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# *VAPOR PRESSURE OF LIQUID HYDROGEN-DEUTERIUM SOLUTIONS BELOW 20.4 K*

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The vapor pressure of liquid $eH_2 - eD_2$ solutions is measured at temperatures from 20.4° K down to the freezing point. Mixtures of $eH_2 - eD_2$ with concentrations of 85.0, 73.6, 60.2, 49.6, 39.8, 30.4, 19.7 and 6.0% of $eH_2$ are investigated. Deviations of the vapor pressure of liquid $eH_2 - eD_2$ solutions from the Raoult law for ideal solutions are determined.

## 1. INTRODUCTION

IN our earlier studies of the phase equilibrium in the $eH_2 - eD_2$ system, we measured the melting diagram of this system[1], the lines of dew and frost points in the temperature interval 20–14° K, and the projection of the three-phase lines on the (P, T) plane[2]. This enabled us to plot a three-dimensional phase diagram of the $eH_2 - eD_2$ isotope solution[1)] in terms of the coordinates P, T, and x[2]. However, the vapor-pressure lines of the liquid and solid solutions were marked on this diagram tentatively, without a direct measurement. We have now determined experimentally the vapor-pressure line of liquid $eH_2 - eD_2$ solutions.

## 2. APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental setup is illustrated in Fig. 1. The main part of the instrument is a massive copper block with two equal cylindrical chambers, each approximately 2 cm³ in volume. One of the chambers (2) is intended for the investigated mixture, and the other (3) is a condensation thermometer. The thermometric material was $eH_2$. To ensure rapid assumption of the ortho-para equilibrium state by the mixtures and by pure hydrogen at the temperature experiment, we placed in each chamber a small amount of catalyst for the ortho-para transformation $(CrOH)_3$. The gas was fed to the chambers through capillaries of 1 mm inside diameter. The vacuum jackets around the capillaries prevented the gas from condensing in them. Identical magnetic stirrers were installed inside the two chambers, making it possible to stir the entire liquid mass continuously. This ensured homogeneity of the concentration of the entire liquid, including its surface. The stirrers were actuated by a magnet. The pressures in the chambers were measured with mercury manometers that were read with cathetometers accurate to 0.02 mm Hg. Small pressure differences between the chambers could be measured with a differential oil manometer.

Before performing the experiments, the previously prepared $H_2 - D_2$ mixture was condensed from flask 11 into the thick-wall copper vessel 12. This vessel was then closed with a valve and heated to room temperature. The amount of mixture in it could be monitored with manometer 13. There was always enough mixture to perform several experimental runs, using each time a new batch of mixture from vessel 12. Such a procedure ensured a constant mixture concentration from run to run.

The quantity of mixture that had to be condensed in the measurement chamber to measure vapor pressure reliably was determined from the filling curves—the dependence of the pressure in the chamber on the quantity of condensed mixture at constant temperature. It was established that as the measuring chamber becomes filled with the mixture, the pressure in it first increases, but starting with a certain degree of filling (0.9 liter of gas under normal conditions for all the investigated mixtures) the pressure ceases to vary within ± 0.2 mm Hg. This limiting pressure corresponds to the vapor pressure of the investigated mixture. In all the measurements of the vapor pressure we used equal quantities of mixture (1.3 liter of gas under normal conditions), corresponding to a reliable measurement of the vapor pressure.

To measure the vapor pressure, the mixture was condensed from vessel 12 into the measuring chamber at 20.4° K. The temperature was then successively lowered and the vapor pressure measured at each new temperature. Most experiments were performed while the temperature was lowered. In experiments in which the

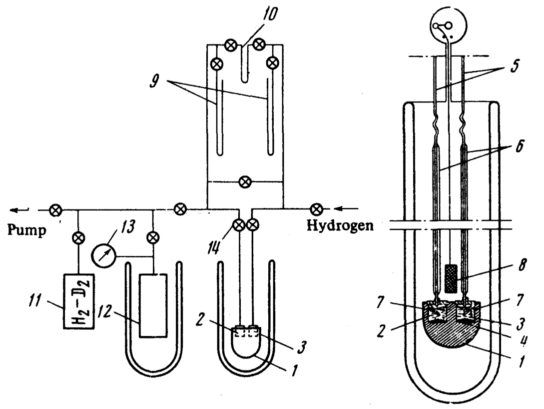

FIG. 1. Apparatus for measuring the vapor tension of liquid $eH_2$–$eD_2$ solutions: 1—copper block, 2, 3—cylindrical chambers, 4—catalyst, 5—capillaries, 6—vacuum jackets, 7—magnetic stirrers, 8—magnet, 9—mercury manometers, 10—differential oil manometer, 11—flask to store the mixture, 12—copper vessel for the mixture, 13—manometer, 14—valve.

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[1)] The symbols $eH_2$ and $eD_2$ denote hydrogen and deuterium that are in equilibrium relative to the ortho-para composition at 20.4°K; the symbols $nH_2$ and $nD_2$ denote the same at room temperature.

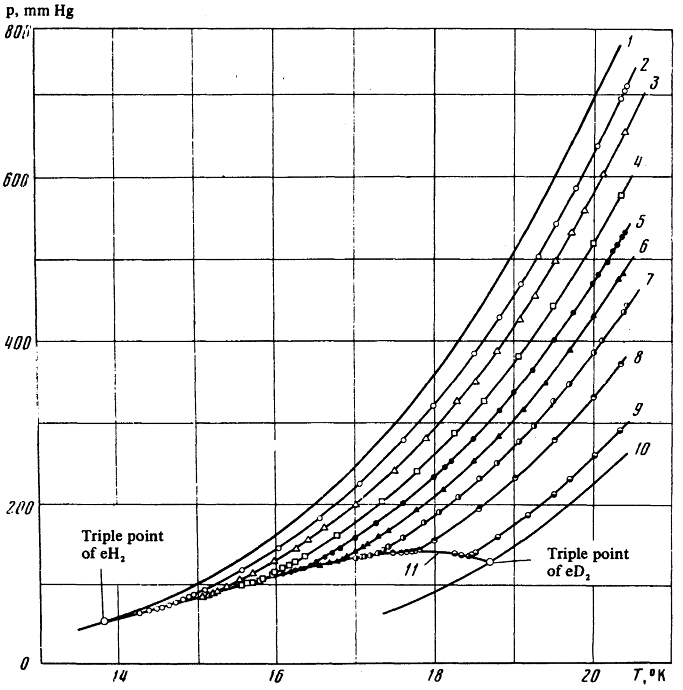

FIG. 2. Vapor-pressure curves of $eH_2$–$eD_2$ solutions: 1–pure $eH_2$, 2–85.0% $eH_2$, 3–73.6% $eH_2$, 4–60.2% $eH_2$, 5–49.6% $eH_2$, 6–39.8% $eH_2$, 7–30.4% $eH_2$; 8–19.7% $eH_2$, 9–6.0 $eH_2$, 10–pure $eD_2$, 11–projection of three-phase lines on the (P, T) plane from [2].

temperature is raised, it is necessary to take into account the danger that the liquid-phase concentration may deviate from the initial value. This change can be due to separation when part of the liquid is evaporated in order to fill the manometer section to a higher pressure. To avoid this, the manometer section was disconnected from the chamber by means of valve 14 before raising the temperature, and was filled with the original mixture from vessel 12 to the required pressure. Only then was the temperature raised, valve 14 opened, and the vapor pressure measured. The results of the measurements at both falling and rising temperature agreed within the spread of the experimental points.

As already noted, the temperature was determined from the $eH_2$ vapor pressure in chamber 3.[2] In addition, the block temperature could be determined from the $nH_2$ vapor pressure in the Dewar. The difference between the temperatures measured by the two methods did not exceed 0.01°K as a rule. Special experiments have shown that the massive copper block ensures equality of the temperatures in chambers 2 and 3 with good accuracy: the difference did not exceed 0.005°K. The block temperature was maintained constant within 0.002°K. The temperature was determined from the P(T) plot for pure hydrogen from[3]. The mixtures were prepared in accord with the partial pressures of the pure gaseous components with an absolute concentration error 0.1%.

## 3. RESULTS AND DISCUSSION

We measured the vapor pressure of the liquid solutions for eight different $eH_2$ – $eD_2$ mixture concentrations: 85.0, 73.6, 60.2, 49.6, 39.8, 30.4, 19.7 and 6.0% $eH_2$. The results are shown in Fig. 2. The experimental points on each curve correspond to several measurement runs, performed with both rising and falling temperature. The scatter of these points relative to the smoothed curve was on the average 0.3 mm Hg.

In the analysis of the results it was necessary to take into account the fact that the catalyst for the ortho-para transformation, which was located in the measuring chamber, adsorbed a small part of the mixture. It was known[4] that the deuterium is adsorbed more readily than hydrogen. Consequently, one could assume a slight increase of the hydrogen content in the liquid mixture, compared with the initial one, owing to the selective adsorption of the catalyst. The value of this concentration difference should depend on the amount m of the catalyst in the chamber, on the amount M of the condensed mixture, and on its concentration x. Auxiliary experiments were performed to determine these relations.

Mixtures having identical initial concentrations were condensed in both chambers at different values of m/M in the two chambers. The resultant difference between the pressures in the chambers was measured with a differential oil manometer (the block temperature was determined in these experiments from the $nH_2$ vapor pressure in the Dewar). The difference between the pressures was 10–30 mm oil or 1–2 mm Hg at 20.4°K, and decreased with decreasing temperature. In the state of three-phase equilibrium (on reaching curve 11 of Fig. 2), the pressure difference vanished completely jumpwise. As a result of the described experiments it was established that the concentration change due to adsorption by the catalyst is proportional to the ratio m/M.

In all the main measurements of the vapor pressure, the amount of catalyst in chamber 2 was 200 mg, and the amount of condensed mixture was 1.3 liter of gas under normal conditions. For these quantities, the dependence of the concentration deviation on the mixture composition is shown in Fig. 3. This curve was used to determine the systematic corrections to the initial concentrations. The indicated values of the investigated

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[2] Under the experimental conditions, the ortho-para conversion of the hydrogen and of the mixture was completed after 10–15 minutes.

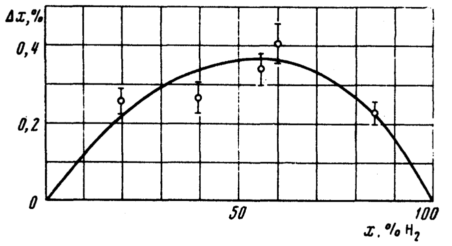

FIG. 3. Change of mixture concentration in the measuring chamber due to adsorption by the catalyst of the ortho-para transformation; Δx—increase of hydrogen concentration, x-concentration of initial mixture.

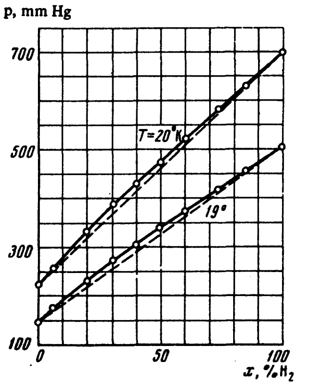

FIG. 4. Deviation of vapor pressure of the $eH_2$–$eD_2$ solutions from Raoult's law for ideal solutions. Solid line—measured vapor pressure, dashed—according to Raoult's law.

concentrations incorporate these corrections. The total concentration error was 0.15%.

It is seen from Fig. 2 that at the instant when the liquid mixture begins to solidify a kink is observed on the vapor-tension curve. The temperature corresponding to this kink is the starting point of the solidification of the given mixture. These points coincide, within the limits of the experimental accuracy, with the temperatures of the start of solidification of the $eH_2 - eD_2$ solutions, measured by us earlier by an independent method in[1]. With further lowering of the temperature, the system remains in three-phase equilibrium, and the corresponding sections of the curves agree well with the projection of the three-phase lines on the (P, T) plane. This projection, which was determined in[2], is shown by the solid line 11 of Fig. 2.

Figure 4 shows plots of the vapor tension against the concentration at 19 and 20° K. The vapor pressure of the $eH_2 - eD_2$ mixtures is seen to deviate appreciably from Raoult's law for ideal solutions. This deviation is maximal at approximately 30% $H_2$ concentration, and amounts to several per cent. There are no other measurements of the vapor pressure of $eH_2 - eD_2$ solutions in the temperature interval 14–20° K. It is possible, however, to compare the results with the data of[5,6], which were obtained in the immediate vicinity of the indicated temperature interval. Newman and Jackson[5] measured the vapor pressure of $nH_2 - nD_2$ solutions above 21° K. They observed a deviation from Raoult's law, of the same magnitude and character as in our measurements. In a class by itself is the result of Blagoĭ and co-workers[6], who measured the vapor tension of several $nH_2 - nD_2$ solutions at 20.3° K. Their deviation from Raoult's law is approximately twice as large.

The vapor-tension lines measured by us, and the dew-point lines determined by us earlier[2], are in essence two branches of the liquid-vapor phase diagram of the $eH_2 - eD_2$ system. It is known that the Gibbs-Duhem equation holds for any diagram in thermodynamic equilibrium. We used this equation in the form given in[7], and verified its satisfaction for the liquid-vapor diagrams at 19 and 20° K. The calculation has shown a high degree of thermodynamic agreement for the two branches of the diagram. The Gibbs-Duhem equation holds within less than 1%.

Thus, the results obtained by us are in good agreement and are thermodynamically reconciled with measurements of other phase-equilibrium lines performed by us earlier.[1,2]

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