Possibility of isotopic separation in H_2–D_2 solutions

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The short-range order and the structure in liquid isotopic solutions and crystals $(p\text{–}H_2)_c(o\text{–}D_2)_{1-c}$ $(0\leqslant c\leqslant 1)$ were investigated by the method of neutron diffraction with a pulsed source. The partial structure factor $S_{cc}(Q)$, characterizing the concentration-concentration correlation, was measured directly for a solution with average neutron coherent-scattering length equal to zero ($c = 0.64$). It was found that $S_{cc}(Q)$ is not constant; this indicates that the isotopic solution deviates from an ideal solution and that concentration fluctuations in short-range order exist. Crystals of the isotopic mixture are single-phase, but additivity breaks down and the excess mixing volume is negative: $\Delta V^E/V \approx -1.2\%$ for $c = 0.5$. These effects are caused by the difference in the zero-point vibrations of the components and indicate a weak tendency toward separation in an isotopic solution.

1. INTRODUCTION

Condensed solutions of isotopes of light elements differ from ideal solutions because the masses and energies of zero-point vibrations of the components differ appreciably. They are characterized by the excess thermodynamic quantities, and as the temperature decreases they can separate into phases of different isotopic composition.[1]

A well-known example is phase separation of the solid solutions ^{3}He–^{4}He at $T < 0.4$ K, first observed in heat-capacity experiments[2] and later widely investigated by different experimental methods (see, for example, the references cited in Ref. 3). Although the kinetics of isotopic separation was complicated and the results depended on the previous history and quality of the samples,[3] the experimental estimates of the critical temperature of separation for the system ^{3}He–^{4}He were found to be close to the theoretical predictions.[4]

A less certain situation has developed in investigations of the phase diagram of solid isotopic solutions of molecular hydrogen. In hydrogen and deuterium crystals the character of the intermolecular interaction and the thermodynamic properties depend on the content of molecules with different rotational states: p–H_2, o–D_2 ($I = 0$; 2; $J = 0$) and o–H_2, p–D_2 ($I = 1$; $J = 1$). This can make it more difficult to interpret the results for H_2–D_2 mixtures with different ortho-para content. Thus, the observation of phase separation even at quite high temperatures ($T \approx 16$ K), close to the melting point, was reported in x-ray measurements,[5,6] performed on solidified hydrogen-deuterium mixtures having a high concentration of molecules with $J = 1$. These results, however, have not been confirmed and were reexamined in Ref. 7 in connection with the suggestion that the H_2–D_2 system can separate not according to isotopes but rather according to ortho-para concentrations.

It was predicted theoretically[1,8,9] that isotopic separation of the H_2–D_2 solution should occur in the temperature interval from 0.8 to 4 K, and the excess thermodynamic functions of the solutions determined from experimental gas–solid and liquid–solid equilibrium diagrams[10–12] suggest that this is most likely to occur at 2–3 K. However, separation was not observed in any of the experiments performed by thermal analysis methods[13–15] in the temperature range 4.2–20 K, heat-capacity measurements[16] in the interval 0.5–5 K, NMR measurements[17] in the range 1.1–12 K, and electron diffraction by thin films[18] at 2.5 K. In Ref. 18 it was concluded that the lack of any observations of indications of separation in the H_2–D_2 system can be explained by the slowness of thermally activated volume and surface diffusion of molecules in the crystal at low temperatures.

Several experiments have been performed on solid solutions of hydrogen and deuterium. These experiments were mainly concerned with the problem of determining the excess mixing volume:

$$\Delta V^E = V - [cV_{H_2} + (1-c)V_{D_2}], \qquad (1)$$

where V, V_{H_2} and V_{D_2} are the molar volumes of the solution and the pure components, respectively, and c is the hydrogen concentration.

In Refs. 19–22, where different methods were employed, it was established that the quantity $\Delta V^E/V$ for liquid solutions H_2–D_2 is different from zero, negative, and equal to about 1% for the equimolar concentration. This result, however, contradicted the conclusion, drawn on the basis of electron-diffraction measurements,[18] that Vegard's relation holds for solidified H_2–D_2 mixtures.

In the present work we investigated the tendency toward separation in liquid isotopic solutions $(p\text{–}H_2)_c(o\text{–}D_2)_{1-c}$ by analyzing with the help of neutron diffraction the structural correlations in their short-range order. The modifications of molecular hydrogen and deuterium having spherically symmetric molecules with isotropic and central interactions and thermodynamically stable at low temperatures were chosen as the components of the solution. This enables us to eliminate the uncertainties associated with ortho-para effects. The neutron coherent-scattering length $b_H = -0.374\cdot 10^{-12}$ cm for scattering by a proton and $b_D = 0.667\cdot 10^{-12}$ cm for scattering by a deuteron different in magnitude and in sign. For this reason, the mixture $(p\text{–}H_2)_c(o\text{–}D_2)_{1-c}$ with concentration $c \approx 0.64$ has, on the average, zero neutron coherent-scattering amplitude, and this makes it possible to investigate directly the

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partial structure factor $S_{cc}(Q)$ characterizing concentration-concentration correlations in an isotopic solution.

2. DETAILS OF THE EXPERIMENT

Structural investigations of the hydrogen-deuterium system by means of neutron diffraction were performed on the pulsed neutron source of the Fakel accelerator at the Kurchatov Institute. A multidetector time-of-flight neutron diffractometer and a setup for working with cryogenic crystals and cryogenic liquids under high pressure were employed.[23,24]

Pure ($\geqslant 98\%$) p–H_2 and o–D_2 modifications were prepared separately by holding liquified hydrogen and deuterium in a converter with $Fe(OH)_3$ catalyst at $T \approx 20$ K and distilling them in different containers. The investigated mixtures with the required composition were prepared according to definite partial pressures of the gaseous components, successively freezing them in the sample chamber, which was placed in a helium cryostat in the neutron beam. The isotopic fractions in the chamber were then melted, evaporated, mixed in the gas phase, and condensed into a liquid. The macroscopic homogeneity, density, and composition of the solution obtained were checked by scanning the sample with a narrow neutron beam, moving the cryostat with the chamber along the vertical and measuring, with the straight-beam detector, the transmission at different points of the sample.

Five $(p\text{–}H_2)_c(o\text{–}D_2)_{1-c}$ isotopic mixtures with concentrations $c = 0, 0.34, 0.50, 0.64$, and 1 were prepared. The liquid samples were investigated at temperatures $T = 20.0$, 18.0, 18.4, 17.5, and 16.5 K, respectively; this is 1.5–2 degrees higher than the solidification temperature of a solution with a given concentration. The rapidly frozen solid samples of the same isotopic mixtures were investigated at $T \approx 4.2$ K.

In each experiment the total $\Sigma_t(\lambda)$ and differential $d\sigma/d\Omega(Q)$ cross sections for scattering of slow neutrons were measured simultaneously as a function of the wavelength λ and the transferred momentum $Q = 4\pi \sin(\theta)/\lambda$ for 16 different scattering angles 2θ in the range 0–165°. The chamber, made of titanium-zirconium alloy,[25] constituted a "zero" matrix for coherent neutron scattering and did not significantly distort the diffraction pattern of the sample. The method used for analyzing the data in order to obtain the structure factor was similar to that employed in investigations of liquid deuterium.[25] The density and concentration (c) of the solution were checked to within better than 1% with the help of measurements of the total cross sections $\Sigma_t(\lambda)$. The lattice parameters and the molar volumes of the crystals of the isotopic mixtures were determined to within 0.05–0.1% from the diffraction data on the solid samples.

3. RESULTS AND DISCUSSION

The measurements of the total macroscopic cross sections $\Sigma_t(\lambda)$ for the interaction of slow neutrons with liquid p–H_2 and o–D_2 and their 50% solution are presented in Fig. 1. The cross section at small wavelengths (high neutron energies), corresponding to scattering by free protons and deuterons, depends only on the nuclear composition and density of the sample and was employed for checking the concentration of the isotopic solution. Incoherent inelastic neutron scattering with excitation of rotational ($J = 0 \rightarrow J = 1,3$) para→ortho ($I = 0 \rightarrow 1$) transitions of a molecule with spin flip predominate in the cross section for p–H_2 at moderate wavelengths (0.5–2 Å). The region of coherent neutron scattering is of interest for analyzing intermolecular structural correlations in solutions. In the p–H_2 case coherent neutron scattering can be observed only at long wavelengths $\lambda > \lambda_m \approx 2.4$ Å, when the neutron energy is less than the excitation energy of the first rotational level ($E < 0.0147$ eV). Even in this region, however, an additional incoherent component, associated with different scattering lengths for neutrons scattered by isotopes, appears in the cross section for solutions. This can be seen by comparing the total cross sections of pure parahydrogen, orthodeuterium, and their mixtures for $\lambda > 2.4$ Å and was taken into account when determining the structure factor.

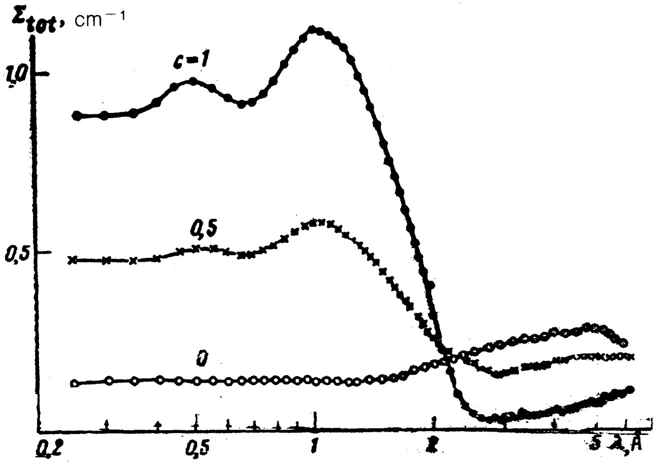

FIG. 1. Total cross sections $\Sigma_{tot}(\lambda)$ for the interaction of neutrons with liquid parahydrogen ($c = 1$), orthodeuterium ($c = 0$), and their solution ($c = 0.5$).

The differential neutron-scattering cross sections $d\sigma/d\Omega(Q)$ at one angle $2\theta = 97°$, which were measured for isotopic solutions of different concentration, are presented in Fig. 2. The lower curve essentially reproduces the behavior of the structure factor of liquid molecular deuterium.[25] In the case of the upper curve for liquid parahydrogen, however, only the first peak in coherent scattering at small Q is manifested. The other structural oscillations are difficult to separate from the background of the strong increase in the inelastic incoherent neutron scattering cross section. Thus in the $(p\text{–}H_2)_c(o\text{–}D_2)_{1-c}$ solutions only a limited region is accessible for analysis of correlations in the short-range order ($Q < Q_m = 4\pi \sin(\theta)/\lambda_m$) and only the first peak in the structure factor can be observed. Regions of coherent scattering were separated in the differential neutron-scattering cross sections measured at different angles, and the structure factor $S(Q)$ was calculated, following the procedure of Ref. 25, by averaging the data in regions overlapping in Q.

The results for $S(Q)$; are presented in Fig. 3. In liquids consisting of a single component (pure parahydrogen and orthodeuterium) the amplitude of the first peak in the structure factor has typical values of 2.8 and 3.5, and the position of the peak shifts from 2.1 to 2.2 Å^{-1}, respectively, due to the change in density. In the binary solutions H_2–D_2 the peak decreases, but does not vanish completely. Figure 4

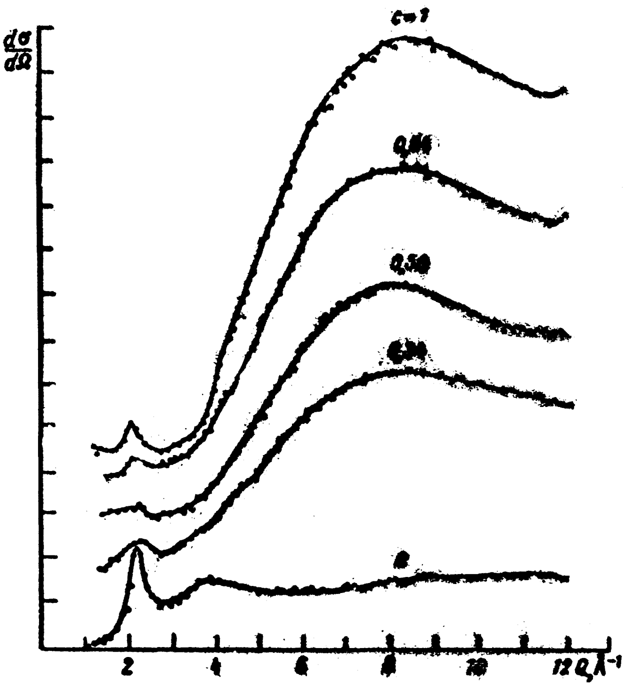

FIG. 2. Differential neutron-scattering cross sections $d\sigma/d\Omega(Q)$ for the liquid solutions $(p\text{-}H_2)_c(o\text{-}D_2)_{1-c}$ (the scattering angle $2\theta = 97°$).

shows the amplitude of the peak and the average neutron coherent-scattering length versus the solution concentration.

For a two-component system the complete structure factor $S(Q)$ can be expressed in terms of the partial structure factors, characterizing the correlation between the density N and concentration c:[26]

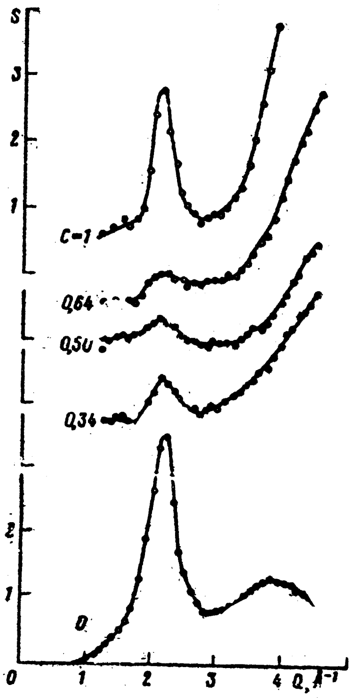

FIG. 3. First peak in the structure factor $S(Q)$ for the isotopic solutions $(p\text{-}H_2)_c(o\text{-}D_2)_{1-c}$.

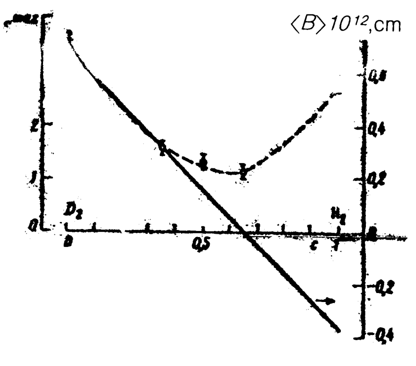

FIG. 4. Amplitude of the first peak in the structure factor $S^{\max}$ and the average neutron coherent-scattering length $\langle b \rangle$ as a function of the concentration c of the isotopic solution $(p\text{-}H_2)_c(o\text{-}D_2)_{1-c}$.

$$S(Q)=\frac{\langle b\rangle^2}{\langle b^2\rangle}S_{NN}(Q)+\frac{(\Delta b)^2}{\langle b^2\rangle}S_{cc}(Q)+\frac{2\langle b\rangle\Delta b}{\langle b^2\rangle}S_{Nc}(Q), \qquad (2)$$

where $S_{NN}(Q)$, $S_{cc}(Q)$, and $S_{Nc}(Q)$ are the partial structure factors of the correlations between fluctuations of the particle number density, between local fluctuations of the concentration, and between density-concentration fluctuations, respectively; and

$$\langle b\rangle = cb_H + (1-c)b_D;\ \langle b^2\rangle = cb_H^2 + (1-c)b_D^2;\ \Delta b = b_H - b_D.$$

For a solution with concentration c, $\langle b \rangle = 0$:

$$S(Q)=\frac{(\Delta b)^2}{\langle b^2\rangle}S_{cc}(Q)=\frac{S_{cc}(Q)}{c(1-c)}, \qquad (3)$$

i.e., the structure factor characterizes directly the partial correlations between the concentration fluctuations in the system. The corresponding radial distribution function $G_{cc}(r)$ is related with it by a Fourier transformation and can be expressed in terms of the partial intermolecular distributions $G_{H_2H_2}(r)$, $G_{D_2D_2}(r)$, $G_{H_2D_2}(r)$:

$$G_{cc}(r)=\frac{2}{\pi}\int_0^\infty Q\left[\frac{S_{cc}(Q)}{c(1-c)}-1\right]\sin(Qr)dQ$$
$$=c(1-c)\left[G_{H_2H_2}(r)+G_{D_2D_2}(r)-2G_{H_2D_2}(r)\right]. \qquad (4)$$

In the case of an ideal solution of isotopes with interchangeable components of identical size all intermolecular distributions are equivalent and $S_{cc}(Q) = c(1-c)$, i.e., the structure factor should not depend on Q.

In our case the solution $(p\text{-}H_2)_c(o\text{-}D_2)_{1-c}$ with concentration $c = 0.64$ corresponds to the condition $\langle b \rangle = 0$. This was confirmed by measurements on a crystal of this mixture. The measurements showed that there were no diffraction peaks in the neutron diffraction pictures at different scattering angles. At the same time, for both liquid and frozen solutions a small diffuse nonmonotonicity appeared in $S(Q)$ near $Q \approx 1.8\text{–}2.5$ Å^{-1} (see Fig. 3). This suggests that an isotopic hydrogen-deuterium solution differs, though weakly, from an ideal solution even at a temperature ~ 17 K. The manifestation of concentration fluctuations in the short-range order reflects a probable tendency for the $H_2\text{–}D_2$ system to separate.

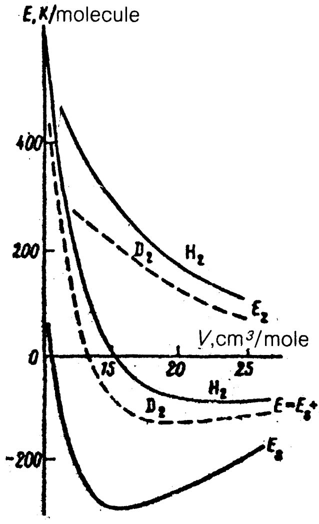

FIG. 5. Total energy $E(V)$, potential energy $E_s(V)$, and zero-point vibration energy $E_z(V)$ for p–H_2 (solid line) and o–D_2 (dashed line) at $T = 0$. The energies were determined from neutron-diffraction data according to the equations of state.[23,24] The minimum of $E(V)$ corresponds to sublimation energies 89.8 K/mole for H_2 (Ref. 27) and 132.8 K/mole for D_2 (Ref. 28).

The function $G_{cc}(r)$ usually characterizes the so-called chemical short-range order, which in a liquid changes with time: mixing and separation processes occur between the H_2 and D_2 components in solution. The existence of concentration fluctuations could be due to the difference in the energy of zero-point vibrations of hydrogen and deuterium molecules. The magnitude of this difference $\Delta E_z = E_z^{H_2} - E_z^{D_2}$ can be estimated from Fig. 5, which shows the total energy $E(V)$, the potential energy $E_s(V)$, and the energy of zero-point vibrations $E_z(V)$ for both isotopes and $T = 0$. These functions were obtained from the experimental equations of state $P(V) = -\partial E/\partial V$ for solid p–H_2 and o–D_2 (Refs. 23 and 24) under the assumption that their interaction potential is identical while the energy of zero-point vibrations is proportional to $(M_i)^{-1/2}$, where M_i is the mass of the ith isotope. In the range of densities of solutions at $P = 0$ the difference ΔE_z to ~ 50 K/molecule, which is appreciably higher than the temperature of the system and necessarily affects the properties of the solution.

Investigations of neutron diffraction by crystals of solidified mixtures H_2–D_2 showed that although these crystals are usually textured, they are single-phase. The neutron-diffraction pictures at different scattering angles contained one set of diffraction peaks (100), (002), and (101), corresponding to a hexagonal close-packed structure. Their intensities were lower than for pure crystals as a result of incoherent scattering, but their widths did not differ appreciably.

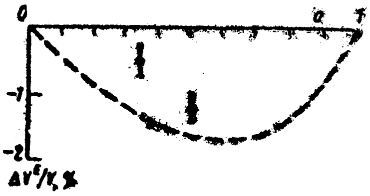

FIG. 6. Relative excess volume $\Delta V^E/V$ in isotopic crystals $(p\text{–}H_2)_c(o\text{–}D_2)_{1-c}$ at $T = 4.2$ K. The dots are the experimental data and the dashed line is the estimate from the equations of state.[23,24]

The crystal-lattice parameters and the excess molar volumes of the crystals determined on the basis of these parameters are presented in Table I. The molar volumes V or pure parahydrogen and orthodeuterium crystals at $T = 4.2$ K and $P = 0$ differ by 15%; this is a direct consequence of the effect of zero-point vibrations (see Fig. 5). The specific volumes of the solutions have intermediate values. The ratio of the parameters c/a in the entire range of concentrations remains close to the ideal ratio for an *hcp* lattice. The quantity $\Delta V^E/V$ could be determined only for $c = 0.34$ and 0.50 (as has already been noted, there were no diffraction peaks for $c = 0.64$). The excess volume for H_2–D_2 crystals was found to be negative, and the sign and magnitude of the ratio $\Delta V^E/V$ are close to the results for liquid solutions.[19-22]

The concentration dependence of $\Delta V^E/V$ can be estimated from the data with the help of the equations of state p–H_2 and o–D_2,[23,24] using the condition[29]

$$cP_{H_2}(V)+(1-c)P_{D_2}(V)=0,$$

where $P_{H_2}(V)$ and $P_{D_2}(V)$ are the pressures to which the pure components must be "compressed" or "expanded," respectively. For deuterium this means that the equation of state must be extrapolated, by a small amount, into the region of negative pressures. The results of such an estimate $\Delta V^E/V = f(c)$ together with the experimental results for H_2–D_2 crystals are presented in Fig. 6. One can see that the estimate correctly predicts the sign of the effect and is close in magnitude.

4. CONCLUSIONS

Structural investigations of liquid isotopic solutions of hydrogen and deuterium by means of neutron diffraction have shown that these solutions differ from ideal solutions and they exhibit a weak tendency toward separation. It is conjectured that this is a result of the difference in the zero-point vibrations, which result in the appearance of concentration fluctuations in the short-range order. It follows from investigations of crystals of isotopic mixtures at low temperature that these crystals are single-phase, but the Vegard

TABLE I. Parameters of the hcp crystal lattice and excess volumes of the solid solutions $(p\text{–}H_2)_c(o\text{–}D_2)_{1-c}$ at $T = 4.2$ K.

c	a, Å	c, Å	c/a	V, cm³/mole	$\Delta V^E/V$, %
0	3,605 (1)	5,882 (2)	1,632 (1)	19,933 (15)	—
0,34	3,662 (1)	5,972 (5)	1,631 (2)	20,88 (2)	—0,5
0,50	3,681 (1)	6,000 (4)	1,630 (2)	21,21 (1)	—1,2
1	3,782 (2)	6,167 (3)	1,631 (1)	23,00 (2)	—

relation for the specific volumes in them is not satisfied. The excess mixing volume is negative, close to the value known for liquid solutions and can be predicted starting from the equations of state of the pure isotopes.

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