

Statistical Mechanics of He³-He⁴ Liquid Mixtures*†

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(Received 21 March 1963)

The partition function method proposed by Feynman for pure liquid He⁴ and previously extended to treat pure liquid He³ by Kikuchi is here applied to liquid mixtures of He³-He⁴. The variation of the λ point with mole fraction He³, the isotopic phase separation curve, and the excess functions of mixing are discussed. The theoretical λ line is interpreted as a cooperative boson transition and follows the experimental results closely up to $X_3=0.5$ irrespective of the effective mass of the He³ atoms while above $X_3=0.5$ the λ temperatures are too high. An asymmetric isotopic phase separation is found in the mixtures at temperatures below a critical temperature that depends slightly on further assumptions in the model but which is of the correct order of magnitude (1°K). The phase separation is due to the quantum dynamical effects as opposed to the purely statistical effects arising out of the different inherent symmetries of the wave functions for He³ and He⁴. The calculated excess Gibbs free energies of mixing become positive in "time" to effect the phase separation but are less positive than the experimental values and are in fact of the wrong sign above 1°K. The calculated excess entropies of mixing are much too positive. The model used assumes zero excess volumes of mixing.

INTRODUCTION

IN 1953 Feynman¹ applied his path-integral method of quantum mechanics² to a system of He⁴ atoms and essentially factored the partition function for the system into two parts, one dependent on the quantum statistics of the atoms, assumed to move in fictitious motion through various permutations as free particles with an effective mass, and the other factor dependent on the actual interatomic potential and in particular on the energy of the system at absolute zero. Assuming the second factor to be a continuous function of temperature, Feynman neglected it and, making a random-walk estimate for the fictitious motions during the permutations, showed that the Bose statistics of He⁴ atoms led to a third-order transition in the thermodynamic functions, a result characteristic of an ideal Bose gas.

One of us³ improved the treatment of Feynman's statistical factor for pure He⁴ by using a lattice model for the permutations. The lattice served as a structure on which permutation paths could be followed by the quasifree atoms without excessive overlap of their force fields and, thus, repulsive effects of the actual potential were implicitly introduced. A second-order

transition in the thermodynamic functions was obtained which is in accord with experiment on the λ transition in He⁴. With the same approximations it was further shown⁴ that pure He³ atoms, treated as fermions, do not exhibit a λ transition.

The permutation types used in I needed extension in order to discuss systems with bosons at temperatures less than 1°K and this extension has recently been developed⁵ and used to treat the problem of pure He⁴ in more detail.

In the present work the complete formalism of I, II, and III has been applied to liquid He³-He⁴ mixtures in order to calculate the variation of the λ point with mole fraction He³ and to determine the curve of isotopic phase separation and to obtain the excess functions of mixing.

THE PARTITION FUNCTION AND ITS PARAMETRIZATION

We treat a mixture of N_3 He³ atoms and N_4 He⁴ atoms with $N_3+N_4=N$. The He³ atoms differ from He⁴ atoms by virtue of their statistics and differ among themselves by having their nuclear spin 'up' or 'down.' He⁴ atoms can only be permuted with other He⁴ atoms as bosons and only He³ atoms of like nuclear spin can be permuted among themselves as fermions. The total partition function of the system is

$$Q = qQ_0, \quad (1)$$

⁴ R. Kikuchi, Phys. Rev. **99**, 1684 (1955); to be referred to as II. It is worth noting that Professor Feynman's comment recorded in Ref. 4 of this reference is equally valid for the present work.

⁵ R. Kikuchi, H. H. Denman, and C. L. Schreiber, Phys. Rev. **119**, 1823 (1960); to be referred to as III.

* Work supported in part by the U. S. Atomic Energy Commission.

† Preliminary reports of this work were presented at the Second Symposium on Liquid and Solid Helium Three, held at the Ohio State University, 1960 and at the Seventh International Conference on Low Temperature Physics, held at the University of Toronto, 1960.

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¹ R. P. Feynman, Phys. Rev. **91**, 1291 (1953).

² R. P. Feynman, Rev. Mod. Phys. **20**, 367 (1948).

³ R. Kikuchi, Phys. Rev. **96**, 563 (1954); to be referred to as I.

with Q_0 , the dynamical factor, incorporating an unknown function of temperature K_β , being

$$\frac{\ln Q_0}{N} = -X_3 \ln X_3 - X_4 \ln X_4 + \frac{3}{2} X_3 \ln \left(\frac{m_3' kT}{2\pi \hbar^2} \right) + \frac{3}{2} X_4 \ln \left(\frac{m_4' kT}{2\pi \hbar^2} \right) + \frac{1}{N} \ln K_\beta \quad (2.1)$$

and q , the statistical factor, being

$$q = \sum_{\text{spin distributions}} \sum_{P_0} \sum_{P_A} \sum_{P_B} (-1)^{P_A+P_B} \times \int \exp \left[\frac{-m_4' kT}{2\hbar^2} \sum_{i=1}^{N_4} (\mathbf{z}_i - P_0 \mathbf{z}_i)^2 \right] \times \exp \left[\frac{-m_3' kT}{2\hbar^2} \sum_{i=1}^{N_3} (\mathbf{z}_i - P_A P_B \mathbf{z}_i)^2 \right] \times \rho(\mathbf{z}_1 \cdots \mathbf{z}_N) d\mathbf{z}_1 \cdots d\mathbf{z}_N. \quad (2.2)$$

In the above equations, P_0 denotes a permutation among the bosons; P_A denotes a permutation among the fermions with spin $+\frac{1}{2}$; P_B denotes a permutation among the fermions with spin $-\frac{1}{2}$; m_3' = effective mass of a He^3 atom; m_4' = effective mass of a He^4 atom; $X_3 = N_3/N$, $X_4 = N_4/N = 1 - X_3$. In obtaining Eq. (2) we have combined the methods of II and III which follow from Eq. (7) of Ref. 1. In this, the following approximations have been made. The actual interatomic potential which depends on \mathbf{z}_i has been replaced by a modulating one, independent of \mathbf{z}_i , and absorbed into the factor K_β in a form proportional to $\exp(-\tilde{U}_0/RT)$, where \tilde{U}_0 is the energy of the system at absolute zero. Thus, we have effectively free particles but with masses greater than the actual masses of He^3 and He^4 atoms. No lattice-model approximation has yet been made but the partition function has been factored into two parts: Q_0 , dependent on the dynamics of the interatomic interaction and on the zero-point energies but independent of statistics, and q , independent of the dynamics but dependent on the quantum statistics. Q_0 as function of T has been assumed to be continuous and to have no effect on the temperature of the λ transition in our mixtures. As we shall see, it is necessary to consider it when calculating the isotopic phase separation but for the moment we will concentrate our attention on q .

The density function $\rho(\mathbf{z}_1 \cdots \mathbf{z}_N)$ is assumed to be zero everywhere except for \mathbf{z} 's located on the sites of a lattice with coordination number c , nearest-neighbor distance d , and total number of sites N . It is then possible to express q as the sum of the product of a combinatorial factor times Boltzmann factors over all possible distributions of polygons in *space* arising from closed chains of permutations among permutable types

Point Configuration	Probability	Weight (a_i)
A	x_1	1
B	x_2	1
•	x_{31}	1
U	x_{32}	c
→	x_{33}	$c(c-1)$
↗	x_{34}	$2c$
○	x_{35}	1

FIG. 1. Point probability parameters. A represents He^3 atoms with nuclear spin $+\frac{1}{2}$, B represents those with spin $-\frac{1}{2}$. All other single sites are occupied by He^4 atoms taken up in various kinds of permutation cycles. → represents a short side of length equal to the nearest-neighbor distance. --- or - - - represents a long side. Δ connects a long side with a short side. ○ is a lattice point between two long sides. The weights are expressed in terms of c , the number of nearest neighbors on the permutation lattice.

(i.e., He^4 only with other He^4 atoms, etc.) that lead to different Boltzmann factors. The combinatorial factor and the arguments of the exponentials of the Boltzmann factors can be shown, as in II and III, to depend in good approximation on parameters representing all single-site and pair configurations that are possible on the lattice on which the permutations are carried out. The most important single term contributing to the sum is then found and used in place of the entire sum itself as is usually done in statistical mechanics by minimizing an appropriate free-energy expression with respect to the independent parameters.

The total number of point and bond configurations are given in Figs. 1 and 2, respectively. The weights assigned to the various configurations in terms of c , the number of nearest neighbors, are the numbers of different ways of obtaining a given configuration due to the symmetry of the lattice. β_{35} , for example, is found by multiplying the number of ways of selecting 2 directions out of $(c-1)$, i.e., $(c-1)!/2!(c-3)!$ by a factor 2 for possible interchange of left and right, and by another factor 2 for the two directions of cyclical permutation possible. In the figures we distinguish between short sides of polygons which are equal in length to a nearest-neighbor distance d , and 'long' sides which are of length equal to any lattice displacement greater than d . An arrow indicates the direction of permutation. At a triangle lattice point Δ a long side meets a short side. An open circle ○ is a lattice point where two long sides meet. In counting β_{ij} in Fig. 2 the two different directions for a long side (when there is no arrow attached to it) are not counted.

We have a total of 39 parameters and define a 40th ζ ,

$$2\zeta = x_1 - x_2, \quad (3.1)$$

so as to be proportional to the excess of $\text{He}^3 + \frac{1}{2}$ spins over the opposite type. In addition to Eq. (3.1) we

have the following requirements:

$$x_{31} + cx_{32} + c(c-1)x_{33} + 2cx_{34} + x_{35} = 1 - X_3, \quad (3.2)$$

$$x_1 + x_2 = X_3, \quad (3.3)$$

$$x_1 = y_1 + y_2 + y_{41} + (c-1)y_{42} + (c-1)(c-2)y_{43} + 2(c-1)y_{44} + y_{45}, \quad (3.4)$$

$$x_2 = y_2 + y_3 + y_{51} + (c-1)y_{52} + (c-1)(c-2)y_{53} + 2(c-1)y_{54} + y_{55}, \quad (3.5)$$

$$x_{31} = y_{41} + y_{51} + y_{61} + (c-1)y_{62} + (c-1)(c-2)y_{63} + 2(c-1)y_{69} + y_{610}, \quad (3.6)$$

$$x_{32} = y_{42} + y_{52} + y_{62} + (c-1)y_{63} + (c-1)(c-2)y_{66} + 2(c-1)y_{611} + y_{612}, \quad (3.7)$$

$$x_{32} = y_{64}, \quad (3.8)$$

$$x_{33} = y_{43} + y_{53} + y_{63} + (c-1)y_{66} + (c-1)(c-2)y_{67} + 2(c-1)y_{613} + y_{614}, \quad (3.9)$$

$$x_{33} = (c-1)y_{68} + y_{617}, \quad (3.10)$$

$$x_{34} = y_{44} + y_{54} + y_{64} + (c-1)y_{611} + (c-1)(c-2)y_{613} + 2(c-1)y_{615} + y_{616}, \quad (3.11)$$

$$x_{34} = (c-1)y_{617} + y_{618}, \quad (3.12)$$

$$x_{35} = y_{45} + y_{55} + y_{610} + (c-1)y_{612} + (c-1)(c-2)y_{614} + 2(c-1)y_{616} + y_{619}. \quad (3.13)$$

Equations (3.2) and (3.3) represent the correct counting up of He⁴ and He³ atoms, respectively, and their sum gives the proper normalization of single-site probabilities. Equations (3.4) through (3.13) are consistency requirements derived in each case by equating the number of lattice sites of given type to the total number of such sites involved in the pairs. The normalization of pair probabilities follows from Eqs. (3) and is not an independent requirement. Because of the 13 Eqs. (3), only 27 of our 40 parameters are independent.

We approximate the total combinatorial factor G_T in the pair approximation of Kikuchi,⁶

$$G_T = GG_{Is}, \quad (4)$$

where

$$\begin{aligned} \ln G = & N(c-1) \sum_{i=1}^2 x_i \ln x_i + N(c-1) \sum_{i=1}^5 \alpha_{3i} x_{3i} \ln x_{3i} \\ & - \frac{Nc}{2} \sum_{i=1}^3 \beta_{2i} y_i \ln y_i - \frac{Nc}{2} \sum_{i=1}^5 \beta_{4i} y_{4i} \ln y_{4i} \\ & - \frac{Nc}{2} \sum_{i=1}^5 \beta_{5i} y_{5i} \ln y_{5i} - \frac{Nc}{2} \sum_{i=1}^{19} \beta_{6i} y_{6i} \ln y_{6i} \end{aligned} \quad (5.1)$$

and G_{Is} is the factor coming from long side jumps in

⁶ R. Kikuchi, Phys. Rev. **81**, 988 (1951).

Pair Configuration	Probability	Weight (θ_{ij})
A-A	y_1	1
A-B	y_2	2
B-B	y_3	1
A •	y_{41}	2
A U	y_{42}	$2(c-1)$
A L	y_{43}	$2(c-1)(c-2)$
A ↗	y_{44}	$4(c-1)$
A ↘	y_{45}	2
B •	y_{51}	2
B U	y_{52}	$2(c-1)$
B L	y_{53}	$2(c-1)(c-2)$
B ↗	y_{54}	$4(c-1)$
B ↘	y_{55}	2
• •	y_{61}	1
• U	y_{62}	$2(c-1)$
U U	y_{63}	$(c-1)^2$
○	y_{64}	1
• L	y_{65}	$2(c-1)(c-2)$
U L	y_{66}	$2(c-1)^2(c-2)$
L L	y_{67}	$(c-1)^2(c-2)^2$
L ↗	y_{68}	$2(c-1)^2$
• ↗	y_{69}	$4(c-1)$
• ↘	y_{610}	2
U ↗	y_{611}	$4(c-1)^2$
U ↘	y_{612}	$2(c-1)$
L ↗	y_{613}	$4(c-1)^2(c-2)$
L ↘	y_{614}	$2(c-1)(c-2)$
↗ ↘	y_{615}	$4(c-1)^2$
↗ ↗	y_{616}	$4(c-1)$
↘ ↗	y_{617}	$4(c-1)$
↘ ↘	y_{618}	2
↗ ↘	y_{619}	1

FIG. 2. Pair probability parameters. Conventions as in Fig. 1.

boson permutations and reads as (see III):

$$\ln G_{Is} = \hat{N} \ln \hat{N} - \hat{N} + \sum_{l>d}^{l_{max}} N_l (\ln \bar{N}_l - \ln N_l), \quad (5.2)$$

with

$$\sum_{l>d}^{l_{max}} N_l \equiv \hat{N} = (cx_{34} + x_{35})N \quad (6.1)$$

and

$$\bar{N}_l = (cx_{34} + x_{35})N_l^{(0)}, \quad (6.2)$$

in which N_l denotes the total number of sides in a configuration having length l between two He⁴ atoms and $N_l^{(0)}$ is a purely geometrical number giving the

number of sites which lie at a distance l from a certain lattice point.

THE FREE ENERGY AND ITS MINIMIZATION

The Helmholtz free energy F is given by

$$F = -kT \ln Q. \quad (7)$$

As shown in (I-II-III), when the sum that is Q is replaced by its maximum term, the minimum free-energy expression has virtual potential energy terms coming from permutations along polygon sides for the bosons of the form

$$(cN\tau_4)kT[y_{64} + (c-1)^2y_{68} + y_{618} + 2(c-1)y_{617}] + \sum_{l>d}^{l_{\max}} kT \frac{l^2}{d^2} \tau_4 N_l,$$

an energy term coming from fermion permutations

$$-kT \sum_{\mathbf{k}} \ln B(\mathbf{k}, \mathbf{k}),$$

a magnetic energy contribution

$$-2\mu H N \zeta,$$

with H the external magnetic field and μ the nuclear magnetic moment of He^3 , and τ_4 , a dimensionless ratio,

$$\tau_4 = (m_4' d^2 k T / 2 \hbar^2). \quad (8)$$

In addition, there are, of course, terms from the logarithm of the complete combinatorial factor.

The symbols in the term arising from fermion permutations will now be explained using further notation defined explicitly in II. In considering the formulation of the determinant that enters into the sum over He^3 permutations it seems that we should always take the origin to be at one of the He^3 atoms so that (in the notation of II) $p(\text{origin}) = 1$ always, even in the limit that $X_3 \rightarrow 0$ because then, as will be seen below, the equations reduce consistently to those for pure He^4 . In any case the difference between an assembly of pure He^4 and one with He^4 atoms plus one He^3 atom should be of no significance. We, thus, use

$$p(\text{origin}) = 1, \quad (9.1)$$

$$p(\text{nearest neighbor}) = y_1 + y_3 \equiv p(d), \quad (9.2)$$

$$p(\text{further neighbor}) \cong p_\infty = x_1^2 + x_2^2. \quad (9.3)$$

We then express the $B(\mathbf{k}\mathbf{k})$ of II after an appropriate unitary transformation as

$$B(\mathbf{k}\mathbf{k}) = \sum_{\mathbf{x}} \{ \exp[-(a_3 |\mathbf{x}|^2 + 2\pi i \mathbf{k} \cdot \mathbf{x})] \} \times \{ p(|\mathbf{x}|) - p_\infty \} + p_\infty B^s(\mathbf{k}\mathbf{k}), \quad (10)$$

in which $B^s(\mathbf{k}\mathbf{k})$ is the value of $B(\mathbf{k}\mathbf{k})$ when all spins are aligned in one direction and is a function of certain

sums expressible in terms of theta functions⁷ and dependent also on the lattice used for the permutations and $a_3 \equiv m_3' k T / 2 \hbar^2$, with \mathbf{k} the general vector of the lattice reciprocal to the space lattice used for permutations. We will replace $\sum_{\mathbf{k}} \ln B(\mathbf{k}\mathbf{k})$ with

$$\frac{N}{\sigma} \int \int \int_{-1/2}^{+1/2} dx dy dz \ln B(\mathbf{k}\mathbf{k}), \quad (11)$$

where

$$\begin{aligned} \sigma &= 1 \text{ for a simple cubic space lattice,} \\ &= 2 \text{ for a face-centered cubic lattice,} \\ &= 4 \text{ for a body-centered cubic lattice.} \end{aligned}$$

The reason for division by the integer σ is that σ is the number of sites per unit cell of the lattice reciprocal to the space lattice used. In Eq. (11) and in the equations below for the $B^s(\mathbf{k}\mathbf{k})$, x, y, z , are variables of integration equal to $\kappa/L, \lambda/L, \mu/L$, respectively, where κ, λ, μ are integers relating to the components of the general reciprocal lattice vector and $L = (N)^{1/3}$.

Selecting 27 independent variables out of our 40 parameters and using Eqs. (3) and (9) in Eq. (10), we find

$$\begin{aligned} B(\mathbf{k}\mathbf{k}) &= (1 - \frac{1}{2} X_3^2 - 2\zeta^2) + (\frac{1}{2} X_3^2 + 2\zeta^2) B^s(\mathbf{k}\mathbf{k}) \\ &+ 2e^{-\tau_3} (\sum \cos) \{ X_3 - \frac{1}{2} X_3^2 - 2\zeta^2 - 2y_2 - y_{41} - y_{51} \\ &- (c-1)y_{42} - (c-1)y_{52} - (c-1)(c-2)y_{43} \\ &- (c-1)(c-2)y_{53} - 2(c-1)y_{44} \\ &- 2(c-1)y_{54} - y_{45} - y_{55} \}, \quad (12) \end{aligned}$$

in which

$$\tau_3 \equiv a_3 d^2 = m_3' d^2 k T / 2 \hbar^2 \quad (13)$$

and $(\sum \cos)$ is a factor which is a sum over cosines dependent on the lattice used.

Recalling that x, y, z , without subscripts are integration variables and not probability parameters, it is convenient to collect here the forms assumed by $(\sum \cos)$ and $B^s(\mathbf{k}\mathbf{k})$ for different lattices:

Square lattice ($c=4$)

$$(\sum \cos) = \cos 2\pi x + \cos 2\pi y, \quad (14.1)$$

$$B^s(\mathbf{k}\mathbf{k}) = \vartheta_3(x, e^{-\tau_3}) \vartheta_3(y, e^{-\tau_3}). \quad (14.2)$$

Simple cubic lattice ($c=6$)

$$(\sum \cos) = \cos 2\pi x + \cos 2\pi y + \cos 2\pi z, \quad (14.3)$$

$$B^s(\mathbf{k}\mathbf{k}) = \vartheta_3(x, e^{-\tau_3}) \vartheta_3(y, e^{-\tau_3}) \vartheta_3(z, e^{-\tau_3}). \quad (14.4)$$

Body-centered cubic lattice ($c=8$)

$$\begin{aligned} (\sum \cos) &= \cos 2\pi(x+y+z) + \cos 2\pi(-x+y+z) \\ &+ \cos 2\pi(x+y-z) + \cos 2\pi(x-y+z), \quad (14.5) \end{aligned}$$

$$\begin{aligned} B^s(\mathbf{k}\mathbf{k}) &= \vartheta_3(2x, e^{-(4/3)\tau_3}) \vartheta_3(2y, e^{-(4/3)\tau_3}) \vartheta_3(2z, e^{-(4/3)\tau_3}) \\ &+ \vartheta_2(2x, e^{-(4/3)\tau_3}) \vartheta_2(2y, e^{-(4/3)\tau_3}) \vartheta_2(2z, e^{-(4/3)\tau_3}). \quad (14.6) \end{aligned}$$

⁷ See, for example, E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1927), 4th ed., Chap. 21.

Face-centered cubic lattice ($c=12$)

$$\begin{aligned} (\sum \cos) = & \cos 2\pi(x+y) + \cos 2\pi(y+z) + \cos 2\pi(z+x) \\ & + \cos 2\pi(x-y) + \cos 2\pi(y-z) + \cos 2\pi(z-x), \end{aligned} \quad (14.7)$$

$$\begin{aligned} B^s(\mathbf{kk}) = & \vartheta_3(2x, e^{-2\tau_3})\vartheta_3(2y, e^{-2\tau_3})\vartheta_3(2z, e^{-2\tau_3}) \\ & + \vartheta_2(2x, e^{-2\tau_3})\vartheta_2(2y, e^{-2\tau_3})\vartheta_3(2z, e^{-2\tau_3}) \\ & + \vartheta_2(2x, e^{-2\tau_3})\vartheta_3(2y, e^{-2\tau_3})\vartheta_2(2z, e^{-2\tau_3}) \\ & + \vartheta_3(2x, e^{-2\tau_3})\vartheta_2(2y, e^{-2\tau_3})\vartheta_2(2z, e^{-2\tau_3}). \end{aligned} \quad (14.8)$$

Two different types of theta functions appear in Eqs. (14) and the different arguments should also be noted carefully. Equation (14.7) is a corrected form of Eq. (5.7) of II in which some terms were omitted by the printer.

We will not be able to combine the face-centered cubic lattice form with our counting of boson permutations since the boson counting is not valid for lattices in which there are pairs of nearest neighbors among the nearest neighbors of a given site. Nevertheless, the fcc equations are included for completeness with regard to the case of pure He³.

We may finally write down the free-energy expression as

$$\begin{aligned} \frac{F}{kT} = & -\ln Q_0 - \frac{2\mu NH\zeta}{kT} - \frac{N}{\sigma} \int \int \int_{-1/2}^{+1/2} dx dy dz \ln B(\mathbf{kk}) \\ & - \ln G + Nc\tau_4[y_{64} + (c-1)^2 y_{68} + y_{618} \\ & + 2(c-1)y_{617}] + \frac{F'}{kT}, \end{aligned} \quad (15)$$

where

$$\begin{aligned} \frac{F'}{kT} = & \sum_{l>d}^{l_{\max}} \tau_4 \frac{l^2}{d^2} N_l + \hat{N} - \hat{N} \ln \hat{N} \\ & - \sum_{l>d}^{l_{\max}} N_l (\ln \bar{N}_l - \ln N_l) - \lambda [\hat{N} - \sum_{l>d}^{l_{\max}} N_l], \end{aligned} \quad (16)$$

and λ in the last term of (16) is a Lagrangian multiplier for the condition (6.1). The only dependence of F on N_l is in F' so that we first minimize F (i.e., F') with respect to N_l . The process is precisely the same as in III. We find

$$N_l = \bar{N}_l \exp \left[-\frac{l^2 \tau_4}{d^2} - (\lambda + 1) \right]. \quad (17)$$

Summing both sides of Eq. (17) over all $l>d$ and using Eq. (6.2), the multiplier λ is determined by

$$B \equiv N e^{(\lambda+1)} = \left(\sum_{l>0}^{l_{\max}} N_l^{(0)} e^{-l^2 \tau_4 / d^2} \right) - 1 - c e^{-\tau_4}, \quad (18)$$

in which a new quantity B has been defined. The B in Eq. (18) is not to be confused with $B(\mathbf{kk})$ from Eq. (12).

The meaning of $N_l^{(0)}$ defined in connection with Eq. (6.2) permits us to express B in terms of more theta functions this time with arguments depending on τ_4 (see III). We have for the simple cubic lattice ($c=6$)

$$B = [\vartheta_3(0, e^{-\tau_4})]^3 - 1 - 6e^{-\tau_4}, \quad (19.1)$$

and for the body-centered cubic lattice ($c=8$)

$$B = [\vartheta_3(0, e^{-(4/3)\tau_4})]^3 + [\vartheta_2(0, e^{-(4/3)\tau_4})]^3 - 1 - 8e^{-\tau_4}. \quad (19.2)$$

The final expression for F' is

$$F'/kT = N(cx_{34} + x_{35}) \{1 - \ln B - \ln(cx_{34} + x_{35})\}. \quad (20)$$

Then using Eqs. (15) and (5.1), the total free energy is

$$\begin{aligned} \frac{F}{NkT} = & \frac{-\ln Q_0}{N} - \frac{2\mu H}{kT} \zeta - \frac{1}{\sigma} \int \int \int_{-1/2}^{+1/2} dx dy dz \ln B(\mathbf{kk}) \\ & - (c-1) \sum_{i=1}^2 x_i \ln x_i - (c-1) \sum_{i=1}^5 \alpha_{3i} x_{3i} \ln x_{3i} \\ & + \frac{c}{2} \sum_{i=1}^3 \beta_i y_i \ln y_i + \frac{c}{2} \sum_{i=1}^5 \beta_{4i} y_{4i} \ln y_{4i} \\ & + \frac{c}{2} \sum_{i=1}^5 \beta_{5i} y_{5i} \ln y_{5i} + \frac{c}{2} \sum_{i=1}^{19} \beta_{6i} y_{6i} \ln y_{6i} \\ & + c\tau_4 [y_{64} + (c-1)^2 y_{68} + 2(c-1)y_{617} + y_{618}] \\ & + [cx_{34} + x_{35}] [1 - \ln B - \ln(cx_{34} + x_{35})]. \end{aligned} \quad (21)$$

This is a function of the parameters given in Figs. 1 and 2 and ζ defined by Eq. (3.1). The 27 independent parameters were chosen to be ζ , x_{35} , y_2 , y_{41} , y_{42} , y_{43} , y_{44} , y_{45} , y_{51} , y_{52} , y_{53} , y_{54} , y_{55} , y_{63} , y_{64} , y_{66} , y_{67} , y_{68} , y_{69} , y_{611} , y_{612} , y_{613} , y_{614} , y_{615} , y_{616} , y_{617} , and y_{619} . The 13 dependent variables are expressed in terms of the independent ones and this substitution is made in Eq. (21) for the free energy which is then minimized with respect to each of the 27 independent variables in turn leading to 27 higher order algebraic equations which must be solved simultaneously.

Minimizing first with respect to ζ it is easily seen that, for vanishing external magnetic field ($H=0$), $\zeta=0$ is a possible solution. We have chosen this case as appropriate, thus, ruling out any ferromagnetic possibility. This is in accord with all the known data on pure He³ and its mixtures with He⁴. We will take $\zeta=0$ throughout the rest of this paper and write $B(\mathbf{kk})_0$ to indicate that $\zeta=0$ in Eq. (12).

Next, minimizing with respect to y_{4i} and y_{5i} there results the 5 relations

$$y_{4i}^2 = y_{5i}^2 (y_1/y_3), \quad 1 \leq i \leq 5,$$

which when substituted into Eqs. (3) requires that

$$y_1 = y_3$$

as is the case in pure He³. This, in turn, leads to

$$y_{4i} = y_{5i}, \quad 1 \leq i \leq 5.$$

Minimizing with respect to y_2 we are led to the relation

$$\frac{c}{2} \ln \left(\frac{y_1 y_3}{y_2^2} \right) = - \int_{-1/2}^{+1/2} \int \int \frac{dx dy dz}{B(\mathbf{k}\mathbf{k})_0} e^{-\tau_3(\Sigma \cos)}. \quad (22)$$

The minimization with respect to the remaining 15 variables follows closely the procedure used in III.

Further details of the algebraic manipulations will be omitted and only the final results given. They appear in terms of two new variables α and γ , where α is defined as

$$\alpha = (c-1) + (z_{610}/z_{65})^{1/2}, \quad (23)$$

in which

$$z_{6i} = y_{6i}/y_{61} \quad \text{for } i=2, 3, \dots, 19, \quad (24)$$

and γ is defined as

$$\gamma = 1 + 2(y_2/y_{61})^{1/2}. \quad (25)$$

The final results are the following two simultaneous equations for α and γ :

$$B = \frac{[\alpha - (c-1)] \{ [\alpha^2 - (c-1)](\alpha+1)^2 e^{-\tau_4} - \alpha [\alpha^2(\gamma-1) + 2\gamma\alpha - (c-1)(\gamma-1)] \}}{(1-X_3)\alpha(\alpha+1)[\alpha^2 - (c-1)]}, \quad (26)$$

$$\frac{c}{2} \ln \left(\frac{y_1}{y_2} \right) = - \int_{-1/2}^{+1/2} \int \int \frac{dx dy dz e^{-\tau_3(\Sigma \cos)}}{B(\mathbf{k}\mathbf{k})_0}, \quad (27)$$

with B given by Eqs. (19) and (y_1/y_2) and $B(\mathbf{k}\mathbf{k})_0$ given explicitly in terms of α and γ by

$$\left(\frac{y_1}{y_2} \right) = \frac{2X_3 e^{-2\tau_4} [\alpha^2 - (c-1)](\alpha+1)^2 - 4X_3 e^{-\tau_4} \gamma \alpha^2 - 2(\gamma-1)\alpha e^{-\tau_4} [\alpha^2 - (c-1)] + (\gamma-1)^2 (1-X_3) [\alpha^2 - (c-1)]}{(1-X_3) [\alpha^2 - (c-1)] (\gamma-1)^2} \quad (28)$$

and

$$B(\mathbf{k}\mathbf{k})_0 = (1 - \frac{1}{2}X_3^2) + \frac{1}{2}X_3^2 B^*(\mathbf{k}\mathbf{k}) + 2e^{-\tau_3} X_3 (\Sigma \cos) (1 - \frac{1}{2}X_3) \frac{\{ 2e^{-\tau_3} (\Sigma \cos) (\gamma-1) [\alpha - \frac{1}{2}(\gamma-1)e^{\tau_4}] (1-X_3) [\alpha^2 - (c-1)] \}}{[\alpha^2 - (c-1)] (\alpha+1)^2 e^{-\tau_4} - \alpha [\alpha^2(\gamma-1) + 2\gamma\alpha - (c-1)(\gamma-1)]}. \quad (29)$$

Upon solution of these equations, the probability parameters may be found as follows:

$$\zeta = 0, \quad (30.1)$$

$$x_1 = x_2 = \frac{1}{2}X_3, \quad (30.2)$$

$$x_{31} = y_{61}(e^{-\tau_4})\alpha, \quad (30.3)$$

$$x_{32} = y_{61}z_{62}(e^{-\tau_4})\alpha, \quad (30.4)$$

$$x_{33} = y_{61}z_{65}(e^{-\tau_4})\alpha, \quad (30.5)$$

$$x_{34} = y_{61}z_{69}(e^{-\tau_4})\alpha, \quad (30.6)$$

$$x_{35} = y_{61}z_{610}(e^{-\tau_4})\alpha, \quad (30.7)$$

$$y_1 = y_3 = \frac{X_3}{2} \frac{y_2}{(\gamma-1)} [2\alpha e^{-\tau_4} - (\gamma-1)], \quad (30.8)$$

$$y_2 = (\gamma-1)^2 y_{61}/4, \quad (30.9)$$

$$y_{61} = y_{41} = y_{61}(\gamma-1)/2, \quad (30.10)$$

$$y_{62} = y_{42} = y_{61}z_{62}(\gamma-1)/2, \quad (30.11)$$

$$y_{63} = y_{43} = y_{61}z_{65}(\gamma-1)/2, \quad (30.12)$$

$$y_{64} = y_{44} = y_{61}z_{69}(\gamma-1)/2, \quad (30.13)$$

$$y_{55} = y_{45} = y_{61}z_{610}(\gamma-1)/2, \quad (30.14)$$

$$e^{\tau_4} (1-X_3) [\alpha^2 - (c-1)]$$

$$y_{61} = \{ [\alpha^2 - (c-1)] (\alpha+1)^2 e^{-\tau_4} - \alpha [\alpha^2(\gamma-1) + 2\gamma\alpha - (c-1)(\gamma-1)] \}^{-1}, \quad (30.15)$$

$$z_{62} = e^{-\tau_4}/\alpha, \quad (30.16)$$

$$z_{63} = z_{62}^2, \quad (30.17)$$

$$z_{64} = e^{-2\tau_4}, \quad (30.18)$$

$$z_{65} = \frac{e^{-\tau_4} [\alpha^2 - (c-1)] - \alpha\gamma}{\alpha [\alpha^2 - (c-1)]}, \quad (30.19)$$

$$z_{66} = z_{62}z_{65}, \quad (30.20)$$

$$z_{67} = z_{65}^2, \quad (30.21)$$

$$z_{68} = z_{65}e^{-\tau_4}, \quad (30.22)$$

$$z_{69} = [\alpha - (c-1)]z_{65}, \quad (30.23)$$

$$z_{610} = [\alpha - (c-1)]^2 z_{65}, \quad (30.24)$$

$$z_{611} = z_{62}z_{69}, \quad (30.25)$$

$$z_{612} = z_{62}z_{610}, \quad (30.26) \quad z_{617} = [\alpha - (c-1)]e^{-\tau_4}z_{65}, \quad (30.31)$$

$$z_{613} = z_{65}z_{69}, \quad (30.27) \quad z_{618} = [\alpha - (c-1)]^2e^{-\tau_4}z_{65}, \quad (30.32)$$

$$z_{614} = z_{65}z_{610}, \quad (30.28) \quad z_{619} = z_{610}^2. \quad (30.33)$$

$$z_{615} = z_{69}^2 = z_{614}, \quad (30.29) \quad \text{When these results are substituted into Eq. (21)}$$

$$z_{616} = z_{69}z_{610}, \quad (30.30) \quad \text{we have}$$

$$\begin{aligned} \frac{F}{NkT} = & \frac{-\ln Q_0}{N} - \frac{1}{\sigma} \int_{-1/2}^{+1/2} \int \int dx dy dz \ln B(\mathbf{k}\mathbf{k})_0 - (c-1)X_3 \ln\left(\frac{X_3}{2}\right) + \frac{c}{2} \left\{ X_3 - (\gamma-1)y_{61} \left[\alpha e^{-\tau_4} - \frac{(\gamma-1)}{2} \right] \right\} \\ & \times \ln \left\{ \frac{X_3}{2} - \frac{(\gamma-1)}{2} y_{61} \left[\alpha e^{-\tau_4} - \frac{(\gamma-1)}{2} \right] \right\} + \frac{c}{4} (\gamma-1)^2 y_{61} \ln \left[\frac{(\gamma-1)^2}{4} y_{61} \right] - (c-1)(1-X_3) \ln x_{31} + \frac{c}{2} (1-X_3) \ln y_{61} \\ & + cx_{34} + x_{35} + c[e^{-\tau_4}\alpha - (\gamma-1)](\gamma-1)y_{61} \ln \left[\frac{(\gamma-1)}{2} y_{61} \right] - \frac{c}{2} (\gamma-1)y_{61} [e^{-\tau_4}\alpha - (\gamma-1)] \ln y_{61}. \quad (31) \end{aligned}$$

THE λ POINT AND ABOVE

As T and, thus, τ_4 is increased from zero it can be seen from Eq. (30) that a T is reached at which y_{65} and, thus, also x_{33} through x_{35} , y_{43} through y_{45} , y_{53} through y_{55} , and y_{66} through y_{619} all become zero. Any further increase in T would result in negative values for these probability parameters which is not possible. Hence, this point is associated with the λ transition. Note that the only polygons describing He⁴ permutations that can be used above the λ point are the double-sided ones. The condition for the λ point is obtained from Eq. (30.19) and is

$$e^{+(\tau_4)\lambda} = \frac{\alpha^2 - (c-1)}{\alpha\gamma}. \quad (32)$$

Using Eq. (32) in Eqs. (26) and (27), the α and γ at the λ point are found from

$$(B)_\lambda = \frac{[\alpha - (c-1)][\alpha^2 + 1 + c(\gamma-1)]}{(1-X_3)(\alpha+1)[\alpha^2 - (c-1)]} \quad (33)$$

and

$$\frac{c}{2} \ln \left(\frac{y_1}{y_2} \right)_\lambda = \frac{2}{\sigma} \int_{-1/2}^{+1/2} \int \int \frac{dx dy dz e^{-(\tau_3)\lambda} (\sum \cos)}{B(\mathbf{k}\mathbf{k})_0}. \quad (34)$$

$$\left(\frac{y_1}{y_2} \right) = \frac{2X_3[2(c-1) + c(r-\gamma)] - (\gamma-1)(r+1)(r-\gamma)(1-X_3)e^{2\tau_4}}{(\gamma-1)^2(1-X_3)(r-\gamma)e^{2\tau_4}} \quad (37)$$

and

$$B(\mathbf{k}\mathbf{k})_0 = (1 - \frac{1}{2}X_3^2) + \frac{1}{2}X_3^2 B^*(\mathbf{k}\mathbf{k}) + 2e^{-\tau_3}X_3(\sum \cos)(1 - \frac{1}{2}X_3) - \frac{e^{-\tau_3}(\sum \cos)(\gamma-1)(r+1)(r-\gamma)(1-X_3)e^{2\tau_4}}{[2(c-1) + c(r-\gamma)]}. \quad (38)$$

Using Eq. (32) it is not difficult to show that at the λ point Eqs. (37) and (38) are identical with Eqs. (28) and (29), respectively, so that γ and, thus, all the probability parameters are continuous at T_λ .

Thus, Eqs. (32)–(34) serve as three simultaneous equations for the three unknowns T_λ , α_λ , γ_λ in a mixture of given X_3 .

For temperatures above the λ point for a given mixture, we must set all probability parameters equal to zero except x_1 , x_2 , x_{31} , x_{32} , y_1 , y_2 , y_3 , y_{41} , y_{42} , y_{51} , y_{52} , y_{61} , y_{62} , y_{63} , y_{64} , and ζ . Then, of course, many of the Eqs. (3) and many of the 27 equations found by minimizing F in Eq. (21) become trivial identities and another set of solutions can be found for the 16 remaining parameters enumerated above. These solutions are given in terms of γ defined by Eq. (25) and a new parameter r , where r is the positive square root of

$$r^2 = \gamma^2 + 4(c-1)e^{-2\tau_4}. \quad (35)$$

It should be noted that the parameter α used in the equations below the λ point does not enter the equations above λ point although at the λ point itself it is easy to show that

$$\alpha_\lambda = \left[\frac{(\gamma+r)e^{+\tau_4}}{2} \right]_\lambda. \quad (36)$$

Above T_λ the single equation that must be solved for γ is still Eq. (27) but now its component parts have changed. Namely,

The probability parameters above T_λ are then given by

$$\zeta = 0, \quad (39.1)$$

$$x_1 = x_2 = \frac{1}{2}X_3, \quad (39.2)$$

$$x_{31} = \frac{2(c-1)y_{61}e^{-2\tau_4}}{(r-\gamma)}, \quad (39.3)$$

$$x_{32} = y_{61}e^{-2\tau_4}, \quad (39.4)$$

$$y_1 = y_3 = \frac{1}{2}X_3 - \frac{1}{4}y_{61}(\gamma-1)(r+1), \quad (39.5)$$

$$y_2 = \frac{1}{4}(\gamma-1)^2y_{61}, \quad (39.6)$$

$$y_{41} = y_{51} = y_{61}(\gamma-1)/2, \quad (39.7)$$

$$y_{42} = y_{52} = y_{61}z_{62}(\gamma-1)/2, \quad (39.8)$$

$$y_{61} = \frac{e^{2\tau_4}(1-X_3)(r-\gamma)}{2(c-1)+c(r-\gamma)}, \quad (39.9)$$

$$z_{62} = (r-\gamma)/2(c-1), \quad (39.10)$$

$$z_{63} = z_{62}^2, \quad (39.11)$$

$$z_{64} = e^{-2\tau_4}. \quad (39.12)$$

When these results are substituted into Eq. (21) we have an expression for the free energy above T_λ :

$$\begin{aligned} & \left[\frac{F}{NkT} + \frac{\ln Q_0}{N} \right] \\ &= -\frac{1}{\sigma} \int_{-1/2}^{+1/2} \int \int dx dy dz \ln B(\mathbf{k}\mathbf{k})_0 - (c-1)X_3 \ln \left(\frac{X_3}{2} \right) \\ & \quad - (c-1)(1-X_3) \ln x_{31} + c \left[\frac{X_3}{2} - \frac{y_{61}}{4}(\gamma-1)(r+1) \right] \\ & \quad \times \ln \left[\frac{X_3}{2} - \frac{y_{61}}{4}(\gamma-1)(r+1) \right] + c \frac{(\gamma-1)^2}{4} y_{61} \\ & \quad \times \ln \left[\frac{(\gamma-1)^2}{4} y_{61} \right] + \frac{c}{2} y_{61}(\gamma-1)(r+2-\gamma) \ln \frac{(\gamma-1)}{2} \\ & \quad + \frac{c}{8} y_{61} [4e^{-2\tau_4} + r^2 + 2r\gamma + 8\gamma - 3\gamma^2 - 4] \ln y_{61}. \quad (40) \end{aligned}$$

SOLUTION OF THE EQUATIONS

All the necessary equations given in the preceding sections of this paper have been solved numerically by the electronic digital computer, MANIAC II, at the Los Alamos Scientific Laboratory. Certain parameters had first to be selected. From Eq. (8) we see that d^2 , the square of the nearest-neighbor distance enters the calculation. In expressing this we have neglected any volume changes on mixing and set the volume of the

mixture equal to

$$\bar{v}_m = X_3 \bar{v}_3 + X_4 \bar{v}_4, \quad (41)$$

so that

$$d^2 = \frac{p}{\bar{N}^{2/3}} [\bar{v}_4 + X_3(\bar{v}_3 - \bar{v}_4)]^{2/3}, \quad (42)$$

with $p=1.0$ for a simple cubic lattice and $p=\frac{3}{4} \times 2^{2/3} = 1.19055$ for a body-centered cubic lattice and where \bar{v}_j is the molar volume of pure isotope j and \bar{N} is Avogadro's number. We have further chosen characteristic values for the molar volumes of the pure components appropriate to the pressure of their saturated vapors at the λ point of pure He^4 and below and assumed them temperature-independent for simplicity. Our values are

$$\bar{v}_3 = 37.7 \text{ cm}^3 \text{ mole}^{-1}, \quad (43.1)$$

$$\bar{v}_4 = 27.5 \text{ cm}^3 \text{ mole}^{-1}. \quad (43.2)$$

From Eq. (13) we see that

$$\tau_3 = (m_3'/m_4')\tau_4. \quad (44)$$

It is, thus, also necessary to specify m_3' and m_4' . The latter, which is the effective mass of He^4 atoms, is chosen so that the experimental λ point in pure He^4 under its saturated vapor pressure (2.172°K) is obtained in the limit of $X_3=0$. This effective mass is

$$m_4' = (1.648)m_4 \text{ for simple cubic lattice} \quad (45.1)$$

$$= (1.671)m_4 \text{ for body-centered cubic lattice.} \quad (45.2)$$

Two choices were made for m_3' :

$$m_3' = (5.25)m_3, \quad (46.1)$$

$$m_3' = (2.00)m_3. \quad (46.2)$$

Equation (46.1) was found necessary by Kikuchi in II to best fit the nuclear magnetic susceptibility data of Fairbank, Ard, and Walters⁸ in the case of permutation counting in pure He^3 on a simple cubic lattice. Equation (46.2) has been suggested by the specific heat measurements of Brewer, Daunt, and Sreedhar.⁹

The results for the λ temperatures as a function of X_3 , still not considering a possible phase separation, are tabulated in Table I. It is gratifying to note that these temperatures do not essentially depend on the arbitrary permutation lattice chosen nor even on the choice of the He^3 effective mass. These results are more in accord with the experimental results of Zinov'eva and Peshkov¹⁰ than with that of Elliott and Fairbank¹¹ or Roberts and

⁸ W. M. Fairbank, W. B. Ard, and G. K. Walters, *Phys. Rev.* **95**, 566 (1954).

⁹ D. F. Brewer, J. G. Daunt, and A. K. Sreedhar, *Phys. Rev.* **115**, 836 (1959).

¹⁰ K. N. Zinov'eva and V. P. Peshkov, *Zh. Eksperim. i Teor. Fiz.* **37**, 33 (1959) [translation: *Soviet Phys.—JETP* **10**, 22 (1960)].

¹¹ S. D. Elliott, Jr., and H. A. Fairbank, in *Proceedings of the Fifth International Conference on Low-Temperature Physics, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 180.

TABLE I. Theoretical λ temperatures in He³-He⁴ liquid mixtures as function of X_3 neglecting possible phase separation.

Permutation lattice	sc	sc	bcc
m_4'	1.65 m_4	1.65 m_4	1.67 m_4
m_3'	5.25 m_3	2.00 m_3	2.00 m_3
X_3	$T(^{\circ}\text{K})$	$T(^{\circ}\text{K})$	$T(^{\circ}\text{K})$
0.00	2.172	2.172	2.172
0.05	2.099	2.099	2.101
0.10	2.026	2.026	2.030
0.15	1.954	1.954	1.958
0.20	1.880	1.880	1.886
0.25	1.806	1.806	1.813
0.30	1.731	1.731	1.739
0.35	1.655	1.655	1.663
0.40	1.577	1.577	1.585
0.45	1.497	1.497	1.504
0.50	1.415	1.414	1.421
0.55	1.329	1.328	1.334
0.60	1.240	1.239	1.242
0.65	1.147	1.144	1.146
0.70	1.047	1.044	1.044
0.75	0.941	0.937	0.934
0.80	0.824	0.821	0.815
0.85	0.695	0.691	0.684
0.90	0.545	0.543	0.534
0.95	0.359	0.358	0.350
1.00	0.000	0.000	0.000

Sydoriak.¹² Since, however, the first mentioned results are believed to be too high¹³ our theoretical results are certainly too high for $X_3 > 0.5$. A graphic comparison is given in Fig. 3.

The λ line is seen to go to zero only when $X_3=1$. Hecht's¹⁴ prediction that the λ line could go to zero with a finite fraction of He⁴ atoms present is seen to be incorrect since it was based on the limited type of permutation cycles used in I and neglected cycles involving jumps of a long-range nature on the permutation lattice. It is just these long-range cycles that are of importance when the temperature is less than 1°K as shown in III. The situation is analogous to the case of Curie points for dilute ferromagnetic materials for which it is known¹⁵ that only if the interaction is strictly nearest-neighbor can the Curie point vanish with a nonzero mole fraction of ferromagnetic centers.

In order to look for an isotopic phase separation at a fixed temperature, it is necessary to consider the second derivatives with respect to X_3 of G , the Gibbs free energy, which for a condensed phase is essentially equal to F given by Eq. (7). If this second derivative is always positive as X_3 varies from 0 to 1, there is no phase separation. If in part of the range the second

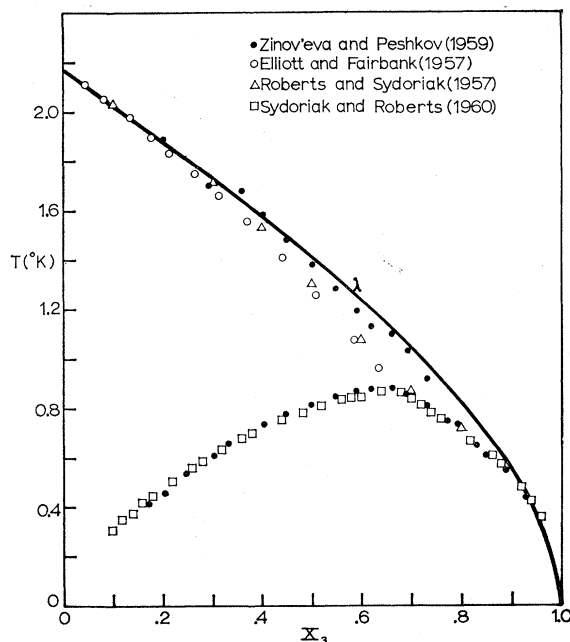


FIG. 3. The theoretical λ line in He³-He⁴ liquid mixtures as function of X_3 for the simple cubic permutation lattice with effective mass ratio $(m_3'/m_4')=2.40$. Various experimental λ temperatures and phase-separation temperatures are also shown.

derivative is negative, a phase separation has occurred and the separated mixtures that are in equilibrium are determined by the two X_3 values outside of the negative second-derivative region for which the first derivatives of G with respect to X_3 are equal, i.e., by the points of a common tangent.¹⁶

Tabulated quantities related to the free energy were produced in terms of the quantity E ,

$$E = \left[\frac{F}{NkT} + \frac{\ln Q_0}{N} \right] - \frac{3}{2} X_3 \ln \frac{m_3'}{m_4'} + X_3 \ln X_3 + X_4 \ln X_4. \quad (47)$$

For one total mole of mixture, using the tilde to indicate molar quantities, identifying F of a condensed phase with G , and using Eq. (2.1), we obtain

$$E = \frac{\tilde{G}}{RT} + \ln \left[\left(\frac{m_4' k T}{2\pi \hbar^2} \right)^{3/2} K \beta^{1/N} \right], \quad (48)$$

where R is the gas constant. At any fixed temperature T as we vary X_3 , we compute E from Eq. (31), as long as X_3 is such that the fixed T is below the λ point of the mixture. When the X_3 is large enough and if our fixed T is below the T_λ of pure He⁴, we will reach a range of X_3 values for which the fixed T is above the λ point of the mixtures and Eq. (40) must be used to compute E .

¹⁶ I. Prigogine and R. Defay, *Chemical Thermodynamics*, translated by D. H. Everett (Longmans Green and Company, London, 1954), Chap. 16.

¹² T. R. Roberts and S. G. Sydoriak, in *Proceedings of the Fifth International Conference on Low-Temperature Physics, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 170.

¹³ T. R. Roberts and S. F. Sydoriak, in *Proceedings of the Second Symposium on Liquid and Solid Helium Three, Columbus, Ohio, 1960*, edited by J. G. Daunt (Ohio State University Press, Columbus, 1960), p. 173.

¹⁴ C. E. Hecht, *Physica* **24**, 584 (1958).

¹⁵ R. Brout, *Phys. Rev.* **115**, 824 (1959).

If we neglect the possible X_3 -dependence of the dynamical quantity K_β in Eq. (48), the second derivative of E with respect to X_3 will be the second derivative of G with respect to X_3 at any constant temperature. Analysis of our results shows clearly that this neglect gives second derivatives which are always positive no matter what the temperature. This indicates no isotopic phase separation due to quantum statistical effects alone and in fact shows that these effects favor an ordered mixture of the isotopic species as the temperature approaches absolute zero, since the molar excess Gibbs function (see below), neglecting the X_3 dependence of K_β , is negative.

ISOTOPIC PHASE SEPARATION CURVE AND EXCESS FUNCTIONS OF MIXING

In view of our result that the quantum statistical effects do *not* lead to isotopic phase separation, we assume the inherent cause of the experimentally observed separation to be due to the difference in zero-point motion of the two isotopes which is empirically manifested by the difference in molar volumes given by Eq. (43). In this we follow the interpretation of Prigogine *et al.*,^{17,18} in principle, but not in detail. It is necessary to make a crude estimate of the functional form of K_β . Without committing ourselves on the complete temperature dependence of K_β , we follow Feynman¹ in assuming K_β proportional to $\exp(-\tilde{U}_0/RT)$, where \tilde{U}_0 is the energy of the system at absolute zero. The dependence of K_β on X_3 may be estimated by expressing \tilde{U}_0 as a sum of nearest neighbor pair energies on a formal space lattice (not to be confused with the formal lattice used earlier for counting permutations). The result is

$$\tilde{U}_0 = \frac{1}{2} \tilde{N} z \{ (1-X_3)\epsilon_{44} + W(0)y_{34} + X_3\epsilon_{33} \}, \quad (49)$$

where

$$W(0) = [2\epsilon_{34} - \epsilon_{33} - \epsilon_{44}], \quad (50)$$

z is the number of nearest neighbors, and y_{34} is the probability of a He³-He⁴ pair. Effective pair potentials ϵ_{ij} have been introduced because of the different molar volumes of the pure components and of the mixtures as determined by Eqs. (41) and (43). This part of our theory is clearly semiphenomenological. We proceed as if we had no phase separation until we note in a certain region of the T - X_3 plane that we obtain unphysical results, i.e., $(\partial^2 G / \partial X_3^2)_T$ less than zero and then conclude that a phase separation has occurred. Hence, as the simplest approximation we can assume that the distribution of the isotopic species prior to phase separation is completely random. This means making a Bragg-Williams approximation for y_{34} such that

$$y_{34} = X_3(1-X_3) \quad (51)$$

¹⁷ I. Prigogine, R. Bingen, and A. Bellemans, *Physica* **20**, 633 (1954).

¹⁸ I. Prigogine, *Molecular Theory of Solutions* (North-Holland Publishing Company, Amsterdam, 1957), Chap. 19.

and yields

$$K_\beta \propto \exp(-c_1 X_3/T) \exp(c_2 X_3^2/T), \quad (52)$$

where

$$c_1 = z(\epsilon_{34} - \epsilon_{44})/k, \quad (53.1)$$

$$c_2 = zW(0)/2k, \quad (53.2)$$

and k is Boltzmann's constant. Furthermore, using a Lennard-Jones form for the ϵ_{ij} and the helium parameters¹⁹

$$(\epsilon/k) = 10.22^\circ\text{K}, \quad \tilde{N}\sigma^3 = 10.06 \text{ cm}^3/\text{mole}, \quad (54)$$

the lattice energy per like pair is

$$\epsilon_{ii} = 4\epsilon \left[\frac{1}{\gamma^4 (v_i^*)^4} - \frac{1}{\gamma^2 (v_i^*)^2} \right], \quad (55)$$

with

$$v_i^* = v_i / \tilde{N}\sigma^3 \quad (56.1)$$

and

$$\gamma = v/a^3, \quad (56.2)$$

where v is the volume per atom and a is the nearest neighbor distance on the space lattice. The average pair energy in a random mixture may be denoted by ϵ_{X_3} , where

$$\begin{aligned} \epsilon_{X_3} &= 4\epsilon \left[\frac{1}{\gamma^4 (v_m^*)^4} - \frac{1}{\gamma^2 (v_m^*)^2} \right] \\ &= 2X_3(1-X_3)\epsilon_{34} + X_3^2\epsilon_{33} + (1-X_3)^2\epsilon_{44}. \end{aligned} \quad (57)$$

From Eq. (57) ϵ_{34} and, thus, $W(0)$ and, thus, c_2 can be estimated for any simple space lattice. There is some ambiguity in this estimate depending on the X_3 value chosen and, hence, the average of the limits as $X_3 \rightarrow 0$ and as $X_3 \rightarrow 1$ was chosen as the appropriate value. The results for cubic space lattices are

$$\text{fcc} \quad c_2 = 3.1^\circ\text{K}, \quad (58.1)$$

$$\text{sc} \quad c_2 = 2.4^\circ\text{K}, \quad (58.2)$$

$$\text{bcc} \quad c_2 = 2.3^\circ\text{K}. \quad (58.3)$$

Equations (48) and (52) lead to

$$\left(\frac{\partial^2 (\tilde{G}/RT)}{\partial X_3^2} \right)_T = \left(\frac{\partial^2 E}{\partial X_3^2} \right)_T - \frac{2c_2}{T}, \quad (59)$$

so that with c_2 positive phase separation is possible if T is low enough, even though the first term on the right of Eq. (59) is always positive. It is of interest to write down an expression for the molar excess Gibbs function of mixing. This is defined as

$$\frac{\tilde{G}^E}{RT} = \frac{\tilde{G}}RT - X_3 \ln X_3 - X_4 \ln X_4 - X_3 \frac{\tilde{G}_3^0}{RT} - X_4 \frac{\tilde{G}_4^0}{RT}, \quad (60)$$

¹⁹ J. de Boer, in *Progress in Low-Temperature Physics II*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Chap. 1.

TABLE II. Theoretical critical He³ mole fractions X_{3c} and critical temperatures T_c for isotopic phase separation as function of permutation and space lattice model combinations.

Permutation lattice	sc		sc		bcc	
	T_c	X_{3c}	T_c	X_{3c}	T_c	X_{3c}
Effective mass ratio	2.40		0.914		0.902	
Space lattice						
fcc	1.3	0.57	1.2	0.56	1.2	0.56
sc or bcc	1.0	0.57	0.9	0.56	1.0	0.56

where \tilde{G}_i^0 is the molar Gibbs function of pure species i . From our previous expressions we have

$$\left(\frac{\tilde{G}^E}{RT}\right) = \left(\frac{\tilde{G}^E}{RT}\right)' + \frac{c_2}{T} X_3(1-X_3), \quad (61)$$

where

$$\left(\frac{\tilde{G}^E}{RT}\right)' \equiv E - X_3 \ln X_3 - X_4 \ln X_4 - X_3 E_3 - X_4 E_4 \quad (62)$$

and

$$E_3 = \lim_{X_3 \rightarrow 1} (E), \quad (63.1)$$

$$E_4 = \lim_{X_3 \rightarrow 0} (E). \quad (63.2)$$

The primed quantity arises from the quantum statistical effects and is always negative. We note that assuming the proportionality in Eq. (52) we can obtain \tilde{G}^E without any ambiguity from Eq. (61) since the natural logarithm of the unknown proportionality function which may depend on T is cancelled in the subtractions of Eq. (62). The molar excess entropy of mixing is given by

$$\tilde{S}^E = - \left(\frac{\partial \tilde{G}^E}{\partial T} \right)_{P, X_3} \quad (64.1)$$

or

$$\begin{aligned} \frac{\tilde{S}^E}{R} = & -T \left(\frac{\partial E}{\partial T} \right)_{P, X_3} + X_3 T \left(\frac{\partial E_3}{\partial T} \right)_P \\ & + (1-X_3) T \left(\frac{\partial E_4}{\partial T} \right)_P - \left(\frac{\tilde{G}^E}{RT} \right)', \end{aligned} \quad (64.2)$$

and the molar excess enthalpy of mixing is obtained from

$$\tilde{H}^E = \tilde{G}^E + T\tilde{S}^E. \quad (65)$$

A numerical analysis of the results of the machine calculation for the E function of Eq. (47) using the methods of Ref. 16 was carried out to obtain critical He³ mole fractions X_{3c} and temperatures T_c . The experimental results for phase separation, based on the work of Zinov'eva and Peshkov¹⁰ and Sydoriak and Roberts²⁰ and also shown in Fig. 3, show a critical point of 0.88°K at $X_{3c}=0.64$. Our results are given in

²⁰ S. G. Sydoriak and T. R. Roberts, Phys. Rev. 118, 901 (1960).

 TABLE III. Comparison of experimental results with rough theoretical X_3 values for coexisting liquid phases below T_c using a simple cubic permutation lattice with effective mass ratio $(m_3'/m_4')=0.914$ and a body-centered cubic space lattice.

T (°K)	Coexisting X_3 values	
	Theory	Experiment
0.8	0.40-0.80	0.472-0.740
0.7	0.30-0.88	0.365-0.805
0.6	...	0.290-0.860

Table II and depend on which combination of permutation and space lattices were chosen for the calculations. We cannot really differentiate between use of an sc or a bcc space lattice since their c_2 values from Eq. (58) are so close. The fcc space lattice leads to T_c values that are too high. Perhaps this is connected with the fact that the eight nearest neighbors on a bcc lattice are more in accord with the actual spatial arrangements in liquid helium as revealed by neutron scattering work,²¹ which indicate that on the average there are 8.5 nearest neighbors, than are the twelve nearest neighbors on a fcc lattice. It is satisfying to note that our calculations predict an asymmetric phase separation curve and in the right direction ($X_{3c} > \frac{1}{2}$). This asymmetric effect arises in these calculations only from the quantum statistical terms but this is probably an artifact of our crude treatment of the dynamical terms and as we shall see below a better treatment of these dynamical terms is certainly required to arrive at correct excess entropies of mixing. In the Prigogine¹⁸ theory of isotopic mixtures, which neglects the effects of quantum statistics, the simplest expression for the excess Gibbs function [Eq. (19.3.7) of Ref. 18] leads to an asymmetrical phase separation but shifted to the wrong side, i.e., $X_{3c} < \frac{1}{2}$. This result of the Prigogine theory has only become calculable since the publication of compressibility data^{22,23} on the pure isotopes.

It is extremely difficult to estimate numerically by the method of common tangents the X_3 values for the two liquid mixtures that are in equilibrium at any given T below T_c . Hence, we shall not attempt to plot a theoretical phase-separation curve. We were premature in doing so in our report to the Toronto Conference²⁴ and, in fact, the E values on which that phase separation curve was based have since been revised. Taking the case of sc permutation lattice with effective mass ratio,^{24a} $(m_3'/m_4')=0.914$ and bcc space lattice for which the T_c is 0.9°K, we compare in Table III some rough estimates

²¹ D. G. Hurst and D. G. Henshaw, Phys. Rev. 91, 1222 (1953); 100, 994 (1955).

²² H. L. Laquer, S. G. Sydoriak, and T. R. Roberts, Phys. Rev. 113, 417 (1959).

²³ R. H. Sherman and F. J. Edeskuty, Ann. Phys. (N. Y.) 9, 522 (1960).

²⁴ C. E. Hecht, R. Kukuchi, and P. R. Stein, in *Proceedings of the Seventh International Conference on Low-Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (The University of Toronto Press, Toronto, 1961), p. 637.

^{24a} Note added in proof. This mass ratio corresponds to $m_3' = 2.00 m_3$ in (46.2) together with m_4' in (45).

of the coexisting X_3 values with the experimental results. Both our calculations and the experimental results show that the phase separation line for He^3 -rich mixtures approaches the temperature axis, as $T \rightarrow 0$, more rapidly than does the line for He^4 -rich mixtures. This is in qualitative accord with the deductions drawn by Edwards and Daunt²⁵ from the theories of Zharkov and Silin²⁶ and Pomeranchuk.²⁷ In fact, the former theory indicates that the phase separation line for He^3 -rich mixtures is asymptotic to the temperature axis as $T \rightarrow 0$, while the latter indicates the possibility of the phase separation line for He^4 -rich mixtures not passing through the origin of the phase diagram thus leading to a stable isotopic mixture at the absolute zero. Our numerical results are not extensive enough to enable us to draw conclusions about an asymptotic approach to the temperature axis on the He^3 -rich side but from Eq. (59) the second derivatives of the molar Gibbs function at fixed T tends to minus infinity as $T \rightarrow 0$ and this means phase separation. Intuitively we would expect from the Third Law of Thermodynamics that this phase separation would be into two pure phases at the absolute zero. However, on a purely phenomenological basis the suggestion of De Bruyn Ouboter and Beenakker²⁸ that the excess entropy of mixing due to nonideal effects could tend to $R[X_3 \ln X_3 + (1-X_3)\ln(1-X_3)]$ (negative) at the absolute zero such that the total entropy of mixing still goes to zero would also be in accord with the Third Law.

Turning to the excess functions of mixing we can compare our calculated results with the values derived by Taconis *et al.*²⁹ from an extensive series of specific heat and vapor pressure measurements. Experimentally the molar excess enthalpy of mixing \bar{H}^E is always positive and increases with increase of temperature. The molar excess entropy of mixing \bar{S}^E is much more complicated being positive always above 1.5°K but negative in the He^4 -rich mixtures at temperatures less than 1.5°K and finally being everywhere negative for temperatures less than 1°K. The molar excess Gibbs function is found always to be positive but measurements have not extended above 1.7°K. Theoretically our excess Gibbs functions are not positive enough and in fact are negative above 1°K if we use the bcc space lattice. They become positive in 'time' to effect the phase separation predicted in Table II. The theoretical \bar{S}^E values are always much too positive and never negative and thus finally the theoretical \bar{H}^E values are much too positive. We should recall that we have neglected any volume change on mixing whereas experi-

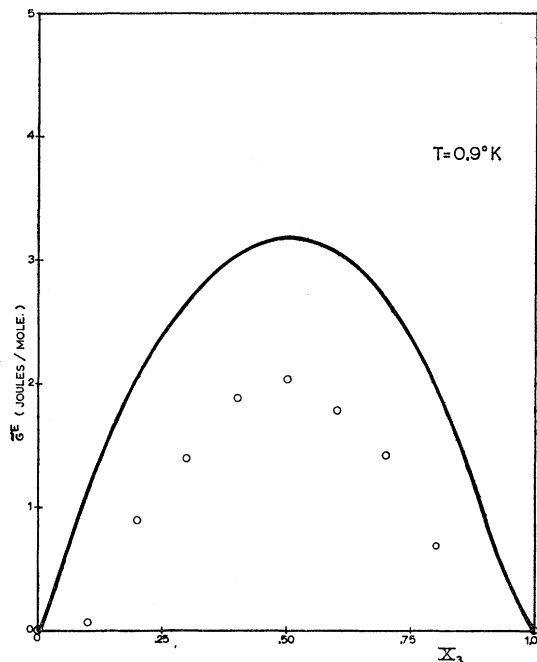


FIG. 4. Excess Gibbs free energies of mixing in He^3 - He^4 liquid mixtures at 0.9°K from theory (circles) and experiment (solid curve) using model combination of a simple cubic permutation lattice with effective mass ratio $(m_3^*/m_4^*)=0.914$ and a simple cubic- or body-centered cubic space lattice.

mentally³⁰ the excess volumes are negative and increasing in absolute magnitude with increase of temperature. This neglect could tend to make our \bar{S}^E values too positive. Nevertheless, it is clear that our theory cannot give a correct description of the behavior of \bar{S}^E which depends so sensitively on the details of both statistical and dynamical effects. It should be noted that from Eq. (64.2) our calculated \bar{S}^E depends only on the statistical effects since our simple way of treating the dynamical effects adds in a regular solution term in the expression for the excess Gibbs function and the excess entropy of mixing for regular solutions is zero.

We have chosen to display our theoretical results for the model combination of sc permutation lattice with effective mass ratio 0.914 and bcc or sc space lattice. The results are not qualitatively different for other model combinations. For fixed temperature of 0.9°K we give in Fig. 4 the experimental \bar{G}^E curve and various calculated points while in Fig. 5 we give the experimental \bar{S}^E curve and various calculated points.

SUMMARY

In this paper the fruitful Feynman treatment of the statistical thermodynamic properties of a system of interacting bosons has been extended to treat semi-

²⁵ D. O. Edwards and J. G. Daunt, *Phys. Rev.* **124**, 640 (1961).

²⁶ V. N. Zharkov and V. P. Silin, *Zh. Eksperim. i Teor. Fiz.* **37**, 143 (1959) [translation: *Soviet Phys.—JETP* **10**, 102 (1960)].

²⁷ I. J. Pomeranchuk, *Zh. Eksperim. i Teor. Fiz.* **19**, 42 (1949).

²⁸ R. De Bruyn Ouboter and J. J. M. Beenakker, *Physica* **27**, 219 (1961).

²⁹ R. De Bruyn Ouboter, K. W. Taconis, C. Le Pair, and J. J. M. Beenakker, *Physica* **26**, 853 (1960).

³⁰ E. C. Kerr, in *Proceedings of the Fifth International Conference on Low-Temperature Physics*, edited by J. R. Dillinger (The University of Wisconsin Press, Madison, 1958), p. 158.

phenomenologically a system of interacting bosons and fermions. This has been applied to liquid He³-He⁴ mixtures and the λ transition characteristic of a cooperative interaction between bosons has been seen to persist in these mixtures as long as any He⁴ atoms are present. The λ line follows the experimental results closely up to $X_3=0.5$ irrespective of the effective mass of the He³ atoms while above $X_3=0.5$ the theoretical λ temperatures are too high. An asymmetric phase separation has been predicted in these mixtures below 0.9°K and the phase-separation curve is estimated to run outside the λ line at sufficiently high He³ concentrations ($X_3>0.85$) so that in this region the experimental λ line will appear to coincide with the phase-separation curve. Experimentally²⁹ this apparent coincidence of λ line and phase-separation curve occurs for $X_3>0.73$.

We have not attempted to calculate the heat capacities of the mixtures and so cannot directly say what our models predict for the nature of the mixture heat capacity at the mixture λ temperature. From the theoretical results in III for pure He⁴, however, we expect that our theory gives a second-order transition at the mixture λ temperatures. Taconis *et al.*²⁹ suggest that the experimental transition in the mixtures may be strictly second-order whereas experiment on pure He⁴ indicates³¹ a transition of a more complicated nature, i.e., a second-order transition combined with a logarithmic singularity in the heat capacity.

Chester³² first pointed out that the quantum dynamical or "diffraction" effects and the statistical effects might be considered as two competing mechanisms in settling the properties of He³-He⁴ liquid mixtures. As a result of the present work we may cite two points supporting this concept. First, the statistical effects alone do not lead to isotopic phase separation but the dynamical effects alone would do so. This has received independent experimental verification from the work of Edwards *et al.*³³ who report isotopic phase separation in *solid* mixtures of He³-He⁴ at pressures in excess of

³¹ M. J. Buckingham and W. M. Fairbank, in *Progress in Low-Temperature Physics* III, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), p. 80.

³² G. V. Chester, in *Proceedings of the Second Symposium on Liquid and Solid Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, 1957), p. 170.

³³ D. O. Edwards, A. S. McWilliams, and J. G. Daunt, *Phys. Rev. Letters* **9**, 195 (1962).

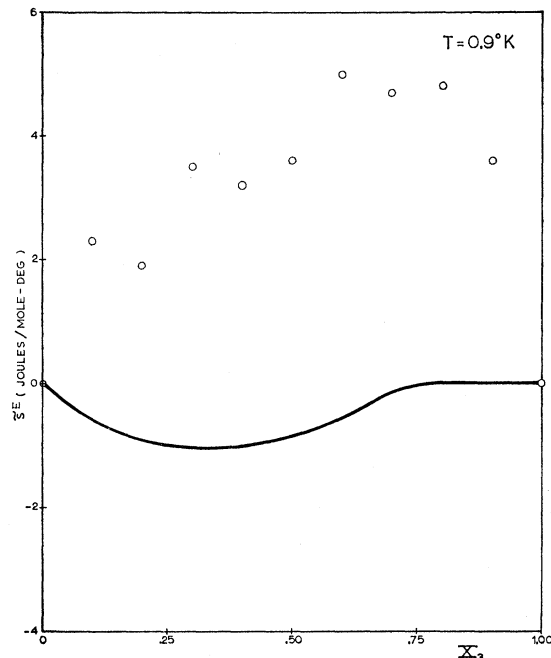


FIG. 5. Excess entropies of mixing in He³-He⁴ liquid mixtures at 0.9°K from theory (circles) and experiment. Conventions as in Fig. 4.

30 atm. In such solid mixtures the atoms are localized and should obey Boltzmann statistics and not exhibit nonideal behavior due to statistical effects. Secondly, the excess entropy at 0.9°K as calculated by our theory depends only on the statistical effects and is much too positive while the excess entropy at 1.4°K as calculated with the neglect of statistical effects from the theory of Prigogine by Simon and Bellemans³⁴ is much too negative. It does not, however, seem that the statistical effects should dominate at lowest temperatures.

ACKNOWLEDGMENTS

The authors wish to thank Mrs. D. Williamson and Miss R. Huitt of the Los Alamos Scientific Laboratory for their work in programming and carrying out the calculations on MANIAC II.

³⁴ M. Simon and A. Bellemans, *Physica* **26**, 191 (1960).