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Abstract

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TEMPERATURE DEPENDENCE OF THE SEPARATION COEFFICIENTS OF THE ISOTOPIC MOLECULES D –H , D –HD, AND HD –H ON SYNTHETIC ZEOLITES NaA AND NaX DURING SORPTION UNDER ISOBARIC CONDITIONS

(Presented by Academician M. M. Dubinin, March 8, 1965)

The study of the selective adsorption of hydrogen isotopes on zeolites is of great interest both for adsorption theory and for practical applications ([1–5]). In a previous communication by the authors ([2]), the separation of hydrogen isotopes on mixed sodium-cobalt cation-exchange forms of type-A zeolite was studied, as was the kinetics of isotopic exchange between gaseous and adsorbed hydrogen. In the present work we have investigated the temperature dependence of the separation coefficients of the isotopic pairs D –H , D –HD, and HD–H during sorption of the three-component mixture D , HD, and H on industrial granulated synthetic zeolites NaA (Grozny) and NaX (Gorky experimental base of VNIINP). The dependence of the separation coefficients on the equilibrium gas pressure above the sorbent was first studied, and it was established that, at all the temperatures investigated (90.4, 77.6, and 62° K), changes in the coefficients over the pressure interval 200–400 mm Hg may practically be neglected*. Thus, the values obtained by us refer to an average pressure of 300 mm Hg. They are close to the smallest limiting values and may be used for a practical estimate of the efficiency of the sorption method for enrichment of deuterium at other temperatures and at a constant pressure of 300 mm Hg.

Experiments to determine the separation coefficients were carried out in a circulation apparatus ([2]). Liquid oxygen and nitrogen were used as cooling liquids. A temperature of 62.0° K was obtained by continuous pumping of liquid nitrogen in a special cryostat. An oxygen condensation thermometer served to measure the temperature. Before the experiments, the zeolites were evacuated for 12 h at a temperature of 350° C to a residual pressure of $5 \cdot 10^{-3}$ mm Hg. The separation coefficients were calculated from the formula $\alpha = R_{\text{zeolite}}/R_{\text{gas}}$, where R_{zeolite} and R_{gas} are the ratios of the concentration of the heavy component to that of the light component in the adsorbed and gas phases, respectively. The

isotope concentrations in the gas were determined mass-spectrometrically, and the concentration in the zeolite was calculated from material-balance equations. Isotopic analysis was performed on an MI-1305 mass spectrometer. The relative error of analysis did not exceed ±1.5%. Since, with decreasing temperature, the gas phase became strongly depleted in heavy isotopes, the concentration of the initial mixture had to be varied from 1 to 10% D and from 5 to 20% HD. At the same time, as in works ([1,2]), no dependence of the separation coefficients on the isotopic composition of the initial mixture was found within the accuracy of the experiment.

Table 1 presents the mean values of the isobaric separation coefficients, as well as the maximum deviations from the mean. Each value represents the average of 4-8 measurements. Taking into account the inaccuracy

* Similar results were obtained in work ([1]) for pressures of 200-750 mm Hg at a temperature of 90° K.

in determining the temperature and in determining the isotopic composition, the reproducibility of 2-3% is satisfactory.

As is seen from the data in Table 1, in all cases the separation coefficients on zeolite NaA are higher than on NaX. This conclusion agrees with the data of works ([1], [3]). However, the absolute values of the coefficients obtained by us are higher than in those works. It is possible that this is explained by the different origin of the zeolites, as well as by differences in the experimental procedure and in the preparation of the sorbents.

As is seen from Fig. 1, the data obtained fall satisfactorily on straight lines in the coordinates $\lg\alpha$–$1/T$. It follows that the temperature dependence of the "isobaric" separation coefficients can be described by the usual equation of the form:

$$\lg\alpha = A + B/T, \tag{1}$$

where α is the separation coefficient of the heavy isotope relative to the light one, A and B are constants, and T is the temperature in °K. The meaning of the coefficients A and B can be revealed if one uses the formal analogy between the separation coefficient and the equilibrium constant of the corresponding isotope-exchange reaction between the gas and sorbed phases. For example, for the pair D_2–H_2:

$$D_{2\,\text{gas}} + H_{2\,\text{sorb}} \rightleftarrows D_{2\,\text{sorb}} + H_{2\,\text{gas}}. \tag{2}$$

Analogous equations can also be written for the pairs D_2–HD and HD–H_2. Assuming that a reaction of type (2) proceeds at a constant equilibrium pressure, equal in our case to 300 mm Hg, and at constant temperature, and also neglecting the mutual influence of the isotopes on the sorption of one another, it

can be shown that the equilibrium constant of reaction (2), written in terms of mole fractions, is identical to the separation coefficient $\alpha_{D_2-H_2}$ at the same equilibrium pressure, i.e. $K_{D_2-H_2} \equiv \alpha_{D_2-H_2}$.

In accordance with the van ' t Hoff isobar equation, the equilibrium constant of reaction (2) depends on two factors: entropic and enthalpic:

$$\lg K_{D_2-H_2} = \lg \alpha_{D_2-H_2} = \Delta S^0/2.3R - \Delta H^0/2.3RT, \quad (3)$$

where ΔS^0 and ΔH^0 are the standard entropy and enthalpy of the isotope-exchange reaction (2). As the standard state in the present case one should take such–

Figure 1: Dependence of the hydrogen-isotope separation coefficients on temperature: 1 –$\alpha_{D_2-H_2}$, 2 –α_{D_2-HD}, 3 –α_{HD-H_2}, 4 –$\alpha_{D_2-H_2}$, 5 –α_{D_2-HD}, 6 –α_{HD-H_2}. 1, 2, 3 –zeolite NaA; 4, 5, 6 –zeolite NaX.

Fig. 1. Dependence of the hydrogen-isotope separation coefficients on temperature:
1 –$\alpha_{D_2-H_2}$, 2 –α_{D_2-HD}, 3 –α_{HD-H_2}, 4 –$\alpha_{D_2-H_2}$, 5 –α_{D_2-HD}, 6 –α_{HD-H_2}.
1, 2, 3 –zeolite NaA; 4, 5, 6 –zeolite NaX.

Table 1

Dependence of the hydrogen-isotope separation coefficients on zeolites NaA and NaX on temperature at a pressure of 300 mm Hg

Separation coefficient	Zeolite NaA, temp., °K: 90.4±0.2	Zeolite NaA, temp., °K: 77.6±0.2	Zeolite NaA, temp., °K: 62.0±0.3	Zeolite NaX, temp., °K: 90.4±0.2	Zeolite NaX, temp., °K: 77.6±0.2	Zeolite NaX, temp., °K: 62.0±0.3
$\alpha_{D_2-H_2}$	2.16±0.05	2.53±0.09	3.67±0.06	1.84±0.02	2.12 ± 0.001	2.72 ± 0.05
α_{D_2-HD}	1.57±0.03	1.75±0.04	2.17±0.05	1.46±0.03	1.58±0.02	1.84±0.04
α_{HD-H_2}	1.38±0.01	1.45±0.03	1.69±0.03	1.26±0.03	1.35±0.01	1.48±0.02

state of the gas-zeolite system at the experimental temperature and a pressure of 300 mm Hg, when the mole fractions of all three isotopes are equal to one another and are identical in both phases. Comparing the right-hand sides of equations (1) and (3), it is easy to find that $A = \Delta S^0/2.3R$ and $B = \Delta H^0/2.3R$. The values of ΔS^0 and ΔH^0 thus found for exchange reactions between the isotopes $D_2 - H_2$, $D_2 - HD$, and $HD - H_2$ are given in Table 2.

Table 2

Entropies and enthalpies of isotopic-exchange reactions of heavy and light isotopes between the gas and adsorbed phases at an equilibrium pressure of 300 mm Hg on zeolites NaA and NaX

	Exchanging molecules	$D_2 - H_2$	$D_2 - HD$	$HD - H_2$
Zeolite NaA	Entropy ΔS^0, e.u.	0.705	0.448	0.256
Zeolite NaA	Enthalpy ΔH^0, cal/mol	201	122	79
Zeolite NaX	Entropy ΔS^0, e.u.	0.467	0.252	0.216
Zeolite NaX	Enthalpy ΔH^0, cal/mol	152	90	62.0

The general conclusion that can be drawn from comparing the data of Tables 1 and 2 is that the higher separating ability of zeolite NaA with respect to hydrogen isotopes, as compared with NaX, is due to the much larger exchange enthalpy on the former zeolite. Since the exchange enthalpy is proportional to the difference between the heats of sorption of the corresponding isotopes, the greater selectivity of NaA is explained by the greater difference in the heats of sorption of the isotopes. Thus, for example, for the $D_2 - H_2$ pair the exchange enthalpies on NaA and NaX are 201 and 152 cal/mol, respectively. This conclusion agrees with the conclusion drawn in work (1) on the basis of measurements of the adsorption isotherms of pure D_2 and H_2. As the comparison of the heats of exchange for the pairs $D_2 - HD$ and $HD - H_2$, first obtained by us for zeolites NaA and NaX (see Table 2), shows, the conclusion made above also holds for them. It is also interesting to note that the separation coefficient on zeolite NaA would be still higher if the entropy of exchange on it were the same as on NaX (0.705 and 0.467 e.u., respectively). This is connected with the fact that the entropy of exchange is negative and decreases the separation coefficient. Evidently, the optimum combination of properties for separation would be a large difference in the heats of sorption with the minimum attainable difference in entropies. In this connection, the natural zeolite chabazite, which has elongated narrow channels, is of interest.

Another important conclusion that follows from the joint analysis of the data in Tables 1-2 concerns the relative difficulty of separating the isotopic pairs $D_2 - HD$ and $HD - H_2$. Although the relative mass difference for the first pair is smaller than for the second, the coefficients α_{D_2-HD} are in all cases higher than α_{HD-H_2}. Similar data were obtained in work (3) for temperatures of 78° K. The apparent deviation of these data from the conclusions of the quantum-mechanical theory of isotope effects can be explained by the influence of the

ortho-para composition of the mixture being separated. In our case, when catalysts of ortho-para conversion were absent, it may be assumed that the mixture had a high-temperature-equilibrium, or "normal," composition. Therefore the mixture contained 75% ortho-H_2, which is extremely close in properties to HD and has practically the same sorbability as the latter ([5,6]). Therefore the separation coefficients found by us are certain effective quantities characterizing the separation of binary mixtures of the ortho-para varieties of H_2 and D_2 with respect to HD.

Using equation 3 and the values of ΔS^0 and ΔH^0 given in Table 2,

one can calculate the values of the separation coefficients at any temperatures, on the assumption that the values of ΔS^0 and ΔH^0 remain constant. It is of interest to compare the quantities thus obtained with analogous quantities for the distillation of hydrogen isotopes. Thus, for example, the separation coefficient at the boiling point of liquid hydrogen (20.4° K) is, for distillation, $\alpha_{D_2-H_2} \approx 3$ [7], whereas for adsorption on NaA $\alpha_{D_2-H_2} = 81$. This indicates the great promise of the adsorption method for enriching deuterium with the aid of synthetic zeolites.

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