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The Solubility of He^3 in Liquid He^4*

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Measurements are reported of the distribution coefficient for He^3 between solutions of He^3 in liquid He^4 and their saturated vapors in the temperature range 1.4°K to 2.6°K. The results obtained below the λ-temperature give values for C_V/C_L higher than those calculable for perfect classical solutions, but in good agreement with the theory previously proposed by Heer and Daunt. Above 2.18°K, the λ-temperature for pure liquid He^4, the measured C_V/C_L also appears greater than that for perfect calssical solutions, as was predicted by Heer and Daunt. A comparison with the theory of de Boer and Gorter is also given.

I. INTRODUCTION

THE experimental study of solutions of He^3 in He^4 has been mainly concerned with measurement of the distribution coefficient, i.e., the ratio of the concentration, C_V, of He^3 in the saturated vapor, to the concentration, C_L, of He^3 in the solution, and this has yielded results which have been both mutually inconsistent and subject to excessive experimental scatter.

A. Above the Lambda-Temperature

Results of measurements[1,2] above the lambda-temperature T_λ for dilute solutions ($C_L \approx 10^{-5}$) indicated values of C_V/C_L in approximate agreement with those calculable from Raoult's law from the equation:

$$C_V/C_L = p_3{}^0/p_4{}^0, \tag{1}$$

where $p_3{}^0$ and $p_4{}^0$ are the vapor pressures of pure liquid He^3 and pure liquid He^4, respectively. More recent work above T_λ by Lane and co-workers[3] and by Weinstock, Osborne, and Abraham[4] using more concentrated solutions (C_L up to 25 percent) indicated qualitatively that the observed C_V/C_L is greater than that calculable from Eq. (1). No exact data however was reported.

B. Below the Lambda-Temperature

It has been in measurements of C_V/C_L below the lambda-temperature that the greatest discrepancies between the various results have been evidenced, and these discrepancies have been mainly the result of a lack of uniformity in the distribution of He^3 throughout the volume of the liquid of the solution. This lack of homogeneity in the liquid phase is primarily the result of (*a*) the much larger heat influxes to the experimental arrangements at temperatures below the λ-temperature and (*b*) the fact that He^3 in solution in liquid He^4 does not partake in superfluid flow.[5,6]

The results obtained by Daunt, Probst, and Smith[2] and by Lane and co-workers[7] for C_V/C_L below T_λ were all much smaller than would be given by Raoult's law; whereas the experimental results by Taconis *et al.*[8] and by Lane and co-workers[9] were very much larger than those predictable form Raoult's law. From their results, Taconis *et al.* proposed the hypothesis that He^3 in liquid He^4 below T_λ could be regarded as being in solution with the "normal" constituent of liquid He^4 only. Assuming such a limited solubility to observe the laws for perfect solutions, this empirical rule leads to the

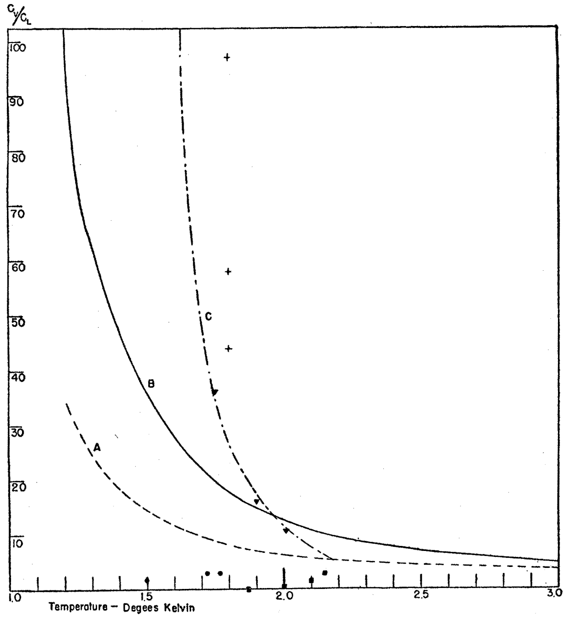

FIG. 1. Plot of C_V/C_L *versus* T from experiment (previous to this paper) and theory for dilute solutions of He^3 in He^4. ($C_L \leqslant 10^{-4}$.) Curve *A*, Raoult's law for perfect classical solutions; Curve *B*, theory of Heer and Daunt (reference 11); Curve *C*, calculated from Taconis's rule (reference 8). ▼ experimental results of Taconis *et al.* (reference 8), + experimental results of Lane and co-workers (reference 9), ■ experimental results of Lane and co-workers (reference 7), and ● experimental results of Daunt and co-workers (reference 2).

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* Assisted by a contract between the AEC and the Ohio State University Research Foundation.

[1] Fairbank, Lane, Aldrich, and Nier, Phys. Rev. **71**, 311 (1947).

[2] Daunt, Probst, and Smith, Phys. Rev. **74**, 494 (1948).

[3] Fairbank Reynolds, Lane, McInteer, Aldrich, and Nier, Phys. Rev. **74**, 345 (1948).

[4] Weinstock, Osborne, and Abraham, Phys. Rev. **77**, 400 (1950).

[5] Daunt, Probst, Johnston, Aldrich, and Nier, Phys. Rev. **72**, 502 (1947).

[6] Daunt, Probst, and Johnston, J. Chem. Phys. **15**, 759 (1947).

[7] Fairbank, Lane, Aldrich, and Nier, Phys. Rev. **73**, 729 (1949).

[8] Taconis, Beenakker, Nier, and Aldrich, Phys. Rev. **75**, 1966 (1949) and Physica **15**, 733 (1949). See also Taconis, Beenakker, and Dokoupil, Phys. Rev. **78**, 171 (1950).

[9] Lane, Fairbank, Aldrich, and Nier, Phys. Rev. **75**, 46 (1949).

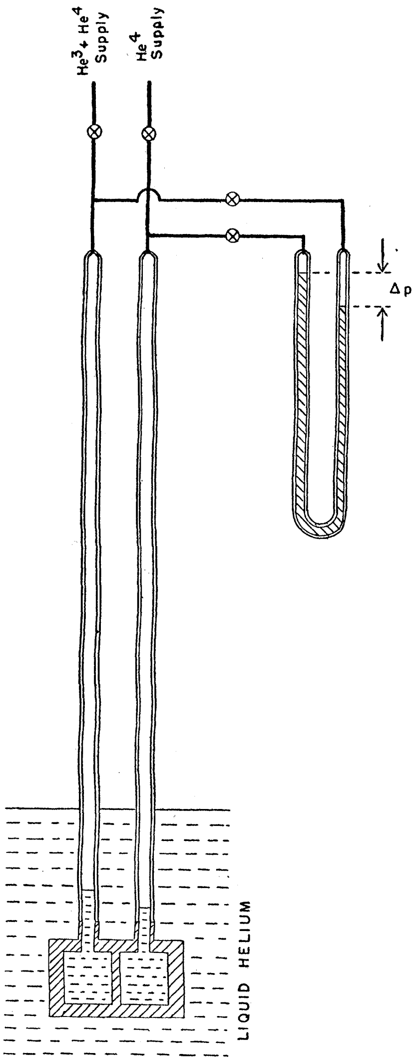

FIG. 2. Diagram of apparatus reported in this paper for measurement of C_V/C_L for solutions of He^3 in He^4.

following formulation for C_V/C_L, for very dilute solutions

$$C_V/C_L=(\rho/\rho_n)(p_3^0/p_4^0), \tag{2}$$

where ρ and ρ_n are the total density of liquid He^4 and the density of the "normal" constituent of He^4, respectively. The value of C_V/C_L according to Eq. (2) is shown in Fig. 1. It should be emphasized that if the laws for classical perfect solutions are continued to be assumed valid, above the λ-temperature there should be no difference between Eqs. (2) and (1), since above the λ-temperature $\rho_n/\rho=1$. This means therefore, according to Taconis, that Raoult's law should be at least approximately valid above the λ-temperature for dilute solutions. de Boer and Gorter[10] have extended this hypothesis of Taconis by calculating the properties of such solutions when the concentration of He^3 may be appreciable.

An entirely different theoretical approach has been made by Heer and Daunt,[11] who have shown that solutions of He^3 in liquid He^4 can be regarded as solutions of model liquids which are represented respectively by ideal Fermi-Dirac and ideal Bose-Einstein gases situated in smoothed potential wells. For such model liquids the quantum effects associated with the degeneracy of the B.E. statistics lead to marked deviations from Raoult's law. The theoretical calculation of C_V/C_L for such dilute solutions is also shown in Fig. 1.

In view of the conflicting experimental data and the interest theoretically in such solutions of He^3 in He^4, the experiments reported herewith were carried out in an attempt to narrow the margin of experimental scatter of results and to measure C_V/C_L over as wide a temperature range as possible.

II. EXPERIMENTAL TECHNIQUE EMPLOYED

The experimental arrangement used by us for the evaluation of C_V/C_L is shown diagramatically in Fig. 2. Two vessels of internal diameter 3.2 mm and volume 40 mm^3 were drilled out of a solid block of pure copper, so that they were in good thermal contact with each other. The vessels were connected to their external gas supplies by capillary tubing of 0.79-mm internal diameter, part of which was of glass so that the levels of the liquids in the two volumes could be observed directly, and the vessels immersed in a bath of liquid helium.

One vessel was filled with pure liquid He^4 and the other with a solution of He^3 in liquid He^4, having a value of C_L of about 1.5 percent, until the levels were visible in the capillaries and at any desired temperature the difference in vapor pressure between the solution and the pure liquid He^4 could be observed with an external differential oil ("Octoil, *S*") manometer of very small dead (gas) volume (see Fig. 2).

Significant dimensional data are collected together in Table I.

Provision was made also for making a differential comparison between the vapor pressure of the pure liquid He^4 in the vessel and the vapor pressure of the helium bath. (For simplicity this arrangement is not shown in Fig. 2.)

Our experimental arrangement was chosen as one

TABLE I. Dimensional data of apparatus.

Internal diameter of each copper vessel	3.2 mm
Volume of each copper vessel (Experiments of 21st and 22nd December, 1950)	40 mm^3
Volume of each copper vessel (Experiments of 14 December, 1950)	50 mm^3
Diameter of glass capillaries, leading from copper vessels to room temperature	0.79 mm
Average volume of gas "dead" space at room temperature on He^3+He^4 line	3.5 cm^3

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[10] J. de Boer and C. J. Gorter, Physica 16, 228, 667 (1950).

[11] C. V. Heer and J. G. Daunt, Phys. Rev. 81, 447 (1951).

which would minimize systematic errors for the following reasons:

(a) The maximum height of the solution, measured from the bottom of its containing vessel, was 50 mm, which for 1.0 percent average value of solution concentration would result in ebullition at the bottom of the vessel for a concentration excess of 15 percent at 1.5°K. At 1.8°K the error is 7.5 percent. This would therefore provide adequate automatic stirring, and would provide a surface concentration within 15 percent of the measured average value at the lowest temperature and better accuracy at higher temperatures.

(b) By having both vessels in the same copper block, the temperatures of both vessels should remain the same even above the λ-temperature.

(c) By measuring differential vapor pressure, an equilibrium measurement is made, which also is independent of the two-phase convection in the filling tubes. Moreover, for all temperatures used, the correction for thermo-molecular pressure differences is negligible.

If Δp is the observed excess pressure of the solution over that of pure liquid He^4, then for our dilute solutions,

$$C_V/C_L=[\Delta p/(p_4^0+\Delta p)](1/C_L), \tag{3}$$

to within the accuracy of the experiment.

(d) By observation of the height of the liquid levels, the liquid and vapor volumes could be computed at all temperatures, and hence, C_L could be evaluated from a knowledge of the He^3 concentration in the unrefrigerated gas.

III. THE EXPERIMENTS

He^3, kindly supplied by the AEC, was used, diluted with He^4 ("well" helium) to form a mixture having an unrefrigerated He^3 concentration, C_3, of 1.0±0.10 percent, as estimated by volume measurements made during the dilution process. Subsequent mass-spectrographic analysis of the sample of the unrefrigerated mixture carried out at three different establishments[12] gave values of $C_3=0.99$ percent; 1.60 percent and 1.65 percent. These discrepancies are disturbing and have forced us to give out results in the form of ranges of C_V/C_L within which the true values of C_V/C_L may be located.

Observations were made on three independent runs. In the last two runs, the vessels were of dimensions given above, whereas in the first run a different copper block was substituted having a vessel volume = 50 mm^3, the dimensions of other parts of the apparatus being kept the same.

TABLE II. The results.

Experiment	T°K	Δp cm oil	Δp cm Hg	C_V/C_L[a]
December 14, 1950	2.33	7.60	0.527	5.4– 8.9
	2.27	7.15	0.496	5.8– 9.5
	2.18	5.30	0.368	5.4– 8.9
	1.99	4.60	0.319	7.5–12.4
	1.75	3.90	0.271	12.7–21.0
	1.45	2.70	0.187	23.8–39.3
	2.49	9.20	0.638	4.8– 7.9
December 21, 1950	2.12	4.95	0.344	5.6– 9.3
	1.66	3.95	0.274	12.4–20.4
	1.43	2.70	0.187	25.4–42.0
	2.59	11.50	0.798	4.9– 8.0
December 22, 1950	2.60	8.90	0.617	3.8– 6.3
	2.31	7.70	0.534	5.8– 9.5
	2.19	7.20	0.500	7.0–11.5
	1.93	4.45	0.308	8.5–14.0
	2.30	5.70	0.396	4.4– 7.3
	2.18	5.30	0.368	5.4– 8.9
	1.50	3.0	0.208	23.2–38.2

[a] The two columns under C_V/C_L give the limits of the ranges of the calculated values of C_V/C_L. The lower numerical values of C_V/C_L were obtained by taking $C_L=C_3=1.65$ percent and the higher values were obtained by taking $C_L=C_3=1.00$ percent.

The temperature of the helium bath was measured by vapor pressure measurements in the usual way, and above the λ-temperature the bath was well stirred and measurements made only on diminishing the temperature from a higher value.

At all temperatures of measurement no measurable difference of vapor pressure was observable between that of the bath and that of the vessel containing the pure He^4, indicating negligible thermo-molecular pressure difference corrections.

The observed results are given in Table II, in which are tabulated the observed temperatures (1949 scale[13]), the observed vapor pressure differences, Δp, between the He^3 and He^4 solution, and the pure liquid He^4, given both in cm of oil and cm of Hg, and the calculated range of values of C_V/C_L obtained from Eq. (3). In this evaluation of C_V/C_L, the numerical value of C_L has been set throughout equal to C_3, the He^3 concentration of the unrefrigerated gas, and the range of values of C_V/C_L has been calculated for $C_3=1.0$ percent to 1.65 percent. In assessing the possible deviations of C_L from the concentration of the unrefrigerated gas, estimates have been made of the quantity of He^3 present in the vapor phase at each temperature. These estimates have been made in two ways: (*a*) by estimation of the effective (*NTP*) volume available to the vapor from observation of the meniscus heights of liquid in the capillary and in the main liquid helium bath, and (*b*) by noting the change in the meniscus height of the solution in the capillary when the temperature was reduced from the temperature of interest to a low temperature ($T\approx 1.4$°K) where the vapor pressure is negligibly small. By both these methods it was concluded that at the highest temperature of measurement, namely $T\approx 2.6$°K, (where the "effective" vapor volumes are largest) the amount of He^3 in the vapor phase was not larger than

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[12] We are indebted to Dr. Mohler of the National Bureau of Standards, to the General Electric Company and to the AEC for the analyses.

[13] H. Van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

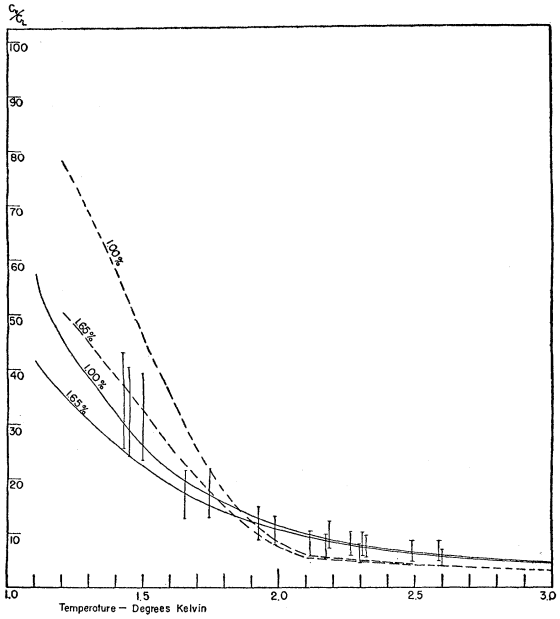

FIG. 3. The full curves are calculated from the theory of Heer and Daunt (reference 11) for He^3 concentrations of 1.00 and 1.65 percent. The broken curves are calculated from the theory of de Boer and Gorter (reference 10) for He^3 concentrations of 1.00 and 1.65 percent. The experimental results (this paper) are given by the vertical lines. The lower ends of the vertical lines correspond to $C_3 = 1.65$ percent and the upper ends to $C_3 = 1.00$ percent.

12 percent of the total amount of He^3. At these temperatures, therefore, C_L may be different from C_3 by 12 percent, and at lower temperatures correspondingly smaller differences must occur. The uncertainty, however, in measurement of the unrefrigerated gas concentration, as detailed above, introduces greater possible errors, and consequently it was not thought worthwhile to make the corrections for the differences between C_L and C_3.

The results are shown in Fig. 3.

IV. CONCLUSION

The results reported herewith on the experimental evaluation of C_V/C_L, although not of high accuracy, do narrow the region of uncertainty and scatter, which was evidenced by previous work (see Fig. 1), and enable a further check with theory to be made. In Fig. 3, the lower numerical values of our results for C_V/C_L correspond to taking the value 1.65 percent for the concentration of the unrefrigerated gas and the higher values correspond to taking 1.00 percent for the same quantity. It seemed natural therefore to make numerical computations from the theories of Heer and Daunt[11] and of de Boer and Gorter[10] for the two liquid concentrations of 1.65 and 1.00 percent. The results of these computations are shown in the curves of Fig. 3.[14]

The comparison of the theories and the experimental results given in Fig. 3 shows that broadly both theories are in general agreement with experiment below T_λ, both showing values of C_V/C_L well above those calculable from the laws for classical solutions.

For temperatures above T_λ the accuracy of the results is unfortunately insufficient to allow a definite conclusion to be drawn; but it might be inferred that the laws for classical perfect solutions are probably insufficient to describe the results. It appears that for the concentration range used in these experiments, the crucial test of theory lies in measurements above T_λ and, consequently, further measurements in this temperature range would be of value.

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[14] More extensive computations are to be published by Daunt, Tseng, and Heer.