PHASE DIAGRAM OF THE eH_2-eD_2 VAPOR-LIQUID-CRYSTAL SYSTEM AT TEMPERATURES BETWEEN 14° AND 20°K[1]

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Condensation curves are measured for five mixtures containing 14.3, 25.2, 40.1, 49.5, and 75.4% of D_2 by the dew-point method between 14° and 20°K. The projections of the three-phase lines of the eH_2-eD_2 system on the P, T plane are measured. The topology of the vapor-liquid-crystal phase diagram of this system is determined from the aggregate data.

1. INTRODUCTION

THE isotopes of hydrogen are known to have very different thermodynamic properties, especially in their condensed phases. In addition, a number of theoretical and experimental studies have shown that mixtures of hydrogen isotopes are far from being ideal mixtures. Thus it is impossible to calculate in advance the phase diagram of a binary system of these isotopes from only the properties of the pure components. Interest in the investigation of the actual complete phase diagram encompassing the regions of two-phase and three-phase equilibrium in a broad range of temperatures, pressures, and concentrations is not based only on the prospect of determining the topology precisely. Knowledge of the complete diagram enables us also to evaluate the degree of nonideality of the binary systems in different phases for different values of the external parameters and to calculate the excess thermodynamic potentials of the corresponding phases.

The phase diagrams of H_2-D_2 solutions have been studied by several workers. In [1] two dew points of the nH_2-nD_2 system were measured (in mixtures containing 49.9% H_2 at 19°K and 44.0% H_2 at 20°K). In [2] the vapor-liquid phase diagram of the nH_2-nD_2 system was determined in the 21°–25°K interval. The dependence of the vapor pressure[2] on the concentration of nH_2-nD_2 solutions at 20.3°K is shown in [3]. Liquid-solid phase (or melting-point) diagrams of the H_2-D_2 system are given in [4-6]. However, the results did not permit a unique determination of the topology of this diagram and particularly the location of the "solidus" curve (representing complete solidification of the mixtures). Finally, the only measurements for the eH_2-eD_2 vapor-solid diagram are given in [5] pertaining to the eH_2 triple point (13.81°K) alone.

The foregoing review of the literature shows that insufficient data have been available for a complete phase diagram of the H_2-D_2 system including curves representing the equilibrium of the vapor, liquid, and solid phases. Our work was begun for the purpose of obtaining all the data needed to construct this diagram. In the first stage we obtained the melting-point diagram of the eH_2-eD_2 system.[7] Having used special precautions to ensure the rapid establishment of concentration equilibrium, we were able with sufficient reliability to determine the topology of the diagram (having the form of a smooth cigar) and the positions of the solidus and liquidus. In the present work we measured the condensation curves of several eH_2-eD_2 mixtures both to the liquid phase (dew points) and to the solid phase (frost points) in the range 14°–20°K. For this system we also determined the projections of the three-phase lines on the P, T plane (a single projection for all the three-phase lines). The investigated H_2-D_2 system was in ortho-para equilibrium; this enabled us to exclude errors associated with the possibility of conversion to a low-temperature modification during the experimental work.

2. EXPERIMENT AND RESULTS

A. Dew-point and frost-point curves. The condensation curve in the coordinates P and T represents the temperature dependence of the pressure P at which a gaseous mixture of given concentration (X of the vapor) begins to condense.

The dew and frost points were measured as follows. At a given temperature a chamber of variable volume (a bellows) was filled with a gaseous mixture of the isotopes in a known concentration. The volume of the chamber was gradually reduced by successive compressions to a small constant value. Following each successive volume change we measured the pressure of the mixture and plotted the dependence of the pressure on the degree of compression of the bellows. A break of the curve clearly indicated the onset of condensation, which was determined with 0.1 Torr accuracy. Temperatures were determined from the eH_2 vapor pressure, using data in [8], with 0.01°K accuracy.

Figure 1 shows the results. The vapor-liquid equilibrium curves for pure components are based on data in [8] with which our measurements of the eH_2 and eD_2 vapor pressure are in good agreement. The condensation curves were determined for five concentrations of the eH_2-eD_2 mixture. The average pressure spread of

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[1] The notation eH_2 and eD_2 refers to hydrogen and deuterium in ortho-para equilibrium at 20.4°K. In the text nH_2 and nD_2 designate normal hydrogen and deuterium (i.e. in ortho-para equilibrium at room temperature).

[2] In the literature, for liquid mixtures in addition to the expression "vapor pressure of the solution" the expression "boiling point of the solution" is often used. We prefer the first expression, which is also used for equilibrium pressure above the solid phase.

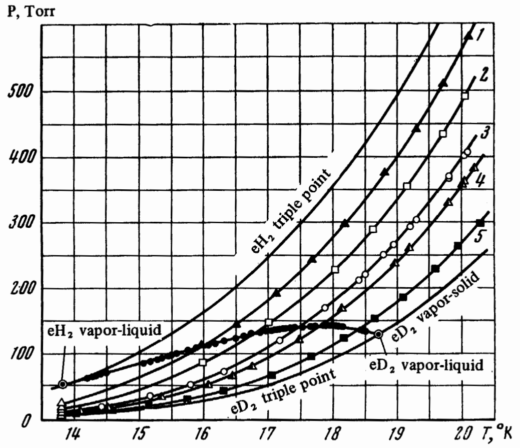

FIG. 1. Condensation curves of eH_2-eD_2 mixtures for five different concentrations of D_2: 1–14.3%, 2–25.2%, 3–40.1%, 4–49.5%, 5–75.4%. Δ–data of Simon for 13.81°K; [5] ●–projection of the three-phase lines of the eH_2-eD_2 system on the P, T plane.

the experimental points from the smooth curves is 0.3 Torr. At 13.81°K frost-point data from [5] are given, to which our results are seen to extrapolate well. It is difficult to make a detailed comparison with data given in [1,2], where measurements were performed mainly at higher temperatures for the nH_2-nD_2 system.

B. Projection of three-phase lines on the P, T plane. Since the condensation curve measurements were performed in a temperature range that lies mainly between the triple points of the pure components, each curve represents partly condensation to the liquid phase (dew points) and partly condensation to the solid phase (frost points). To determine the boundary between the regions where liquid and solid solutions exist in the P, T plane, it was necessary to measure the projections of the three-phase lines on this plane. This projection represents the temperature dependence of a pressure that is common to all three coexisting phases.

Our measurements were performed as follows. We determined the pressure above a condensed eH_2-eD_2 solution while lowering the temperature. Two typical experimental curves for two different concentrations are shown in the lower right-hand corner of Fig. 2. Each curve has two sharp bends, corresponding to the onset (a and a′) and the termination (b and b′) of solidification of the liquid solution. Obviously, at pressures and temperatures in the region between the bends all three phases exist. It must be emphasized that for the given measurements it is unnecessary to know the concentration of each phase and their ratio; it is sufficient to determine simply the segment of the P(T) curve that corresponds to their coexistence. This segment will always belong to the projection of the three-phase lines on the P, T plane. Our measurements for eight different eH_2-eD_2 solutions enabled us to locate this projection in detail. The results are shown in Figs. 1 and 2 (on a larger scale). Temperatures were determined with 0.01°K accuracy. The average pressure spread of the experimental points about the smooth curves is 0.2 Torr.

In Figs. 1 and 2 the maximum of the three-phase line projection occurs at 17.90°K and 141.8 Torr. This means that the eH_2-eD_2 liquid solutions begin to solidify at pressures somewhat higher than the pressure at the eD_2 triple point. In Fig. 2 the dot-dash curve represents our calculated projection for ideal eH_2-eD_2 solutions. At the maximum point there is about 5% pressure difference between the real and ideal curves.

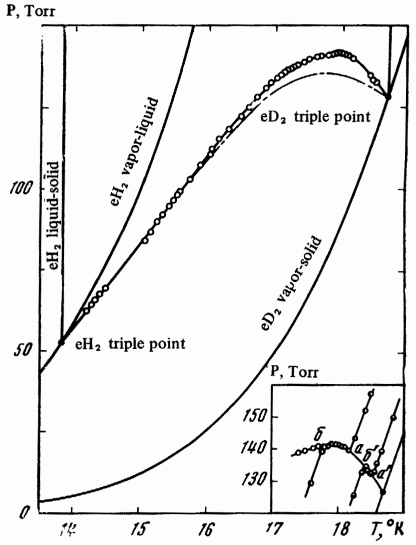

FIG. 2. Projection of the three-phase lines of the eH_2-eD_2 system on the P, T plane. The graph in the lower right-hand corner shows typical experimental curves for two solutions; the segments a, b and a′, b′ correspond to the coexistence of three phases. The dot-dash curve corresponds to the projection of the three-phase lines for ideal eH_2-eD_2 solutions.

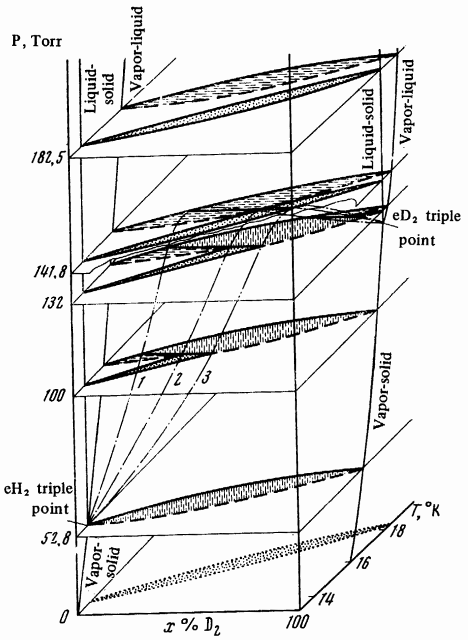

FIG. 3. Vapor-liquid-solid phase diagram of the eH_2-eD_2 system.

3. TOPOLOGY OF THE THREE-DIMENSIONAL eH_2-eD_2 PHASE DIAGRAM

The data for the melting-point curve that we obtained in the present and in earlier[7] work have enabled us to determine almost completely the vapor-liquid-solid phase diagram in three-dimensional P, T, X space for the eH_2-eD_2 system at 14°–20°K. This three-dimensional diagram, seen in Fig. 3, shows graphically how the topology of the phase diagram is altered by a change of any one of the system parameters. Figure 3 shows several characteristic cross sections for different constant pressures.

In the cross section at 182.5 Torr we see two separate vapor-liquid and liquid-solid phase diagrams, corresponding to a continuous series of eH_2-eD_2 solutions in all three phases. Similar diagrams are obtained at higher pressures up to the pressure at the critical point of eH_2.

In the cross section at 141.8 Torr, which corresponds to the maximum of the three-phase line projection, tangency of the separate diagrams occurs and a peritectic form appears, corresponding to equilibrium of the three phases.

In the cross sections between 141.8 Torr and 128.5 Torr (at the eD_2 triple point) we observe in each case two peritectic points (at 132 Torr, for example). Below 128.5 Torr one peritectic remains (at 100 Torr), which disappears at the eH_2 triple point (in the cross section for 52.8 Torr). This corresponds to the complete freezing of the liquid phase. At still lower pressures a vapor-solid phase diagram remains.

In states of three-phase equilibrium different concentrations of all three phases correspond to an identical pressure and temperature. Therefore in P, T, X space three-phase lines will exist, connecting sets of P, T, X values for the vapor, liquid, and solid states. These lines are seen in Fig. 3 as dot-dash curves which represent the intersections of two-phase equilibrium surfaces. Figure 3 also shows their identical projection on the P, T plane, which has already been mentioned.

It should also be noted that the melting-point diagram in [7] was derived from a thermal analysis of condensed eH_2-eD_2 mixtures under saturated vapor pressure in a constant volume. Therefore the onset and termination of solidification corresponded, in general, to different vapor pressures. Thus the actually measured melting-point diagram is the projection of the three-phase lines 2 and 3 on the T, X plane; this projection is shown in the lowest cross section in Fig. 3. However, the properties of the condensed phase are almost independent of pressure up to a few tens of atmospheres. This is supported by the practically vertical form of the liquid-solid equilibrium curves for the pure components in Fig. 3. We can therefore quite confidently consider that for different constant pressures those parts of the diagram that pertain to liquid-solid equilibrium are known to us and coincide either completely with the experimental melting-point diagram or with a portion of it for pressures below 141.8 Torr (the pressure at the maximum of the three-phase lines).

The dashed lines in Fig. 3 are the vapor pressure curves above liquid and solid eH_2-eD_2 solutions; up to the present moment these curves have not been measured. They were plotted in Fig. 3 by taking into account their points of intersection with the melting-point diagrams (these points comprise the three-phase lines 2 and 3) and making a reasonable interpretation of vapor pressure data in [2,5] for the H_2-D_2 system in the 14°–20°K range. The positions of the three-phase lines in P, T, X space is completely determined, since in [7] the projections of three-phase lines 2 and 3 on the T, X plane were obtained, while in the present work we have obtained a single projection for all three three-phase lines on the P, T plane as well as the condensation curves of the mixtures.

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