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On Solutions of He^3 in He^4

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Elementary thermodynamics has been applied to recent data on the equilibrium concentrations of He^3 in the liquid and vapor phases of He^4. The differences between He^3 and He^4 as regards partial molar heat and entropy have been calculated and briefly discussed. Above the λ-point the energy of He^3 in the liquid is greater than that of He^4 by about 13 cal. mole^{-1}, an amount which can be accounted for theoretically by the difference in zero-point energy. But below the λ-point the energy and entropy of He^3 are considerably lower than those of He^4 in the same solution ($\Delta\bar{H}_3 - \Delta\bar{H}_4 \approx -170$ cal. mole^{-1}). The entropy decrease per He^3 atom dissolved is equivalent to the entropy contents of about 50 He^4 atoms in pure liquid helium II. An explanation of this strange result is suggested by Tisza's hypothesis that below the λ-point helium may be considered to be a mixture of a "normal" and a "superfluid" phase. The thermal data obtained lead to the conclusion that the λ-transition of pure He^4 might become a transition of first order in dilute solutions of He^3 in He^4. On this basis, the effect of concentration of He^3 on the λ-point has been considered.

RECENTLY, Fairbank, Lane, Aldrich, and Nier[1] have measured the equilibrium concentrations of He^3 in the liquid and vapor phases of He^4. These measurements provide valuable information which can serve to calculate the energy and entropy of solution of He^3 in He^4. Since the knowledge of energy and entropy is important for an understanding of the structure of these solutions, we thought it worth while to make an elementary analysis of these data.

1. THERMODYNAMICS OF THE LIQUID-VAPOR EQUILIBRIUM

Using the chemical potential μ in the usual way,[2] we apply the equation

$$d\mu_i = -\bar{S}_i dT + \bar{V}_i dp, \qquad (1)$$

to the components in the liquid, under the condition that the composition of the liquid phase is kept constant. $\bar{S}_i$ is the partial molar entropy of component i ($i=3$ for He^3 and $i=4$ for He^4), $\bar{V}_i$ the partial molar volume, T the absolute temperature, and p the pressure. We assume that in the gas phase the two components form an ideal solution, which is certainly justified below the normal boiling point of helium as the pressure becomes less than one atmosphere. If this assumption is valid we can write, using primes to designate quantities peculiar to the vapor phase,

$$\mu_i' = \mu_i^{0\prime} + RT\ln x_i' \qquad (2)$$

where $\mu_i^{0\prime}$ is the chemical potential of the pure component i in the vapor phase, at a pressure equal to the total pressure p of the system, and where x_i is the mole fraction of the component i. Differentiating this, and noting that $\mu_i^{0\prime}$ will obey an equation similar to Eq. (1), we obtain

$$d\mu_i' = -S_i^{0\prime}dT + V_i^{0\prime}dp + R\ln x_i' dT + RTd(\ln x_i'). \qquad (3)$$

Since, for an ideal solution $\bar{S}_i' = S_i^{0\prime} - R\ln x_i'$ this may be written

$$d\mu_i' = -\bar{S}_i'dT + V_i^{0\prime}dp + RTd(\ln x_i'). \qquad (4)$$

Applying $d\mu_3 = d\mu_3'$ (from $\mu_3 = \mu_3'$, one of the conditions for equilibrium between liquid and vapor phases which continue to hold under a change of temperature) we find

$$\Delta\bar{S}_3 = \bar{S}_3 - \bar{S}_3' = (\bar{V}_3 - V_3^{0\prime})dp/dT - RTd\ln x_3'/dT. \qquad (5)$$

Applying $d\mu_4 = d\mu_4'$ we find

$$\Delta\bar{S}_4 = \bar{S}_4 - \bar{S}_4' = (\bar{V}_4 - V_4^{0\prime})dp/dT - RTd\ln x_4'/dT. \qquad (6)$$

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[1] H. A. Fairbank, C. T. Lane, L. T. Aldrich and A. O. Nier, Phys. Rev. **71**, 911 (1947) and **73**, 729 (1948). We wish to thank Dr. Lane for sending us some of these data before publication.

[2] As, e.g., in F. H. MacDougall, *Thermodynamics and Chemistry* (John Wiley and Sons, Inc., New York, 1939), third edition, Chapter X.

We now assume that

$$\bar{V}_3 dp/dT(=p\bar{V}_3 d(\ln p)/dT)$$

and

$$\bar{V}_4 dp/dT(=p\bar{V}_4 d(\ln p)/dT).$$

are small[3] compared to $RTd(\ln x_3)/dT$; we assume also that $V_3^{0\prime}=V_4^{0\prime}$, which seems reasonable for the vapor phase, and which, while not required thermodynamically, is suggested by the assumption that the vapor phase is an ideal solution.[4] We also note that when the solution is very dilute in He^3 the last term in Eq. (6) becomes negligible. We may, therefore, write for the difference of entropy of condensation:

$$\Delta\bar{S}_3-\Delta\bar{S}_4=-RTd(\ln x_3')/dT \qquad (7)$$

or, for the difference in enthalpy of condensation:

$$\Delta\bar{H}_3-\Delta\bar{H}_4=T(\Delta\bar{S}_3-\Delta\bar{S}_4)=Rd(\ln x_3')/d(T^{-1}). \qquad (8)$$

Since $H=-T^2[\partial(F/T)/\partial T]$ and since the free energy F has to be continuous, it follows from (8) that x_3' has also to be continuous.

In the case where the composition of the liquid phase is not kept constant, we may still make use of Eqs. (7) and (8), provided Henry's law holds for the He^3, which appears reasonable to assume at very low concentrations. We need merely to replace x_3' by C_V/C_L the fraction of the concentrations of He^3 in the vapor and in the liquid phase. Thus if we plot $\log(C_V/C_L)$ against T^{-1}, the slope should give directly $(\Delta\bar{H}_3-\Delta\bar{H}_4)/2.3R$.

2. DISCUSSION OF THE MEASUREMENTS

Such a plot is shown in Fig. 1. The measured values shown are the results of Fairbank, Lane, Aldrich, and Nier.[1] These values fall quite well along two straight lines which meet at the λ-point ($T_\lambda=2.19$°K).[5] From their slopes we obtain the following values for the difference of the enthalpies of condensation (compare, e.g., (8)):

$$\Delta\bar{H}_3-\Delta\bar{H}_4=13\pm2 \text{ cal. mole}^{-1} \quad \text{for} \quad T>T_\lambda, \qquad (9)$$

$$\Delta\bar{H}_3-\Delta\bar{H}_4=-168\pm20 \text{ cal. mole}^{-1} \quad \text{for} \quad T<T_\lambda. \qquad (10)$$

The entropy difference, after subtracting the entropy of mixing, is given by

$$\Delta S_3^0-\Delta S_4^0=(\Delta\bar{H}_3-\Delta\bar{H}_4)/T+2.3R\log(C_V/C_L). \qquad (11)$$

With the above values we obtain

$$\Delta S_3^0-\Delta S_4^0=2.5 \text{ cal. deg}^{-1}\text{ mole}^{-1} \quad \text{for} \quad T>T_\lambda, \qquad (12)$$

$$\Delta S_3^0-\Delta S_4^0=-80 \text{ cal. deg}^{-1}\text{ mole}^{-1} \quad \text{for} \quad T<T_\lambda. \qquad (13)$$

Since we have used straight lines in Fig. 1 it follows that we obtain one constant for each slope.

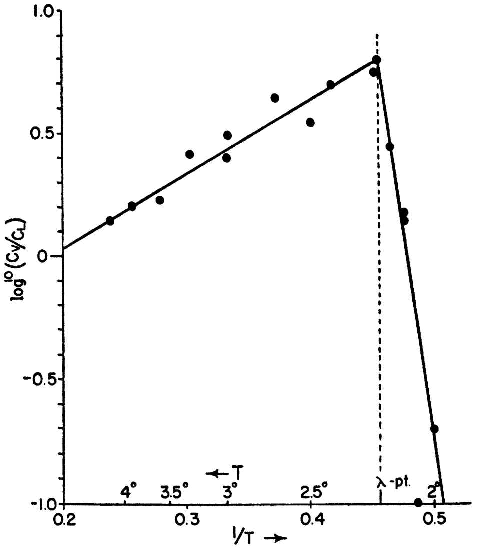

FIG. 1. Equilibrium concentrations of He^3 in He^4 in vapor (C_V) and in liquid (C_L) as function of $1/T$. The dots indicate the measured values of Lane and co-workers (reference 1).

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[3] At the normal boiling point of He^4 we have for the liquid phase $pV_4^0=32$ cc atmos. mole^{-1}; this is small compared to $RT=82.1\cdot4.2=345$ cc atmos. mole^{-1}. Since experiment indicates that $d\ln x_3'/dT$ is of the same order of magnitude as $d\ln p/dT$, or greater, it seems reasonable to neglect the terms $\bar{V}_3 dp/dT$ and $\bar{V}_4 dp/dT$.

[4] See R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939), pp. 353.

[5] We have assumed that the measurements really dealt with a thermodynamic equilibrium although the question may be raised as to whether evaporation from the superfluid film carrying He^4 only could have falsified the results during the sampling below the λ-point. According to a discussion with Dr. Lane it seems, however, that this effect could at most call for a correction of about 10 percent and could in no way account for the enormous decrease of the He^3 concentration in the vapor phase below the λ-point. In favor of our interpretation we may add the remark that if the measurements were very far from equilibrium conditions it would be a most improbable coincidence that the two curves of C_V/C_L should meet just at the λ-point, the continuity of C_V/C_L being a requirement of thermodynamics, of course only for equilibrium concentrations.

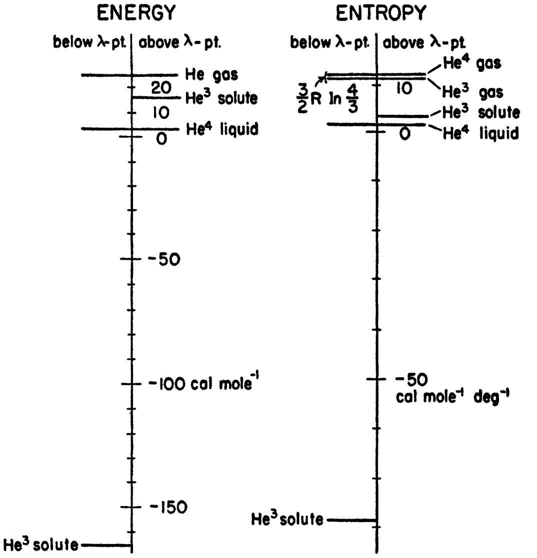

FIG. 2. Partial molar energy and entropy of He^3 and He^4 in close neighborhood to the λ-point. The zeros of the scales are chosen so as to coincide with the values of the entropy and energy of pure liquid He^4 at absolute zero. The energies in the gaseous state of He^3 and He^4 are set equal.

In Fig. 2 these results are represented in the form of energy- and entropy-level schemes taken closely above and below the λ-point. We used the value of 22 cal. mole^{-1} as heat of vaporization of He^4 near the λ-point.

3. INTERPRETATION OF RESULTS

We consider first the value of $\Delta\bar{H}_3 - \Delta\bar{H}_4 = 13$ cal. above the λ-point. It can roughly be accounted for by the different zero-point energies due to the different masses of the two isotopes. The zero-point energy in liquid He^4 has been estimated by one of us to be between 34 and 46 cal. mole^{-1} near absolute zero.[6] If we assume that the zero-point energy of He^3 is given simply by multiplication of that of He^4 by 4/3, the ratio of the masses,[7] we obtain a value between 45 and 61 cal. mole^{-1}. If this were the sole effect we would have $\Delta\bar{H}_3 - \Delta\bar{H}_4 = 13 \pm 2$ cal. mole^{-1}. The value derived from Lane's measurements just fits into this interval. However, it is not to be expected that it is the whole effect, since the entropy of He^3 in solution is higher than that of He^4 by about 2.5 entropy units. This corresponds to a free volume of He^3 about 3.5 fold that of He^4 in the same solution. The exact reason for this difference is not clear.

The values of $\Delta\bar{H}_3 - \Delta\bar{H}_4$ and $\Delta S_3{}^0 - \Delta S_4{}^0$ below the λ-point are truly astonishing. If the value of $\Delta S_3{}^0 - \Delta S_4{}^0 = -80$ cal. deg^{-1} were to be interpreted by a change of free volume, it would mean that He^3 has a free volume equal to only 10^{-17} times that of the free volume of He^4 in the same solution. It seems absurd to imagine that such a difference in free volume could occur. We are practically driven to the conclusion that this is an effect of He^3 on the solvent, He^4. The presence of the He^3 must then be able to induce a change involving very many atoms of He^4. Since the entropy per mole He^4 below the λ-point is smaller than 1.6 cal. deg^{-1} while we obtained for $\Delta S_3{}^0 - \Delta S_4{}^0 = -80$, it follows that one single He^3 atom must be able to "disentropize" about 50 He^4 atoms.

We may try to explain this effect by a simple mechanism which is suggested by the model proposed by Tisza[8] and F. London[9] of two inter-penetrating phases, a "normal" and a "superfluid" one in liquid helium below the λ-point. A He^3 atom could presumably move without collision through the superfluid phase of He^4 but not through the normal one. If it found itself in a portion of the superfluid phase it would have an extremely long free path, and its zero-point energy would be low. It might thus be expected to draw around itself a small lake of superfluid He^4. This would mean that the presence of He^3 would cause the appearance of small globules of superfluid He^4 which would have abnormally small entropy (approximately zero, according to Tisza) and abnormally low energy. The question arises as to whether these globules of pure superfluid He^4 can be large enough to account for the large energy and entropy of dissolving of He^3 below the λ-point.

Tisza has pointed out that the thermohydro-

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[6] F. London, Proc. Roy. Soc. **A153**, 576 (1936); J. Phys. Chem. **43**, 49 (1939).

[7] We multiply by the ratio of the masses rather than by its square-root as for a harmonic oscillator because there is evidence that the field in which a helium moves, resembles a square-well potential energy more closely than a Hooke's law field. See reference 6 and also M. E. Hobbs, J. Chem. Phys. **7**, 318 (1939).

[8] L. Tisza, Nature **141**, 913 (1938); C. R. Paris, **207**, 1035, 1186 (1938); J. de phys. et rad. **1**, 165, 350 (1940); Phys. Rev. **72**, 838 (1947).

[9] F. London, Phys. Rev. **54**, 947 (1938).

dynamic effects can be explained by his model if one assumes that the normal He atoms in the liquid below the λ-point have a sort of partial pressure, which may be measured by a semipermeable piston which allows the superfluid helium, but not the normal helium, to pass through.

Let us imagine a He^3 atom within a globule of superfluid helium acting much like such a semipermeable piston, holding the normal He^4 atoms beyond a radius r, but allowing the superfluid He^4 to pass into the sphere. The He^3 atom, then, must exert an outward pressure to balance the partial pressure of the normal He^4 atoms outside r. Indeed it exerts such a pressure by virtue of its zero-point energy. Our idea is that the equilibrium of these two pressures determines the size of the globule and thus the number of normal He^4 atoms which are disentropized by one He^3 atom. This is, of course, a very idealized picture.

Since we are interested only in obtaining a rough estimate we shall make the calculation as though the globules were spherical and shall further assume that each one contains only one He^3 atom.

The zero-point energy of an atom of mass m, radius a, which is locked within a spherical cavity of the radius r, is

$$E_0=\frac{h^2}{8m(r-a)^2}. \tag{14}$$

Its zero-point pressure is given by differentiation with respect to the volume $v=(4\pi/3)r^3$

$$p_0=-\frac{\partial E_0}{\partial v}=\frac{h^2}{4m(r-a)^3}\,\frac{1}{4\pi r^2}. \tag{15}$$

On the other hand, the thermal pressure exerted by liquid helium II on a semipermeable wall, behind which the pure superfluid is contained, is approximately given by [10]

$$p=4.6\cdot 10^3 T^{6.6}\ \text{dyn/cm}^2. \tag{16}$$

Thus, equilibrium is established for the radius r_0 given by equalizing the two pressures:

$$\frac{h^2}{16\pi m r_0{}^2(r_0-a)^3}=4.6\cdot 10^3 T^{6.6}, \tag{17}$$

or

$$(r_0-a)^3 r_0{}^2=3.8\cdot 10^{-35}/T^{6.6}.$$

At $T=2.1°K$ and for $a=1.4A$ (range of the repulsive forces between helium atoms) one obtains the radius $r_0=5.8A$ or the volume $(4\pi/3)r_0{}^3=815A$. The molecular volume of liquid helium is about 45A. Hence, there would be about 815:45 = 18 He^4 molecules in such a globule. At 2.1°K the entropy of liquid helium is about 1.3 cal. deg^{-1} $mole^{-1}$. Accordingly, we would be able to account for about 24 cal. deg^{-1} $mole^{-1}$ of the 80 obtained by the evaluation of Lane's experiments.

The significance of this result might still be a matter of opinion, and we do not wish to push this particular picture unduly; it is to be taken merely as a tentative suggestion. In particular, it is still necessary to show why one should consider the zero-point energy of a He^3 atom as determined by the space left free from the normal phase of He^4 alone, whereas we know that the zero-point energy of pure He^4 at 0°K is essentially determined by the space left between *all* He^4 atoms.

4. INFLUENCE OF He^3 ON THE λ-TRANSITION OF He^4

The thermal data (9), (10), (12), (13), which we have derived from the vapor-liquid equilibrium consentration, can be used to calculate the effect on the λ-transition of He^4 caused by the presence of He^3.

While it cannot be said with certainty, it appears to be strongly suggested, if one looks at the data assembled in Fig. 1, that the C_V/C_L-curve has a *discontinuous slope* at the λ-point. This, at any rate, lay at the root of our previous discussion of the measurements. This means that $\bar{H}_3-\bar{H}_4$ has a discontinuity in the liquid phase at the λ-point (9), (10), or rather that the solutions of He^3 in He^4 will have a *first-order transition* instead of a λ-point. The *transition heat* is directly given by (9), (10) to be about 180±20 cal. per mole He^3 dissolved. This is quite similar to the transition of a superconductor in a magnetic field, which also is a first-order transition except for one point on the transition line, namely, for the magnetic field zero, where there is no transition heat, only a discontinuity

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[10] F. London, Rev. Mod. Phys. **17**, 310 (1945), Eq. (14).

of specific heat, quite as it is here the case in the (x_3, T) plane for $x_3=0$.

Further, there might be an effect on the *transition temperature.* Our data enable us to calculate the coefficient $(dT/dx_3)_{x_3=0}$, i.e., the *change of the transition temperature* with the concentration x_3 in the limit of very small concentration.

Since we have a phase transition of first order, we may expect an equilibrium in which two solutions of He I and He II co-exist side by side (similar to the "mixed" state of superconductors in a magnetic field). The equilibrium concentrations, x_3^+ and x_3^-, at a given temperature, will not necessarily be the same.

We assume constant pressure. Then, according to (9), (10), (12), (13), the chemical potentials μ^+ and μ^- above and below the λ-point may be written for small concentrations x_3^+ and x_3^-:

$$\begin{aligned}\mu_3^+ &= \mu_3^{0\prime}+\Delta\bar{H}_3^+-T\Delta\bar{S}_3^++RT\ln x_3^+\\ &= \mu_3^{0\prime}+\Delta\bar{H}_4^+-T\Delta\bar{S}_4^++13\\ &\qquad -2.5T+RT\ln x_3^+\\ &= \mu_3^{0\prime}+\mu_4^{0+}-\mu_4^{0\prime}+13-2.5T+RT\ln x_3^+;\end{aligned} \tag{18a}$$

$$\begin{aligned}\mu_3^- &= \mu_3^{0\prime}+\Delta\bar{H}_3^--T\Delta\bar{S}_3^-+RT\ln x_3^-\\ &= \mu_3^{0\prime}+\Delta\bar{H}_4^--T\Delta\bar{S}_4^--168\\ &\qquad +80T+RT\ln x_3^-\\ &= \mu_3^{0\prime}+\mu_4^{0-}-\mu_4^{0\prime}-168+80T+RT\ln x_3^-;\\ \mu_4^+ &= \mu_4^{0+}-RTx_3^+;\\ \mu_4^- &= \mu_4^{0-}-RTx_3^-;\end{aligned} \tag{18b}$$

where $\mu_4^{0\pm}$ are the chemical potentials of pure liquid He^4 above and below the λ-point, respectively, and $\mu_3^{0\prime}$ and $\mu_4^{0\prime}$ are the chemical potentials of pure He^3 and He^4 in the vapor phase, respectively. Since there is no discontinuity in the properties of the vapor phase, we do not need to distinguish between the values of $\mu_i^{0\prime}$ above and below the λ-point.

The conditions of equilibrium,

$$\mu_3^+(x_3^+, T)=\mu_3^-(x_3^-, T), \tag{19a}$$

$$\mu_4^+(x_3^+, T)=\mu_4^-(x_3^-, T) \tag{19b}$$

furnish for small concentrations the following two equations:

$$\mu_4^{0+}-\mu_4^{0-}=82.5(T-T_\lambda)-RT\ln(x_3^+/x_3^-), \tag{20a}$$

$$\mu_4^{0+}-\mu_4^{0-}=RT(x_3^+-x_3^-). \tag{20b}$$

We are only interested in the neighborhood of the λ-point and call $T-T_\lambda=\tau$. At the λ-point, μ_4^0 and $\partial\mu_4^0/\partial T=-S_4^0$ are both continuous (no transition heat). Hence, for small τ:

$$\begin{aligned}\mu_4^{0+}-\mu_4^{0-} &\approx \frac{1}{2}\left(\frac{\partial^2\mu_4^{0+}}{\partial T^2}-\frac{\partial^2\mu_4^{0-}}{\partial T^2}\right)\tau^2\\ &= \frac{C_p^--C_p^+}{2T_\lambda}\tau^2,\end{aligned} \tag{21}$$

where $C_p^--C_p^+\approx 7.6$ cal. deg^{-1} mole^{-1} is the well-known discontinuity of the specific heat at the λ-point ($T_\lambda=2.19$°K). Hence,

$$\mu_4^{0+}-\mu_4^{0-}\approx(7.6/2\cdot 2.19)\tau^2=1.73\tau^2.$$

Accordingly, the two Eqs. (20a) and (20b) can be written in the form

$$1.73\tau^2=82.5\tau-RT_\lambda\ln(x_3^+/x_3^-), \tag{22a}$$

$$1.73\tau^2=RT_\lambda(x_3^+-x_3^-). \tag{22b}$$

Eliminating x_3^+ gives the following equation for x_3^-:

$$82.5\tau-1.73\tau^2=RT_\lambda\ln(1+1.73\tau^2/x_3^-RT_\lambda),$$

or for small τ:

$$82.5\tau=1.73\tau^2/x_3^-.$$

This equation has two solutions for τ:

1. $\tau=0$ independent of x_3^-,
2. $\tau\approx x_3^-82.5/1.73=48x_3^-$,

to which belong, according to (22b), the following values of x_3^+

1. $x_3^+=x_3^-$,
2. $x_3^+=x_3^-+(1.73/RT_\lambda)(48x_3^-)^2$.

However, only the first solution, $x_3^+=x_3^-$, $\tau=0$ independent of $x_3^\pm$, can have physical significance; the other one, occurring at a higher temperature, would correspond to a return to He II, evidently the consequence of an illegitimate extrapolation of the free energy branch of He II to higher temperature.

5. CONCENTRATED SOLUTIONS

It is clear that we have to expect marked deviations from Henry's law below the λ-point as soon as the concentration becomes so large that the spheres of influence of the He^3 atoms (Eq. (17))

have a chance to overlap. This will happen when $x_3 \approx 1/100$. Obviously not more entropy than originally contained within the liquid He^4 can be taken away by dissolving He^3. In other words, the difference $\Delta\bar{H}_3 - \Delta\bar{H}_4$, which below the λ-point was found to be negative (Eq. (10)) for very small concentrations x_3, should change sign and should become positive for larger x_3.

Moreover, it is almost certain that pure He^3 cannot exist in a liquid phase at any temperature, at least not for normal pressure.[11] Hence, if He^3 is present in abundance one will have a gaseous phase, which is practically pure He^3 below 1°K, in equilibrium with a liquid phase which is predominantly He^4, and it appears most questionable whether solutions of much more than 1 percent He^3 could exist in the liquid phase.

According to our ideas the Brownian movement of a He^3 globule would essentially be determined by the local state of motion of the normal phase of He^4, which is the one which carries most of the heat content. Hence, in the presence of a heat current in He II, the He^3 atoms will have to follow the direction of the heat transfer which below the λ-point occurs through bodily transfer by motion of the atoms of the normal phase rather than by ordinary heat conduction. This can have a most disturbing effect on the establishment of the vapor-liquid equilibrium. If, for instance, liquid helium is evaporated at constant temperature by pumping off the vapor a heat current is produced towards the surface. In this case the He^3 atoms will be swept towards the surface where the concentration of He^3 will be enriched eventually to the degree that the deviations from Henry's law mentioned above become important and the He^3 can no longer remain dissolved in the liquid phase and will evaporate. Observations which support this view have recently been communicated to us by Lane and will be published by him in the Physical Review in the near future.

SUPPLEMENT TO SECTION 4

Only after concluding the above paper we became aware that the deviations from Henry's law below the λ-point predicted in section 5 for larger concentrations may have an effect of *first* order on the change of the λ-temperature with x_3 calculated in section 4. We may account for this effect by adding to μ_3^- a correction term linear in x_3 which expresses an increasing antipathy of He^3 against being dissolved in liquid He^4 below the λ-point as the concentration x_3 becomes greater.

Thus instead of (18a) we write now:

$$\mu_3^- = \mu_3^{0\prime} + \mu_4^{0-} \mu_4^{0\prime} - 168 + 80T + RT \ln x_3^- + a x_3^-. \qquad (18a')$$

The term ax_3^- in Eq. (18′) expresses a deviation from Henry's law. One can easily show that a is directly given by:

$$a = (\partial/\partial x_3) \ln(C_V/C_L).$$

If the solubility of He^3 is to decrease *monotonically* starting with the smallest concentrations, then a has to be positive.

Accordingly we now obtain the equation

$$1.73\tau^2 = 82.5\tau - RT \ln(x_3^+/x_3^-) + a x_3^-, \qquad (22a')$$

instead of (22a). Equation (22b) is obtained as before.

Elimination of x_3^+ from (22a′) and (22b) yields now the following equation for small τ and small x_3^-:

$$1.73\tau^2/x_3^- - 82.5\tau - a x_3^- = 0$$

with the solutions

$$\tau/x_3^- = 24 \pm (576 + a/1.73)^{\frac{1}{2}}.$$

The solution with the minus sign is the only one which has physical significance. It is the one which corresponds to the solution $\tau = 0$ in section 4. Accordingly we expect $\tau/x_3^- < 0$, i. e., a *decrease* of the λ-temperature with increasing x_3, if indeed our assumption $a > 0$ of a monotonically decreasing solubility is correct.

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[11] That He^3 cannot exist in the liquid state at any temperature and normal pressure appears most probable in view of the estimates of the zero-point energy of liquid He^4 in reference 6. Replacing this zero-point energy by one 4/3 times as large (see reference 7) one obtains a repulsion more than sufficient to compensate entirely the potential energy of the Van der Waals cohesion for any density assumed. The difference in statistics is in this estimate not yet accounted for. Its consideration, of course, would still contribute in the same direction.