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Tensile Strengths of Liquid Argon, Helium, Nitrogen, and Oxygen

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The tensile strengths of several liquids at low temperature were measured by a linear deceleration method. The values found were as follows (expressed in atmos): argon = 12, nitrogen = 10, oxygen = 15, and helium = 0.16. The values are somewhat lower than those calculated from the theory.

LIQUIDS at temperatures somewhat below their boiling points are well known to have measurable tensile strengths of appreciable magnitude. If it is assumed that the liquid fracture takes place simultaneously into two portions along a plane surface, then it can be shown from thermodynamic theory that the internal pressure or tensile strength $p_i$ is given by the relation

$$p_i = \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v - p_v = T \frac{\alpha}{\beta} - p_v,$$

(1)

where $p_v$ is the vapor pressure of the liquid, $E$ the internal energy, $T$ the absolute temperature, $V$ the volume, $\alpha$ the coefficient of thermal expansion, and $\beta$ the coefficient of compressibility. If the liquid obeys Van der Waals' equation and the vapor pressure $p_v$ is small in comparison to $p_i$, the internal pressure is given approximately by $p_i = a/\nu^3$ where $a$ is Van der Waals constant. Care, of course, must be taken in using Eq. (1) in cases such as water between 4°C and 0°C or for liquid helium below the lambda point where $a$ is negative. In all cases so far investigated, the measured values are considerably lower than those predicted from Eq. (1) or from Van der Waals' coefficients. Fisher has pointed out that Eq. (1) should give values which are too large because a liquid under high enough tension would become metastable and in time should change spontaneously into a two-phase system of liquid and vapor, i.e., vapor bubbles should form and grow until the liquid fractures under the negative pressure. By application of nucleation theory he has shown that the tensile strength is given by the relation

$$p_i = -\left[ \frac{16\pi}{3} \frac{\sigma^3}{kT \ln \frac{NkT}{\mu} - f_0} \right] + p_v,$$

(2)

where $k$ is Boltzmann's constant, $h$ is Planck's constant, $f_0$ is the free energy of activation for the motion of a molecule of liquid into or away from the bubble surface, $t$ is the time between the application of the tension and the fracture, and $\sigma$ is the surface tension at the interface between the bubble and the liquid. Although the values estimated by Eq. (2) are much smaller than those calculated by Eq. (1), they are still considerably larger than those found by experiment. If nuclei exist around which vapor bubbles may form and grow in the liquid or on the interface between the liquid and its container, then, as pointed out by many different investigators, it is easy to account for the experimental results.

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cracks in the container filled with gas or vapor are especially effective nuclei for bubble formation.

In the present experiments an attempt is made to measure the tensile strengths of some liquids at low temperatures in the hope that better agreement with theory might be obtained. It is believed that properly prepared liquids at low temperatures may have fewer gaseous nuclei than those at room temperature. Also because of its superfluid properties, liquid helium II should flow into the cracks of the container and thus help to eliminate gaseous nuclei at the interface between the liquid and the container. In order to minimize the effect of nuclei formed by cosmic rays and other background radiation the tensile stresses were applied to a comparatively small liquid cross section for not greater than $10^{-3}$ sec.

The experimental method consists in applying the stress to the liquid by means of a known linear deceleration of the liquid. Figure 1 shows a schematic diagram of the apparatus. The diagram is not to scale and the $x$'s indicate cuts in the drawing. The liquid completely fills the glass inverted U tube. Its arms are vertical and their open ends extend just below the liquid surface. The U tube is then given a velocity downward by a spring mechanism $S$ and quickly decelerated to zero velocity by the stop $B_1$. When the U tube is being stopped the liquid tends to continue its downward motion and creates a tensile stress in the liquid in the upper part of the U tube. From the deceleration, and the height of the liquid in the U tube the tensile stress is determined. In most of the experiments the U tube was flamed Pyrex glass. It was carefully cleaned first with detergents and a potassium dichromate-sulfuric acid cleaning solution followed by a careful rinsing with distilled water. Care was taken to avoid dust contamination as far as practicable. The arms of the U tube were 10 cm long and 3 mm to 5 mm i.d. The U tube is supported by a hollow cylindrical transparent container as shown in Fig. 1. This was filled with the liquid at approximately the same temperature as that under test in the U tube. In some experiments a metal shield was used instead. The shield was supported by a 0.16-cm stainless steel rod $R$, 91 cm long, which passes through the vacuum oil and wax glands $G_1$ and $G_2$ and the journal bearing guides $B_1$, $B_2$, and $B_3$. The metal stops $E_1$ and $E_2$ are firmly fastened to $R$. A small brass rod $H$ is fastened to the end of the stainless steel rod at $F$ as shown in Fig. 1. This passes through an air core solenoid $C$ and the guide bearing $B_2$. Firmly attached to $H$ at $M$ was a brass housing which carried a permanent magnet $M$. A small stylus $P$ rigidly attached to $R$ produced a trace on the rotating disk $I$. The U tube is surrounded by coaxial glass Dewar flasks $D_1$ and $D_2$. $D_1$ usually contains liquid nitrogen or liquid air and is silvered except for a thin viewing strip. $D_2$ contains the liquid under test and is sealed to the metal cap by a vacuum-tight joint made of sealing tape and wax. $D_2$ was filled and evacuated through $F_1$, $F_2$ is a small space which was evacuated to compensate for possible leakage through the gland $G_1$.

The inner Dewar $D_2$ was first evacuated to less than $10^{-3}$ mm of Hg by pumping through $F_1$ and $F_2$. Pure gas of the liquid to be used was next admitted until the pressure was slightly above an atmosphere. $D_1$ is then filled with liquid nitrogen or air depending upon the temperature desired. In the cases of argon and oxygen, liquid nitrogen was placed in $D_1$ and a glass tube replaced the Dewar $D_2$ so that the gas could be condensed in the tube directly. In the case of nitrogen and helium, the liquid was introduced into $D_1$ by filling tubes. The pumps were then started and the U tube moved alternatively above and below the liquid surface until the U tube was completely filled with the liquid. It was then lowered to a few centimeters
above the bottom of \( D_3 \) and the pumping continued until the desired temperature was reached as determined by the vapor pressure. The U tube was placed in the position shown in Fig. 1 with the spring compressed and the trigger at \( T \) supporting the tension. The trigger was next released, which allows the spring to give the U tube a velocity downward. This velocity can be determined at any instant by the trace of the stylus on the rotating disk \( I \). At the same time the moving permanent magnet \( M \) induces an emf in the coil \( C \) which is recorded on an oscillograph. When the stop \( E_1 \) reaches \( B_1 \), the U tube is rapidly decelerated. \( B_1 \) contains lead washers which were adjusted to give a roughly uniform deceleration, over most of the period of deceleration. The deceleration is measured by the change in emf across the coil as \( M \) is stopped together with the velocity determined by the trace on \( I \). This process was repeated with the spring tension gradually increased until the liquid in the U tube broke. Then from the height of the liquid in the arms of the U tube, the deceleration and the vapor pressure of the liquid in \( D_3 \), the tension required to fracture the liquid was determined. In some of the experiments the U tube was replaced by a tube sealed at the upper end and dipping into the liquid at the lower end. In the case of liquid helium it was difficult to observe visually whether or not the liquid column was broken immediately after the deceleration so a carbon resistor was mounted inside the U tube just below the top of the U. By determining its resistance just before and just after the deceleration, thus avoiding the complication of thermal pressure, the fracture of the liquid column could be observed.

The results with the resistor were in agreement with the visual observations. In all cases care was taken to make sure that the vapor pressure of the liquid when once broken inside the U tube, was approximately equal to or slightly greater than that of the same liquid in \( D_2 \). Under these conditions the liquid level in the U tube drops after the break.* The results are shown in Table I.

The first column gives the values calculated from the Van der Waals constants, the second that computed from Fisher’s nucleation theory, and the third, the measured values. The fourth column gives the temperatures and the fifth the values of the surface tension \( \sigma \) given in The American Institute of Physics Handbook.4 The measured values for argon, nitrogen, and oxygen could be repeated to about 1 atm whereas the helium value could be repeated to about \( \pm 0.03 \) atm. It will be observed that the value found for helium II is about the same as that found previously by the centrifugal method5 and the value for nitrogen is somewhat greater than that found by the bellows method of Misener and Hedgecock.

It will be noted that the measured values are less than those given by nucleation theory. Although this theory might not be expected to hold for liquid helium II it probably should hold for the other liquids measured. In Eq. (2) the measured values of the surface tension4 were used in computing the values listed in column two of Table I. These values may be considerably different from the effective surface tension on the interface between a very small bubble and the liquid.7,8 However this correction probably could not account for all of the discrepancy between theory and experiment. The work \( W \) associated with the formation of a spherical vapor bubble inside a liquid is

\[
|W| = 4\pi r^2 \sigma + \frac{3}{2} \pi r^3 (p_i - p_v),
\]

where \( r \) is the radius of the bubble. If \( W \) is plotted versus \( r \), for a negative value of \( p_v \) the curve has a maximum for a radius \( r_{\max} = -2/(p_i - p_v) \), i.e., for bubbles with \( r \) less than \( r_{\max} \) additional free energy is required for growth and for \( r \) greater than \( r_{\max} \) the bubble will grow freely. If the measured values of \( p_i \) and the values of \( \sigma \) in the table are used to

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* I am greatly indebted to Dr. R. B. Jacobs of the National Bureau of Standards and to Dr. H. Parker, University of Virginia, who pointed out to me that the siphon experiments to which I referred [Phys. Rev. 104, 880 (1956)] were not sufficient to establish definitely the presence of a finite tensile strength in liquid helium. However, recently similar siphon experiments with helium II were carried out with a “head” of 160 mm of helium II in the siphon and a vapor pressure of 0.5 mm of Hg which, it is believed, demonstrate a tensile strength.

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calculate $r_{\text{max}}$ it is found that for argon, nitrogen, and oxygen the value is approximately $2.5 \times 10^{-6}$ cm, whereas for helium it is about $10^{-5}$ cm. This suggests that gaseous nuclei were probably still present. If such large nuclei exist in the liquid they should, if given sufficient time, settle out in a centrifugal field but the values obtained by the centrifugal method for helium II were almost the same as those by the present method. Also very large holes in helium might possibly lower the dielectric strength of the liquid. However some very rough measurements indicated that the dielectric strength as measured by impulsively applied voltages ($10^{-3}$ sec) to the liquid helium was at least the order of $10^9$ v/cm, which was as high as the method could measure reliably. Gaseous nuclei also may exist on the interface between the liquid and the glass U tube.

Experiments⁹ on the flow of helium II through fine channels such as are in Vicor glass show that the helium II does not exhibit superfluid properties until its temperature is reduced to the order of $1.3^\circ$.

Consequently it may be that the helium II did not fill all of the smaller cracks in the Pyrex glass U tube used in the present experiments. In order to test this, the glass U tube was replaced by a U tube made of stainless steel instead of glass. The change in resistance of a carbon resistor was used to register the liquid fracture. The results obtained were in substantial agreement with those found with the glass U tube. An attempt also was made to observe whether the initial vapor bubble formed on the wall or in the liquid. Both visual and rapid motion picture methods were used to observe the phenomena. The bubble formed near the upper surface of the U tube but it was not possible to determine whether or not it was on the wall or in the liquid. In the process of decelerating the U tube, vibrations no doubt were set up in the long stainless steel rod $R$ although care was taken to damp them to a minimum. This may have increased the effective tension applied to the liquid and thus made the measured values in Table I too small. However, the effect is believed not to be important except possibly in the case of liquid helium.