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SURFACE TENSION OF NORMAL HYDROGEN SOLUTIONS IN NEON

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The surface tension σ of normal hydrogen solutions in neon is measured in the region of solubility at temperatures between 24.59 and 29°K. It is shown that σ decreases rapidly as the hydrogen concentration increases. The hydrogen adsorption on the neon surface is calculated; this significantly affects the decrease of surface tension and its temperature dependence $\sigma = f(T)$. The results are compared with the molecular-statistical theory of Englert-Chwoles and Prigogine[2] and the important role of quantum effects at low temperatures is shown.

IN earlier[1] measurements of surface tension σ that were performed on solutions of substances having spherically symmetric molecules and very different intermolecular force parameters at temperatures above the boiling point of nitrogen it was shown that σ decreases drastically with increase in the amount of dissolved surface-active components. The results agreed satisfactorily with the molecular-statistical theory of Englert-Chwoles and Prigogine[2] for classical liquids. However, a comparison of this theory with results obtained for nH_2—Ne solutions revealed large discrepancies that evidently resulted from quantum effects at low temperatures, as had previously been observed for solutions of isotopes of hydrogen[3] and of helium.[4] As in the cases of the isotope solutions, the nH_2—Ne system is characterized by a small difference of the intermolecular force parameters, although the masses of hydrogen and neon differ by a factor of 10. We can therefore infer that the effects observed in the given system result, as for the isotopes, from a difference of the quantum parameters λ.

The surface tension σ of nH_2—Ne solutions was measured in the region of solubility[1)] at temperatures 24.59°—29°K using the method of differential capillary rise. The test liquid was contained inside two connected capillaries of different diameters ($d_1 = 0.0293$ cm and $d_2 = 0.2667$ cm) placed in a cryostat with automatically regulated temperature. The cryostat differed only insignificantly from that described in[5].

To reduce the time required to establish equilibrium in the solutions, the capillary of larger diameter contained an agitator that was moved by means of an electromagnet supplied by a multivibrator. By changing the vibration frequency of the agitator, circulation of the liquid was induced in the capillaries, thus providing for good mixing of the solution. The equilibrium time was determined by observing when the meniscus level difference in the capillaries ceased to change. The concentrations of the solutions were calculated from the liquid-vapor phase equilibrium diagrams given in[6]. The required vapor pressure of the solution was measured with Class-0.4 standard manometers. The error of the concentration did not exceed ±0.2 mol.%. The temperature in the cryostat was measured and maintained within 0.01°—0.02°K.

$T°$, K	ΔH, cm	P, atm	$c_{H_2}^{\text{liquid}}$, mol. %	σ, dyne/cm
24.59	0.223	1.91	1.44	4.09
24.59	0.202	2.03	1.57	3.70
24.59	0,180	2.52	2,16	3,30
24,59	0,172	2,50	2.13	3,13
26.33	0.232	2,06	1.22	4.15
26,33	0.205	2.49	1,71	3.63
26.33	0,171	3.31	2.83	2,98
26.33	0.143	3,99	4.11	2.45
27.15	0.214	2,49	1,58	3.75
27.15	0.175	3,38	2,73	3.00
27.15	0.154	4,09	3.84	2.60
27.15	0.111	4,93	5,88	1.83
29.00	0.206	2.80	1.20	3.51
29,00	0.191	3.36	1,94	3,22
29,00	0.180	3.77	2.54	3.00
29.00	0.147	4,89	4.48	2.37
29.00	0.113	5.90	7.38	1.73

The surface tension was calculated from the formula

$$\sigma = (\Delta H/2)(\rho_1 - \rho_2)\frac{r_1 r_2}{r_2 - r_1}g;$$

ΔH is the difference between the meniscus levels in the capillaries, ρ_1 and ρ_2 are the densities of the liquid and the vapor of the solution, g is the acceleration in free fall, r_1 and r_2 are the radii of curvature of the meniscuses and were computed by successive approximations from the capillary radii using Sugden's tables.[7] Just as for the majority of liquefied gases, zero contact angle is assumed for the wetting of glass by an nH_2—Ne solution. This assumption at liquid hydrogen temperature is supported by our investigations,[5] which showed that liquid hydrogen easily wets many metallic and nonmetallic surfaces. The density of the liquid was calculated assuming that the molar volumes of the components are additive. With a low hydrogen concentration no large error can result from this hypothesis. The densities of the pure components were taken from[8,9]. In calculating the vapor density we used the equation of state in its virial form with the second virial coefficients B determined for the solutions from the equation

$$B = B_{11}c_1^2 + 2B_{12}c_1c_2 + B_{22}c_2^2;$$

B_{11} and B_{22} are the second virial coefficients for neon and hydrogen. B_{12} and B_{11} were calculated by the procedure described in[10], while experimental values given in[11] were taken for B_{22}.

The measurements are given in the accompanying table; the curves in Fig. 1 show the temperature depen-

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[1)] The system nH_2—Ne is characterized by limited solubility for $T < 29°K$.

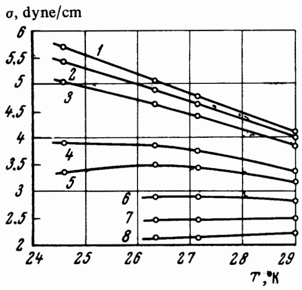

FIG. 1. Temperature dependence on the surface tension of nH₂—Ne solutions. 1—Ne; 2—0.2%, 3—0.5%, 4—1.5%, 5—2%, 6—3%, 7—4%, and 8—5% of H_2.

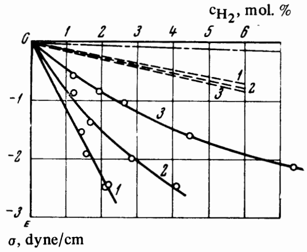

FIG. 2. Dependence of excess surface tension on hydrogen concentration. Dot-dash curve—calculated from classical theory; solid curves—experimental results; dashed curves—calculated from Eq. (1). T = (1) 24.59°K, (2) 26.33°K, (3) 27.15°K.

dence of the surface tension at different concentrations, as plotted from graphs of σ(c). The points on the curves correspond to certain cross sections of the isotherms and characterize the concentration spread of the results. A considerable reduction of surface tension is noted with increasing hydrogen concentration despite its low solubility in neon. For example, at T = 24.59°K, P = 2.5 atm, and c_{H_2} = 2.13 mol.% we find that σ has decreased 40% from its initial value; at T = 29°K and c_{H_2} = 7.38 mol.% the reduction is 50%. Figure 1 shows that at the same time σ(T) departs considerably from linearity. With decreasing temperature and increasing hydrogen concentration the slopes of the curves are reduced, and they become almost horizontal for c_{H_2} = 4 mol.%. Moreover, for some concentrations a clear sign reversal of $(\partial\sigma/\partial T)_c$ is observed (curves 5–8 in Fig. 1). The curves representing the concentration dependence of σ lie considerably below the additive values. Consequently, the "excess" surface tension σ^E that characterizes the deviation of σ from additivity ($\sigma^E = \sigma - \sigma_{add}$) has a quite large negative value (Fig. 2). The deviation is also seen to increase steeply with decreasing temperature.

The described effects appear to be associated mainly with strong adsorption of the hydrogen, since the surface tensions of the components differ considerably. Even at low concentrations the adsorption (G) calculated from Gibbs' formula[12] has an appreciable magnitude (Fig. 3). At T = 24.59°K and c_{H_2} = 2 mol.% we find G = 10^{-9} mole/cm². If we assume adsorption mainly into a monomolecular film, this value indicates that the surface concentration has increased 60 mol.% above the volume concentration (multiplication by a factor of 30). The value of G is also strongly temperature dependent, and varies by a factor of 4 in the interval 24.59°–29°K.

In order to determine the influence of quantum effects on the surface tension of the solutions we compared our results with the molecular-statistical theory of Englert-Chwoles and Prigogine.[2] It has previously been found that the classical calculation yields values of σ that are two orders of magnitude below the experimental results.

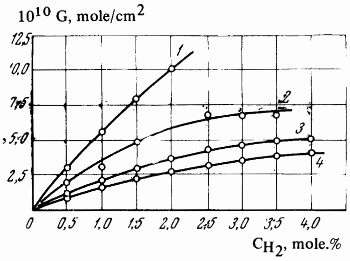

FIG. 3. Dependence of adsorption (G) on hydrogen concentration. T = (1) 24.59°K, (2) 26.33°K, (3) 27.15°K, (4) 29°K.

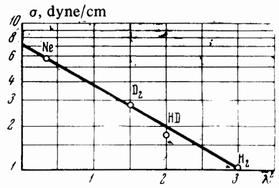

FIG. 4. Dependence of σ on $\tilde{\lambda}^2$ at 24.59°K.

This was accounted for by the difference of the quantum parameters $\tilde{\lambda} = h/d^*\sqrt{me^*}$ (h is Planck's constant, d* and ε* are parameters of the Lennard-Jones potential, and m is the mass). From de Boer's quantum theorem of corresponding states and the classical-liquid equation for σ^E given by Englert-Chwoles and Prigogine we obtained the following formula:

$$\sigma^E = -\frac{1}{2}c_1c_2[\partial^2/\partial(\tilde{\lambda}^2)^2]_{11}(\tilde{\lambda}_{11}{}^2 - \tilde{\lambda}_{22}{}^2)^2 - \frac{1}{2}c_1c_2\frac{\omega}{kT}(\sigma_{11} - \sigma_{22})^2, \quad (1)$$

where c_1 and c_2 are the neon and hydrogen concentrations. Here ω is the area per molecule of the surface film when close packing is assumed. The function $\sigma(\langle\tilde{\lambda}^2\rangle)$ was determined from the experimental surface tensions of the pure substances at an identical reduced temperature. The calculation of $\partial^2\sigma/\partial(\tilde{\lambda}^2)^2$ was facilitated by the fact that σ depends on $\tilde{\lambda}^2$ exponentially; this is shown clearly by the semilogarithmic plot in Fig. 4. Neon was the standard substance used in the calculation.

Figure 2 compares the experimental results with the calculations of σ^E based on the theory of Englert-Chwoles and Prigogine for classical liquids and on (1). Agreement as to sign is observed, but there is a difference of almost two orders in the absolute values. The isotherms (dashed lines) in Fig. 2 represent $\sigma^E(c)$ calculated with quantum corrections according to (1). At 24.59°K these calculations differ from experiment by a factor of 3 to 7, while at 29°K they differ by a factor of 2 or 3. However, although the disagreement between theory and experiment diminishes with increasing temperature, this temperature dependence of σ^E must be regarded as unsatisfactory. Evidently the adsorption is not taken into account adequately, although it is represented by the last term in (1); the contribution of ~20% to the calculated value of σ^E changes little with increasing temperature, in contradiction with experiment. We can thus expect better agreement between theory and experiment at higher temperatures, when less adsorption is observed; this effect is actually verified.

It is also important that the accuracy of calculations using (1) is affected greatly, aside from possible errors contained in the model itself, by deviations from the law of corresponding states for pure substances, thereby introducing some error into the determination of $\partial^2\sigma/\partial(\tilde{\lambda}^2)^2$.

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