SOVIET PHYSICS JETP VOLUME 22, NUMBER 5 MAY, 1966

SURFACE TENSION OF HYDROGEN NEAR THE CRITICAL POINT

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Submitted to JETP editor June 22, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 1453-1456 (November, 1965)

Measurements were made of the surface tension of normal hydrogen in the temperature range from 20°K to the critical temperature. The results obtained near the boiling point agreed with data of earlier papers, within the limits of experimental error (≈ 1%). A form of the analytic dependence of σ on temperature is proposed.

THE surface tension of normal liquid hydrogen between the triple point and the boiling point under equilibrium pressure has been investigated by a number of workers.[1,2] It was found that the value of σ varied linearly with temperature. However, the extrapolation of this dependence to higher temperatures gave results which were known to be wrong since the straight line intersected the temperature axis below the critical point. Moreover, the linear dependence was not observed over a wide range of temperatures for other liquids. An investigation of the surface tension of hydrogen over the whole range of its existence in the liquid phase is of interest both from the point of view of practical applications and from the point of view of the modern theory of liquids.

The measurements were carried out using the difference between the liquid levels in two capillaries of different diameters. The apparatus is shown schematically in Fig. 1. The capillaries, 0.0639 and 0.2025 cm in diameter,[1] joined as shown, were placed inside a double-walled glass chamber, located in a Dewar flask containing liquid hydrogen. The inner space of the chamber was filled with a thermostatting liquid which was hydrogen for temperature up to 28°K and neon for higher temperatures. The space between the walls of the chamber was filled with helium at low temperatures (near 20°K) and pumped out at higher temperatures. To better equalize the temperature a copper cylinder 2 was placed in the inner chamber, to which a carbon resistance thermometer 5 (which served as the probe for the temperature control system) and two heaters 4 were attached.

The temperature was controlled automatically using the circuit shown in Fig. 2. The carbon resistance thermometer T was connected to a dc bridge B, whose out-of-balance signal was applied to a control potentiometer EP, which switched on the heater H_1. The second heater H_2 was operated continuously and the power was selected to suit the working temperature. Using this circuit, the temperature was kept constant to within ≈ 0.02 deg K near the critical point and to within ≈ 0.01 deg K at low temperatures. The capillaries were calibrated by means of mercury and by direct measurement of the diameters at several points using a horizontal comparator, IZA-2 (the accuracy of the measurements was 2×10^{-3} mm). The

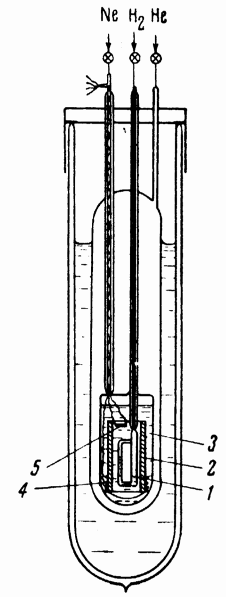

FIG. 1. Device for measuring the surface tension of hydrogen; 1) capillaries; 2) copper cylinder; 3) thermostatting liquid; 4) heaters; 5) carbon resistance thermometer.

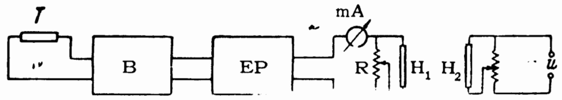

FIG. 2. Automatic circuit for temperature control in the cryostat: T – carbon resistance thermometer; B – dc bridge; EP – electronic potentiometer; R – rheostat; H_1 and H_2 – heaters.

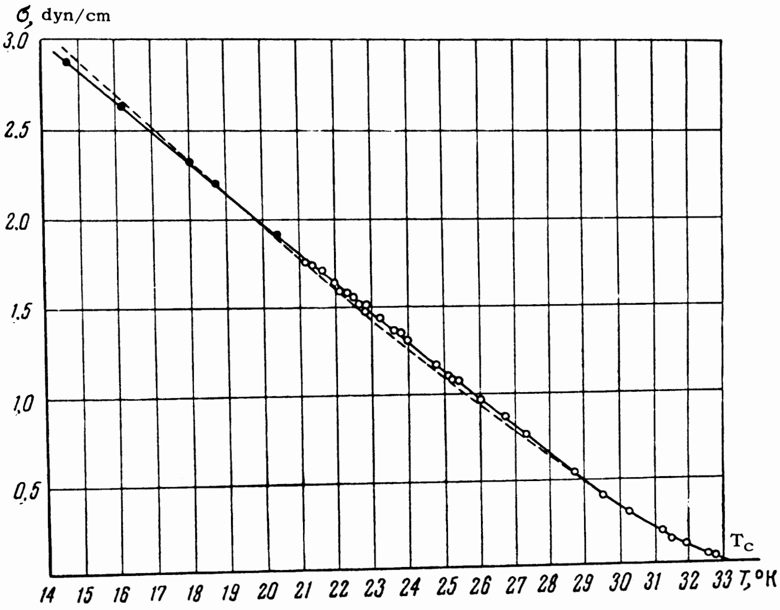

FIG. 3. Temperature dependence of the surface tension of hydrogen: ○ – our data; ● – data of Kammerlingh-Onnes and Kuypers.

measurement error, allowing for variation in diameter along the length, did not exceed 0.5%.

The temperature was measured from the vapor pressure of the thermostatting liquid using a differential mercury manometer up to 1000 mm Hg, while at higher vapor pressures it was measured using a manometer of 0.4 grade with a scale up to 6 atm. The measurement error at low temperatures was 0.02–0.03 deg K and it did not exceed 0.05 deg K at higher temperatures. The values of the vapor pressure of neon were taken from [3] and those of hydrogen from [4].

The difference between the levels of hydrogen in the two capillaries was determined with a cathetometer, KM-6. At each value of temperature, 10–12 measurements were carried out. The average scatter of the results did not exceed 0.04 mm.

To calculate the surface tension using the capillary method, it is necessary to know the value of the wetting angle. Usually, the wetting angles of liquid gases, in particular hydrogen, are assumed to be zero when in contact with glass. To check this assumption we carried out special measurements on hydrogen, which showed that the wetting angle was equal to zero within 1°30′.

T, °K	ΔH, cm	σ, dyn/cm	T, °K	ΔH, cm	σ, dyn/cm
21.15	1.146	1.755	24.77	0.850	1.171
21.40	1.122	1.715	24.98	0.831	1.136
21.98	1.084	1.633	25.16	0.814	1.100
22.13	1.062	1.594	25.25	0.809	1.089
22.31	1.054	1.575	25.37	0.802	1.073
22.43	1.051	1.565	26.05	0.747	0.969
22.65	1.024	1.516	26.72	0.691	0.869
22.83	1.020	1.502	27.31	0.630	0.767
22.84	1.011	1.486	28.68	0.491	0.540
22.86	1.006	1.481	29.49	0.408	0.401
23.25	0.983	1.431	30.27	0.328	0.303
23.28	0.977	1.421	31.23	0.244	0.193
23.62	0.951	1.361	31.49	0.203	0.149
23.80	0.948	1.351	31.90	0.173	0.116
23.98	0.923	1.307	32.57	0.109	0.053
24.33	0.857	1.244	32.77	0.106	0.0459

The surface tension was calculated using the formula

$$\sigma = \frac{\Delta H(\rho_l - \rho_v)g}{2}\,\frac{r_1 r_2}{r_2 - r_1}$$

where ΔH is the difference between the meniscus levels in the capillaries; ρ_l and ρ_v are the densities of the liquid and vapor; r_1, r_2 are the meniscus curvature radii. The meniscus curvatures were determined by the method of successive approximations using Sugden's tables.[5] The densities of the liquid and vapor phases were taken from [6]. The absolute error in the determination of σ did not exceed 0.02 dyn/cm.

The table lists the values of the level differences in the capillaries and the values of the surface tension at all measurement temperatures. The temperature dependence of σ is shown in Fig. 3. The same figure includes the revised data of Kammerlingh-Onnes and Kuypers below the boiling point of hydrogen. The difference between the two sets of results lies within the measurement error.

It is evident from Fig. 3 that at high temperatures there is a marked deviation from the linear dependence of σ, proposed earlier for the range below 20°K. Consequently, it is difficult to select a simple empirical equation which would describe the temperature dependence of the surface tension over the whole range of temperatures.

Two equations are proposed. In the temperature range below 26–27°K

$$\sigma = 5.38 - 0.170 \cdot T \, (\mathrm{dyn/cm}) \pm 0.02 \, (\mathrm{dyn/cm}). \qquad (1)$$

This equation agrees, to within 0.5%, both with our data and with the results of Kammerlingh-Onnes and Kuypers. We must mention that the coefficients in Eq. (1) are different from the values obtained by Grigor'ev and Rudenko, which were 5.25 and 0.162. However, because Grigor'ev and Rudenko[2] do not give the numerical values of the surface tension, it is difficult to compare these two sets of results.

At higher temperatures, near the critical point, we may expect the temperature dependence of the surface tension to be described by the equation obtained first by van der Waals:[7]

$$\sigma = \sigma_0 (1 - T / T_c)^n. \qquad (2)$$

The values of the constants σ_0 and n for hydrogen, determined from the experimental data, are 6.1 dyn/cm and 1.23. The latter value agrees with the value n = 11/9, obtained by Guggenheim for a number of other liquids. The dashed curve in Fig. 3 shows the values of the surface tension calculated using Eq. (2). Above 27°K, the difference between the experimental values and this curve does not exceed 0.02 dyn/cm, i.e., it is within the limits of accuracy of the measurements, but at lower temperatures the difference reaches the value 0.05—0.06 dyn/cm.

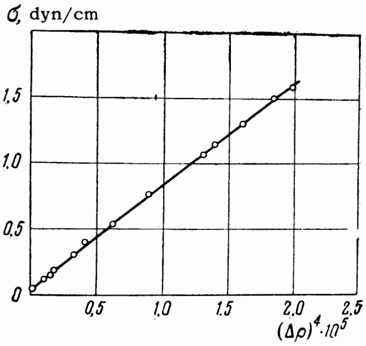

FIG. 4. Dependence of σ on $(\Delta\rho)^4$. ○ – our data.

There is also good agreement between our experimental data and the equation of Bachinskiĭ: $\sigma = k(\rho_l - \rho_v)^4$.

Figure 4 shows the dependence of σ on $(\rho_l - \rho_v)^4$. It is evident from Fig. 4 that the points in this graph fit relatively well the straight line shifted by 0.05 dyn/cm with respect to the origin of coordinates, which may be due to errors in the determination of σ or $(\rho_l - \rho_v)$ near the critical point.

The authors are grateful to G. P. Kropachev for his help in the measurements.

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Translated by A. Tybulewicz
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