ANALYSIS OF He^3 - He^4 MIXTURE SPECIFIC HEAT DATA

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Analysis of He^3 - He^4 Mixture

Specific Heat Data

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CHAPTER I

Introduction

Specific-heat data for Helium-3-Helium-4 mixtures in the vicinity of the tricritical point were taken by Alvesalo et al. in 1968 and 1969 and were subsequently presented and partially analyzed in two Physical Review papers.^{1,2} My work has been stimulated by a need to analyze this data set further, in an effort to understand better the nature of the phase transitions, as well as to look at the other thermodynamic properties of the system, especially those that have been investigated by some other method.

A. The He^3 - He^4 System

Beginning with a mixture of liquid helium containing both isotopes, the mole concentration of the He^3 in the mixture can be denoted by x , where $x = N_3/(N_3 + N_4)$, N_3 = number of moles of He^3 , and N_4 = number of moles of He^4 . Previous experiments have shown that the second-order phase transition of normal fluid into a

superfluid--the lambda, or λ , transition--takes place with the temperature of the transition decreasing with increasing concentration of He^3 . Also, at low enough temperatures, and for a wide range of molar concentration, the fluid which is otherwise homogeneous will separate into two distinct phases, one of which is He^4 rich, and is superfluid, the other of which is He^3 rich, and behaves like the normal fluid. The phase boundary, called the phase-separation curve, also will be referred to as the σ boundary. The lambda transition line meets this second-order phase-separation curve at what is called the tricritical point.³ In the analysis by Alvesalo et al., which didn't take gravity effects into account, this point was determined to exist at the temperature of $T_c = .871 \pm .002$ K and concentration $x_c = .6735 \pm .003$ at the saturated vapor pressure. The whole phase diagram is shown in Figure 1.

B. Thermodynamics

Let G , the free energy of a binary fluid at constant pressure, be defined to be equivalent to $U - TS + VP$, with the symbols having their usual thermodynamic meanings. Then, if G is known as a function of temperature and concentration, all other thermodynamic functions can be calculated. Using the independent variables of temperature T and concentration x , and dealing only with molar quantities, denoted by lower case letters, the following thermodynamic functions are defined;

Figure 1

Phase Diagram of He^3 - He^4 Mixtures
at Saturated Vapor Pressure

The diagram also shows the region of x and T space where the specific-heat data was taken.

molar free energy:	$g = u - sT + vP$
molar entropy:	$s = -(\partial g / \partial T)_x$
molar specific heat:	$c_x = T(\partial s / \partial T)_x$ $= -T(\partial^2 g / \partial T^2)_x$
difference of chemical potentials:	$\Delta = \mu_3 - \mu_4$ $= (\partial g / \partial x)_T$
not designated:	$\psi = g - (x - x_0)\Delta$

where μ_3 and μ_4 are the chemical potentials per mole of the He^3 and He^4 in the mixture, respectively. In addition, there are two other quantities of interest because they are experimentally obtainable: $(\partial \Delta / \partial T)_x = (\partial^2 g / \partial x \partial T)$ and $(\partial \Delta / \partial x)_T = (\partial^2 g / \partial x^2)_T$.

Unfortunately, g is never explicitly measurable. But, with a knowledge of the specific heat c_x , g can be calculated by integrating twice at constant x :

$$g(x, T) = \int_0^T \int_0^{T'} - \frac{c_x(x, T'')}{T''} dT'' dT' \\ = \int_0^T \int_0^{T'} \left[- \frac{c_x(x, T'')}{T''} \right] dT'' dT' + F_1(x) + TF_2(x),$$

where in the second expression, the integral is indefinite. The two functions totally dependent on x , $F_1(x)$ and $F_2(x)$, can be found partially by using plausibility arguments and the thermodynamic boundary conditions: in x and T space, the entropy, free energy, and difference of chemical potentials are continuous across all phase boundaries, and at a given temperature, Δ , as well as ψ , has the same value on both branches of the phase-separation curve. There are also two other relations which can be derived;

$$(\partial\Delta/\partial T)_{T,\sigma} = (d\Delta/dT)_{\sigma} - \delta(-c_{p,x}/T)/[(dx/dT)_{\sigma}] \quad (1)$$

$$(\partial\Delta/\partial x)_{T,\sigma} = \delta(-c_{p,x}/T)/[(dx/dT)_{\sigma}^2], \quad (2)$$

where δ refers to the difference in the values between the homogeneous region and the two-phase region, and σ denotes evaluation along the phase-separation curve.

Therefore, given a fairly complete knowledge of the specific heat as a function of concentration and temperature, a reasonably complete picture of several other thermodynamic functions can be found through analysis.

C. Data

The data analyzed in this report were that of Alvesalo et. al. taken for the specific heat of $\text{He}^3 - \text{He}^4$ mixtures at the saturated vapor pressure, in the temperature range from about .6 K to 1.5 K, at eight discrete concentration values ranging between .5297 and .7307. The data were corrected using thermodynamic considerations to obtain $c_{p,x}(x,T)$, the molar specific heat at constant pressure and concentration evaluated at the saturated vapor pressure, as a function of concentration and temperature. These data were transformed to $c_{p,x}/T$ in order to make a more convenient thermodynamic function. The actual transformed data will be presented in graphical form in Chapter III.

In this region of x and T , the λ line is approximately a straight line, whereas the phase-separation boundaries have a slight curvature away from the tricritical point. The phase-transition

values of concentration and temperature as observed from the data are tabulated in Table 1.

D. Scaling Theory

Because the region under investigation contains a line of critical points, the λ line, it seems natural to attempt an analysis which takes into account present theory involving critical phenomena. In a single-component system, the theory states that various thermodynamic functions of variables each tend to act in accordance with a power law in one of the independent variables as the critical point is approached, when the other independent variables are at their critical values. For example, the theory indicates that C_v , the specific heat at constant volume, and K_T , the isothermal compressibility, are both dominated by functional behavior proportional to $|(T - T_c)/T_c|^{-A}$ as T approaches T_c , where T_c is the critical temperature and A is called a critical exponent. The critical exponent A will differ for different thermodynamic functions and as to whether T_c is approached from above or below.

One direction of investigation in which the theory of critical phenomena has been going involves scaling theory, originally formulated mathematically by Widom and later supported with plausibility arguments by Kadanoff and others.^{4,5} The basic assumption of this theory is that the Gibbs free energy behaves like a "homogeneous" function near the critical point, where a homogeneous function $F(x,y)$ is defined as one that obeys the relation

$$F(\lambda^a x, \lambda^b y) = \lambda F(x, y), \quad (3)$$

Table 1

Values of the Concentration and Temperature Along
the Phase Boundaries for He^3 - He^4 Mixtures

Concentration	Temperature of λ Transition (K)	Temperature of Phase Separation (K)
.5297	1.2229	.8063
.5800	1.0995	.8331
.6100	1.0270	.8459
.6500	.9290	.8622
.6720	.874	----
.6800	----	.8605
.7008	----	.8292
.7307	----	.7871

where a and b are certain numbers and the equation is valid for all values of the parameter λ . This assumed property of the free energy, together with the existence of critical exponents for some thermodynamic functions, implies certain behavior in other thermodynamic functions. When a proposed theoretical functional form approximating a given thermodynamic function follows these scaling implications, the terms making up the function are called scaling terms, and the function itself is called a scaling function.

Scaling theory becomes more complicated when dealing with a region containing a tricritical point. In this case, the theory describing the thermodynamic behavior is called tricritical scaling theory. Because the present work merely compares results with established theory, any further presentation of the theory will be avoided. A great deal of work already has been done both theoretically and experimentally on the scaling hypothesis, and I refer the reader to the literature. Of particular interest is the thesis work of G.J. Goellner, which motivated the investigation of scaling forms in the present work.⁶

CHAPTER II

Procedure and Analysis

The $c_{p,x}/T$ data were first divided into three blocks corresponding to the three physical regions in temperature-concentration space--the normal fluid with 335 data points, the superfluid with 245 data points, and the two-phase region containing 283 data points. Then each region was analyzed separately, trying out different functional forms which would describe the behavior of the data, with the hope of discovering a form adequate in this regard. Following this analysis, the homogeneous region was analysed collectively, and next the two-phase region was reanalyzed taking into consideration the results of the single-phase regions. This procedure gave a reasonable mathematical functional form for $c_{p,x}/T$ in the regions of interest. Next, a free-energy functional form consistent with the $c_{p,x}/T$ functional form was proposed, and then the relevant parameters were determined so that the boundary conditions and the other thermodynamic considerations outlined previously would be satisfied as well as possible. Finally, a composite,

partially self-consistent fit was made, allowing most of the parameters involved to vary. A total collective analysis could not be performed due to limitations in computer time and difficulty with the convergence.

A. Method of Analysis

The problem of data reduction involving large numbers of data points and many parameters is always a difficult one. In the usual least-squares analysis, the data is to be represented by a function, often a polynomial form, so that the dependent variable y is approximated by the form:

$$y(x) = \sum_{j=1}^n b_j X_j(x), \quad (4)$$

where x represents the independent variables, the $X_j(x)$'s are simple functions of the independent variables, the b_j 's are the parameters to be determined, and n is the number of parameters. In the above case, the function being fit to is linear in the parameters, which means that the function can be written simply as the sum of products of the parameters and the lesser functions X_j containing no parameters. When the fitting function cannot be written so that the lesser functions X_j are independent of any of the parameters, then the function is nonlinear.

The least-squares approximation attempts to minimize Φ as a function of the parameters, where Φ is the sum of the squares of the differences between the actual values of the dependent variable y_i and the predicted values $y(x_i)$ derived from the functional form

evaluated at the values of the independent variable x_1 corresponding to the dependent y_1 variable. Thus

$$\Phi = \sum_{i=1}^N [y_1 - y(x_1)]^2, \quad (5)$$

where N is the number of data points. Minimizing Φ as a function of the parameters gives n equations, where

$$0 = \frac{\partial \Phi}{\partial b_k} = \frac{\partial}{\partial b_k} \sum_{i=1}^N [y_1 - y(x_1)]^2 \quad (6)$$

$$= \frac{\partial}{\partial b_k} \sum_{i=1}^N [y_1 - \sum_{j=1}^n b_j X_j(x_1)]^2, \quad (7)$$

which in the case of the linear fitting function becomes equal to

$$= 2 \left[- \sum_{i=1}^N y_1 X_k(x_1) + \sum_{j=1}^n b_j \sum_{i=1}^N X_j(x_1) X_k(x_1) \right] \quad (8)$$

$$\text{or} \quad 2 \sum_{i=1}^N y_1 X_k(x_1) = 2 \sum_{j=1}^n b_j \sum_{i=1}^N X_j(x_1) X_k(x_1). \quad (9)$$

This last equation can be put in terms of a matrix equation:

$$\vec{\beta} = \vec{b} \underline{\alpha}. \quad (10)$$

where the elements of the vectors and matrix are defined as:

$$\beta_k = 2 \sum_{i=1}^N y_1 X_k(x_1)$$

$$b_j = j^{\text{th}} \text{ parameter}$$

$$\alpha_{jk} = 2 \sum_{i=1}^N X_j(x_1) X_k(x_1).$$

Solving for the parameters:

$$\vec{b} = \vec{\beta} \underline{\alpha}^{-1}. \quad (11)$$

If all the X_j are linearly independent, the above solution is exact. However, when the functional form is nonlinear, complications arise, for the partial derivatives in Equation (7) do not all simplify.

Various simple methods of analysis have been devised for the nonlinear case, but the methods of interest in this work are the gradient method and the parabolic extrapolation method. In the gradient method, initial guesses are made for the parameters at the beginning of the i^{th} iteration, with the parameters being designated as $\vec{b}^i$. Then the gradient of Φ , where

$$\vec{\nabla} \Phi(\vec{b}^i) = \sum_{j=1}^n \frac{\partial \Phi(\vec{b}^i)}{\partial b_j} \hat{b}_j \quad (12)$$

is computed. Here the hat represents a unit vector, and the derivative in Equation (12) is being evaluated using the $\vec{b}^i$ parameter set. With a step size Δa being chosen, new parameter sets $\vec{b}_m^{i+1}$ are created using the formula

$$\vec{b}_m^{i+1} = \vec{b}^i - m(\Delta a) \vec{\nabla} \Phi, \quad (13)$$

where m is an integer. A new $\Phi(\vec{b}_m^{i+1})$ is computed for increasing m until the value of Φ begins to increase over the previously computed value. The $\vec{b}_m^{i+1}$ set that gave the smallest value of Φ then is used for the initial guesses in the next iteration. Thus, the parameters change in a way that follows the steepest descent of Φ in parameter space. The method initially approaches the minimum fairly rapidly, but eventual convergence to the minimum is rather slow.

The second method involves making a parabolic extrapolation of Φ in parameter space. If initial guesses b_j^1 are made for the parameters, then the minimum of Φ , Φ_0 , can be approximated by a Taylor's Series about the initial parameters, keeping only the first three terms:

$$\begin{aligned}\Phi_0 \cong \Phi(\vec{b}^1) + \sum_{j=1}^n \left[\frac{\partial \Phi(\vec{b}^1)}{\partial b_j} \right] \delta b_j^1 \\ + \frac{1}{2} \sum_{j=1}^n \sum_{k=1}^n \left[\frac{\partial^2 \Phi(\vec{b}^1)}{\partial b_j \partial b_k} \right] \delta b_j^1 \delta b_k^1.\end{aligned}\quad (14)$$

where the δb 's are the differences between the parameters that would produce minimum Φ and the initial parameters. Because Φ_0 is assumed to be a minimum, it must be a minimum with respect to each of the increments δb_k in Equation (14), so that

$$0 = \frac{\partial \Phi_0}{\partial (\delta b_k^1)} \cong \frac{\partial \Phi(\vec{b}^1)}{\partial b_k} + \sum_{j=1}^n \left[\frac{\partial^2 \Phi(\vec{b}^1)}{\partial b_j \partial b_k} \right] \delta b_j^1, \quad (15)$$

which is a set of n simultaneous linear equations in n unknowns.

Letting g_k^1 be the ^{negative} gradient component, $g_k^1 = -\partial \Phi(\vec{b}^1)/\partial b_k$, and

$\alpha_{jk}^1 = \partial^2 \Phi(\vec{b}^1)/\partial b_j \partial b_k$, then

$$\vec{g}^1 = \underline{\alpha} \vec{\delta b}^1 \quad (16)$$

and
$$\vec{\delta b}^1 = (\underline{\alpha}^1)^{-1} \vec{g}^1. \quad (17)$$

When these increments $\vec{\delta b}^1$ are calculated, they are added to the initial parameter guesses $\vec{b}^1$, obtaining a new set of parameters which should yield a lower value of Φ . In practice, this method

converges rapidly to a minimum value of Φ when the initial parameters are chosen so that they lie close to their optimum values, for then the parabolic approximation is fairly good. However, far from the region of minimum Φ in parameter space, convergence can become extremely slow, for the approximation fails.

Some statistical results are available when using this latter method. The standard error of the fit, which represents the predicted uncertainty in each of the data points, can be defined by the following equation:

$$\text{Standard Error} = s = \sqrt{\Phi / (N - n - 1)}. \quad (18)$$

Once the minimum of Φ has been found, the uncertainties in the parameters can be obtained also. The standard error associated with the parameter j , which is called σ_j , is defined by:

$$\sigma_j = s \sqrt{(cc^{-1})_{jj}}. \quad (19)$$

These statistical results are taken from Bevington's book on data reduction.⁷

The actual method of analysis used for this problem utilized the Marquardt Algorithm (sometimes called the Levenberg-Marquardt Algorithm), which contains a convergence sensitivity so that an interpolation between the gradient method and the parabolic extrapolation method is made.⁸ That is, in the initial stages of finding the least-squares best-fit parameters, the method approximates the gradient method, whereas near the minimum of Φ in parameter space, the method approximates the method of parabolic extrapolation.

This process is accomplished by initially defining a scaled matrix $\underline{A}$ and a scaled vector $\vec{g}^*$ such that

$$A_{ij} = \alpha_{ij} / \sqrt{\alpha_{ii}} \sqrt{\alpha_{jj}} \quad (20)$$

$$g_j^* = g_j / \sqrt{\alpha_{jj}}, \quad (21)$$

where α_{ij} and g_j are defined as in the parabolic method. If this transformation were the only change, then the Taylor's Series approximation at the i^{th} iteration would yield the equation

$$\underline{A}^i \vec{\delta b}^i = \vec{g}^i, \quad (22)$$

where $\vec{\delta b}^i$ are the scaled increments and are related to the real increments $\vec{\delta b}$ by $\delta b_j^* = \delta b_j / \sqrt{\alpha_{jj}}$.

However, the method of the Marquardt Algorithm at the i^{th} iteration is to introduce a parameter λ^i and solve the equation

$$[\underline{A}^i + \lambda^i \underline{I}] \vec{\delta b}^i = \vec{g}^i \quad (23)$$

for $\vec{\delta b}^i$, and thus get the new parameters:

$$\vec{b}^{i+1} = \vec{b}^i + \vec{\delta b}^i. \quad (24)$$

It can be shown⁹ that if $\vec{\Phi}$ is not already at a minimum at the i^{th} iteration, then there exists a sufficiently large λ^i such that $\vec{\Phi}^i(\lambda^i) < \vec{\Phi}^{i-1}$. At large values of λ , the diagonal terms of the matrix dominate, so that the increments $\vec{\delta b}$ become proportional to the ^{negative} gradient $\vec{g}$. At small values of λ , the problem degenerates to $\underline{A} \vec{\delta b} = \vec{g}^*$, which is equivalent to the parabolic extrapolation method. By monitoring the convergence, λ can be

increased or decreased as necessary to reduce $\bar{\Phi}$, with the intent of eventually getting λ as low as possible.

A computer program that incorporates this method (and the program that was used) is NONLIN, a Share program by D.W. Marquadt. The strategy used by NONLIN for changing λ is to first compute $\bar{\Phi}$ using initial parameter guesses, set $\lambda = .01$, and solve the matrix Equation (23) for the increments, getting a new set of parameters $\vec{b}^1$. If these parameters yield a lower value of $\bar{\Phi}$, they are kept for use in the next iteration, λ is divided by ten, and the first iteration is complete. If not, then λ is multiplied by ten and new parameters $\vec{b}^1$ are found. This multiplication of λ is continued until the new $\bar{\Phi}$ is lower than the initial $\bar{\Phi}$. Then the values of λ and the parameters that gave the lower $\bar{\Phi}$ are retained for the next iteration, and the present iteration is finally complete. This whole process is continued for each iteration using the accepted parameters from the last iteration as starting parameters for the next iteration until some form of convergence criterion is met.

B. Parametric Thermodynamic Functions

Initially functional forms describing the $c_{p,x}/T$ data had to be constructed. In working only in x and T space, and with all of the data being in the vicinity of the tricritical point, the scaled variables $\chi = x - x_c$ and $\tau = T - T_c$ were used, where x_c and T_c , the concentration and the temperature at the tricritical point, had the experimental values of .6735 and .871 K respectively.

This construction was easy for the two-phase region, where thermodynamic theory states that $c_{P,X}/T = F(\tau) + \chi G(\tau)$, where F and G are functions of τ alone. Polynomials were used for F and G because more complicated functions were not suggested by experiment.

The single-phase region presented a problem, however, for a singularity exists along the λ line. The data show that far from the tricritical point, the slopes of $c_{P,X}/T$ from both sides appear to go to infinity at the λ line, but as the tricritical point is approached, the slopes become finite. Thus, near the λ line the data could not be described by a simple polynomial in χ and τ .

Various exotic forms were tried. Usually a polynomial background was used in conjunction with some form of nonanalytic function. Examples of the nonanalytic functions tried were $\chi^n |\tau - q\chi|^{-\alpha}$, $\tau^n |\xi|^{-\alpha}$, $\tau \theta^{-\alpha}$, and $|\xi/\sqrt{\xi^2 + \tau^2}|^{-\alpha}$, where $\xi = \chi - q\tau$, q equals the slope of the lambda line, $(d\chi/d\tau)_\lambda$, $\theta = \arctan(\xi/\tau)$, and n is a low-valued integer. Sometimes polynomials in $\sin \theta$ and $\cos \theta$ were added to these terms. Though the fits employing θ were satisfactory, further exact analysis was impossible because the functional forms were not twice integrable in closed forms, so that this method of analysis was dropped. Of the other analyzable forms, the most satisfactory was the approximation:

$$-c_{P,X}/T = \sum_{n=0}^{n+m=3} [(n+2)!/n!] g_{n+2,n} \tau^n \chi^m + (\gamma_1 \tau + \gamma_2 \tau^2) |\chi - q\tau|^{-\alpha}, \quad (25)$$

where the g 's, γ 's, and α are parameters to be determined, and differ for the normal and superfluid sides. Here the main consid-

eration in the fit was goodness of fit (all data points well approximated), low sum of the squares of the differences (χ^2), and a minimum number of parameters, for analysis facility. Under these conditions, the form of Equation (25) was the most successful in fitting the data.

Although good agreement was obtained when different parameters were used for the separate regions, it was hoped that a scaling form could be found describing both regions simultaneously. This form would have a common background plus scaling terms. In attempted fits of this kind very poor agreement was found. As a compromise, a partially common background was attempted with extra, nonscaling terms, so that the final fitting function became:

$$\begin{aligned}
 -c_{P,X}^{\pm} / T = & 2g_{20} + 20g_{50}\tau^3 + 12g_{41}\tau^2\chi + 6g_{32}\tau\chi^2 + 2g_{23}\chi^3 \\
 & + 6g_{30}^{\pm}\tau + 2g_{21}^{\pm}\chi + 12g_{40}^{\pm}\tau^2 + 6g_{31}^{\pm}\tau\chi + 2g_{22}^{\pm}\chi^2 \\
 & + (Y_1^{\pm}\tau + Y_2^{\pm}\tau^2) |\chi - q\tau|^{-\alpha^{\pm}},
 \end{aligned} \tag{26}$$

where the "-" refers to the superfluid region and the "+" refers to the normal region. However, continuity across the λ line of the first order terms in the $c_{P,X}/T$ form seems to be required by the data, so that with this assumption g_{30}^+ can be written as a linear combination of g_{30}^- , g_{21}^- , and g_{21}^+ in Equation (26). This form in Equation (26) then corresponds to a twenty-parameter fit of 580 data points.

The form for the specific heat in the two-phase region was approximated by the form:

$$\begin{aligned}
 -c_{p,x}/T = & 2f_{20} + 6f_{30}\tau + 12f_{40}\tau^2 + 20f_{50}\tau^3 \\
 & + \chi(2f_{21} + 6f_{31}\tau + 12f_{41}\tau^2) .
 \end{aligned}
 \quad (27)$$

Because of the observed continuity of the specific heat at the tricritical point, the parameter f_{20} in Equation (27) must equal the parameter g_{20} in Equation (26).

In order to find the molar free energy, $-c_{p,x}/T$ must be integrated twice in the variable τ . In a single-phase region where the specific heat is represented by the function in Equation (25), these integrations yield, when keeping polynomials to the fifth degree:

$$g = \sum_{n=0}^{n+m=5} g_{nm} \tau^n \chi^m + \iint [-c_{p,x}/T]_s d\tau \cdot d\tau + F_{1s}(\chi) + F_{2s}(\chi), \quad (28)$$

where the subscript s in the specific-heat term refers to the non-analytic term in Equation (25), and the F 's are functions singular in χ , assuming that the polynomial terms in the summation already describe the nondivergent behavior. However, the existence of these F functions would imply that singularities exist in the free energy along lines of constant χ in χ, τ space, a rather unphysical situation. Thus, these singular functions were rejected. Because the free energy and the entropy must be continuous across the λ line, the parameters g_{14} , g_{05} , g_{11} , g_{02} , g_{10} , g_{01} , and g_{00} do not have different values in the normal and superfluid phases. Therefore, g , the molar free energy was approximated by the functional form:

$$\begin{aligned}
g^{\pm} = & g_{00} + g_{10}T + g_{01}\chi + g_{20}T^2 + g_{11}T\chi + g_{02}\chi^2 + g_{50}T^5 \\
& + g_{41}T^4\chi + g_{32}T^3\chi^2 + g_{23}T^2\chi^3 + g_{14}T\chi^4 + g_{05}\chi^5 \\
& + g_{30}T^3 + g_{21}T^2\chi + g_{12}T\chi^2 + g_{03}\chi^3 + g_{40}T^4 \\
& + g_{31}T^3\chi + g_{22}T^2\chi^2 + g_{13}T\chi^3 + g_{04}\chi^4 + g_s^{\pm},
\end{aligned} \quad (29)$$

where

$$\begin{aligned}
g_s^{\pm} = & \frac{(\delta_1^{\pm}T + \delta_2^{\pm}T^2)|\xi|}{q^2(1-\alpha^{\pm})(2-\alpha^{\pm})} \pm \frac{(2\delta_1^{\pm} + 4\delta_2^{\pm}T)|\xi|}{q^3(1-\alpha^{\pm})(2-\alpha^{\pm})(3-\alpha^{\pm})} \\
& + \frac{6\delta_2^{\pm}|\xi|}{q^4(1-\alpha^{\pm})(2-\alpha^{\pm})(3-\alpha^{\pm})(4-\alpha^{\pm})}
\end{aligned} \quad (30)$$

In the two-liquid-phase region the form for the free energy is much simpler:

$$g = \sum_{n=0}^5 f_{n0}T^n + \chi \sum_{n=0}^4 f_{n1}T^n. \quad (31)$$

Once the form of g has been established, the other thermodynamic functions can be calculated by differentiation: $\Delta = (\partial g / \partial x)_T$, $(\partial \Delta / \partial T)_x = (\partial^2 g / \partial T \partial x)$, and $(\partial \Delta / \partial x)_T = (\partial^2 g / \partial x^2)$. However, all of the parameters mentioned in g are not linearly independent, for once again, continuity of entropy and the free energy across the λ line make two each of the third and fourth-order parameters linearly dependent on the other parameters. In the actual fits, g_{12}^+ , g_{03}^+ , g_{13}^+ , and g_{04}^+ were replaced by linear combinations of the other parameters. Nevertheless, this simplification left thirty-one independent, unknown parameters in the homogeneous region.

C. Options for Fitting the Non-Specific-Heat Parameters

Once the fits for the specific-heat data have been established, there are still twelve more parameters that are unknown: $\epsilon_{00} = f_{00}$, $\epsilon_{10} = f_{10}$, $\epsilon_{01} = f_{01}$, f_{11} , ϵ_{11} , ϵ_{02} , ϵ_{14} , ϵ_{05} , ϵ_{13} , ϵ_{04} , ϵ_{12} , and ϵ_{03} . The equalities that occur between the f and g parameters are the result of equalities of entropy Δ and free energy at the tricritical point. The conditions left to be satisfied are that Δ , g , ψ , and s are continuous across the σ boundary (only any two conditions of which are independent of the others), and that at a given temperature, Δ , as well as ψ , has the same value on both normal and superfluid branches of the σ boundary. However, a third set of conditions exists based on the two thermodynamic relations cited before in Equations (1) and (2):

$$\left(\frac{\partial \Delta}{\partial T}\right)_{x,\sigma} = \left(\frac{\partial \Delta}{\partial T}\right)_{\sigma} + \frac{\frac{C_{p,x}}{T}(1 \text{ phase}) - \frac{C_{p,x}}{T}(2 \text{ phase})}{(dx/dT)_{\sigma}} \quad (32)$$

$$\left(\frac{\partial \Delta}{\partial x}\right)_{T,\sigma} = - \frac{\frac{C_{p,x}}{T}(1 \text{ phase}) - \frac{C_{p,x}}{T}(2 \text{ phase})}{[(dx/dT)_{\sigma}]^2} \quad (33)$$

The only unknown in these equations, the slope of the g boundaries, can be found by fitting the data points from Table 1 to a polynomial form and then obtaining the slope by differentiation.

Each of the three sets of conditions described above can be used in a fitting procedure to obtain theoretically seven of the twelve unknown parameters; the combination $\epsilon_{11} = f_{11}$ also can be found. However, four of the parameters can never be found using

only specific heat data: g_{00} , g_{10} , g_{01} , and f_{11} . It also should be noted that the value of $(\partial\Delta/\partial T)_{x,\sigma}$ that is worked with is not the true value, but is missing the term f_{11} , where f_{11} equals the value of $(d\Delta/dT)_{\sigma}$ at the tricritical point. Further reference to $(\partial\Delta/\partial T)_{x,\sigma}$ will imply having the f_{11} term subtracted off. This situation will not affect the evaluations of the other parameters.

The actual method used in the present work was to fit the functional forms of $(\partial\Delta/\partial T)_{x,\sigma}$ and $(\partial\Delta/\partial x)_{T,\sigma}$ to points along the boundary determined by the thermodynamic relations in Equations (32) and (33). By fitting the specific-heat data, the resulting functional form could be used to generate values of $c_{p,x}/T$ along the phase-separation boundary, which in turn could be used to generate data for $(\partial\Delta/\partial T)_{x,\sigma}$ and $(\partial\Delta/\partial x)_{T,\sigma}$. Because the functional forms of the first derivatives of Δ contain parameters included in the specific-heat functional form, a simultaneous fit of $c_{p,x}/T$, $(\partial\Delta/\partial T)_{x,\sigma}$ and $(\partial\Delta/\partial x)_{T,\sigma}$ parameters could be made. It was hoped that when this was done, the results would be self-consistent--the specific-heat parameters would yield values of the first derivatives of Δ consistent with the other parameters found.

It should be noted that there is a degree of inconsistency in treating both the two-phase region and the phase-separation boundaries separately. Indeed, once the form of the free energy is assumed in the homogeneous region, the phase boundary automatically results. However, the shape of the phase-separation boundary is known to a certain extent, whereas the real form of the free energy is not known. In addition, the complexity of evaluation involved

with treating the phase boundary as dependent upon the homogeneous region looked prohibitive. The best course of action appeared to be to assume a form for the free energy, hope it was reasonably accurate, and try to make that form consistent with the known ϕ phase boundaries.

CHAPTER III

Parametric Evaluation Results

It is unfortunate that no theory exists which would predict the functional form of the nonanalytic terms describing the specific-heat data. Therefore, the only recourse was to try different nonanalytic terms, which appeared to have the requisite behavior on a trial and error basis. Criteria for acceptance of these nonanalytic terms plus polynomial backgrounds as a good fit to the data have been outlined previously. Coupled with these criteria was the need to have the nonanalytic term simple enough so that it could be integrated twice in closed form for ease of analysis.

The form which gave the best results in the homogeneous region using these criteria was that given in Equation (26), for which a listing of the parameters, as well as their standard errors, is given in Table 2.* This fit of 580 data points yielded a $\bar{\chi}$

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* Note that although the parameters have dimensions, no formal units have been attached to the parameters in any of the listings. The units are implied, so that a parameter of the form g_{nm} or f_{nm} has units of Joules/mole- $(K)^n$, γ_n has units of Joules/mole- $(K)^{n+2}$, and α is dimensionless.

Table 2

List of Parameters Giving the Best Fit for $-c_{p,x}/T$
Using Equation (26) in the Single-Phase Region

(Standard errors are given in parentheses,
units are implied.)

Parameter	Superfluid Value ("-" side)	Common Value	Normal Fluid Value ("+" side)
ϵ_{20}		-4.38804 (.00236)	
ϵ_{30}	-.166965 (dependent)		3.01307 (.03956)
ϵ_{21}	-4.57619 (.13778)		18.7698 (.1425)
ϵ_{40}	1.02520 (.13369)		-4.33689 (.05530)
ϵ_{31}	11.2641 (.6810)		-24.1384 (.3167)
ϵ_{22}	14.5946 (2.0647)		-60.5905 (2.0231)
ϵ_{50}		.826031 (.032561)	
ϵ_{41}		10.2215 (.2702)	
ϵ_{32}		40.9270 (1.9396)	
ϵ_{23}		36.0389 (8.9812)	
λ_1	17.2233 (1.5251)		7.07886 (.43013)
λ_2	-7.19610 (3.17218)		23.7962 (1.3480)
α	-.501331 (.055263)		-.253327 (.020558)

equal to .73366, which gives a standard error of .036195, utilizing twenty independent parameters. Slightly better fits were attained by adding extra polynomial terms to the existing polynomial, but this addition violated one of the fitting criteria, so that these fits were rejected for use in further analysis of the data.

Other fits were attempted using different nonanalytic terms or different forms of the background polynomial common to both sides. Table 3 contains a listing of some of these attempted fits. In the Table are a description of the nonanalytic term, the total number of independent parameters, and the resultant values of $\bar{\Phi}$ and the standard error. In addition, the number of terms involving parameters common to both sides is indicated. Only those fits in which actual convergence of some kind was attained are included in the Table. Other functional forms which were tried and for which convergence was not attained are not included.

As stated previously, the two-phase region was much easier to work with, for the functional form was a simple polynomial in the scaled concentration and temperature variables. The actual functional form used was that as given in Equation (27). There are two results that are of interest: the first is an unconstrained fit of the functional form to the parameters; the second takes into account the observed continuity of the specific heat^{at} the tricritical point, setting the constant term in the two-phase region, f_{20} , equal to the value of the constant term in the single-phase region, g_{20} . In this seven-parameter fit of 283 data points the former method results in a value of $\bar{\Phi}$ equal to .19859, with a

Table 3

Functional Forms Used in Trying to Fit
the Single-Phase Specific-Heat Data

Number of Independent Parameters	Number of Common Parameters	Nonanalytic Terms or Nonpolynomial Terms	$\bar{\chi}$	Standard Error
21	9	$\tau \theta ^{-\alpha}, \tau\theta, \tau\theta^2, \tau\theta^3$	2.10145	.061313
21	9	$\tau \theta ^{-\alpha}, \tau\sin\theta, \tau\cos\theta, \tau\sin^2\theta$	2.1791	.06244
18	6	$\tau^2 \theta ^{-\alpha}$	1.0716	.04367
18	6	$\tau^2 \xi ^{-\alpha}$	1.0185	.04257
20	6	$(\gamma_1\tau + \gamma_2\tau^3) \xi ^{-\alpha}$	.73366	.036195
22	2	$\tau^2 \xi ^{-\alpha}$	.7653	.03703
23	9	$(\gamma_1\tau + \gamma_2\tau^2) \xi ^{-\alpha}$	.6226	.03415
26	12	$(\gamma_1\tau + \gamma_2\tau^2) \xi ^{-\alpha}$	.4974	.03069

where $\xi = \chi - q\tau$
 $\theta = \arctan(\xi/\tau)$

standard error of .026824, while the latter method, in which f_{20} is assigned the value of g_{20} resulting from the best single-phase fit, yields a $\bar{\Phi}$ of .20265 and a standard error of .027048, representing an increase of $\bar{\Phi}$ of a little over 2%. This minor change appears acceptable. A listing of both sets of parameters is presented in Table 4.

Ideally, the most accurate method of analysis would entail simultaneously fitting the data of the homogeneous region and the data of the two-phase region. In this way, the common constant term would be more validly determined. However, this approach would constitute a twenty-six parameter fit involving 863 data points, which is a bit cumbersome for the computer to handle. In view of the restrictions in computer time and in the convergence ability of the computer program being used, it was decided that the most fruitful course of action in subsequent fits would be to analyze the two-phase region separately, setting the constant term f_{20} equal to the term g_{20} that would result from the homogeneous region fit. It was believed that the effects of this action would be minor.

Therefore, if the best single-phase fit is taken in conjunction with the two-phase region fit, we have a functional form which accurately describes the $c_{p,x}/T$ data and which is the best functional form of those forms investigated, given the restrictions outlined previously. This set of parameters involved in these particular fits will be referred to as Parameter Set I. Graphs of the functions resulting from Parameter Set I and Equations (26) and

Table 4

List of Parameters Giving the Best Fit for $-c_{p,x}/T$
Using Equation (27) in the Two-Phase Region

(Standard errors are given in
parentheses, units are implied.)

Parameter	Unconstrained Fit Values	Constrained Fit Values
f_{20}	-4.38163 (.002699)	-4.38804 (dependent)
f_{30}	3.51432 (.02968)	3.45255 (.01444)
f_{40}	3.34923 (.12849)	3.12179 (.08643)
f_{50}	2.12898 (.18575)	1.84289 (.14262)
f_{21}	-3.66398 (.06283)	-3.67269 (.06325)
f_{31}	1.32074 (.32262)	1.27189 (.32466)
f_{41}	.280840 (.508047)	.202118 (.511208)

(27) are presented in Figure 2, parts (a) through (h). The actual $c_{p,x}/T$ data points also are graphed for comparison.

There is a drawback to this set of functions, however. Though this set describes the data accurately within experimental error, it does not predict precisely the observed behavior near the tricritical point, which could ultimately lead to inaccuracies or inconsistencies if the functional form is used as an exact description of the region near the tricritical point. Possible explanations for the difficulties in this region will be discussed in a later chapter.

In order to determine the other free-energy parameters, it was necessary to know the shape of the two branches of the phase-separation curve. This was done by making a least-squares fit of the known points on the curve to a polynomial of the form:

$$\chi = P_1 T + P_2 T^2 + P_3 T^3 \quad (34)$$

The parameters resulting from this fit are given in Table 5. Also included in this table is the slope of the λ line, $q = (dx/dT)_\lambda$.

Because functional forms predicting $c_{p,x}/T$ from given concentration and temperature values were available from the fitting process described above, and the shapes of the phase-separation boundaries were known, use was made of the thermodynamic identities given in Equations (32) and (33) to generate fifty artificial data points for $(\partial\Delta/\partial T)_x$ and $(\partial\Delta/\partial x)_T$ along both branches of the σ boundary as functions of the independent variable T . Then the functional forms of $(\partial\Delta/\partial T)_x$ and $(\partial\Delta/\partial x)_T$ were fit to these fifty

Figure 2, parts (a) through (h)

The Quantity $c_{p,x}/T$ as Predicted from Equations (26) and (27) and Parameter Set I, and a Plot of the Data

Each of the parts (a) through (h) represents a single concentration value corresponding to one of the eight discrete values of concentration given by the data. These graphs are plots of the best $c_{p,x}/T$ fit found. The fitting function is represented by the solid lines whereas the actual data points are marked with a "+".

(a)

(b)

(c)

(d)

(e)

(f)

(9)

(h)

Table 5

Parameters Giving the Shape of the Phase-Separation
Boundaries Using Equation (34); and the Slope of
the Lambda Line

Parameter	Superfluid Value	Normal-Fluid Value
P_1	2.660625	-.62220716
P_2	3.146142	-.71133029
P_3	-55.93173	0.0 (constrained to that value)
$q = \text{slope of } \lambda \text{ line} = (dx/dT)_\lambda = .4086$		

generated data points, a fit involving the eight parameters $\bar{g}_{12}$, $\bar{g}_{13}$, $\bar{g}_{14}$, $\bar{g}_{02}$, $\bar{g}_{03}$, $\bar{g}_{04}$, $\bar{g}_{05}$, and the combination $\bar{g}_{11} - f_{11}$. The specific-heat parameters were not allowed to vary in this particular fit. It should be noted that the specific-heat parameters predict that both $(\partial\Delta/\partial T)_x$ and $(\partial\Delta/\partial x)_T$ should vanish at the tricritical point because of the continuity of $c_{p,x}/T$ there. The data generated for $(\partial\Delta/\partial x)_{T_{1c}}$ agreed well with values obtained by Alvesalo *et. al.* in their initial analysis of the data.¹⁰

Because of this apparent vanishing at the tricritical point of the two first derivatives of Δ , it was decided that the functional form for these derivatives should be constrained to have a zero value at that point. This decision implied setting $\bar{g}_{02}$ and $\bar{g}_{11} - f_{11}$ equal to zero, so that the actual fit degenerated into

into a six-parameter fit of fifty data points.

The resultant fit was not encouraging. Yielding a Φ of 1.3747, the fit had systematic oscillations appearing near the tricritical point on the superfluid side and all along the normal-fluid side for both $(\partial\Delta/\partial T)_{x_{10}}$ and $(\partial\Delta/\partial x)_{T_{10}}$. These six parameters, along with the parameters set equal to zero, g_{02} and $g_{11} - f_{11}$, will be referred to as Parameter Set II. A listing of Parameter Set II is given in Table 6, and graphs of the predicted points, compared with the generated data points for $(\partial\Delta/\partial T)_{x_{10}}$ and $(\partial\Delta/\partial x)_{T_{10}}$ are given in Figure 3 and Figure 4, respectively. As a means of comparison, another fit was run in which the parameters g_{02} and $g_{11} - f_{11}$ were not constrained to the value of zero. Although the value of Φ was about half of the previous value of Φ in this new eight-parameter fit, the systematic oscillations were still present. The difference was that the amplitude of the oscillations had diminished. In an attempt to obtain a better fit with g_{02} and $g_{11} - f_{11}$ set equal to zero, first two, and then four parameters were added as coefficients of higher order terms in the fitting function. At best, Φ was lowered only by a little more than a fourth of the previous value of Φ in the six-parameter fit, and the oscillations still were present. Apparently, something is critically wrong.

One possible explanation for the inability of this functional form to describe the data reasonably lies in the constraints dictated by the continuity of the entropy and the free energy in going from the normal region to the superfluid region across the

Figure 3

The Quantity $(\partial\Delta/\partial T)_{x_{10}}$ vs. x

The values of $(\partial\Delta/\partial T)_{x_{10}}$ result either from a) the thermodynamic relations and Parameter Set I or b) the parametric form and Parameter Sets I and II. Note that there is a difference in scale between the superfluid and the normal sides.

Figure 4

The Quantity $(\partial\Delta/\partial x)_{T_{10}}$ vs. x

The values of $(\partial\Delta/\partial x)_{T_{10}}$ result from either a) the thermodynamic relations and Parameter Set I or b) the parametric form and Parameter Sets I and II. Note that the value of $(\partial\Delta/\partial x)_{T_{10}}$ for the parametric form becomes negative, which is unphysical because it represents thermodynamically unstable states. Also note the change in scale between the superfluid and normal sides.

Table 6

Parameter Set II: Parameters Involved in the
Fitting Functions for $(\partial\Delta/\partial T)_{x,0}$ and $(\partial\Delta/\partial x)_{T,0}$

(Units are implied.)

$g_{11} - f_{11}$	0.0	g_{02}	0.0
g_{12}^-	8.19144	g_{03}^-	6.79865
g_{13}^-	-19.8728	g_{04}^-	-60.3355
g_{14}	94.9144	g_{05}	-137.462

The following are obtainable from the above parameters
and Parameter Set I:

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g_{12}^+	65.3226	g_{03}^+	53.4015
g_{13}^+	-66.1459	g_{04}^+	-49.8434

λ line. In a totally unconstrained fit, with the specific-heat parameters already having been determined, there would be sixteen different parameters to be determined, consisting of eight each on the normal and superfluid sides: $g_{11}^+ - f_{11}$, g_{02}^+ , g_{12}^+ , g_{03}^+ , g_{13}^+ , g_{04}^+ , g_{14}^+ , and g_{05}^+ . However, the λ -line constraints dictate what the exact difference is between a superfluid parameter and the corresponding parameter on the normal side, and this difference is a function of the specific-heat parameters. The form of this difference function allows a small error in a specific-heat parameter to be multiplied by as much as 35.8. Because some of the standard

errors in the specific-heat parameters are fairly large, this multiplication of error could be a serious problem.

In an effort to control somehow the accidental effects of the λ -line constraints, a simultaneous fit of $c_{p,x}/T$ and the generated data points involving the two first derivatives of Δ was attempted. In this fit it was hoped that any strong effects caused by the λ -line constraints would be smoothed out due to the ability of the specific-heat parameters to readjust themselves. In order to reduce the computer time necessary for analysis, it was decided to utilize only every other data point of the original specific-heat data. This also had the effect of reducing the tendency of the fit to weight the specific-heat part of the fit more than the other parts. At the same time, the number of generated data points for $(\partial\Delta/\partial T)_{x_{10}}$ and $(\partial\Delta/\partial x)_{T_{10}}$ was increased to seventy. The ultimate result was a fit of 290 $c_{p,x}/T$ data points and 35 data points each for $(\partial\Delta/\partial T)_{x_{10}}$ and $(\partial\Delta/\partial x)_{T_{10}}$, a total attempted fit of 360 points by six interrelated functions (three each for superfluid and normal fluid) using twenty-six independent parameters.

A great deal of difficulty was encountered in trying to find a minimum Φ for this data set, for it turned out that Φ was not strongly dependent upon the nonlinear parameters. The net result was that Φ was not parabolic in parameter space except in the immediate vicinity of the minimum, so that only a very inefficient gradient search was utilized.

For this particular total fit, the criterion for acceptance was a low value of Φ , with no large systematic deviations from

the data. Initially, a linear fit was attempted keeping the values of the exponents fixed at those values found in the independent single-phase fit for $c_{p,x}/T$ performed previously and listed in Parameter Set I. The result with $\alpha^- = -.5013$ and $\alpha^+ = -.2533$ was $\bar{\Phi} = 1.15827$. Later, after a tortuous gradient fit in which all parameters were allowed to vary, a minimum $\bar{\Phi}$ was found. The result of this fit was:

$$\alpha^- = -.1140 ; \alpha^+ = -.1460 ; \bar{\Phi} = 1.09232.$$

Note that in order to effect a reduction of $\bar{\Phi}$ of only 5.7%, the superfluid exponent was changed by over 77% and the normal-fluid exponent by over 42%. The net result was the reduction of the large deviations previously seen in the predictions of the first derivatives of Δ , in conjunction with a slight increase in the magnitude of the deviations in the specific-heat predictions. Thus the sum of the squares of the deviations for $(\partial\Delta/\partial T)_{x,0}$ and $(\partial\Delta/\partial x)_{T,0}$ has been reduced to about .3479, while $\bar{\Phi}$ for the 290 $c_{p,x}/T$ points has been increased to about .7445, which represents an effective doubling of the sum of the squares of the deviations over the previous best single-phase specific-heat fit. Clearly, the specific heat is not very well described by these parameters. And even though the derivatives of Δ appear to be somewhat more adequately predicted, fairly large discrepancies still are occurring. The set of parameters resulting from this fit will be referred to as Parameter Set III and is listed in Table 7. Also, plots of the predicted points for $(\partial\Delta/\partial T)_{x,0}$ and $(\partial\Delta/\partial x)_{T,0}$, along with the generated data points are presented in Figure 5 and Fig-

Table 7

Parameter Set III

A List of the Parameters Giving the Best Total Fit

Parameter	Superfluid Value	Common Value	Normal-Fluid Value
ϵ_{20}		-4.38333	
ϵ_{30}	-.925404		2.18801
ϵ_{21}	-3.96975		18.8872
ϵ_{40}	1.16588		-3.22136
ϵ_{31}	10.2374		-24.6258
ϵ_{22}	30.9122		-72.7949
ϵ_{50}		1.26719	
ϵ_{41}		12.0491	
ϵ_{32}		51.1645	
ϵ_{23}		116.792	
χ_1	12.0483		12.6853
χ_2	-19.8520		-3.54110
α	-.114		-.146
ϵ_{11}		0.0	
ϵ_{12}	26.7223		82.6568
ϵ_{13}	57.8600		-80.5534
ϵ_{14}		43.1561	
ϵ_{02}		0.0	
ϵ_{03}	32.4614		78.0880
ϵ_{04}	47.2486		-23.9913
ϵ_{05}		-198.163	

(Cont.)

Table 7 (cont.)

Two-Phase Parameters Associated with the Above Set:

f_{20}	-4.38333
f_{30}	3.49779
f_{40}	3.28812
f_{50}	2.05193
f_{21}	-3.66621
f_{31}	1.30863
f_{41}	.261493

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ure 6, respectively.

But how acceptable is this total fit? Once again there is some inaccuracy near the tricritical point in the predictions of the specific heat. Another shortcoming of the fit is that there is a slight tendency on the normal side to predict higher values of $c_{p,x}/T$ at high temperatures and slightly lower values of $c_{p,x}/T$ near the λ line than those present in the data. These inaccuracies are not large, however, and do not seriously affect the credibility of the fit.

On the other hand, the values of the first derivatives of Δ are not well predicted. Though the values have been improved considerably over the values resulting from Parameter Set II, large systematic deviations still occur, and thus $(\partial\Delta/\partial T)_{x,c}$ and $(\partial\Delta/\partial x)_{T,c}$ are not adequately predicted. There also is some inconsistency within Parameter Set III, for the values of $(\partial\Delta/\partial T)_{x,c}$ and $(\partial\Delta/\partial x)_{T,c}$ using the thermodynamic relations of Equations (32) and (33) and Parameter Set III do not agree with the values resulting from the parametric form and the same parameter set. Something is critically wrong.

Figure 5

The Quantity $(\partial\Delta/\partial T)_{x,0}$ vs. x

The values of $(\partial\Delta/\partial T)_{x,0}$ result either from a) the thermodynamic relations and Parameter Set I, b) the thermodynamic relations and Parameter Set III or c) the parametric form and Parameter Set III. Note the change in scale between the superfluid and normal sides.

Figure 6

The Quantity $(\partial\Delta/\partial x)_{T_{10}}$ vs. x

The values of $(\partial\Delta/\partial x)_{T_{10}}$ result either from a) the thermodynamic relations and Parameter Set I, b) the thermodynamic relations and Parameter Set III or c) the parametric form and Parameter Set III. Note the change in scale between the superfluid and normal sides.

CHAPTER IV

Scaling

Several researchers already have attempted to see if scaling theory applies to the thermodynamics of $\text{He}^3 - \text{He}^4$ mixtures. If scaling does hold for the specific heat along the λ line and near the tricritical point, it would be expected that the functional form describing the behavior of $c_{p,x}/T$ in the single-phase region should contain a general, nondivergent background plus some function, unique on either side of the λ line, which would dominate the behavior as either the λ line or the tricritical point is approached and which contains the singularity present in the data. Hopefully, the functions unique to both sides would dominate only near the λ line, with the background dominating far away from the λ line.

In his doctoral thesis, G.J. Goellner discussed a theory of scaling for a region near a tricritical point. One of the results of that theory was that in the appropriate region near a tricritical point, the following holds:

$$\left(\frac{\partial \Delta}{\partial \chi}\right)_T = |\chi|^{\delta-1} W_{1\pm}(\tau/|\chi|^{1/\beta}) \quad (35)$$

where δ and β are critical exponents, and W is a function characteristic of the system, with the "+" indicating that W differs for positive and negative χ . If Equation (35) is integrated with respect to χ twice and differentiated with respect to τ twice, the tricritical form for $-(\partial s/\partial T)_\chi$, which equals $-c_{p,\chi}/T$ becomes apparent:

$$\Delta = f(\tau) + |\chi|^\delta W_{1\pm}(\tau/|\chi|^{1/\beta}), \quad (36)$$

where $W_{1\pm}$ is defined by the equation:

$$W_{1\pm}(z) = \pm \left\{ \delta W_{1\pm}(z) - \frac{z}{\beta} \frac{dW_{1\pm}}{dz} \right\},$$

$$\left(\frac{\partial \Delta}{\partial \tau}\right)_\chi = f'(\tau) + |\chi|^{\delta-\frac{1}{\beta}} W_{2\pm}(\tau/|\chi|^{1/\beta}) = -\left(\frac{\partial S}{\partial \chi}\right)_T, \quad (37)$$

where $W_{2\pm}(z) = \frac{dW_{1\pm}}{dz},$

$$-S = \chi f'(\tau) + g(\tau) + |\chi|^{\delta-\frac{1}{\beta}+1} W_{3\pm}(\tau/|\chi|^{1/\beta}), \quad (38)$$

where $W_{3\pm}$ is defined by the equation:

$$W_{2\pm}(z) = \pm \left\{ (\delta - \frac{1}{\beta} + 1) W_{3\pm}(z) - \frac{z}{\beta} \frac{dW_{3\pm}}{dz} \right\},$$

$$-c_{p,\chi}/T = -\left(\frac{\partial S}{\partial \tau}\right)_\chi = \chi f''(\tau) + g'(\tau) + |\chi|^{\delta-\frac{1}{\beta}+1} W_{4\pm}(\tau/|\chi|^{1/\beta}) \quad (39)$$

$$= \chi f''(\tau) + g'(\tau) + |\tau|^{\beta(\delta-\frac{1}{\beta}+1)-2} v_{\pm}(\chi/|\tau|^\beta), \quad (40)$$

where $|\chi|^{\delta-\frac{1}{\beta}+1} W_{4\pm}(\tau/|\chi|^{1/\beta}) = |\tau|^{\beta(\delta-\frac{1}{\beta}+1)-2} v_{\pm}(\chi/|\tau|^\beta),$

and $W_{4\pm}(z) = \frac{dW_{3\pm}}{dz},$

and the "+" subscript on the function v now indicates that v differs as to whether the variable τ is positive or negative. Hence there does exist a scaling form for $c_{p,\chi}/T$ which follows from

the scaling form for $(\partial\Delta/\partial\chi)_T$.

Now if a comparison is made at a given temperature between a value of $c_{P,X}/T$ at an arbitrary value of scaled concentration and a value of $c_{P,X}/T$ at a value of the scaled concentration, $\bar{\chi}(\tau)$, such that $\bar{\chi} \propto |\tau|^\theta$, then a test on scaling can be made:

$$\frac{c_{P,X}}{T}(\bar{\chi}, \tau) - \frac{c_{P,X}}{T}(\chi, \tau) = (\chi - \bar{\chi}) f''(\tau) + |\tau|^{-\alpha} \bar{v}_2\left(\frac{\chi - \bar{\chi}}{|\tau|^\theta}\right), \quad (41)$$

where $\bar{v}_2\left(\frac{\chi - \bar{\chi}}{|\tau|^\theta}\right) = v_2(\chi/|\tau|^\theta) - v_2(\bar{\chi}/|\tau|^\theta)$

and $\alpha = 2 - \theta(6 + 1)$,

or
$$\frac{\frac{c_{P,X}}{T}(\bar{\chi}, \tau) - \frac{c_{P,X}}{T}(\chi, \tau)}{(\chi - \bar{\chi})} = f''(\tau) + \frac{|\tau|^{-\alpha}}{\chi - \bar{\chi}} \bar{v}_2\left(\frac{\chi - \bar{\chi}}{|\tau|^\theta}\right) \quad (42)$$

$$= f''(\tau) + |\tau|^{-\alpha-\theta} \bar{v}_2\left(\frac{\chi - \bar{\chi}}{|\tau|^\theta}\right) \quad (43)$$

In order to proceed, values of the critical exponents α and β are needed. The exponent α , the power-law-behavior parameter for $c_{P,X}$ in the form $c_{P,X}(\text{singular}) \approx [T - T_c]^{-\alpha}$, is experimentally determined to be approximately -1. The results of Goellner¹² indicate that $\beta = .97 \pm .05$. If the actual values of α and β are approximated by $\alpha = -1$ and $\beta = 1$, Equation (43) simplifies:

$$\Gamma(\chi, \tau) \equiv \frac{\frac{c_{P,X}}{T}(\bar{\chi}, \tau) - \frac{c_{P,X}}{T}(\chi, \tau)}{(\chi - \bar{\chi})} = f''(\tau) + \bar{v}_2\left(\frac{\chi - \bar{\chi}}{\tau}\right), \quad (44)$$

which must hold if Goellner's form of scaling is valid over the region. To check the validity of this equation, one needs only to compute Γ as a function of $(\chi - \bar{\chi})/\tau$ at a constant τ value for several different values of τ . This procedure will generate a

family of curves, one for each value of T . If scaling holds, the curves should all be "parallel" to each other, being displaced vertically by differing values of $f''(T)$.

In order to check the scaling hypothesis as indicated in Equation (44), a functional form for the specific heat is necessary, for the values cannot conveniently be read from the data itself because of the discreteness of the concentration values. The values used were those obtained from the fits of the individual specific-heat regions involving Parameter Set I. The total fit of all the parameters was not used here because the fit with Parameter Set I gave the best overall agreement to the specific-heat data.

It should be noted in passing that if the scaling Equation (44) actually does hold throughout the region of investigation, the correct functional form for specific heat is restricted. Although the actual fitting function is not itself a function obeying Equation (44), the accuracy with which it can predict values of $c_{P,x}/T$ indicates that use of it for a scaling check is quite valid.

Two tests were performed utilizing the scaling Equation (44). The first used $\bar{x} = -.51424T$, and T was varied so that T took on the six values .90, .95, 1.00, 1.05, 1.10, and 1.20, while $\Gamma(\chi, T)$ was found for two hundred values of $(\chi - \bar{x})/T$ for each value of fixed temperature. The second test used the value of $\bar{x} = 0$, the value at the tricritical point, and the procedure was the same as in the first test. Some of the results of the latter check are presented graphically in Figure 7. In no case was there clear

Figure 7

Scaling Test

This test plots Γ , equal to $[c_{p,x}(\bar{x},\tau) - c_{p,x}(x,\tau)]/T(x - \bar{x})$, versus $(x - \bar{x})/\tau$ using Parameter Set I to obtain values for $c_{p,x}/T$. If scaling does work in this region, the curves should have the same shape but be displaced vertically from each other. Only four of the six temperature values have been graphed.

evidence that one curve was displaced vertically from any other curve by a constant amount in both the normal and superfluid regions, which would be attributed to the differing values of $f''(T)$. The net conclusion from this result is that scaling of the form presented by Goellner does not hold completely in the general region of the tricritical point. In order to test the theory more completely, a scaling check should be performed only in the close vicinity of the λ line and the tricritical point.

These results seem to contradict the results of Goellner, who found that Equation (36) was valid for his $(\partial\Delta/\partial x)_T$ data. However, Goellner performed his analysis on data taken from a region somewhat closer to the tricritical point than the region analyzed in my work. Therefore it would seem that the region of investigation probably should be narrowed greatly before any concrete conclusions can be made. Unfortunately, this is a difficult thing to do, for the data near the λ line does not appear to behave in a consistently regular manner, and hence the computer fit, which smooths out the irregularities somewhat, does not describe the observed behavior precisely. One possibility for future investigation would involve taking only the data in the immediate vicinity of the tricritical point and doing a detailed analysis on them.

CHAPTER V

Conclusions

Specific-heat functional forms have been discovered which adequately describe the data of Alvesalo et al. Additional parameters also have been tabulated for forms corresponding to the first derivatives of Δ , which are somewhat consistent with the forms of the specific heat. Finally, a scaling form has been checked in the gross region of the tricritical point, with no success of confirmation of that form.

Although these fits have been adequate, they are not very illuminating in showing fine details of other thermodynamic functions, as was one of the intentions of this research. But the research as presented in this paper has only scratched the surface. There are other methods of analysis which should be attempted, and there are two general approaches which can be made.

The first approach involves continuing the analysis begun as reported in this paper. Other methods have been outlined for obtaining the non-specific-heat parameters in Chapter II, and one or

more of these methods could be tried, either alone or in conjunction with another method. This approach, though it could possibly be successful, does not appear to carry a lot of promise. The fits of $(\partial\Delta/\partial T)_x$ and $(\partial\Delta/\partial x)_T$ have indicated some basic inconsistency between the specific-heat forms that have been obtained from the data and other thermodynamic functions. Regardless of the method of analysis of these non-specific-heat parameters, it appears that the first derivatives of Δ still would not be accurately described.

Another, more promising method would entail freeing up the continuity constraints of the free energy and entropy along the λ line, making these constraints just another function to minimize in the total fit. In this way, the λ -line constraints would be treated the same as the ϕ -boundary constraints in the total fitting of the parameters.

The second approach would involve starting virtually at the beginning. The present method has been to attempt an analysis of the whole region, with the hope that scaling theory might apply. However, if scaling does apply, the region of application is very likely to be restricted to be close to the λ line and/or the tricritical point. Thus, it seems possible that a scaling form for the specific heat might work close to the critical regions and fail further away, and that a nonscaling form would do just the opposite. Therefore, it might be fruitful to use a functional form for the specific heat that scales along the λ line, but does not necessarily follow a scaling form away from the critical regions. In this way, the problems resulting from the present form, which

approximately averages a scaling form with a nonscaling form, might be eliminated. In order to achieve this, the functional form for the specific heat would have to be changed, and finding a form that adequately describes the data has been the most difficult task of the present project.

An alternative approach to the entire problem is a bit more subtle. Perhaps the variables of concentration and temperature are not the natural variables of the system. There has been some indication from other researchers through success of analysis that the difference in chemical potential Δ is a more desirable independent variable than x when trying to describe some observed phenomena, such as the scattering of light, the osmotic pressure, and the vapor pressure. The analysis of the specific-heat data might be easier if the data were converted into $c_{p,\Delta}$, and if it were made a function of T and Δ instead of T and x . But because of the lack of knowledge about Δ , this conversion could be rather difficult.

Regardless of the next method of analysis chosen, there still remains a great deal of work before any major conclusions can be drawn. Besides the problems outlined previously, a careful analysis would have to take into account the effects of gravity as well as some minor inconsistencies in the data, problems that were completely ignored in the present analysis.

Appendix

In the final stages of the writing of this thesis, it was decided that the results near the λ line should be examined more closely. As a first step, four graphs, corresponding to the four concentrations .5297, .5800, .6100, and .6500, were made of the data, as well as the best-fit functional form resulting from Equation (26) and Parameter Set I, for temperatures within about 50 millidegrees of the corresponding lambda temperature. This graphing entailed a tenfold increase in the temperature scale as compared to the graphs of Figure 2.

Although these graphs were made too late for inclusion in the main body of the thesis, it was felt that they were important enough to be added to the thesis nonetheless. This addition is justified by the revelations they give about the inconsistencies and spread in the data and the difficulties and inaccuracies of the best fitting function near the different lambda points, as well as insights into the λ transition behavior as a function of increasing concentration. It is hoped that these detailed graphs, which are presented in Figure 8, parts (a) through (d), might be of some interest to the reader.

Figure 8. parts (a) through (d)

The Quantity $c_{P,x}/T$ Near the λ line as Predicted from Equation (26) and Parameter Set I, and a Plot of the Data

Each of the Parts (a) through (d) represents a single concentration value. The fitting function is represented by the solid lines, whereas the actual data points are marked with a "+".

(a)

(b)

(c)

(d)

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