

FURTHER CONSIDERATIONS REGARDING He³-He⁴ MIXTURES

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1. INTRODUCTION

In a recent paper (Bhagat and Katti, 1955) (henceforth referred to as I) we have developed the thermodynamic properties of a model mixture of a Bose-Einstein and a Fermi-Dirac 'liquid'. The basic assumptions for this model are: (a) the mixture is treated as a quasi-gaseous assembly of particles formed by one sub-assembly of particles obeying Bose and another statistically independent sub-assembly obeying Fermi statistics; (b) the particles in either sub-assembly are envisaged as moving in constant potential wells, say $-\chi_F^0$ and $-\chi_B^0$; (c) the liquids are treated as being incompressible. In other words, the total volume of a mixture of N_F Fermi and N_B Bose particles is written as:

$$V = N_F V_F^0 + N_B V_B^0 \quad \dots \quad (1)$$

where the subscripts F and B refer to the Fermi and the Bose particles, respectively, and V_F^0 , V_B^0 represent the respective atomic volumes; (d) the one-particle energy-momentum spectrum is taken in the form:

$$\epsilon(p) = Bp^n, \quad \dots \quad (2)$$

where B and n are constants. In particular, this would reduce to the ideal-gas expression (the case discussed earlier by Heer and Daunt, 1951) when $n = 2$ and $B = \frac{1}{2}m$. Next, an integration in phase space involves an integration over the three components of momentum and the volume element in momentum space is of the form $p^2 dp \sin \theta d\theta d\phi$. It is evident, therefore, that if we transform to the energy variable and take account of assumption (b), expression (2) leads to distribution functions of the form

$$N(\epsilon)d\epsilon = \frac{N V^0 C \epsilon^{s-1} d\epsilon}{A \exp\left(\frac{\epsilon - \chi^0}{kT}\right) \pm 1}, \quad \dots \quad (3)$$

with negative sign for the Bose and positive sign for the Fermi particles. Also, $s = \frac{3}{n}$, C is a constant (closely related to B) and A is the well-known degeneracy parameter.

Again, it may be noted that the introduction of an energy-momentum relation of the form (2) implies that we are considering that each particle of the sub-assembly is moving in a self-consistent field formed by its neighbours. Since the sub-assemblies are being treated as statistically independent, in the mixture, this self-consistent field must be interpreted as arising from particles belonging to the same sub-assembly. In other words, we assume that the process of mixing does not entail any alteration in the energy-momentum relation. In this connection it is of interest to note that Dingle (1952) has pointed out that the introduction of such an energy

spectrum leads to a considerable improvement in the theory based on the Bose-Einstein, that is, the London (1938), approach to pure liquid He⁴.

Further, it was shown in I that some of the observed properties of the solutions of liquid He³ in He⁴ agree rather well with those obtained theoretically for the mixture in case (i)—liq. F (liquid He³) Boltzmannian—in the ideal-gas approximation (cf. Secs. 4 and 8, Ref. I). Now, it is well known that the specific heat of pure liquid He⁴ (below the λ -temperature) shows a T^6 dependence (at least above 1.6°K.), and also that the density of the normal component varies as T^{-6} . Such a temperature dependence would be obtained theoretically if we take the distribution function for liquid He⁴ in the form (3) (negative sign), with $s = 6$. Consequently, in I we carried out calculations for some of the properties of He³-He⁴ mixtures taking $s = 6$ for liquid He⁴ and treating liquid He³ as an ideal Boltzmannian gas. Unfortunately, as will be shown more explicitly in the following section, the calculations were performed erroneously and thus led to a discontinuity in the total vapour pressure of the mixture at its transition-temperature. In this paper we present some of the results of the recalculation for the vapour pressures. It is interesting to note that the theory gives remarkable agreement with experiment, especially for low concentrations. Further, we notice that the present theory, in agreement with the purely thermodynamic argument of de Boer and Gorter (1952), leads to discontinuities, at the λ -line, in the partial vapour pressure of liquid He³ (as a function of temperature) and the total pressure of the mixture (as a function of liquid He³ concentration). This fact is also borne out rather well by experiment, as pointed out by Mikura (1954).

2. THE VAPOUR PRESSURES

In order to calculate the total vapour pressure of a solution of liquid He³ in He⁴ as a function of temperature we refer to the relations (17), (18), (28) and (29) of I.* Replacing the subscripts F and B used in I by 3 and 4 (corresponding to liquid He³ and liquid He⁴, respectively) and putting $s_4 = 6$, $s_3 = 3/2$ we have (i) below the transition-temperature of the mixture:

$$\frac{p_3}{p_3^0} = X_3' \exp \left[-\frac{V_3^0}{V_4^0} \frac{\zeta(7)}{\zeta(6)} X_4' \left(\frac{T}{T_\lambda} \right)^6 + X_4' \right], \quad \dots \dots (4)$$

$$\frac{p_4}{p_4^0} = \exp \left[-\frac{V_4^0}{V_3^0} X_3' \right], \quad \dots \dots (5)$$

and (ii) above the transition-temperature of the mixture:

$$\frac{p_3}{p_3^0} = X_3' \exp \left[\left(1 - \frac{V_3^0}{V_4^0} \right) X_4' + X_4' \frac{V_3^0}{V_4^0} \left\{ b_2 \zeta(6) \left(\frac{T_\lambda}{T} \right)^6 + b_3 [\zeta(6)]^2 \left(\frac{T_\lambda}{T} \right)^{12} + \dots \right\} \right], \quad \dots \dots (6)$$

$$\frac{p_4}{p_4^0} = X_4' \exp \left[\left(1 - \frac{V_4^0}{V_3^0} \right) X_3' - b_2 \zeta(6) \left(1 + X_3' - \frac{1}{X_4'} \right) \left(\frac{T_\lambda}{T} \right)^6 - \frac{b_3}{2} [\zeta(6)]^2 \left(1 + 2X_3' - \frac{1}{(X_4')^2} \right) \left(\frac{T_\lambda}{T} \right)^{12} - \dots \right], \quad (7)$$

* It is useful to recall that these expressions have been derived under the assumption that the vapours may be treated as perfect gases.

where

$$X'_3 = 1 - X'_4 = \frac{N_3 V_4^0}{N_3 V_3^0 + N_4 V_4^0}, \quad b_2 = \frac{1}{27}, \quad b_3 = \frac{2}{37} - \frac{1}{48}$$

and ζ denotes the Riemann zeta function. Also, T_λ denotes the transition-temperature of the mixture; which is related to that of pure liquid He⁴ (say T_λ^0) by the expression (theoretical) (cf. Eq. (9), Ref. I)

$$\frac{T_\lambda}{T_\lambda^0} = (X'_4)^{1/6} \quad \dots \quad (8)$$

Now, while calculating the total vapour pressure for a 20 per cent solution of liquid He³ in He⁴ in I we used Eq. (4) in form

$$\frac{p_3}{p_3^0} = X'_3 \exp \left[- \frac{V_3^0}{V_4^0} \frac{\zeta(7)}{\zeta(6)} \left(\frac{T}{T_\lambda^0} \right)^6 + X'_4 \right], \quad \dots \quad (4')$$

that is, the first term in the exponential in Eq. (4) was transformed using (8). No such replacement was, however, made in Eqs. (6) and (7) where for T_λ we used

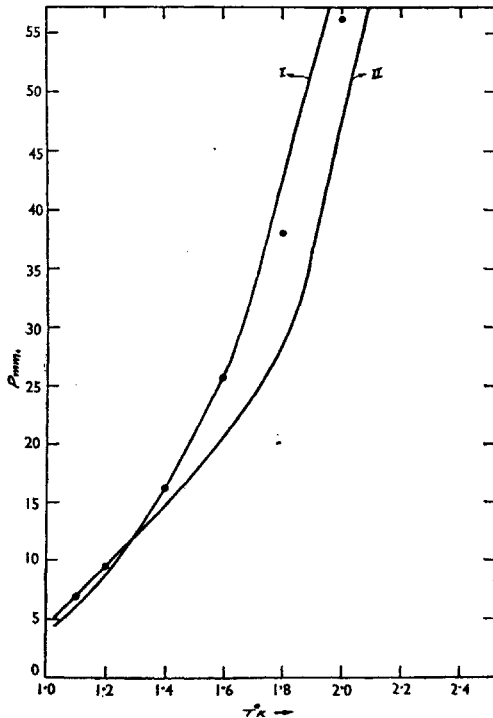


FIG. 1(a). Recalculated plots of the total vapour pressure for a 20 per cent He³-He⁴ solution (cf. Fig. 2, Bhagat and Katti, 1955).
 Curve I: $s_4 = \frac{3}{2}$ (Heer and Daunt, 1955).
 Curve II: $s_4 = 6$.
 Experimental data (dark circles) of Weinstock *et al.* (1950) are for a 20.3 per cent solution.

the observed value (Abraham *et al.*, 1949) 1.63°K. Subsequently, we realised that this replacement is hardly justifiable since the expression (8), with $T_\lambda^0 = 2.186^\circ\text{K.}$, would give $T_\lambda \approx 1.9^\circ\text{K.}$, which is far from being in agreement with experiment. Consequently, it was decided that, pending the development of a more correct expression for the transition-temperature of the mixture within the framework of the present theory, we should substitute for T_λ the values observed experimentally (Abraham *et al.*, 1949; Eselson *et al.*, 1950). We have carried out subsequent calculations with this assumption.

For the saturated pressures p_3^0 and p_4^0 we have used the observed values due to Abraham, Osborne and Weinstock (1950). For $N_0V_3^0$ and $N_0V_4^0$ (where N_0 is the Avogadro number, 6.02×10^{23}) we have used the molar volumes 37.6 c.c. and 27.6 c.c. referring to the absolute zero of temperature. The results* of calculation for a 20 per cent, 10 per cent, 5 per cent and 1 per cent solution of liquid He³ in He⁴ have been presented in Figs. 1(a), 1(b), 1(c) and 1(d), respectively. For the sake of comparison we have included also the observed pressures due to Weinstock, Osborne and Abraham (1950) for the 20 per cent and due to Sommers (1952) for the other concentrations. The agreement is rather close, especially for low

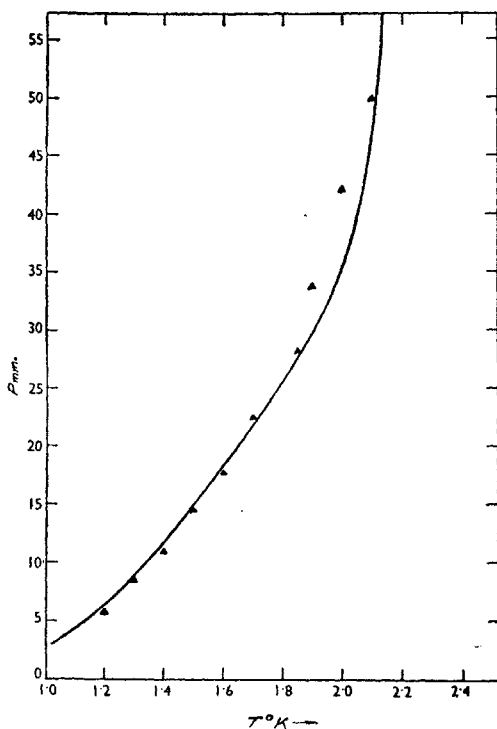


Fig. 1(b). Computed vapour pressure for a 10 per cent solution. The triangles represent Sommers' (1952) smoothed data.

* The values of T_λ employed are 1.63°K., 1.92°K., 2.00°K., and 2.18°K. for the 20, 10, 5 and 1 per cent solutions respectively. It may, however, be noted here that the calculated value of the total pressure is quite insensitive to the exact value of the λ -temperature and therefore one should not expect any significant changes in the calculated vapour pressure curve if subsequent experiments give somewhat different values for the λ -temperatures of these solutions.

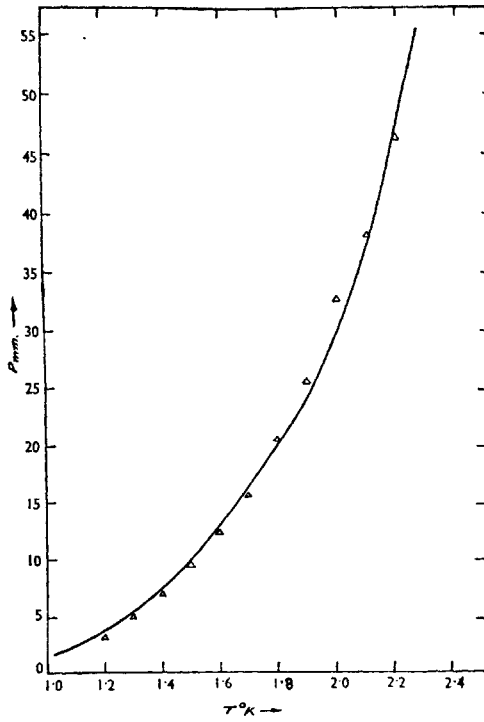


FIG. 1(c). Computed vapour pressure for a 5 per cent solution. The triangles represent Sommers' (1952) smoothed data.

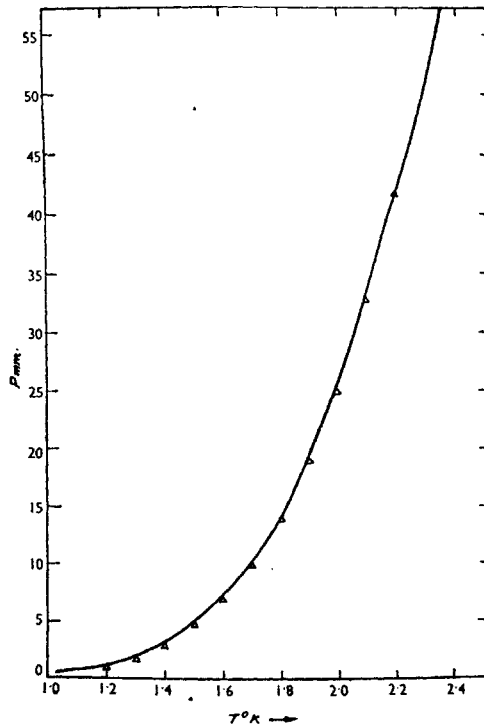


FIG. 1(d). Computed values of the vapour pressure for a 1 per cent solution. The triangles represent Sommers' (1952) smoothed data.

concentrations. As we shall see in somewhat greater detail in Sec. 5 the present theory should not be expected to apply accurately for high concentrations and therefore the discrepancy is hardly surprising.

3. THE DISTRIBUTION COEFFICIENT

The experimental study of the solutions of liquid He³ in He⁴ has involved many measurements of the so-called distribution coefficient, that is, the ratio of the relative concentration, $X_V = N_3^V/N_4^V$ of He³ in the saturated vapour phase to the relative concentration $X_L = N_3^L/N_4^L$ of He³ in the liquid phase. In I we presented the results of calculation of the distribution coefficient for solutions with very low He³ concentration. However, as was also pointed out there, the experimental measurements are subject to excessive scatter and therefore nothing decisive could be stated regarding the applicability of the theory. However, the detailed measurements carried out by Sommers (1952) for more concentrated solutions are fairly reliable and therefore the calculation of the distribution coefficient and its comparison with experiment seems to be of interest.

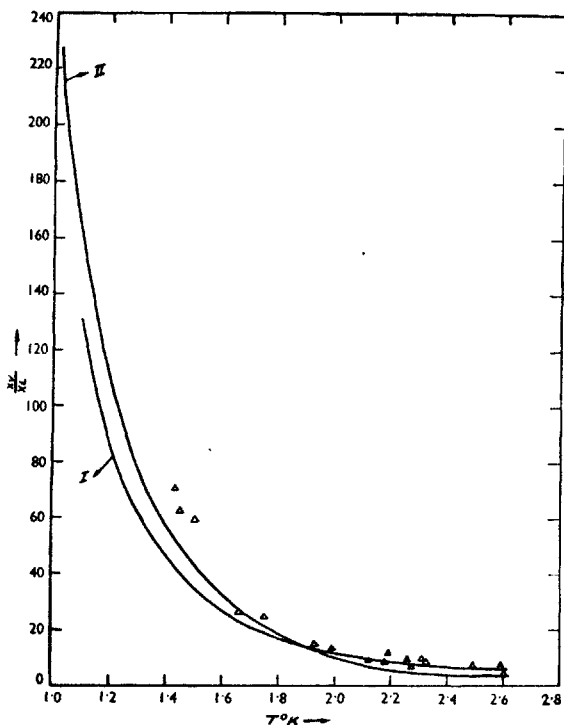


Fig. 2(a). $\frac{X_V}{X_L}$ as a function of temperature for a 1 per cent solution.

Curve I: Theory of Heer and Daunt (1951).

Curve II: Present theory.

Triangles: Observations of Daunt (1952).

Recalling that the vapours are being treated as perfect gases we have:

(i) below the transition-temperature of the mixture:

$$\frac{X_V}{X_L} = \frac{p_3^0}{p_4^0} \cdot X'_4 \frac{V_3^0}{V_4^0} \exp \left[-\frac{V_3^0 \zeta(7)}{V_4^0 \zeta(6)} X'_4 \left(\frac{T}{T_\lambda} \right)^6 + X'_4 + X'_3 \frac{V_4^0}{V_3^0} \right], \quad \dots \quad (9)$$

and (ii) above the transition-temperature of the mixture:

$$\begin{aligned} \frac{X_V}{X_L} = & \frac{p_3^0}{p_4^0} \cdot \frac{V_3^0}{V_4^0} \exp \left[(X'_4 - X'_3) - \left(X'_4 \frac{V_3^0}{V_4^0} - X'_3 \frac{V_4^0}{V_3^0} \right) + \right. \\ & + \left(1 + X'_3 - \frac{1}{X'_4} + X'_4 \frac{V_3^0}{V_4^0} \right) b_2 \zeta(6) \left(\frac{T}{T_\lambda} \right)^6 + \\ & \left. + \left(1 + 2X'_3 - \frac{1}{(X'_4)^2} + 2X'_4 \frac{V_3^0}{V_4^0} \right) \frac{b_3 [\zeta(6)]^2}{2} \left(\frac{T}{T_\lambda} \right)^{12} + \dots \right]. \quad \dots \quad (10) \end{aligned}$$

The solution concentrations chosen for calculation were 1 per cent, 5 per cent and 10 per cent. Our computations, from Eqs. (9) and (10), as well as the observed

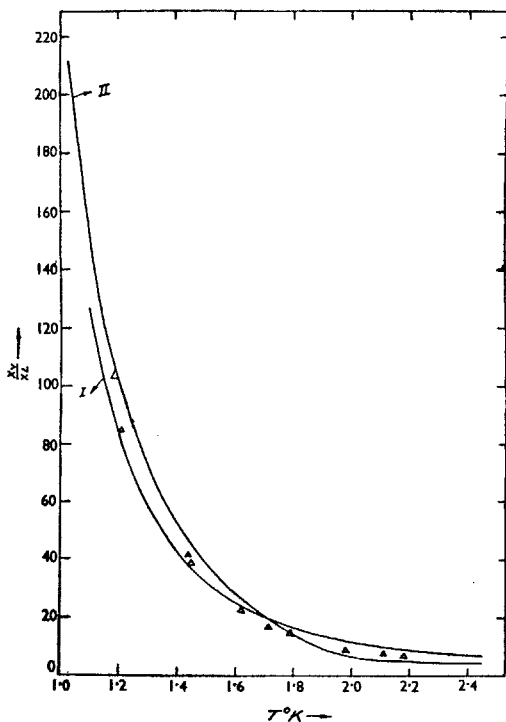


Fig. 2(b). $\frac{X_V}{X_L}$ as a function of temperature for a 5 per cent solution.

Curve I: Theory of Heer and Daunt (1951) (see Daunt, Tseng and Heer, 1952).

Curve II: Present theory.

Triangles: Observations of Sommers (1952) for a 5.21 per cent solution.

values (Sommers, 1952; Daunt, 1952) are shown in Figs. 2(a), 2(b) and 2(c), respectively. Sommers' (1952) data are for solutions of concentrations 5.50 per cent and 9.49 per cent. For the 1 per cent solution the data are taken from Daunt (1952). Further, for the sake of comparison we have given in Figs. 2(a), 2(b) and 2(c) the

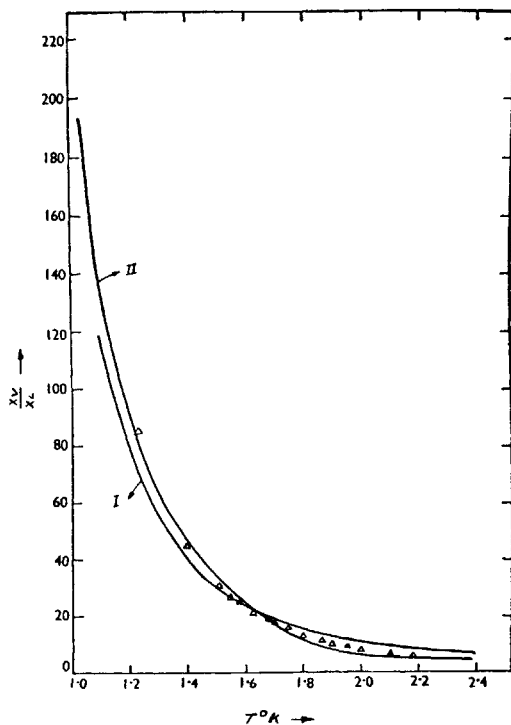


FIG. 2(c). $\frac{X_V}{X_L}$ as a function of temperature for a 10 per cent solution.

Curve I: Theory of Heer and Daunt (1951) (see Daunt, Tseng and Heer, 1952).

Curve II: Present theory.

Triangles: Observations of Sommers (1952) for a 9.49 per cent solution.

results computed by Daunt, Tseng and Heer (1952) for the ideal-gas approximation, $s = 3/2^*$. It is useful to notice that the present theory gives results which are appreciably different from those of the Heer-Daunt theory (1951) (ideal-gas approximation) in the low-temperature region. Hence, further experiments in this region of temperatures would be of great interest.

* It may be noted here that our definition of the distribution coefficient is somewhat different from that of Daunt, Tseng and Heer (1952). They take $C_V = p_3/(p_3 + p_4)$ and $C_L = N_3/(N_3 + N_4)$ so that we may express our X_V/X_L in terms of their C_V/C_L as:

$$\frac{X_V}{X_L} = \frac{C_V}{C_L} \cdot \frac{1 - C_V}{1 - C_L}.$$

4. PARTIAL VAPOUR PRESSURE OF He³ AS A FUNCTION OF TEMPERATURE

In 1952, de Boer and Gorter (1952) pointed out some interesting features regarding the discontinuities, in various thermodynamic functions attendant upon the transition of a solution of liquid He³ in He⁴ through the lambda-temperature. For instance, they showed that if the transition is regarded as a transition of the second order (that is, second derivatives of free energy discontinuous, but first derivatives continuous), then it follows, from purely thermodynamic considerations, that the temperature derivatives of the partial pressures would show discontinuities at the λ -line. On the basis of these results, which do not depend on the choice of any particular model, de Boer and Gorter (1952) criticised the theory of Heer and Daunt (1951). It seems, therefore, interesting to investigate how far the present theory gives results in agreement with these predictions, especially when it is recalled that Ziro Mikura (1954) has recently reported that his theory gives results which are in accord with these thermodynamic considerations.

Before we present the results of calculations it seems to be of interest to note that Mikura (1954) has evaluated, from the total vapour pressure data (Sommers, 1952), the values of the partial pressure of liquid He³ and has shown that the p_3 vs. T plots clearly show breaks, especially for relatively high concentrations, 9.49, 13.0, 20.3 and 25.5 per cent. On the other hand, no breaks are found in the partial pressure curves for the more dilute solutions.

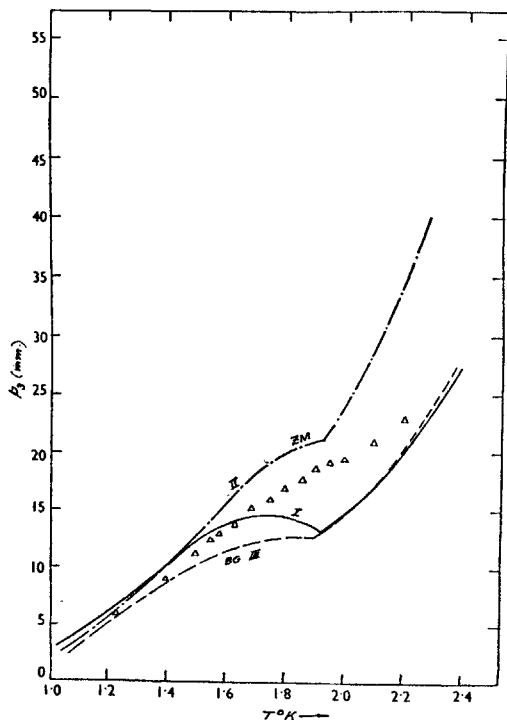


FIG. 3. Partial pressure, p_3 , of He³, in solution with liquid He⁴, as a function of temperature. Curve I: Present theory (10 per cent solution). Curve II: Mikura's modified Bose-Einstein theory (9.49 per cent solution). See Mikura, 1954. Curve III: de Boer and Gorter's theory (9.49 per cent solution). See Mikura, 1954. Experimental points: Mikura's (1954) reevaluation of Sommers' (1952) data.

Next, we have carried out calculations for a 10 per cent solution of liquid He³ in He⁴. The results are presented in Fig. 3 (Curve I). In Fig. 3, for the sake of comparison, we have included also the results obtained from Mikura's modified Bose-Einstein theory (1954*a*) (Curve II) and de Boer and Gorter's theory (1950) (Curve III). The experimental points are derived from Sommers' data for a 9.49 per cent solution and have been taken from Mikura's paper (1954), along with the computed curves II and III. Since the Heer-Daunt theory does not give a break in the p_3-T curve it has not been thought worth while to present their results in this study.

It is interesting to note that the present theory gives, more or less, the best agreement with experiment, below the lambda-temperature. Above the lambda-temperature, however, there is not even qualitative agreement; but this is not entirely unexpected. It will be recalled that the value $s = 6$ was chosen for liquid He⁴ by reference to the observed variation of the specific heat of pure liquid He⁴ below the lambda-temperature, and it is well known that this would not lead to a correct temperature dependence for the specific heat above the lambda-temperature. Consequently, one may not expect the theory to hold very accurately in this region of temperatures. Incidentally, it may also be noted that a similar discrepancy exists also in Mikura's theory.* Another interesting feature of Fig. 3 is the almost complete accord in the results obtained, above the lambda-temperature, from the present theory and the theory of de Boer and Gorter (1950).

5. THE TOTAL VAPOUR PRESSURE AS A FUNCTION OF He³ CONCENTRATION

Another interesting conclusion which followed from the thermodynamic considerations of de Boer and Gorter (1952) was that the derivative, with respect to He³ concentration, of the total vapour pressure of a solution of liquid He³ in He⁴ should show a discontinuity at the λ -line. Although the observations on the total vapour pressure are too few for one to come to any decisive conclusion regarding the existence of such discontinuities still it seems to be of interest to place on record some of the results of calculation for eventual comparison with experiment.

Now, so far the total vapour pressure has been measured for solutions of concentration only up to 25.5 per cent. We have chosen 1.6°K. as the temperature at which to carry out the calculations for the total vapour pressure as a function of He³ concentration, since at this temperature the discontinuity, if any, should be expected to appear at about 20 per cent.

The results of calculation for the present theory as well as those for the earlier theories are presented in Fig. 4.

It is seen that the present theory gives a rather close agreement with experiment for the relatively lower concentrations. On the other hand, at high concentrations the calculated results are too low. However, this is not very surprising when one recalls that in our model for the mixture we have assumed that the process of mixing entails no change in the strength of the self-consistent field for the particles of either liquid. It is clear that whereas this assumption may be valid to a certain extent for lower concentrations it can hardly be justified when more concentrated solutions are concerned. Hence the high concentration part of Curve I must be regarded with a due amount of reserve. One may not, therefore, stress the drastic difference between the results obtained on the basis of the present theory

* Recently Mikura (private communication) has shown that this discrepancy can be accounted for by modifying the dependence, on concentration, of the gap Δ in the low energy part of the one-particle energy spectrum $\epsilon(p) = \frac{p^2}{2\mu} + \Delta$ introduced by him. However, the introduction of such a large number of adjustable parameters can hardly be regarded as satisfactory.

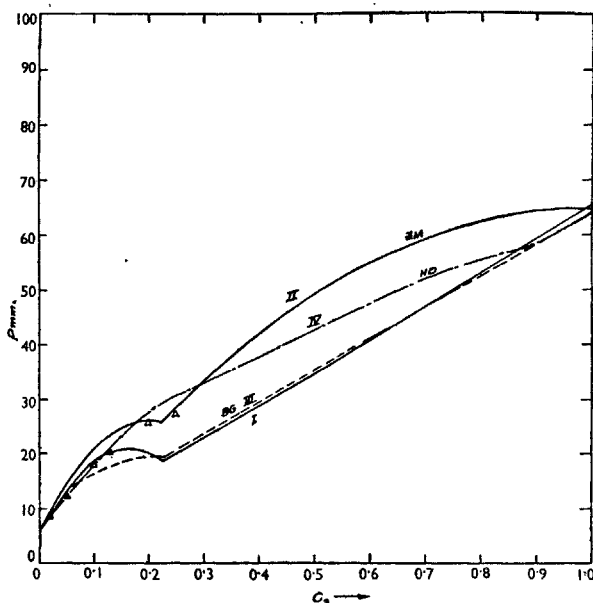


Fig. 4. Variation of the total vapour pressure (p_3+p_4) with He^3 concentration, at 1.6°K .

Curve I: Present theory.

Curve II: Mikura's theory (Mikura, 1954).

Curve III: de Boer and Gorter's theory (Mikura, 1954).

Curve IV: Theory of Heer and Daunt (Mikura, 1954).

The experimental points are due to Sommers (1952) for 5, 10 and 13 per cent solution, and Weinstock *et al.* (1950) for 20.3 and 25.5 per cent solution.

and those given by Mikura in the high concentration range. Further developments of this work are in progress and will be published elsewhere.

In conclusion, the author wishes to express his sincere thanks to Prof. F. C. Auluck, F.N.I., for his valuable guidance and to Prof. D. S. Kothari, F.N.I., for his constant encouragement during the course of this work. He is also thankful to Drs. P. K. Katti and V. S. Nanda for many helpful discussions.

ABSTRACT.

A constant potential model with a generalised energy spectrum has been applied to a study of some of the observed properties of $\text{He}^3\text{-He}^4$ mixtures. The vapour pressure and the distribution coefficient, especially for relatively low concentrations (≤ 10 per cent), are found to agree well with experiment. Further, it is shown that the partial vapour pressure of He^3 , as a function of temperature, has a break at the λ -line, in agreement with experiment as well as the thermodynamic predictions of de Boer and Gorter (1952). This is also found to be the case with the total vapour pressure as a function of concentration.

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