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SURFACE TENSION OF LIQUID HYDROGEN ISOTOPES AND HYDROGEN-DEUTERIUM SOLUTIONS

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Experimental data are presented on the temperature dependence of the surface tension of hydrogen, deuterium, deuterohydrogen and hydrogen-deuterium solutions. The data on the surface tension of hydrogen satisfactorily agree with the results obtained by Kamerlingh-Onnes, whereas the results previously obtained by Van Itterbeek and Van Paemel[10] for deuterium are too high by ~ 5%. The surface tension of the solutions is several per cent smaller than the additive values, in quantitative agreement with Prigogine's calculations.

RECENT research on the density and mixing volumes of solutions of hydrogen isotopes[1-3] has shown that the experimentally observed relatively large decrease in volume (~ 1%) when hydrogen and deuterium solutions are formed cannot be explained within the framework of the simplest theoretical considerations. Calculations based on the Prigogine theory[4,5] or on the quantum theorem of corresponding states[6] lead to results which qualitatively contradict the experiments. The causes of such a contradiction still remain unexplained. It can be hoped that information on other properties of hydrogen-isotope solutions may be useful for a clarification of this question. The present work is devoted to measurements of surface tension. Since it is necessary to know the surface tension of pure isotopes in order to compare the data on the solution with the calculations based on the quantum theory of corresponding states, the first part of the paper presents results of measurements of the surface tension of hydrogen, deuterohydrogen, and deuterium. These measurements are also of independent interest, since the handbook literature contains hydrogen surface-tension data which are somewhat in disagreement, casting doubts also on the data pertaining to deuterium, since analogous setups were used in both cases for the measurements.

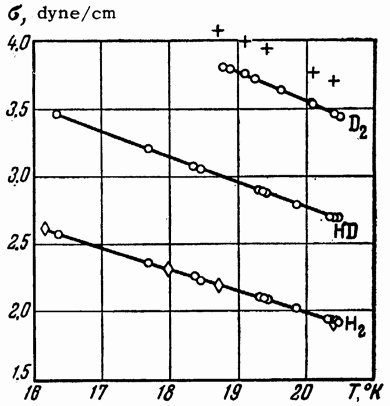

FIG. 1. Temperature dependence of the surface tension of hydrogen isotopes: ○ – present work ◇ – data of Kamerlingh-Onnes and Kuypers, modified in[9], + – data of Itterbeek and Paemel[10].

1. SURFACE TENSION OF PURE HYDROGEN ISOTOPES

The surface tension was determined from the difference of the heights to which the liquid rises in two capillaries of different diameters. The instrument and the procedure were described in detail earlier[7]. The measurements were made from 20.4°K almost to the solidification point for deuterium and deuterohydrogen and to 15°K for hydrogen.

The temperature dependence obtained for the surface tension $\sigma(T)$ of pure isotopes is shown in Fig. 1. In the investigated temperature interval, the temperature dependences are described, within the limits of the measurement accuracy (~ 0.5%), by linear equations of the form $\sigma = A - BT$. The coefficients A and B are listed in Table I. A striking fact is the very small difference between the temperature coefficients B for the different isotopes.

Figure 1 shows also the hydrogen surface-tension data of Kamerlingh-Onnes and Kuypers[8], modified in[9], and also the data of Van Itterbeek and Van Paemel[10] for deuterium. We see that the results for hydrogen are in good agreement, the difference for deuterium amounting to about 5%. The reason for the discrepancy is that Van Itterbeek and Van Paemel[10] improperly calculated the corrections for the curvatures of the

Table I

Isotope	A, dyne/cm	B, dyne/cm-deg	p
H_2	5.25	0.162	17.1
HD	6.53	0.188	16.6
D_2	7.90	0.218	16.2

menisci in the coaxial capillaries; they used the same method for calculating the corrections as Kamerlingh-Onnes and Kuypers[8], but, as shown in[9], this method leads to a noticeable overestimate of the surface tension. We corrected for the meniscus curvature using Rayleigh's formula and Sugden's tables[11]. Both methods gave results within 0.1%.

The Sugden parachores $p = \mu\sigma^{1/4}/(\rho^l - \rho^v)$ were calculated for all isotopes (μ—molecular weight, ρ^l and ρ^v—densities of the liquid and of the vapor). These were found to be temperature-independent within the limits of experimental accuracy. The last column of Table I gives the mean values of the molecular parachores p. They turned out to be somewhat different for the isotopes under consideration, but according to Sugden the parachore of deuterohydrogen is exactly equal to the sum of the atomic parachores of hydrogen and deuterium.

It must be noted that hydrogen and deuterium with normal ortho-para composition were used for the measurements (75% orthohydrogen). According to the preliminary experiments, the difference between the surface tensions of the ortho- and parahydrogen amounts to ~2%.

2. SURFACE TENSION OF SOLUTIONS OF HYDROGEN AND DEUTERIUM

The measurements of the surface tension of the solutions were made with the aid of the same instrument[7]. The mixtures consisted of pure isotopes. The production method and the concentration measurement were the same as described in [2]. The correction to the liquid concentration, brought about by the presence of the gas phase, did not exceed 0.5%. The values of the liquid density, necessary to calculate the surface tension from the rise of the liquid in the capillaries, were taken from [2].

Special attention was paid to ensuring equilibrium between the liquid and the vapor. To accelerate this process, use was made of the fact that when a certain part of the instrument is disconnected from the volume immersed in the liquid, sufficiently intense thermal acoustic oscillations are produced in the liquid, sometimes causing gushing of the liquid in the instrument. Periodic repetition of this process has made it possible to reduce by several times the equilibrium establishment time, which in this case ranged from 10 minutes at high temperatures to 40 minutes at low ones, when the

Table II

T, °K	σ, dyne/cm	$-\frac{\Delta\sigma}{\sigma}$, %
$c_{D_2} = 7.2\%$		
20.44	1.98_1	1.4
19.98	2.04_4	1.9
19.66	2.11_4	1.0
19.28	$2,18_2$	1.2
18.82	2.25_7	1.0
18.48	2.31_4	—
18.23	2.35_6	—
17.94	2.40_4	—
$c_{D_2} = 15.2\%$		
20.44	2.09_7	1.2
20.43	2.10_0	1.0
19.61	2.24_2	1.1
19.17	2.31_5	1.3
18.80	2.38_6	0.8
18.35	2.45_3	—
17.74	2.57_7	—
$c_{D_2} = 23.6_5\%$		
20.43	2.19_8	2.3
20.41	2.20_6	2.0
20.08	2.26_7	1.8
19.48	2.37_1	1.8
19.43	2.38_1	1.8
18,69	2.52_5	1.4
18.08	2.62_5	—
17.47	2.71	—
16.44	2.86_8	
$c_{D_2} = 32.8\%$		
20.42	2.31_3	2.9
20.41	$2,31_7$	2.9
20.41	2.31_7	2.7
19.27	2.53_3	2.4
18.86	2.60_2	2.4
18.25	2.70	—
18.48	$2,67_6$	—
17.92	$2,76_9$	—
$c_{D_2} = 38.6\%$		
20.45	2.34_3	3.2
20.44	2.37_3	2,6
20.46	2.37_0	2.5
20.44	$2,36_6$	2,5
20.43	2.35_9	3.2
20.39	$2,39_1$	2.1
20.32	2.39_3	2,6
19.46	2.33_4	3.2
18,85	$2,63_4$	3.6
18,40	2.76_6	—
17.21	2.92_1	—
17,14	$2,95_4$	—
$c_{D_2} = 49.9\%$		
20.46	2.62_5	3,7
20.44_5	$2,62_5$	3.2
20.44	2,63	3.8
20.43	2,64	4.0
19.96_5	2.72_1	2.5
$19,39_5$	$2,82_6$	2.7
18,94	2.91_1	3.2
$18,40_5$		—
18.93	2.91_3	2,8
17.93		—
17.34		—
16,77		—
16.69		—
$c_{D_2} = 74.1\%$		
20.44	2.89_3	3.2
20.44	2.89_5	3.1
20,43	2.90_3	2.9
19,99	$2,97_9$	3,1
19.94	$2,98_8$	3.3
19.39	3.10	3,0
18.96	3.18_4	3.0
18.56	3.24_2	—
18.42	3.29_5	—
18.14	3.30	—
17.81	3.37_2	—
$c_{D_2} = 82.3\%$		
20.38	3.00_9	3.3
20,36	3.01_8	3,2
19.48	3.17_3	4.2
19,17	3.24_1	4,2
18.27	$3,40_1$	—
17,9	$3,47_2$	—

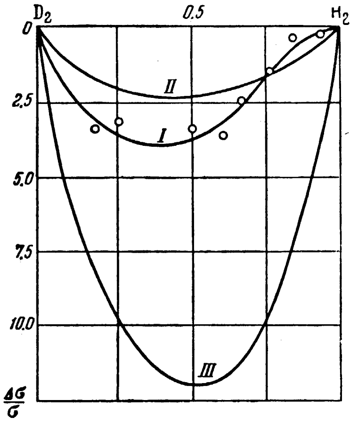

FIG. 2. Concentration dependence of the excess surface tension of hydrogen and deuterium solutions at T = 20.4°K: I – experimental curve, II – excess surface tension due to adsorption, III – curve calculated from formula (1).

oscillation intensity was noticeably lower. Equilibrium was deemed to be established when the results obtained by measurements while lowering the temperature agreed with the results obtained in the opposite direction. Control experiments with pure isotopes have shown that the overheating due to the thermal acoustic oscillations disappears one or two minutes after the stopping of the oscillations.

Table II lists the surface tensions at eight solution concentrations and at temperatures from 20.4°K to the solidification points. Like in pure isotopes, the surface tension decreases linearly with increasing temperature. The temperature coefficient increases smoothly with increasing deuterium concentration. The data obtained were compared with the additive values of the surface tension. The relative deviations from additivity, $\Delta\sigma/\sigma$, are listed in column 3 of Table II. For all the solutions, the surface tensions are smaller than the additive values, and $\Delta\sigma/\sigma$ is independent of the temperature within the limits of experimental error. The concentration dependence of $\Delta\sigma/\sigma$ for T = 20.4°K is plotted in Fig. 2.

3. DISCUSSION OF RESULTS

It is well known that the thermodynamic properties of isotope solutions deviate from ideal because of the influence of quantum effects. These deviations can be calculated with the aid of the quantum theorem of corresponding states, proposed by deBoer[6]. For the surface tension, however, it is also necessary to take into account a purely classical phenomenon, connected with the fact that the concentration of components with lower surface tensions increases in the surface layer. The influence of this surface adsorption can be determined with the aid of the well known Gibbs formula.

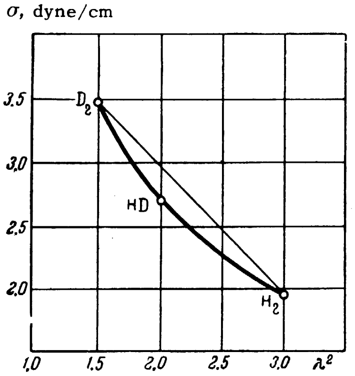

FIG. 3. Dependence of surface tension of solutions of hydrogen isotopes on the value of the deBoer quantum parameter.

The surface tension of the isotopes solutions was calculated with allowance for these two factors by Englert-Chwoles and Prigogine[12], who obtained the following formula for the excess surface tension of binary solutions:

$$\Delta\sigma = \frac{1}{2}c_1c_2\frac{\partial^2\sigma}{\partial(\lambda^2)^2}(\lambda_1^2 - \lambda_2^2) - \frac{1}{2}c_1c_2\frac{\omega}{kT}(\sigma_1 - \sigma_2)^2, \quad (1)$$

where c_1 and c_2—concentrations of the isotopes in the liquid, ω—surface area per molecule, k—Boltzmann constant, and λ—quantum parameter. According to deBoer, $\lambda = h/r_0\sqrt{\mu\epsilon}$ (h—Planck constant, r_0 and ϵ—Lennard-Jones potential parameters; for isotopes of the same element r_0 and ϵ are the same).

It is seen from (1) that to calculate $\Delta\sigma$ it is necessary to know the dependence of $\sigma(\lambda^2)$ at the given reduced temperature. Unfortunately, the temperature interval of liquid hydrogen corresponds to such values of the reduced temperatures, at which all substances with higher boiling temperature are in the solid state, while helium is at above-critical temperature. Therefore the $\sigma(\lambda)$ curve shown in Fig. 3 is constructed only from the values of the surface tension of the three hydrogen isotopes. In view of the equality of the parameters ϵ, equal reduced temperatures correspond in this case to equal ordinary temperatures. The curve of Fig. 3 pertains to 20.4°K. It is easy to see that ideal behavior of the surface tension of solutions of the isotopes hydrogen and deuterium would correspond to a straight line joining the hydrogen and deuterium points. As shown by Prigogine[4], the calculated deviation from ideality turns out to be in this case equal to the difference between the ordinates of the line joining the points of the true components, and the $\sigma(\lambda^2)$ curve for $\lambda_c^2 = c_1\lambda_1^2 + c_2\lambda_2^2$. The values of $\Delta\sigma$ obtained in this manner coincide within 10—20% with the values given by the first term of formula (1).

Curve III on Fig. 2 shows the concentration dependence of the calculated values of $\Delta\sigma/\sigma$. We see that although in this case the signs of the calculated and experimental quantities are equal, the absolute values differ by a factor of three. This difference becomes even larger if only the quantum additions are compared, i.e., if we subtract from the calculated and from the experimental data the adsorption terms (curve II of Fig. 2), which have been accurately measured. It must be noted that the relation between the calculated and experimental surface-tension data is approximately the same for both hydrogen-isotope solutions and for helium-isotope solutions[13], but whereas the mixing volumes of the helium isotopes are sufficiently well described by the analogous theory, a qualitative contradiction is observed in the case of those of hydrogen.

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16