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Lambda-Temperatures of Solutions of He^3 in He^4

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An expression for the effect of He^3 on the lambda-point of He^4 is developed from thermodynamic principles. Use is made of the idea that normal He^4 and superfluid He^4 are in equilibrium with each other and that the lambda-temperature is the temperature at which superfluid first appears. This expression contains the difference in enthalpy of normal fluid and superfluid. The lambda-points of mixtures containing large amounts of He^3 are discussed on the basis of various assumptions regarding this difference in enthalpy as a function of temperature.

An equation

$$dT_\lambda/dx_3 = -T_\lambda[x_3(1-x_3)(1+6x_3) + (1-x_3)7.6/6R], \quad (1)$$

representing the shift in the lambda-temperature T_λ with the mole fraction x_3 of He^3 has been developed by J. W. Stout.[1] While based upon a thermodynamic development which is certainly correct, Stout's expression is restricted in its application by his assumption that the discontinuity of the specific heat at the lambda-point, ΔC_{p4}, remains constant and equal to its value in pure He^4 which Keesom gives as -7.6 cal. per mole per degree. This assumption means that Stout's equation will be accurate only in very dilute solutions of He^3. It represents accurately data obtained by Abraham, Weinstock, and Osborne.[2]

Another equation,

$$dT_\lambda/dx_3 = -RT_\lambda(r+1)/rS_\lambda, \quad (2)$$

involving different quantities, was developed by O. K. Rice.[3] In this equation S_λ is the molal entropy of liquid helium at the lambda-point, R is the gas constant, and r is a constant in the empirical equation for pure He^4

$$S = S_\lambda(T/T_\lambda)^r, \quad (3)$$

which gives the entropy below the lambda-point as a function of temperature.[4] Equation (2) also has a thermodynamic basis, but with the additional assumption that He^4 below the lambda-point can be considered to be a mixture of two fluids, normal He^4 and superfluid, and that these two are in equilibrium with each other. Equation (2) was derived only for very dilute solutions of He^3 in He^4, and in this concentration range it agrees well with the results obtained from Eq. (1) and with the experimental data.

It seems desirable to extend these considerations to concentrated solutions of He^3, and this will be the principal object of the present paper. We summarize herewith the assumptions and observations which we shall use as the basis of this further development:

(A) Superfluid helium may be considered either as a component or as a "phase" as was suggested by Tisza.[5] We assume that it has the character of a component in that the chemical potential of superfluid helium depends on the amount present. If it is treated as a phase, as was suggested by F. London,[4] it must not be regarded as a phase in the usual phase-rule sense. The lambda-transition is considered to be a second-order transition taking place without latent heat whether or not He^3 is present. According to the picture given by Rice[3] the lambda-transition initiates the formation of superfluid in a sort of fibroid form, and the superfluid continues to form over a range of temperatures below the lambda-point.

(B) The superfluid component (or "phase") is exceptional in that the partial molal entropy of superfluid is finite even under the condition that the concentration of superfluid approaches zero. This partial molal entropy of superfluid depends only on the mixing of superfluid with normal fluid[3] and with the isotope He^3.

(C) The lamba-point is the temperature at which the chemical potential of superfluid helium at zero concentration becomes equal to the chemical potential of the normal fluid. It was shown by Rice that essentially this statement follows from the assumption that the two forms of He^4 are in equilibrium with each other. It is probable that superfluid begins to appear slightly above the lamba-point, but it is in a different form (globules[3]) and may be neglected. We also neglect any effect which may result from the globules persisting below the lambda-point.

(D) The partial molal enthalpy of superfluid helium is independent of temperature and arbitrarily set equal to zero.*

We use notation as follows: μ_i equals chemical potential of component i ($i=3$, $4n$, or $4s$ for He^3, He^4 normal fluid, and He^4 superfluid, respectively); x_i equals mole fraction of component i; $\bar{S}_i$ equals partial molal entropy of component i; $\bar{H}_i$ equals partial molal enthalpy of component i; and subscript λ is used to indicate values at the lambda-point of the particular solution considered.

If we consider a closed system at constant pressure

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[1] J. W. Stout, Phys. Rev. 76, 864 (1949).
[2] Abraham, Weinstock, and Osborne, Phys. Rev. 76, 864 (1949).
[3] O. K. Rice, Phys. Rev. 76, 1701 (1949).
[4] F. London, Rev. Mod. Phys. 17, 310 (1945).
[5] L. Tisza, Phys. Rev. 72, 838 (1947).
* See W. Band and L. Meyer, Phys. Rev. 74, 386 (1948).

containing a mole fraction x_3 of isotope He^3, a mole fraction x_{4n} of normal He^4, and a mole fraction x_{4s} of superfluid He^4, then, at the lambda-temperature where the mole fraction of superfluid is zero

$$d\mu_{4s,\lambda} = (\partial\mu_{4s}/\partial T_\lambda)dT_\lambda = -\bar{S}_{4s,\lambda}dT_\lambda,$$
$$d\mu_{4n,\lambda} = (\partial\mu_{4n}/\partial T_\lambda)dT_\lambda + (\partial\mu_{4n}/\partial x_3)_\lambda dx_3$$
$$= -\bar{S}_{4n,\lambda}dT_\lambda + (\partial\mu_{4n}/\partial x_3)_\lambda dx_3.$$

In a perfect solution

$$\mu_{4n} = f(T, P) + RT \ln x_{4n},$$
$$\partial\mu_{4n}/\partial x_3 = (RT_\lambda/x_{4n})(\partial x_{4n}/\partial x_3)_\lambda = -RT_\lambda/x_{4n}$$

since along the lambda-curve where $x_{4s}=0$, $dx_{4n}/dx_3 = -1$. Therefore,

$$d\mu_{4n,\lambda} = -\bar{S}_{4n,\lambda}dT_\lambda - (RT_\lambda/x_{4n})dx_3.$$

The chemical potential of the normal fluid is equal to the chemical potential of superfluid helium at the lambda-temperature (C). Consequently,

$$d\mu_{4s,\lambda} = d\mu_{4n,\lambda}$$

and

$$-\bar{S}_{4s,\lambda}dT_\lambda = -\bar{S}_{4n,\lambda}dT_\lambda - (RT_\lambda/x_{4n})dx_3. \qquad (4)$$

Further, since the chemical potential is the partial molal free energy, it follows that

$$\mu_{4s,\lambda} = \bar{H}_{4s,\lambda} - T_\lambda\bar{S}_{4s,\lambda}, \quad \mu_{4n,\lambda} = \bar{H}_{4n,\lambda} - T_\lambda\bar{S}_{4n,\lambda}.$$

Subtraction of the second expression from the first shows that

$$\bar{S}_{4s,\lambda} - \bar{S}_{4n,\lambda} = (\bar{H}_{4s,\lambda} - \bar{H}_{4n,\lambda})/T_\lambda = -\bar{H}_{4n,\lambda}/T_\lambda$$

since the partial molal enthalpy of superfluid is zero (D). With this substitution, Eq. (4) can be written

$$dT_\lambda/dx_3 = -(RT_\lambda^2)/\bar{H}_{4n,\lambda}(1-x_3). \qquad (5)$$

At the normal lambda-point Eq. (5) is identical with Eq. (2) above if one makes use of the value of $H_\lambda(=\bar{H}_{4n,\lambda})$ which follows from Eq. (3).

The equation is logical as was indicated by Rice[3] in that it indicates a lowering of the lambda-temperature with increase in the mole fraction of He^3. This would be expected because addition of He^3 lowers the escaping tendency (chemical potential) of the normal fluid and therefore shifts the equilibrium between superfluid He^4 and normal He^4.

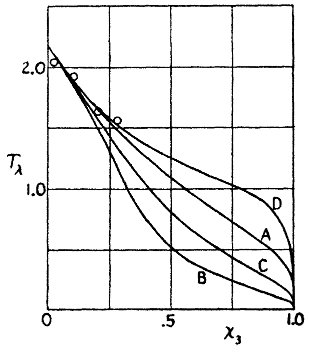

FIG. 1. Lambda-temperature *vs.* the mole fraction x_3. Experimental points circled.

If it is assumed that $\bar{H}_{4n,\lambda}$ is constant, and if the experimental value of 3.01 cal. per degree[3] for He^4 at the lambda-point is used (since at the lambda-point He^4 is practically all normal fluid) the solution of Eq. (5) is[6]

$$-1/T_\lambda = 1.52 \log(1-x_3) - 0.457.$$

The locus is given as curve A in Fig. 1 where the points in circles are the recent experimental values of Abraham, Weinstock, and Osborne.[2]

However, $\bar{H}_{4n,\lambda}$ will not be strictly constant, and some adjustment should be made for the variation in it which must occur as the lambda-point shifts to lower temperatures. Specific heats just above the temperature where the lambda-point anomaly sets in may be considered to refer to the normal fluid, and we may attempt to extrapolate to temperatures below the lambda-point in order to gain some idea as to how the molal enthalpy of normal fluid will behave in this region.

Keesom[7] has recorded data on the specific heat of He^4 determined experimentally by Keesom and Clusius, by Dana and Kamerlingh Onnes, and by Keesom and Miss Keesom. The 1932 data of Keesom and Miss Keesom might indicate a region in which the heat capacity is constant at about 2.2 cal. per mole per degree just prior to the anomalous behavior of the specific heat as the lambda-point is approached. Unfortunately, the data are given for only a short range of temperature above the lambda-anomaly in the specific heat so that it cannot be said with assurance that there is not some slope in the specific heat curve. If the value of the heat capacity of normal fluid has become essentially constant at 2.2 cal. per mole per degree, the enthalpy should go to zero in less than one and a half degrees, and the entropy even sooner. To avoid this one might assume that the heat capacity remained constant over a short range of temperature and then followed a T^3-law to the absolute zero.

On the other hand, it would appear from the data of Keesom and Clusius, and from that of Dana and Kamerlingh Onnes that the specific heat of He^4 just above the lambda-anomaly might be a decreasing function of the temperature, and that as a first approximation the heat capacity might go to zero linearly as the temperature goes to zero.

Both cases seemed likely enough to deserve consideration. Each has been treated with respect to its effect on Eq. (5) and the results are represented by curves B and C, respectively, in Fig. 1. For purposes of comparison, the curve obtained by Stout[1] is also shown as curve D in Fig. 1. His curve is about the same as curve A until the mole fraction of He^3 becomes equal to 0.2.

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[6] Just as we were finishing this paper we received a copy of a Letter to the Editor of the Physical Review by C. J. Gorter and J. de Boer, very kindly sent to us by Professor de Boer, in which a similar but not entirely equivalent expression for T_λ as a function of x_3 was given. See Phys. Rev. **77**, 569 (1950).

[7] W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., New York, 1942), see p. 215.

In treating the first possible behavior of the specific heat curve discussed above, it was assumed that the heat capacity remained constant at 2.2 cal. per mole per degree down to 1.46°K. The temperature of 1.46°K resulted from the imposed condition that the entropy of the normal fluid (known to be 1.62 cal. per mole per degree at the lambda-point) should go to zero as T goes to zero. Below this temperature it was assumed that the heat capacity followed a T^3-law,

$$C_{p4n}=0.707T^3.$$

The constant 0.707 resulted from the condition that the heat capacity is 2.2 cal. per mole per degree at 1.46°K. Under the condition of constant heat capacity, Eq. (5) takes the form (with $H_\lambda=\text{constant}=3.01$ cal. mole^{-1})

$$dT_\lambda/dx_3=-RT_\lambda^2[H_\lambda-(2.19-T_\lambda)2.2]^{-1}(1-x_3)^{-1} \qquad (6)$$

above 1.46°K, which can be integrated to give the part of curve B of Fig. 1 above 1.46°K. From the expression for the heat capacity used below 1.46°K,

$$\bar{H}_{4n}=0.177T^4+0.60.$$

The constant of integration is derived from the experimental fact that the total enthalpy of the normal fluid at the normal lambda-point is 3.01 cal. per mole. (With the heat capacity constant from the normal lambda-point to 1.46°K, the enthalpy at 1.46°K is found to be 1.404 cal. per mole.) Substitution of this expression for $\bar{H}_{4n,\lambda}$ in Eq. (5) gives

$$(0.177T_\lambda^2+0.60/T_\lambda^2)dT_\lambda=[-R/(1-x_3)]dx_3. \qquad (7)$$

The solution of this differential equation is

$$0.059T_\lambda^3-0.60/T_\lambda=R\ln(1-x_3)+0.242. \qquad (8)$$

The value of the constant of integration was found from the condition obtained from the integration of Eq. (6) that x_3 is 0.21 when T_λ is 1.46°K. Equation (8) gives curve B of Fig. 1 below 1.46°K.

In treating the second possible behavior of the specific heat curve we assume as noted that it is a straight-line function of zero intercept.

$$C_{p4n}=bT.$$

From the data of Keesom and Clusius and from those of Dana and Kamerlingh Onnes, the heat capacity is about 2.4 cal. per mole per degree when the temperature is 3°K from which b is found to be 0.8. This actually results in an entropy of the normal fluid which is slightly negative at 0°K, indicating that before 0°K is reached the value of C_{p4n} must drop below $0.8T$. However, the discrepancy is small, and no correction has been made for it.

From this expression for the heat capacity, the enthalpy becomes

$$\bar{H}_{4n}=0.4T^2+k.$$

And since the experimental value of H_λ is 3.01 cal. per degree at the normal lambda point (2.19°K), k is 1.09. Substitution of this expression for $\bar{H}_{4n,\lambda}$ in Eq. (5) gives

$$(0.4T_\lambda^2+1.09)dT_\lambda/T_\lambda^2=-Rdx_3/(1-x_3).$$

The solution of this differential equation is

$$0.4T_\lambda-1.09/T_\lambda=4.58\log(1-x_3)+0.378.$$

The constant is found to be 0.378 from the condition that T_λ is 2.19°K when x_3 is zero. This equation produced the values for curve C of Fig. 1.

The assumptions made have an interesting consequence. The constant in the expression for $\bar{H}_{4n}$ makes the enthalpy finite in each case at 0°K. It is, in fact, necessary that there should be an intercept in the enthalpy *vs.* temperature curve in order that the entropy of the normal fluid may not become negative. Since the enthalpy of superfluid is presumably constant and has been set equal to zero (D), this would indicate that superfluid helium has lower enthalpy at 0°K than normal fluid. It implies that if one could by-pass the lambda-transition and could cool He^4 to 0°K, the product would be supercooled normal fluid and not superfluid. In his recent article on the thermodynamics of liquid helium, Rice[3] has suggested that the superfluid condenses out in ordinary space as well as in momentum space. The superfluid is, nevertheless, in a highly dispersed state and, as we have noted in (A), has the character of a component rather than of a phase. Nevertheless, as Rice has pointed out, it would be necessary for the superfluid condensed in ordinary space to have an especially low energy in order to be stable. It need, therefore, occasion no surprise if the attempt to extrapolate the properties of normal fluid to 0°K indicates a residual enthalpy greater than that of the superfluid.

From the experimental results curve C would appear to be more probable than curve B. It seems likely that the true curve lies somewhere between curve A and curve B, and probably it is not far from curve C.

The equations and conclusions derived from this development depend, of course, upon the validity of the original assumptions. Further, in obtaining Eq. (5) the chemical potential of the normal fluid was found by using the thermodynamic expression for a perfect solution. In this regard, the most recent work of Weinstock, Osborne, and Abraham[8] seems to indicate that these solutions are not exactly ideal even above their lambda-temperatures in that their vapor pressures exceed those which would result from application of Raoult's law, so some modifications will be called for.

Note added in proof: J. G. Daunt and C. V. Heer [Bull. Am. Phys. Soc. **25** (No. 1), 38 (1950)] mention measurements of the lambda-point with solutions containing as much as 90 percent He^3. The two points they give fall close to curve C.

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