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DENSITY MEASUREMENT IN LIQUID H₂-D₂ SOLUTIONS

Yu. A. Milenko and R. M. Sibileva

UDC 532.7

Molar and excess molar volumes of liquid H₂-D₂ solutions are determined by dielectric constant measurements.

Because of quantum effects, the thermodynamic properties of the condensed phases of hydrogen isotopes differ markedly from each other, and their solutions are nonideal, being characterized by excess quantities, in particular, an excess molar volume:

$$V^E = V(p, T) - [V_1(p, T)c_1 + V_2(p, T)c_2], \quad (1)$$

where V is the molar volume of the mixture at a given pressure T and pressure p ; $V_{1,2}$, molar volumes of the pure components under the same conditions; and $c_{1,2}$, component molar concentrations in the solution.

The excess molar volumes of H₂-D₂ solutions at temperatures $T \leq 20.4^\circ\text{K}$ have been measured previously in [1-3]. The results of those studies show that $V^E < 0$, agree qualitatively with each other, but show large quantitative differences.

In the present study molar volumes of H₂-D₂ solutions were determined by measuring the dielectric constant ϵ . This method requires knowledge of the polarization (Clausius-Mossotti function) P of the pure materials and the concentration dependence of P for the mixture. The polarization of H₂ and D₂ for $T \leq 20.4^\circ\text{K}$ has been determined previously [4,5]. The function $P(c)$ was assumed linear.

The resonant frequency ($\sim 10^{10}$ Hz) of an empty and completely filled resonator was measured to determine ϵ .

This method and experimental technique have been used previously to measure ϵ in mixtures of *o*- and *p*-hydrogen, and *o*- and *p*-deuterium [4,5].

The experimental uncertainties were: in frequency, ± 0.2 MHz, which corresponds to an ϵ uncertainty of $\pm 0.8 \cdot 10^{-4}$; in temperature (parahydrogen condensation thermometer) $\pm 0.01^\circ\text{K}$ ($\Delta\epsilon \approx 4 \cdot 10^{-5}$). Data on *p*-H₂ saturation pressure were taken from [6].

The mixtures were prepared at room temperature, measuring the partial pressures of the pure components and using the equation of state of an ideal gas. Practically no change in liquid concentration due to liquid-vapor separation occurred, since the quantity of vapor phase was negligibly small. The uncertainty in concentration determination was 0.15% ($\Delta\epsilon = \pm 0.8 \cdot 10^{-4}$). The total uncertainty in ϵ determination was not more than $\pm 2 \cdot 10^{-4}$.

Equilibrium with respect to *o*-*p* composition at 20.4°K of the H₂ and D₂ (*p*-H₂ and *e*-D₂) was obtained by maintenance in an Fe(OH)₃ catalyst. Room temperature equilibrium H₂ and D₂ (*n*-H₂ and *n*-D₂) were prepared by holding the gas in a glass tube in the presence of an incandescent platinum filament. It should be noted that this method cannot produce normalization of previously prepared H₂-D₂ mixtures, since the HD formation reaction occurs intensely under these conditions.

Dielectric constants of liquid H₂-D₂ solutions with the following compositions were measured: 30.2, 49.6, 69.9 mol. % D₂ for mixtures of *n*-H₂-*n*-D₂, and 29.9, 49.9, 69.7 mol. % D₂ for *p*-H₂-*e*-D₂ mixtures along the liquid-vapor equilibrium line at temperatures from the

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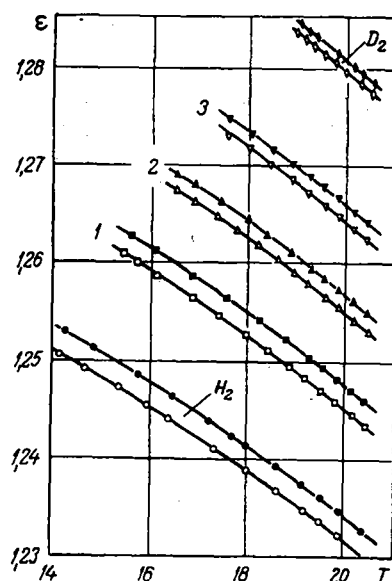


Fig. 1. Dielectric constants of H_2 , D_2 , and their mixtures versus temperature (shaded points, normal o-p compositions; open points, equilibrium): 1) ~ 30 mol. % D_2 ; 2) ~ 50 mol. % D_2 ; 3) ~ 70 mol. % D_2 . ϵ , dimensionless; T , $^{\circ}K$.

solution triple point to $20.4^{\circ}K$. Figure 1 shows the functions $\epsilon(T)$ for the pure components and mixtures studied.

We will assume that the polarization is linearly dependent on concentration for the mixtures studied:

$$P = \frac{\epsilon - 1}{\epsilon + 2} V = P_1 c_1 + P_2 c_2, \quad (2)$$

where $P_{1,2}$ are the polarizations of the pure materials.

Using the data obtained herein on ϵ , Eq. (2), and data on polarization of the pure components from [4,5] the molar volumes of the solutions $n-H_2-n-D_2$, $p-H_2-e-D_2$, and pure $e-D_2$ were determined for temperatures of $18.8-20.4^{\circ}K$ (Table 1). The excess molar volumes of the mixtures were determined (data on V of the components were taken from [1,7,8]), $V^E < 0$. For the 50% mixture $V^E/V = -0.65\%$ ($n-H_2-n-D_2$) and -0.7% ($p-H_2-e-D_2$) in the interval $18.8-20.4^{\circ}K$. The accuracy of v measurement comprises $\Delta V/V \approx 0.1\%$ at $\Delta P/P = \Delta P_{1,2}/P = 0.05\%$.

Figure 2 presents all available data on excess molar volumes of H_2-D_2 mixtures at $20.4^{\circ}K$. For the equimolar solution $n-H_2-n-D_2$ $V^E/V \approx -0.5\%$ [1] and -1.2% [2].*

* In [2] the measurements were conducted under vapor pressure; in [1, 3] under constant pressure. The correction which must be introduced in this connection in order to compare the values of V^E is small due to the low condensability of liquid H_2 and D_2 .

TABLE 1. Molar Volumes V , cm^3/mol , and Excess Molar Volumes V^E , cm^3/mol , for Solutions $n-H_2-n-D_2$ and $p-H_2-e-D_2$

$T, ^{\circ}K$	v	$-v^E$	v	$-v^E$	v	$-v^E$
	$c_{D_2} = 30.2 \text{ mol.}\%$		49.6		69.9	
$n-H_2-n-D_2$						
20.4	26.82	0.15	25.87	0.17	24.94	0.14
20.0	26.67	0.14	25.73	0.17	24.80	0.14
19.5	26.48	0.14	25.55	0.17	24.64	0.13
19.0	26.28	0.14	25.38	0.16	24.49	0.12
18.8	26.21	0.15	25.31	0.16	24.43	0.12
$T, ^{\circ}K$	v	$-v^E$	v	$-v^E$	v	$-v^E$
	$c_{D_2} = 29.9 \text{ mol.}\%$		49.9		69.7	
$p-H_2-e-D_2$						
20.4	26.94	0.15	25.93	0.18	25.00	0.15
20.0	26.79	0.14	25.79	0.18	24.87	0.14
19.5	26.59	0.14	25.61	0.17	24.71	0.14
19.0	26.40	0.14	25.44	0.17	24.54	0.14
18.8	26.33	0.14	25.37	0.17	24.48	0.14
100 ($e-D_2$)						

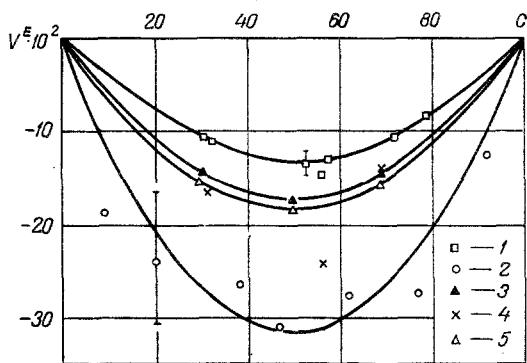


Fig. 2

Fig. 2. Excess molar volume V^E of H_2 - D_2 liquid solutions versus D_2 concentration, n - H_2 - n - D_2 : 1) data of [1]; 2) [2]; 3) present study; p - H_2 - e - D_2 : 4) data of [3]; 5) present study. V^E , cm^3/mol ; c , mol. % D_2 .

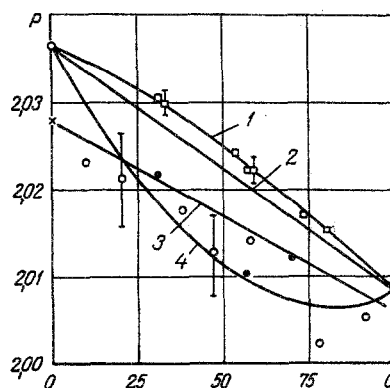


Fig. 3

Fig. 3. Polarization P of liquid H_2 - D_2 solutions versus D_2 concentration: 1) data of [1]; 4) [2] (n - H_2 - n - D_2); 2, 3) calculated with Eq. (2) for H_2 - D_2 mixtures normal and equilibrium in o - p composition, respectively; dark circles, calculated with Eq. (3) (p - H_2 - e - D_2). P , cm^3/mol ; c , mol. % D_2 .

estimated the measurement accuracy to be $\approx 0.02\%$ [1] and $\approx 0.2\%$ [2]. It is obvious that our results for the system n - H_2 - n - D_2 are close to the data of [1], the difference being 0.15%. For the system p - H_2 - e - D_2 the data of [3] and our results agree within the range of scattering of [3]. The absolute value of V^E for p - H_2 - e - D_2 mixtures is much larger than in n - H_2 - n - D_2 mixtures (present study), which agrees with the presence of a small positive excess molar volume in mixtures of the o - and p -modifications of H_2 and D_2 [4,5].

The data obtained on ϵ may be used to determine the form of the concentration dependence of the mixture polarization. Figure 3 shows the polarization of H_2 - D_2 mixtures as a function of mixture composition. Curve 1, calculated with use of [1], is close to linear, the nonlinearity comprising 0.15%, while curve 4 (using data of [2]) is strongly nonlinear - by 0.6-0.7%. Lines 2 and 3 were constructed with Eq. (2). Two of the three points for p - H_2 - D_2 mixtures [3] fit well on line 3.

The following factors favor a linear (or close to linear) dependence of P upon c for H_2 - D_2 solutions: 1) the measurement accuracy of [1] was higher than that of [2]; for p - H_2 - e - D_2 solutions (using [3]) the function $P(c)$, although in fact nonlinear, is only slightly so (see Fig. 3); 2) the mixture polarization P , as in the case of the pure components, may be written in the form of a series in powers of $1/V$:

$$P = A + B/V + C/V^2 + \dots, \quad (3)$$

where A , B , C are dielectric virial coefficients of the mixture. The basic component A of the polarization depends linearly on the mixture concentration:

$$A = \frac{4}{3} \pi N (\alpha_1 c_1 + \alpha_2 c_2), \quad (4)$$

where $\alpha_{1,2}$ are the polarizabilities of the components. The quantity $B/V + C/V^2 + \dots$ is a small correction to the Clausius-Mossotti equation $P = A$. For the pure components it comprises tenths of a percent. Therefore, it can be expected that its component nonlinear in c is negligibly small. The coefficients B and C for H_2 - D_2 mixtures at $T = 50^\circ K$ were calculated with the formulas proposed in [9,10] (applicable at $T \geq 50^\circ K$), and it was found that the quantity $B/V + C/V^2$ is linearly dependent on concentration to sufficient accuracy.

The available data (accuracy in V measurement, character of the function $P(c)$) permit us to consider the results of the present study and [1] as preferable.

In conclusion, we note that measurement of excess molar volumes of H_2 - D_2 mixtures at

higher temperatures, especially in the range of the H₂ and D₂ critical temperatures, is also of interest.

NOTATION

V, molar volume; V^E, excess molar volume; p, pressure; T, temperature; c, concentration of components in solution; ε, dielectric constant; α, polarizability of a molecule; P, polarization (Clausius-Mossotti function); N, Avogadro's number; A, B, C, dielectric virial coefficients.

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SPONTANEOUS NUCLEATION FREQUENCY IN SUPERHEATED LIQUID

XENON AND KRYPTON

A. M. Kaverin, V. G. Baidakov,
and V. P. Skripov

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An experimental study is made of spontaneous boiling up in superheated liquid xenon and krypton. Results are compared with calculations using the Volmer-Zel'dovich-Frenkel homogeneous nucleation theory.

Boiling processes may be accompanied by significant superheating of the liquid involved. The case where boiling up occurs at centers of a fluctuation nature is of physical interest. In the absence of external fields the kinetics of such a process are described by the well-known Volmer-Zel'dovich-Frenkel theory [1], which produces the following expressions for the stationary nucleation frequency:

$$J = N_1 B \exp(-W_*/kT), \quad (1)$$

where

$$W_* = \frac{16\pi\sigma^3}{3(p_s - p)^2 (1 - v'/v)^2} \quad (2)$$

Division of Physicotechnical Energetics Problems, Ural Scientific Center, Academy of Sciences of the USSR, Sverdlovsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 38, No. 4, pp. 680-684, April, 1980. Original article submitted July 4, 1979.