

and which asymptotically equals  $\cos(kr + \eta)$ . Let  $V(r)$  and  $U(r)$  be two potentials,  $\eta$  and  $\xi$  the corresponding phase shifts, and  $v_1, v_2$  and  $u_1, u_2$  the associated wave functions. Set  $Y_k(r) = u_1 v_1$ , and  $Z_k(r) = u_1 v_2 + u_2 v_1$ . Hylleraas asserts the general validity of the equation

$$V(r) - U(r) = (4/\pi)(d/dr) \int_0^\infty \sin(\eta - \xi) Z_k(r) dk. \quad (15)$$

[The foregoing equation differs from Hylleraas' (cf. (H 13)) in two minor points. (a) In order to avoid the appearance of divergent integrals we have interchanged differentiation with respect to  $r$  and integration with respect to  $k$ . (b) The signs of  $V$  and  $U$  are inverted, because Hylleraas'  $V$  corresponds to our  $-V$  in the Schrödinger equation (cf. his Eq. (3)).] One would infer from (15) that  $\eta = \xi$  implies  $V(r) = U(r)$ , whereas we have seen above that  $V(r)$  is not uniquely determined by  $\eta$ .

Hylleraas bases his proof on the assumption that his equations (H 14) and (H 15) are equivalent, and that it is therefore sufficient to establish (H 14). In reality, these two equations are independent, since (H 14) corresponds to an orthogonality relation, and (H 15) to a completeness relation. The latter appears particularly doubtful if either one of the potentials  $V, U$  gives rise to a bound state, because then the solutions of the Schrödinger equation which belong to the continuous spectrum do not form a complete system of functions.

The writer has checked Eq. (H 15) for  $V = K[2, \beta, \lambda]$ ,  $U = K[2, \beta', \lambda']$ . Then the func-

tions  $Y_k$  and  $Z_k$  may be computed from (7), (3), and (14), and the integral in (H 15) evaluated explicitly. The following result was obtained: (H 15) holds if and only if the Schrödinger equations for both  $V$  and  $U$  have no discrete spectra, i.e., if  $\beta \leq 1$  and  $\beta' \leq 1$ . This seems to indicate that Hylleraas' formula (cf. Eq. (15) above) may be generally valid if neither  $V$  nor  $U$  give rise to bound states. (Note that this holds for the example which Hylleraas discusses at the end of his paper.) The writer has not attempted a proof of this conjecture.

#### APPENDIX

For arbitrary values of  $\sigma$ , the function  $f(k, r)$  associated with the potential  $V(r) = K[\sigma, \beta, \lambda]$  (cf. (6)) is found to be

$$f(k, r) = e^{-ikr} (1 + \beta e^{-\lambda r})^\tau F(\tau + (2ik/\lambda), \tau, 1 + (2ik/\lambda), -\beta e^{-\lambda r}), \quad (16)$$

where  $\tau = \frac{1}{2}(1 - (1 + 4\sigma)^{\frac{1}{2}})$ , and  $F$  is the hypergeometric function. If  $\sigma = n(n+1)$  [ $n = 1, 2, \dots$ ], then  $\tau = -n$ , and  $F$  is a polynomial of  $n$ -th degree. One obtains the expressions (7) and (10) by setting  $n = 1$  and  $2$ , respectively, and inserting  $(\lambda + \mu(r))/(\lambda - \mu(r))$  for  $\beta e^{-\lambda r}$ .

*Note added in proof:* In the meantime the writer has worked out a number of additional examples. In particular, it is possible to construct potentials which (for  $S$ -waves) give equal phase shifts, but bound states of different energy values. This fact is of interest with respect to the theory of the  $S$ -matrix. It is also possible to find a non-vanishing potential which does not give any  $S$ -scattering. A detailed account will be published later.

## Condensation of Pure He<sup>3</sup> and Its Vapor Pressures between 1.2° and Its Critical Point

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ON October 13, 1948 the authors succeeded in condensing<sup>1</sup> pure He<sup>3</sup> prepared by E. S. Robinson and R. M. Potter of the laboratory.

<sup>1</sup> Although the evidence is not conclusive, indications are that we have observed a transition to a liquid rather than a solid state. This is suggested by the similarity of Fig. 1

The isotope was "grown" from pure tritium solutions by  $\beta$ -decay of the tritium. The latter

to what one would expect for a gas-liquid transition and by the approximate agreement between observed densities and those calculated from the critical constants by use of van der Waal's and Dieterici's equations of state.

was initially separated from traces of  $\text{He}^4$  by passage through a palladium valve. The  $\text{He}^3$  was purified by absorption of  $\text{H}_2$  and  $\text{T}_2$  in uranium, followed by repeated passages successively over (1) hot  $\text{CuO}$  followed by a liquid air trap and (2) hot  $\text{Ca}$ , thus removing all other impurities except the rare gases.

These results seem especially interesting since so much doubt has existed over the properties of  $\text{He}^3$ . London and Rice<sup>2</sup> suggested that this isotope would not liquefy at all, at least not under any "normal" conditions. Their argument was based on the large zero-point energy calculated for  $\text{He}^3$  which they found to be sufficient to compensate entirely the potential energy of the van der Waal's cohesive energy. Tisza<sup>3</sup> also doubted that  $\text{He}^3$  would liquefy unless "entirely unheard of properties" of viscosity were exhibited by the liquid. Fairbank, Reynolds, and Lane<sup>4</sup> measured the vapor pressure difference between  $\text{He}^4$  and solutions enriched to 0.16 percent  $\text{He}^3$  in the temperature range from 1.3° to 4.2°K. Using ideal solution concepts, they calculated vapor pressures of pure  $\text{He}^3$ . An extrapolation of  $\log P$  vs.  $1/T$  led to a normal boiling point of 2.9°K.

In these experiments 20 cc S.T.P. of  $\text{He}^3$  was used. The  $\text{He}^3$  was permitted to condense into the bottom of a 1.2-mm I.D. stainless steel capillary immersed in a bath of liquid well helium at depths of, usually, 5 or 10 mm. The

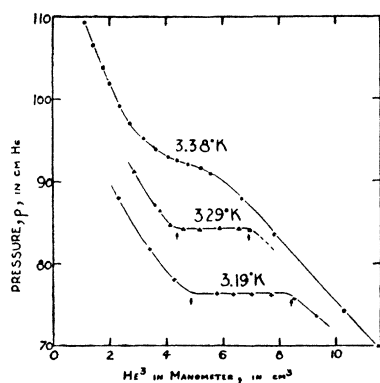


FIG. 1. "Isotherms" in the vicinity of the critical point.

<sup>2</sup> F. London and O. K. Rice, *Phys. Rev.* **73**, 1188 (1948).

<sup>3</sup> Laszlo Tisza, *Physics Today* **1**, 26 (1948).

<sup>4</sup> Fairbank, Reynolds, Lane, McInteer, Aldrich, and Nier, *Phys. Rev.* **74**, 345 (1948).

immersion depth was held constant by gradually raising the Dewar as the bath evaporated, the capillary being fixed with respect to its vacuum system. A double Wilson seal surrounding the capillary made this immersion adjustment possible even when pumping on the bath. In order to minimize the effect of the dead volume of the capillary in the temperature region between bath and room temperature, the upper part of the capillary was surrounded by two shells of heavier tubing in thermal contact with the capillary at the top (room temperature) end and at a point 4 cm from the bottom. Being far better heat conductors than the capillary, these shells had the effect of raising the temperature of the capillary at all points on the capillary not immersed in the liquid, thus greatly reducing the dead space.

The room temperature end of the capillary was connected to a combined mercury manometer and simple Toepler pump such that by raising the mercury levels in the manometer,  $\text{He}^3$  could be transferred into the capillary and its pressure there measured. Condensation was assumed to be taking place if the equilibrium pressure in the capillary was independent of the volume of helium remaining in the manometer.

Figure 1 shows the data for three different temperatures. Flats on the two lower curves indicate the vapor pressures of  $\text{He}^3$  corresponding to 3.19°K and 3.29°K. The upper curve corresponds to a temperature of 3.38°K which is believed to be above the critical temperature  $T_c$ , since at  $T_c$  a horizontal inflection would be observed. From these data and other runs at intermediate temperatures we have chosen  $T_c = 3.34^\circ\text{K}$  corrected as explained below.

As a check on the equilibrium temperature inside the capillary,  $\text{He}^4$  was condensed there. Its vapor pressure was found to be greater than the bath pressure by an amount corresponding to a temperature difference of 0.01<sub>2</sub>°K. The same temperature excess inside the capillary was observed at bath temperatures of 4.0, 3.3, and 1.4°K. We are tentatively assuming that the same temperature excess existed when  $\text{He}^3$  was being condensed and have adjusted our temperatures accordingly.

It has been previously observed that open and closed bulb vapor pressure thermometers may

indicate different bath temperatures, but no satisfactory explanation for this has been advanced.<sup>5</sup> Our observations lead us to suggest that a heat flow down to the bulb may give rise to an appreciable temperature gradient through the walls of the immersed portion of the bulb. This thermal flow appears to be due to both conduction in the capillary wall and convection of the gas within it. Since an open-bottomed tube communicates directly with the liquid, the vapor pressure measured with such a device should correspond more closely to the bath pressure.

The possibility of a pressure difference due to the surface tension of the liquid should also be considered.

The vapor pressure measurements are summarized in Table I and in Fig. 2, which also shows vapor pressures for He<sup>4</sup> determined at Leiden in 1937. It is interesting to note that at 1.2°K the vapor pressure of He<sup>3</sup> is 35 times as great as that of He<sup>4</sup>, suggesting the potential usefulness of He<sup>3</sup> for thermometry at low temperatures. At 1°K He<sup>4</sup> vapor pressures are near the limit of accurate measurement. Indications are that He<sup>3</sup> could be used down to 0.5°K or perhaps even lower. The pressure at 0.5°K is 0.12 mm Hg if our data are extrapolated on the assumption of constant latent heat below 1.4°K.

TABLE I. Vapor pressures of He<sup>3</sup> from 1.2° to 3.3°K.

<i>T</i> , °K	<i>P</i> , mm Hg
1.21 <sub>1</sub>	23
1.33 <sub>4</sub>	32
1.52 <sub>4</sub>	54
1.63 <sub>5</sub>	70
1.79 <sub>5</sub>	99
1.97 <sub>7</sub>	141
2.04 <sub>7</sub>	159
2.15 <sub>2</sub>	195
2.32 <sub>7</sub>	255
2.58 <sub>0</sub>	366
2.81 <sub>7</sub>	495
3.03 <sub>2</sub>	634
3.20 <sub>1</sub>	764
3.29 <sub>7</sub>	842
3.33 <sub>5</sub>	872
(3.3 <sub>4</sub> )	(875) critical point
(3.2 <sub>0</sub> )	(760) boiling point

<sup>5</sup> W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., New York, 1942), p. 193.

A curve through the experimental points shows the normal boiling point to be 3.2<sub>0</sub>°K. Extrapolation to the critical temperature gives for the critical pressure  $p_c=875$  mm Hg. Putting these values of  $p_c$  and  $T_c$  in van der Waal's equation, we find the critical density to be  $\rho_c=0.036$  g/cm<sup>3</sup>. By Dieterici's equation we find  $\rho_c=0.046$ . Since for He<sup>4</sup> the accepted value of  $\rho_c$  lies midway between the values calculated from these two equations, we have chosen  $\rho_c=0.041$  g/cc.

It is possible to determine the density of the liquid from these data provided one knows to what level the liquid rises in the immersed

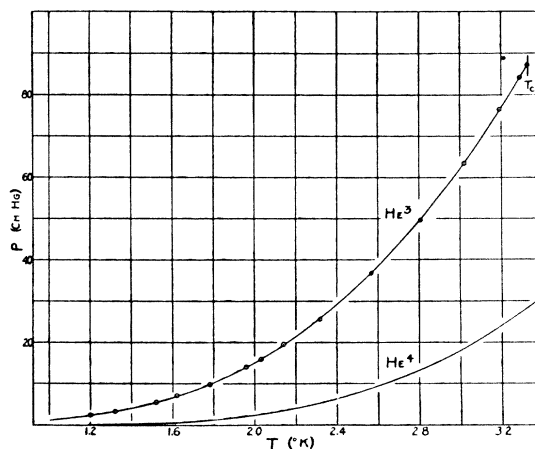


FIG. 2. Vapor pressures of He<sup>3</sup> and He<sup>4</sup>.

capillary before a significant rise in its vapor pressure occurs. This gives the volume corresponding to the mass of gas admitted at constant vapor pressure (plus a correction for the dense gas displaced in the process). With our capillary the level inside is found to rise some millimeters above the bath when He<sup>4</sup> is being condensed, and it is therefore necessary to get data for two or more immersion depths in order to make a reasonable estimate of the liquid density. The evidence so far is that near  $T_c$  the densities calculated above are approximately correct and that with decreasing temperature a very rapid rise in density occurs. At 2.8° it may be as much as a factor of two higher. We are now prepared to risk using a glass capillary in order to check these density estimates.