 1. Relation between logarithm of Henry constant and reciprocal temperature.
Fig. 2. Relation between isosteric adsorption heat and adsorption value in region of ideal gas phase.

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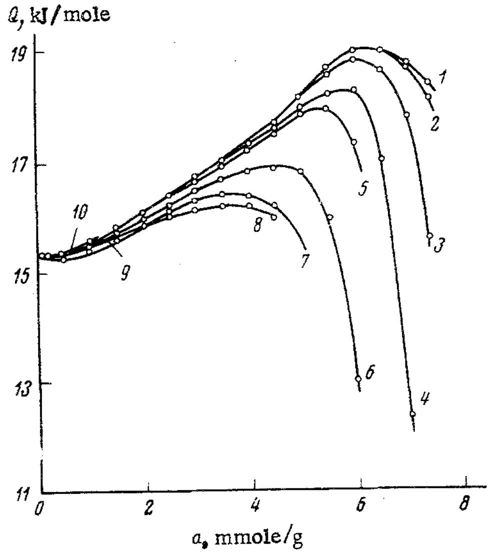

Fig. 3. Relation between adsorption heat and adsorption value at various temperatures, °K, 1) 120; 2) 140; 3) 170; 4) 200; 5) 220; 6) 270; 7) 320; 8) 370; 9) 500; 10) 600.

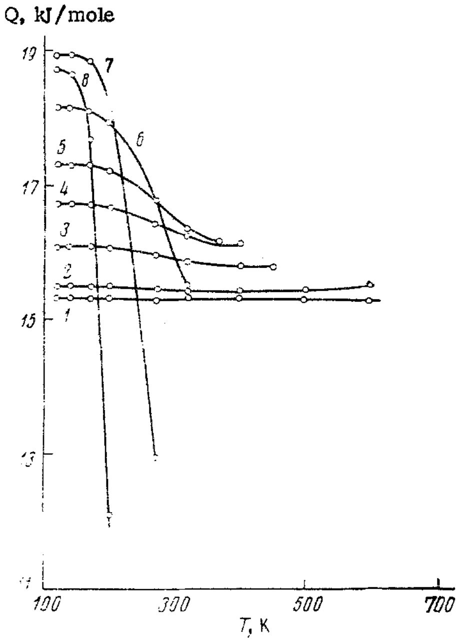

Fig. 4. Relation between adsorption heat and temperature under isosteric conditions, mmole/g: 1) 0.1-0.5; 2) 1; 3) 2; 4) 3; 5) 4; 6) 5; 7) 6; 8) 7.

where $\overline{V}_{ad}$ is the partial mole volume of the adsorbate, V_t is the mole volume of the equilibrium gas phase, $Z = PV_g/RT$ is the compressibility factor of the gas phase, $(d\ln P/dT^{-1})_a$ is the slope of the isostere in the coordinates ln P vs 1/T, and a is the adsorption. For wide-pored adsorbents, when the adsorbate represents a separate phase, the partial mole volume of the adsorbate is equal to the average mole volume. In the case of a microporous adsorbent, under the condition that the volume of the adsorbent remains constant during adsorption, the partial mole volume $\overline{V}_{ad}$ is equal to zero [3]. Consequently, the following equation was used to calculate the isosteric heats of krypton adsorption on zeolite NaX:

$$Q = -ZR\left(\frac{d\ln P}{dT^{-1}}\right)_a \tag{3}$$

in which for linear isosteres the term $R(d\ln P/dT^{-1})_a = Q_{id}$ represents the isosteric adsorption heat when the gas phase is ideal. Consequently,

$$Q = ZQ_{id} \tag{4}$$

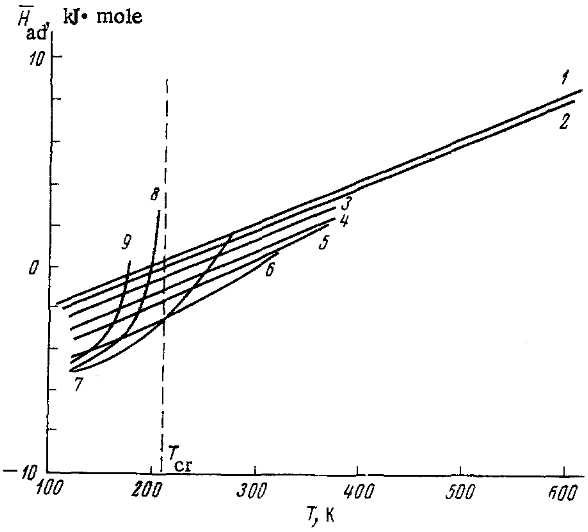

Fig. 5. Partial molar enthalpy of adsorbate as a function of temperature under isosteric conditions, mmole/g: 1) 0.5; 2) 1; 3) 2; 4) 3; 5) 4; 6) 5; 7) 6; 8) 7; 9) 7.4.

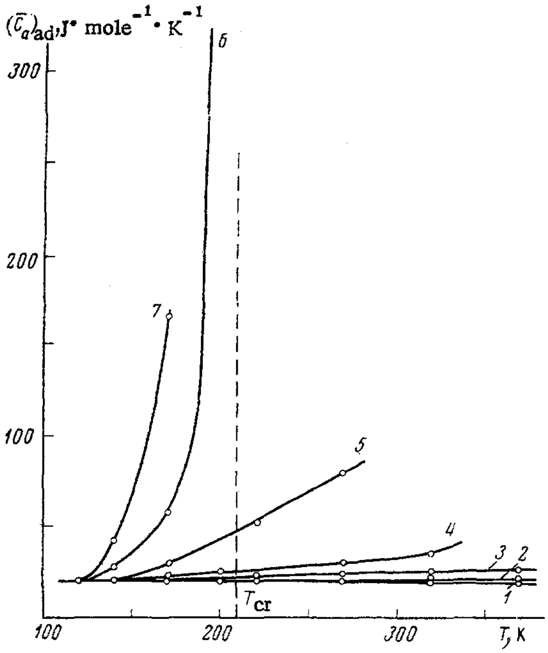

Fig. 6. Partial molar isosteric heat capacity of adsorbate as a function of temperature, mmole/g: 1) 0.5; 2) 3; 3) 4; 4) 5; 5) 6; 6) 7; 7) 7.4.

The adsorption heat Q_{id} of krypton on zeolite NaX is plotted in Fig. 2. The initial points on the curve were calculated from the Henry constants, while the other values were obtained from the solpe of the linear isosteres. Initially the heat remains approximately constant, and then it begins to rise smoothly, passes through a maximum at a = 6-6.6 mmoles/g, and then drops. A nonideality of the gas phase means that $Z \neq 1$, and consequently at high pressures the adsorption heat depends not only on a, but also on T, as a consequence of which substantial deviations of Q from Q_{id} are observed in this region. In Fig. 3 is shown the function: Q vs a when T = const (i.e., along the adsorption isotherm), while in Fig. 4 are given the curves for the function: Q vs T when a = constant (i.e., along the adsorption isostere) for the system: krypton–zeolite NaX. The isosteric adsorption heat represents the difference between the molar enthalpy of the gas phase and the partial molar enthalpy of the adsorbate [3]. On the basis of this ratio we calculated the partial molar enthalpy of the adsorbate $\bar{H}_{ad}$ as a function of T for a number of isosteres (Fig. 5). The enthalpy of the gas phase was determined from the data given in [4]. The partial molar isosteric heat capacity of the adsorbate (C_a) was found by differentiating the function $\bar{H}_{ad} = f(T)_a$ with respect to T when a = const. In Fig. 6 are given the curves $(\bar{C}_a)_{ad} = f\ (T)_a$, which show that the partial molar isosteric heat capacity remains constant at small values of a, and increases with temperature at large adsorption values.

CONCLUSIONS

1. The initial heat of krypton adsorption on zeolite NaX is 15.3 kJ/mole.

2. The partial molar enthalpy of the adsorbate under isosteric conditions increases with increase in the temperature.

3. The partial molar isosteric heat capacity of the adsorbate is independent of the temperature at small adsorption values, and increases with temperature at high adsorption values.

LITERATURE CITED

1. L. L. Seliverstova, A. A. Fomkin, and V. V. Serpinskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, No. 1,
2. A. A. Fomkin and V. V. Serpinskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 2108.
3. B. P. Bering, V. V. Serpinskii, and A. A. Fomkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 2111.
4. V. A. Rabinovich, A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, Heat Physical Properties of Neon, Argon, Krypton, and Xenon [in Russian], Izd. Standartov, Moscow (1976), p. 474.