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

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In the two-fluid theory of liquid helium, assumptions concerning superfluid He thermodynamic properties can be tested by comparing, in theory and experiment, values both of dT_λ/dx_3 and of T_λ for isotopic mixtures of helium. Comparison of T_λ values is shown to be the more practical plan, since experimental excess chemical potentials in dilute solution are available for use in solving the fundamental differential equations. Error contributed by uncertainty in normal fluid heat capacity is shown to be reasonably unimportant for the dilute cases considered. The differential equations are solved and theoretical values of lambda temperatures are presented so that comparison can be made when experimental lambda points become available.

I. INTRODUCTION

IN the numerous recent thermodynamic treatments of helium isotope solutions based on the two-fluid theory, the undetermined nature of thermodynamic properties both of normal fluid below the lambda point and of superfluid has left a number of interpretations open to question. Variety in values employed for superfluid partial molal entropy has lead to variety in results of thermodynamic calculations. In particular, Gorter[1] has used a vanishing partial molal superfluid entropy, whereas Rice[2] has used a vanishing partial molal superfluid enthalpy. Since determination of the thermodynamic properties of superfluid is a matter of considerable importance, it is worth while to see what experimental evidence can be used to check the validity of the above assumptions. Rice[3] has suggested that extremely precise determination of the rate of change of the lambda temperature with respect to He^3 concentration would serve as a test. The fundamental two-fluid theory equation for the derivative in question is $dT_\lambda/dx_3=(\partial\mu_{4n}/\partial x_3)_\lambda/(\bar{S}_{4n}-\bar{S}_{4s})$. For the Gorter case the equation becomes

$$dT_\lambda/dx_3=(\partial\mu_{4n}/\partial x_3)_\lambda/\bar{S}_{4n}, \tag{1}$$

and for the Rice case

$$dT_\lambda/dx_3=T_\lambda(\partial\mu_{4n}/\partial x_3)/\bar{H}_{4n}. \tag{2}$$

The ratio of the slopes would be $\bar{H}_{4n}/T_\lambda\bar{S}_{4n}$ which, at 2.186°K is 0.849, since $\bar{H}_{4n}=2.95$ cal/mole and $\bar{S}_{4n}=1.59$ cal/deg mole at the normal lambda point. In spite of the proximity of the ratio to unity, a fact which makes differentiation on the basis of dT_λ/dx_3 a very difficult task, the scheme which would compare theoretical values with the experimental slope at $x_3=0$ has some important features to recommend it. These immediately become apparent when one attempts the alternative scheme of dealing with the integrated theoretical equations,[3-5] in other words, comparing lambda temperatures rather than slopes. In order to integrate the differential equations and to obtain the theoretical lambda point shift with changing He^3 mole fraction, one must know how thermodynamic properties of normal fluid He^4 change with temperature and with He^3 concentration. Evaluation of the slope at $x_3=0$, that is, at the normal lambda point, can be done without such specialized information; the theoretical slope result is, at this point, unambiguous with respect to the heat capacity of normal fluid and to the nonideality of the solution.

Recent experimental investigation of vapor-liquid equilibria,[6] which made possible determination[7] of excess chemical potentials of He^3 and of He^4 in liquid solution, has made a reconsideration of advantages advisable. Calculation of lambda temperatures for dilute solutions can be put on a firm basis if one works

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[1] C. J. Gorter, Physica **15**, 523 (1949).
[2] O. K. Rice, Phys. Rev. **76**, 1701 (1949).
[3] O. K. Rice, Phys. Rev. **79**, 1024 (1950).
[4] O. G. Engel and O. K. Rice, Phys. Rev. **78**, 55 (1950).
[5] J. C. Morrow, Phys. Rev. **84**, 502 (1951).
[6] H. S. Sommers, Jr., Phys. Rev. **88**, 113 (1952).
[7] J. C. Morrow, Phys. Rev. **89**, 1034 (1953).

TABLE I. Nonideality values at the lambda point.

x_3	$\ln\gamma_3$
0.0058	0.364
0.0198	0.461
0.0521	0.445
0.0949	0.491
0.130	0.523

in the composition range $0.02 \leq x_3 \leq 0.13$, for which the experimental excess potentials are known. The low He^3 composition range is important not only because excess potentials are available but also because the corresponding lambda temperatures are very close to the normal lambda point. Thus uncertainty in T_λ introduced through uncertainty in heat capacity of normal fluid below the normal lambda point is made very slight.

The desirability of dealing with the slope of the lambda line near $x_3 = 0$ appears small indeed when the advantages of direct comparison of lambda temperatures are noted. Comparisons of the latter type have, of course, been made previously both for ideal solutions[3] and for solutions with nonideality calculated from theory.[5] These previous efforts cannot be described as being completely free from uncertainty as far as the distinction between the Gorter and Rice assumptions is concerned, although the results seem to point in a definite direction. In previous work comparisons of theory and experiment were made with results for concentrated solutions. The Gorter and Rice difference is more exaggerated for concentrated than for dilute solutions, but the advantage of greater difference is offset somewhat by the uncertainties in heat capacity and in nonideality in the concentrated region. The purpose of this paper is to provide for the Gorter and Rice equations solutions describing mixtures dilute enough that heat capacity uncertainties are unimportant and that experimental nonideality terms can be used and yet sufficiently concentrated to provide differences greater than reasonable experimental error.

II. SOLUTION OF THE DIFFERENTIAL EQUATIONS

In the solution of Eqs. (1) and (2), it is convenient to express $(\partial\mu_{4n}/\partial x_3)$ as $-x_3(1-x_3)^{-1}(\partial\mu_3/\partial x_3)$. The chemical potential of isotope three is given by $\mu_3{}^0 + RT\ln x_3 + RT\ln\gamma_3$; $\mu_3{}^0$ is the standard potential, x_3 is the mole fraction of He^3, and γ_3 is the mole fraction activity coefficient. Then

$$(\partial\mu_{4n}/\partial x_3)_\lambda = -RT_\lambda(1-x_3)^{-1}[1 + x_3(\partial\ln\gamma_3/\partial x_3)]. \quad (3)$$

For each of the five mixtures examined by Sommers,[6] the activity coefficients are available.[7] Table I presents the values of $\ln\gamma_3$ at lambda points corresponding to indicated concentrations. Only the last three refer to a concentration range in which there is enough difference in the results of Eq. (1) and Eq. (2) to make distinction reasonable. Examination reveals that $\ln\gamma_3$ is linear in x_3 for these three values, and nearly linear for all five. Focusing attention on the practical range $0.02 \leq x_3 \leq 0.13$, one notes that, since $\ln\gamma_3$ is linear in x_3, $(\partial\ln\gamma_3/\partial x_3)_\lambda$ can be given the constant value 0.915. This result is important because it makes analytic solution possible for most of the differential equations.

Three types of normal fluid heat capacity temperature dependence[5] are employed so that the influence of uncertainty in C_p can be ascertained. In the dilute solutions considered, influence of heat of mixing on the results of Eq. (2) is so slight that the heat of mixing can be neglected. In subsequent sections, constants of integration are to be evaluated from the fact that $T_\lambda = 2.13$°K at $x_3 = 0.02$. All treatments regardless of assumptions about heat capacity, superfluid thermodynamic properties, and the like, produce this value because of the extreme dilution of the mixture described.

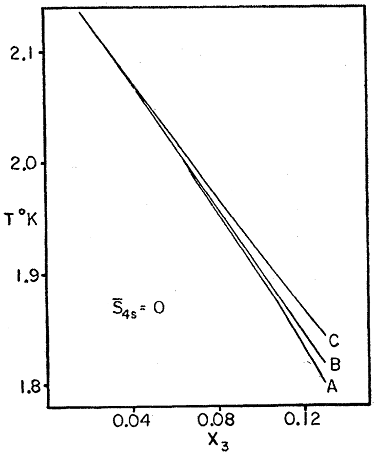

FIG. 1. Lambda temperature *vs* He^3 mole fraction for various heat capacity assumptions.

Cases for which $\bar{S}_{4s} = 0$

Substitution of 0.915 for $(\partial\ln\gamma_3/\partial x_3)_\lambda$ in Eq. (3) combined with Eq. (1) produces a differential equation for the Gorter cases,

$$dT_\lambda/dx_3 = (-RT_\lambda/\bar{S}_{4n})(1-x_3)^{-1}(1+0.915x_3). \quad (4)$$

For Case A, $C_p = 2.2$ cal/deg mole, the value at the normal lambda point and $\bar{S}_{4n} = 2.2\ln T - 0.135 - R \times \ln(1-x_3)$. The resulting differential equation has been integrated numerically over the range $0.02 \leq x_3 \leq 0.13$ in steps of 0.005 in x_3. In this range the lambda temperatures can be represented (correct in the thousandths place) by the empirical expression $T_\lambda = 2.1845 - 2.7x_3 - 2x_3{}^2$. Similarly in Case B, where $C_p = 0.725$ cal/deg mole and $\bar{S}_{4n} = 0.725T - R\ln(1-x_3)$, numerical integration produces $T_\lambda = 2.185 - 2.74x_3 - 0.78x_3{}^2$.

For Case C, $C_p = 0$. Then $\bar{S}_{4n} = 1.59 - R\ln(1-x_3)$ cal/deg mole and $dT_\lambda/dx_3 = -RT_\lambda(1-x_3)^{-1}(1+0.915x_3) \times [1.59 - R\ln(1-x_3)]^{-1}$. The variables are easily separated, and the solution is

$$\ln(T_\lambda/T_0) = [0.915 \exp(1.59/R) - 1.915] \times \ln(m/m_0) + 0.915 \exp(1.59/R) \sum_{i=1}^{\infty} (m^i - m_0^i)/(i)(i!),$$

where $m \equiv (1.59/R) - \ln(1-x_3)$ and subscript zero refers to known values. Rapid convergence of the sum simplifies calculation of T_λ from this equation.

Cases for which $\bar{H}_{4s} = 0$

Analytic solution of Eq. (2) can be given for all three heat capacities. In Case D, with the constant C_p of 2.2 cal/deg mole and $\bar{H}_{4n} = 2.2T - 1.868$, Eq. (2) has the solution

$$1.868(T_\lambda^{-1} - T_0^{-1}) + 2.2 \ln(T_\lambda/T_0) = 1.915R \ln(1-x_3)/(1-x_{3,0}) + 0.915R(x_3 - x_{3,0}).$$

For Case E, with the linear heat capacity and $\bar{H}_{4n} = 1.21 + 0.3625T^2$, the solution is

$$1.21(T_0^{-1} - T_\lambda^{-1}) + 0.3625(T_\lambda - T_0) = 1.915R \ln(1-x_3)/(1-x_{3,0}) + 0.915R(x_3 - x_{3,0}).$$

Finally, for Case F, with vanishing C_p and constant $\bar{H}_{4n} = 2.95$, the integrated form is

$$2.95(T_0^{-1} - T_\lambda^{-1}) = 1.915R \ln(1-x_3)/(1-x_{3,0}) + 0.915R(x_3 - x_{3,0}).$$

III. DISCUSSION OF RESULTS

In Fig. 1, the values of the lambda temperature from Cases A, B, and C are plotted against He^3 mole fraction in order to display the influence of heat capacity assumptions on the results. Even on such a large scale plot as Fig. 1, the two more realistic heat capacities are very close indeed. Even at the largest x_3, separation between the extreme $C_p = 0$ case and the mean of A and B is but 0.03°. Having noted the relatively insignificant effect in these dilute solutions even for rather radical variation in C_p, one finds the retention of interest in the rather unlikely vanishing C_p cases hard to justify. Results in concentrated solutions[5] lend further support to the suggestion that Cases C and F can be ignored.

It is clear that one should not seek to identify the temperature dependence of C_p by making comparisons in the dilute range discussed. One can, then, focus attention on the difference between Gorter and Rice cases by dealing with two curves: (1) the mean of A and B, and (2) the mean of D and E. The difference of a parent curve from its mean curve is in no case greater than 0.008°. These mean curves are presented in Fig. 2, which shows that, for $0.11 \leq x_3 \leq 0.13$, the separation of temperatures Δ is given by $0.050° \leq \Delta \leq 0.061°$.

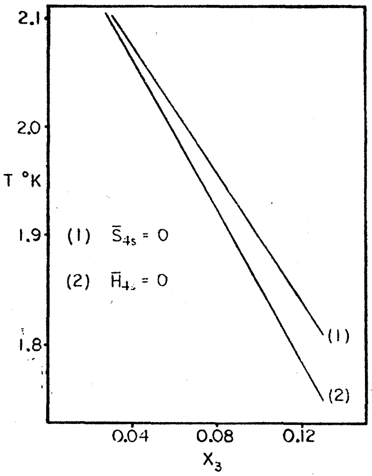

FIG. 2. Lambda temperature *vs* He^3 mole fraction for Gorter (1) and Rice (2) assumptions.

IV. CONCLUSION

With the use of experimentally determined excess potentials which remove uncertainty about mixture nonideality and with the demonstration that radical variation in assumed temperature dependence of normal fluid heat capacity has only slight effect on T_λ, one removes limitations on testing the basic Gorter and Rice assumptions by comparison of calculated and experimental lambda temperatures for dilute mixtures. Demands on precision of experimental data are much smaller for this type comparison than for comparison of slopes in the neighborhood of $x_3 = 0$. Differences in the Gorter and Rice cases near He^3 mole fraction of about 0.12 are of such magnitude that experimental investigation of the lambda temperatures should give significant information about validity of the two assumptions. Careful measurements in the dilute range thus can be of much value and significance in elucidating the nature of superfluid thermodynamic properties. Equally worth while would be vapor-liquid equilibria studies in concentrated mixtures. Such work, in making available the concentrated mixture nonideality, would permit extension of the above calculations and, indirectly, would provide information not only about the Gorter and Rice assumptions but about the normal fluid heat capacity as well.