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THE DENSITY OF H_2-D_2 *MIXTURES*

V. N. GRIGOR'EV and N. S. RUDENKO

Physico-Technical Institute, Academy of Sciences, Ukrainian S.S.R.

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The density of the binary system H_2-D_2 has been measured in the range from the melting point to 20.4°K, and the relative excess volumes $\Delta V/V$ determined. For all mixtures $\Delta V/V < 0$ and is independent of temperature within the experimental accuracy. For an equimolar mixture $\Delta V/V \approx -0.01$. The theoretical calculations of $\Delta V/V$ for the H_2-D_2 system[9,11] do not agree with the experimental data.

INTRODUCTION

THE influence of quantum effects on the microscopic properties of matter can be revealed by a study of the physical properties of mixtures of isotopes. As is well known, isotopic mixtures behave ideally in any phase according to classical considerations,[1] so that a contribution from quantum effects to the thermodynamic functions is characterized by a departure from ideality. These effects are most marked for isotopes of the light elements at low temperatures. The properties of the He^3-He^4 system have been studied fairly thoroughly,[2] but for H_2-D_2 mixtures only the liquid-vapor[3] and liquid-solid[4] diagrams are known. The data obtained indicate a considerable departure in the behavior of these systems from the laws for ideal mixtures. This is shown especially clearly in the investigations of Kogan, Lazarev and Bulatova[4] who found a separation of a mixture of H_2 and D_2 into two phases at temperatures below the melting point.

The present work was undertaken for the further study of the deviation of the hydrogen isotopes system from ideality. The density of mixtures of H_2 and D_2 was measured in order to calculate the excess mixing volume

$$\Delta V = V - (c_H V_H + c_D V_D); \qquad (1)$$

where V, V_H and V_D are the molar volumes of the mixture, of hydrogen and of deuterium and c_H and c_D are the molar concentrations of hydrogen and deuterium.

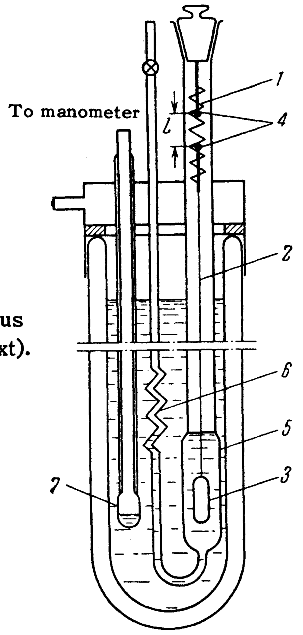

FIG. 1. Diagram of the apparatus (the description is given in the text).

EXPERIMENTAL SECTION

The measurements were made by the method of hydrostatic weighing on a spring balance (Fig. 1). A quartz float 3 of weight ≈ 200 mg and volume ≈ 0.05 cm^3 is hung from the spring 1 by a 0.03 mm diameter copper wire. The distance L between the quartz markers 4 attached to the lower and upper ends of the spring was measured with a KM-6 cathetometer. If L is the distance between the markers when the float is immersed in liquid, and L_0 the corresponding distance in vacuum, then $L_0 - L = k\rho$, where ρ is the liquid density and k is a coefficient of proportionality, depending on the sensitivity of the spring and the volume of the float.

The spring was made of 0.08 mm diameter tungsten wire and had 130 turns of diameter ~ 8 mm, which gave a sensitivity of about 50 cm/g. After the spring had been prepared it was kept under a load of 200 mg to prevent any zero drift. During the measurements this drift did not exceed 0.01 mm per day. The pure isotopes H_2 and D_2

T•, K	ΔV/V, %	T, °K	ΔV/V, %	T, °K	ΔV/V, %	T, °K	ΔV/V, %
c_D =91.1%		c_D =76.95%		c_D =61.6%		c_D =57.3%	
20.39	0.52	20,46	1,14	20,46	1.11	20,40	0,95
20.09	0.52	19.82	1.08	19,96	1,00	19,89	1,00
18,36	0.53	19.79	1.02	19.20	1,05	19,79	0.93
		19.08	0,90	19,15	1.10	19,10	1.04
		18,58	0,96	18,44	1.06	19,08	0,99
		18,44	1.03	18,67	0.95	19,09	0,98
		18,39	0,98	17,52	1.05	18,51	0.98
		17,79	0,96	16,97	1,09	18.38	0,98
		17,75	0,96			17.82	0,91
c_D = 47.75%		c_D = 38,3%		c_D = 20,35%		17.61	0,98
20,44	1,22	20,43	1.0	20,38	0,86	16,78	0,83
19,81	1.16	19.69	1,12	19,83	0.94	16,76	0,89
19,80	1.27	19,67	1,05	19.76	0,81	16,74	0,82
19,26	1,15	19.03	1.00	19.23	0,91	c_D = 9,7%	
19,24	1.14	18.99	1,00	19.00	0.82	20,42	0,70
18.46	1.19	18,38	1.06	18.55	0,89	14,97	0,71
18,42	1,10	18.31	1,09	18,29	0,78	14,86	0.74
17,79	1,16	17.71	1,07	17,73	0.90	14,48	0,85
17.70	1.18	17,52	1.14	17.58	0.85		
17.11	1,15	16,85	0.99	16,81	0,72		
17,06	1.13	16.77	0,97	16.64	0.78		
16,38	1,19	16.10	1.04	16.05	0.70		
16,36	1,14	15,84	1.08	15.46	0,85		
				15,13	0,75		

were used to determine the magnitude of k. The stretch of the spring was measured with vessel 5 filled with liquid hydrogen or deuterium at various temperatures, and from the known densities we found

$$k = 25{,}09 \pm 0{,}02 + (0{,}040 \pm 0{,}004)(L_0 - L) \text{ cm}^4/\text{g}.$$

This method of calibration removes additional errors related to the determination of the float volume, and reduces the error arising from the action of surface tension on the support 2. We note that according to the data of Forziati et al.[5] the latter effect is less than the experimental errors. A dependence of k on $L_0 - L$ is explained by the change in sensitivity of the spring with elongation, since the angle between the coils increases for large elongations. Several repeat calibrations between the measurements of the mixtures gave the same values of k, within the limits of error.

The measurement of the elongation introduced a noticeable error in addition to the calibration errors. The errors associated with maintaining and measuring the temperature and with the preparation of the mixtures were negligibly small. The total error in measuring the density was 0.1 — 0.2%.

In preparing the mixtures, the hydrogen and deuterium were thoroughly cleaned by being passed through a glass coil cooled in liquid hydrogen. Further purification took place on condensing the mixture into the apparatus through the spiral 6. Mixing was achieved by many successive condensations and evaporations. The concentrations of the mixtures were calculated from the partial pressures. The temperature was obtained by pumping liquid hydrogen, and was measured by the saturated vapor pressure of pure hydrogen, contained in vessel 7.

The measurements were made in the range from the melting point of the mixture to 20.4° K, both for the temperature decreasing by steps and increasing. The hydrogen and deuterium had the room temperature equilibrium ortho-para concentrations. No noticeable change in density due to the ortho-para conversion was found, even after keeping for several hours. This was evidently due to the high purity of the hydrogen and the absence of any catalysts. To achieve these conditions, the investigated mixture was replaced by a fresh one when the smallest trace of cloudiness appeared in coil 6.

The good agreement between results obtained with a given mixture on different days indicates the absence of appreciable HD formation in the mixtures.

The densities of eight mixtures were measured with D_2 concentrations from 10 to 90%. From the densities obtained, the molar volumes of the mixtures $V = \mu/\rho$ (μ is the molecular weight of a mixture) were calculated, and the excess mixing

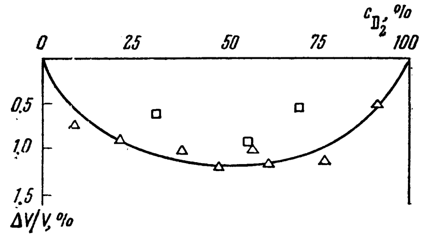

FIG. 2. The dependence of the excess mixing volume on the concentration of the mixture at T = 20.4°K: Δ — data of the present work, □ — Lambert's data.[6]

volume derived from (1). In the calculation account was taken of the difference between the concentration of the liquid and that of the original mixture, due to the presence of the vapor. The correction introduced into the concentrations did not exceed 0.15%. The values of V_D for temperatures below the melting point of D_2 were calculated from an extrapolation formula.

The values of $\Delta V/V$ for all the mixtures studied are shown in Table I. The concentrations given in the table are mean values. The true concentrations do not differ by more than 0.05% from the means, due to various corrections to the gas phase. Figure 2 shows the dependence of $\Delta V/V$ on concentration at a temperature $T = 20.4°K$. It can be seen from the table that the relative excess volume is independent of temperature within the limits of error, and the $\Delta V/V(c)$ isotherms for other temperatures have the same appearance as shown in Fig. 2. The figure also shows data taken from a preliminary report by Lambert,[6] who measured ΔV at 20.3°K. The results agree qualitatively, but the difference is apparently somewhat greater than the errors in measuring (the accuracy of the measurements is not stated by Lambert).

DISCUSSION OF THE RESULTS

The experimental results obtained indicate a relatively large departure from ideality for mixtures of the hydrogen isotopes. Over the whole range of temperature and concentration studied the mixing volume is negative, and is of the same order of magnitude as for binary systems of liquefied gases[7] such as O_2-Ar, O_2-N_2 etc. Simon and Bellemans[9] have recently published a theoretical calculation of $\Delta V/V$ for isotopic mixtures, based on the work of Prigogine et al.[8] They obtain $\Delta V/V \approx 1\%$ for an equimolar mixture of H_2 and D_2, i.e., the calculated volume is positive, which is contrary to the experimental data. We should note that the calculations for the He^3-He^4 and D_2-H_2 systems according to Progogine's theory agree qualitatively with the experimental data.[8,10]

Blagoĭ, who studied mixtures of liquefied gases, found good agreement between the experimental data and calculations made according to the formula proposed by Meares.[11] Meares considered that the total volume change on mixing two liquids of approximately equal molar volumes consists of two terms

$$\Delta V = \Delta V_I + \Delta V_{II}. \qquad (2)$$

The first term, which is related to the energy of mixing, was calculated by Scatchard.[12] According to Scatchard

$$\Delta V_I = \beta \Delta E_v, \qquad \Delta E_v \approx \Delta H - T\alpha \Delta V/\beta, \qquad (3)$$

where β is the compressibility of the mixture, ΔE_V is the excess mixing energy at constant volume, ΔH is the excess mixing enthalpy and α is the thermal expansion coefficient of the mixture. The second term, which arises because of the difference in compressibilities and internal pressures, p, was obtained by Biron[13] and was somewhat refined by Meares:[11]

$$\Delta V_{II} = \gamma c_1 c_2 (\beta_1 V_1 - \beta_2 V_2)(p_1 - p_2), \qquad (4)$$

where γ is a constant coefficient for all liquids. By comparing the experimental and theoretical data, Meares found $\gamma = 0.4$.

In view of the smallness of ΔV, we can put $\Delta E_V \approx \Delta H$ to a first approximation in calculating the mixing volume. According to Lambert's data,[6] $\Delta H = 12 c_H c_D$ cal/mole for hydrogen and deuterium. The values of α, β and V for the pure isotopes were taken from the compilation of Woolley et al.,[14] and were found from the additivity rule for the mixtures. The internal pressure was determined from the thermodynamic relation $p = T\alpha/\beta$. For an equimolar mixture at $T = 20.3°K$ we found $\Delta V_I = 0.11$ cm^3/mole, $\Delta V_{II} = -0.15$ cm^3/mole, so that $\Delta V = -0.04$ cm^3/mole. This value agrees as to sign with experiment, but is about five times smaller in absolute magnitude. It is interesting to note that the same result can be obtained if ΔV is calculated according to (3) by substituting the value of ΔE_V, derived from Hildebrandt's formula for regular mixtures:

$$\Delta E_v = (c_H V_H c_D V_D / V)\,[(Q_H/V_H)^{1/2} - (Q_D/V_D)^{1/2}]^2,$$

where Q_H and Q_D are the heats of vaporization of hydrogen and deuterium.

Better agreement with experiment can be obtained if the value of the coefficient in (4) is taken as close to unity instead of 0.4, although it is unlikely that such a choice can be justified.

We can thus see that the existing theory of mixtures cannot explain the appreciable compression found experimentally on the formation of mixtures of the isotopes H_2 and D_2.

In conclusion, we may remark that the phase separation of the hydrogen isotopes near the melting point can be explained by considering the correlation in the solid state.[15] It is possible that similar effects in the liquid must be taken into account for a correct calculation of the volume change on mixing.

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