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Distribution of He^3 between Liquid and Vapor He^4

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The relative abundances of He^3 in the liquid and vapor phases of atmospheric helium have been studied as a function of temperature above and below the λ-point. The relative abundance of He^3/He^4 in the vapor (C_v) was determined by means of the mass spectrometer and the corresponding quantity for the liquid (C_L) computed from C_v and the mass balance and composition balance equations. From 5.2°K to the λ-point the ratio C_v/C_L increases as the temperature decreases, whereas below the λ-point this ratio sharply decreases to zero, showing that the vapor in equilibrium with superfluid helium contains no measurable amount of He^3. On the basis of these results a simple method of concentrating He^3 is suggested.

INTRODUCTION

THE helium isotope of mass 3 exists in the helium gas present in the earth's atmosphere to an extent of approximately 1 part per million and this is the richest natural source of He^3 known at present. The He^3 in the well helium from Texas is about 8 times less abundant.[1,2] The thermodynamic properties of He^3 are at present unknown and it is impossible to predict theoretically what they might be. It is possible that He^3 might have a normal boiling point below that of He^4 and indeed it might exist as a gas down to absolute zero.

There are two modifications of liquid He^4, the so-called He I existing between 5.2°K and 2.19°K and He II existing at temperature below 2.19°K. In general the properties of He I are "normal," that is, classical laws are obeyed whereas He II is a decidedly "quantum" liquid. In recent years considerable success has been achieved by treating He II as a liquid obeying Bose-Einstein statistics, modified to take into account atomic interaction not present in an ideal gas, an idea first put forward by F. London. In the case of He^3 this idea would not be admissable since these atoms must obey Fermi statistics.

Liquified atmospheric helium consists of a very dilute solution of He^3 in He^4 and in this paper we have studied some of the properties of this solution, especially in the He II region. Previously a similar study had been made by us in the He I region.[3]

In carrying out this work we had a twofold purpose in mind. First, simply as a study of a solution whose nature is unique insofar that the solvent is a quantum liquid. Secondly, as a means of ascertaining the possibility of separating He^3 from He^4 by cryogenic techniques. In this latter connection, Daunt and collaborators have investigated the separation of He^3 from He^4 by the use of a superleak[4,5] and among other things, have shown that the creeping film (Rollin film) of liquid present with He II does not carry He^3 atoms. They have also reported some measurements on the vapor concentration below the λ-point, the results indicating that the abundance ratio is equal to or less than that for the unrefrigerated gas.

APPARATUS AND EXPERIMENTAL PROCEDURE

Three sets of data, referred to henceforth as Runs I, II, and III, have been taken. Run I was restricted to the helium I region and has been briefly reported in a previous communication.[3] The latter two sets of data include many

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[1] L. W. Alvarez and R. Cornog, Phys. Rev. **56**, 613 (1939); **56**, 379 (1939).

[2] L. T. Aldrich and A. O. Nier, Phys. Rev. **70**, 983 (1946).

[3] H. A. Fairbank, C. T. Lane, L. T. Aldrich, and A. O. Nier, Phys. Rev. **71**, 911 (1947).

[4] J. G. Daunt, R. E. Probst, H. L. Johnston, L. T. Aldrich, and A. O. Nier, Phys. Rev. **72**, 502 (1947).

[5] J. G. Daunt, R. E. Probst, and H. L. Johnston, J. Chem. Phys. **15**, 759 (1947).

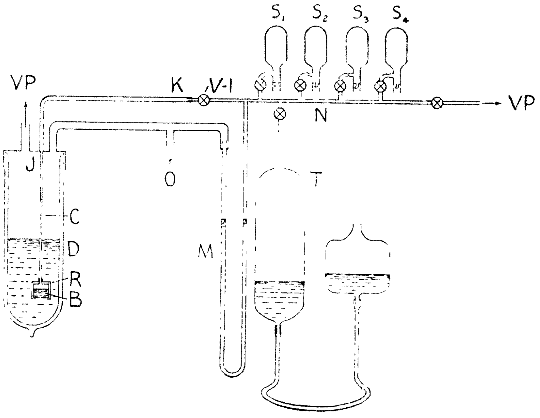

FIG. 1. Schematic diagram of the experimental arrangement.

temperature points in the helium II region where the effect of the creeping film may easily confuse the vapor-liquid equilibrium sufficiently to invalidate the concentration measurements unless the apparatus and method of sampling are carefully designed to minimize this complication. For this reason a rather detailed description of the apparatus and method of sampling will be given. Figure 1 is a schematic diagram of the basic apparatus. The glass Dewar *D* contains a bath of liquid well helium in which a small glass bulb *B* is immersed. This bulb is cylindrical in shape; approximately 31-mm diameter×20 mm long. Bulb *B* is connected via a capillary tube to a capillary glass manifold *N*. The section from *J* to *K* is of copper instead of glass for flexibility and convenience. Attached to the manifold *N* are several break-seal tubes (S_1, S_2, etc.) for collecting the gas samples, a large two-liter mercury Toepler pump *T* to allow easy transfer of an accurately known mass of helium gas to bulb *B* where it can be condensed, and a differential manometer *M* for measuring the difference in the vapor pressure of the liquids and, hence, the difference in temperature inside and outside bulb *B*. Attached at 0 is an absolute oil manometer to measure the vapor pressure of the outer bath of helium, the corresponding absolute temperature being computed from the Leiden 1937 tables.

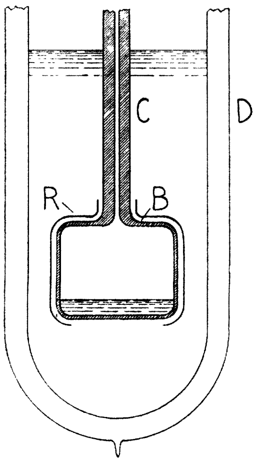

FIG. 2. The sample bulb and radiation shield.

The procedure used in Run II is typical. A charge of 2 liters of Air Reduction Company atmospheric helium was transferred to the Toepler pump *T* by standard methods before the run. After filling Dewar *D* with liquified well helium, the atmospheric helium was condensed in *B*, which has a volume of 12.85 cm^3. With all the stopcocks shown in Fig. 1 closed except *V*-1, the liquid in *B* was allowed to establish equilibrium with the vapor for a period of 30 minutes at a temperature of 2.24°K. The break-seal sample tubes had been previously evacuated and at the end of this time the stopcock to one of them (S_1) was opened and a sample of the vapor withdrawn. The sampling time for this and subsequent samples was one minute. Because the connecting capillary tube between bulb *B* and the manifold *N* has a small but finite volume, it is possible that as much as half of this first sample came from the connecting lines instead of *B*. We therefore took a second sample at this temperature, which must have come substantially from the vapor above the liquid in bulb *B*. In this and subsequent samples in Runs II and III the volumes of the break-seal tubes were adjusted to give a sample size of about 7 standard cc. In every case the mass of vapor in bulb *B* was several times the mass of the sample extracted so that little of the sample obtained is evaporated from the liquid during the short withdrawal time.

Subsequent samples at lower temperatures were obtained in the same manner as the one above. However, for the samples below the λ-point the equilibrium time at each temperature was cut to 15 minutes and in Run II only one sample was taken at each of the other temperatures while in Run III "flushing" samples were taken at each temperature. Of course, as the temperature decreases, the density of the gas decreases and the mass of the gas in the sampling tubing becomes smaller relative to the sample, so little error is introduced from this source.

The effect of the evaporating creeping film in diluting the vapor in He^3 is probably the most serious potential source of error. Presumably, the film will creep up the sides of the capillary from the liquid in bulb *B* to a level at which the temperature exceeds 2.19°K. The evaporated film, depleted in He^3, then diffuses back into bulb *B* to disturb the normal isotope equilibrium between vapor and liquid. Since the rate of creep is proportional to the minimum perimeter of the surface along which it travels, the effect of the creeping film can be minimized by making the connecting capillary *C* small. In these experiments the inside diameter of this glass capillary was 1.5 mm. There is, of course, the possibility that sufficient heat energy could be absorbed by radiation in the walls of bulb *B* itself to evaporate the film before it reached the capillary and in this case the rate of creep would not be limited by the small perimeter of the capillary but by the manyfold larger perimeter of the bulb *B*. This did not appear probable, but inasmuch as no special precautions were taken in Run II to shield the bulb from the radiation through the unsilvered slits in the jacketing Dewars and from the top of the flask, a third run was taken. Figure 2 shows a scale drawing of bulb *B* used in Run III. It is identical to that used in the previous run except for the addition of the aluminum foil radiation shield (*R*) placed around the sides and over the top of the bulb. In this run the sampling method was identical to that in Run II except that two samples were taken at every temperature in order to insure that the second one came substantially from the vapor in bulb *B*.

RESULTS AND DISCUSSION

The ratio of He^3 to He^4 in the vapor, drawn off at the various temperatures, was determined with the mass spectrometer. The corresponding quantity for the liquid, in equilibrium with this vapor, was computed from the balance of mass and balance of composition equations. It may be shown readily that

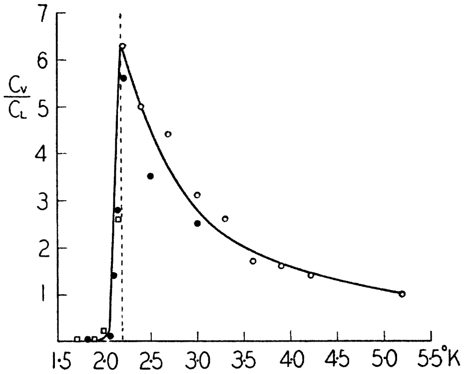

FIG. 3. The ratio of the relative abundances of He^3 in the vapor to that in the liquid as a function of temperature. White circles are the results previously reported (reference 3). Squares are the results of Run II and black circles those of Run III. The vertical broken line passes through the λ-point.

$$\frac{C_v - C_0}{C_0 - C_L} = \frac{\rho_L(\rho_0 - \rho_v)}{\rho_v(\rho_L - \rho_0)},$$

wherein

C_v = He^3/He^4 in vapor,
C_L = He^3/He^4 in liquid,
C_0 = He^3/He^4 in the sample of gas used to produce the liquid and vapor phases,
ρ_L = density of liquid,
ρ_v = density of vapor,
ρ_0 = mass of gas used divided by the volume of the sample bulb.

Since all quantities except C_L in the above expression are known or were measured, the concentration in the liquid could be determined at each temperature. Since the total amount of gas used in each run was around 2000 cm^3 (S.T.P.) and each sample of vapor withdrawn of the order of 6–7 cm^3 (S.T.P.), it was necessary to correct C_0 and ρ_0 at each temperature for depletion due to previous sampling and flushing, and this was done. Below 2.19°K the vapor densities (ρ_v) were not available and in consequence these were computed from Clapeyron's equation using known data for the vapor pressure, latent heat and liquid densities in this region.

In Table I are given the results of Runs II and III; and in Fig. 3 the ratio C_v/C_L is plotted as a function of temperature. For completeness, this graph also includes the results of our previous work (reference 3). One of the points has been omitted from the graph, that at 2.24°K in

TABLE I. Concentrations of He^3 relative to He^4.

Sample	Volume of He in experimental bulb cm³ S.T.P.	C_0 $\times 10^6$	C_v $\times 10^6$	C_L $\times 10^6$	C_v/C_L	T °K	Run
0	1890	0.9	—	—	—	297	2
1*	1883	0.86	11.0	0.53	21	2.24	2
2	1876	0.82	2.2	0.79	2.8	2.15	2
3	1870	0.81	1.2	0.80	1.5	2.10	2
4	1864	0.81	0.17	0.81	0.2	2.00	2
5	1858	0.81	<0.04	0.81	<0.05	1.875	2
6	1852	0.81	<0.04	0.81	<0.05	1.785	2
7	1846	0.81	<0.04	0.81	<0.05	1.700	2
0	2010	1.2	—	—	—	295	3
1	2003	1.2	2.5	1.0	2.5	3.00	3
2	1990	1.2	3.7	1.06	3.5	2.50	3
3	1977	1.18	5.8	1.04	5.6	2.21	3
4	1964	1.16	3.2	1.13	2.8	2.15	3
5	1951	1.16	1.6	1.15	1.4	2.10	3
6	1938	1.16	0.1	1.16	0.1	2.06	3
7	1924	1.16	<0.05	1.16	<0.04	1.82	3

* This point not included in Fig. 3 for reasons given in the text.

Run II. Points taken close to the same temperature in Runs I and III failed to substantiate the very large value of C_v/C_L found in Run II but agreed well with each other. Hence we have discarded this point as being an error of observation.

We have regarded the ratio C_v/C_L as the most significant function to plot since we suppose that with such a highly dilute solution as we have here this ratio should be a constant at a given temperature (Henry's law). In the He I region the variation of the Henry constant with temperature is normal. Helium dissolved in liquid nitrogen shows a somewhat similar behavior.

In the He II region, however, the behavior has no counterpart in any other dilute solution known to us, and appears to be another manifestation of the quantum nature of He II.

In this connection, however, as has been emphasized, it is important to be sure that the effect is a true one and not merely another demonstration of the fact, as has already been established by Daunt and collaborators,[4] that the creeping film transports no He^3. Many of the properties of the Rollin film are now well known, especially the rate at which liquid is transported in the film.[6] In our set-up, as has been mentioned, special precautions were taken to ensure that the film evaporated in the glass capillary and not in the sample bulb itself. Since we had a closed system, the resulting pure He^4 from the evaporating film has necessarily to flow back down the capillary and recondense in the bulb, the heat of condensation being carried away by the outer bath. A simple computation, based on the data for the volume flow rate of the Rollin film (reference 6), shows that it is not possible to account for the present results on the basis of a film effect. For instance, in the case of Sample 4, Run III, the times of operations were as follows. Approximately 6 minutes were taken to reduce the temperature from above the λ-point to 2.15°K. The bulb B remained at this temperature for 15 minutes. A flushing sample was then taken, requiring 1 minute. The measured sample was taken 2 minutes later requiring also 1-minute extraction time. The total elapsed time is accordingly 25 minutes. The rate of creep at 2.15°K is 0.115 cm³ (S.T.P.) per minute,[6] in the 1.5-mm capillary tube. Hence, in 25 minutes, a maximum of 2.9 cm³ (S.T.P.) of helium could have evaporated via the film. If we now make the drastic and unlikely assumptions that all of this helium is recovered in the samples, that it is all He^4, and further that the "true" concentration is the same as that just above the λ-point (5.8×10^{-6}), then the concentration measured at 2.15°K in the two 6.7-cm³ (S.T.P.) samples should have been 4.5×10^{-6}, and this, in view of the above assumptions, is most certainly a lower limit. Actually, the measured concentration on the second sample was $3.2\times 10^{-6}\pm 10$ percent.

The results suggest a rather simple way of concentrating He^3. It would merely be necessary to evaporate a quantity of liquid helium at a temperature well below the λ-point until only a few drops of the liquid remained. These remaining drops would then contain all the He^3 present in the original sample. Since the density of liquid helium is around 800 times that of the gas (S.T.P.) quite sizeable samples of enriched gas should be obtainable, starting with quite modest amounts of liquid.

Finally, we should like to thank Dr. L. Onsager for a number of valuable discussions, and we are indebted also to Mr. Charles Reynolds for material assistance in the low temperature phase of this work.

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[6] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. **A170**, 423 (1939); *ibid.* **170**, 439 (1939).