

EFFECT OF THE VAN DER WAALS' CORRECTIONS ON THE TRANSITION TEMPERATURE OF He³-He⁴ MIXTURES

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INTRODUCTION

The effect of the addition of liquid He³ on the transition temperature of liquid He⁴ has been studied in great detail in recent years. In order to investigate this change in the transition temperature Heer and Daunt (1951) treated liquid He⁴ and liquid He³, respectively, as perfect Bose-Einstein and Fermi-Dirac gases in smoothed potential wells. Assuming the liquids to form statistically independent assemblies in the mixture they showed that the transition temperatures could be predicted with fairly good accuracy. However, the agreement between theory and experiment as reported by them is, more or less, qualitative. It is also well-known that such perfect gas models do not very well represent the actual situation in the pure liquids. Recently, Ziro Mikura (1954) has modified Heer and Daunt's model by introducing a gap in the lowest portion of the one-particle-energy spectrum. But the transition temperatures obtained on the basis of this 'modified Bose-Einstein theory' are too low, for mixtures with He³ concentration greater than about 50 per cent. In this paper we shall show that the transition temperatures can be predicted with somewhat better accuracy when gas 'imperfections' are taken into account.

The imperfections are introduced in a qualitative way as corrections to the perfect gas model so that the liquids may formally be regarded as systems of 'quasi-free particles' obeying Bose and Fermi statistics. Thus, we assume that the total volume accessible to a 'particle' is somewhat less than the actual volume of the liquid (Van der Waals' correction). Next, we attribute to each particle an effective mass somewhat greater than the corresponding atomic mass and introduce in the free energy, terms arising from Lennard-Jones Devonshire type interactions. We shall not discuss here the details of this model. The aim of this paper is to bring out the importance of the Van der Waals' correction so far as the transition temperatures are concerned.

PURE LIQUID HE⁴

Applying the model to liquid He⁴ we write for the free energy the expression (with $y = \epsilon/kT$),

$$F_4^0 = -kT \left[-N_4 \ln A_4^0 - N_4 \ln(1 - A_4^0) - \frac{2\pi(2m_4^* kT)^{3/2}}{h^3} V_{4*} \int_0^\infty \ln\{1 - A_4^0 \exp(-y)\} \times \right. \\ \left. \times y^{1/2} dy \right] - \frac{a_4 N_4^3}{V_4^2} + \frac{b_4 N_4^6}{V_4^4}, \quad \dots \dots \dots (1)$$

where m_4^* is the effective mass, V_{4*} the accessible and V_4 the actual volume and a_4, b_4 are constants to be determined by comparison with observations. Again,

A_4^0 is to be determined by the general condition that the total number of particles is fixed. The conservation of the total number of particles requires that

$$\left(\frac{\partial F_4^0}{\partial A_4^0} \right)_{T, V_4, V_{4e}} = 0, \quad \dots \quad \dots \quad \dots \quad (2)$$

and this equation will evaluate A_4^0 . Next, we introduce the parameter, x , for the fraction of non-condensed particles, i.e. $x = N_4^n/N_4$, and put with London (1938)

$$A_4^0 = 1 - \frac{1}{(1-x)N_4} \quad \dots \quad \dots \quad \dots \quad (3)$$

From eqs. (1), (2) and (3) we obtain

$$x N_4 = \left(\frac{2\pi m_4^* k T}{h^2} \right)^{\frac{3}{2}} V_{4e} \zeta\left(\frac{3}{2}\right) \quad \dots \quad \dots \quad \dots \quad (4)$$

The transition temperature, T_λ^0 is defined by the fact that almost all the particles are non-condensed, i.e. $x = 1$. Hence eq. (4) gives:

$$T_\lambda^0 = \frac{h^2}{2\pi m_4^* k} \left(\frac{N_4}{V_{4e} \zeta\left(\frac{3}{2}\right)} \right)^{\frac{2}{3}} \quad \dots \quad \dots \quad \dots \quad (5)$$

Next, using for the molar volume of liquid He⁴ the value 27.6 c.c. and recalling that the Van der Waals' correction term is 19.2 c.c. per mole we obtain for the accessible volume the value 8.4 c.c. per mole. Comparing eq. (5) with the observed value 2.186° K., of the transition temperature we get

$$m_4^* \approx 3.2 m_4.$$

We shall not, however, discuss the nature of the effective mass in detail because as will be seen below, the transition temperature of the mixture (relative to T_λ^0) is independent of the choice of m_4^* .

Mixtures of He⁴ and He³ and their transition temperatures

In the mixture, interactions between particles of one liquid and those of the other are neglected and therefore we regard the liquids as forming statistically independent systems. Evidently, the mixing process will not affect the nature of the interactions. The actual and accessible volumes of the mixture are written, as for ideal mixtures, in the form

$$V = V_4 + V_3 = N_4 V_4^0 + N_3 V_3^0, \quad ,$$

$$V_e = V_{4e} + V_{3e} = N_4 V_{4e}^0 + N_3 V_{3e}^0,$$

respectively. Here V_4^0 , V_3^0 are the actual and V_{4e}^0 , V_{3e}^0 the accessible volumes per particle of liquid He⁴ and liquid He³, respectively.

According to the present model the free energy of liquid He³ is written as

$$F_3^0 = -kT \left[-N_3 \ln A_3^0 + \frac{4\pi(2m_3^*kT)^{\frac{3}{2}}}{h^3} V_{3e} \int_0^\infty \ln \{ 1 + A_3^0 \exp(-y) \} y^{\frac{1}{2}} dy \right] - \frac{a_3 N_3^3}{V_3^2} + \frac{b_3 N_3^5}{V_3^4}, \dots \dots \dots (6)$$

whence we obtain for the free energy of the mixture

$$F = F_3^0 + F_4^0 + \Delta F = -kT \left[-N_4 \ln A_4 - N_4 \ln(1 - A_4) - \frac{2\pi(2m_4^*kT)^{\frac{3}{2}}}{h^3} V_e \int_0^\infty \ln \{ 1 - A_4 \exp(-y) \} y^{\frac{1}{2}} dy \right] - kT \left[-N_3 \ln A_3 + \frac{4\pi(2m_3^*kT)^{\frac{3}{2}}}{h^3} V_e \int_0^\infty \ln \{ 1 + A_3 \exp(-y) \} y^{\frac{1}{2}} dy \right] - \left(\frac{a_4 N_4^3}{V_4^2} + \frac{a_3 N_3^3}{V_3^2} \right) + \left(\frac{b_4 N_4^5}{V_4^4} + \frac{b_3 N_3^5}{V_3^4} \right) \dots \dots \dots (7)$$

A₄ and A₃ being determined by the conservation conditions:

$$\left(\frac{\partial F}{\partial A_4} \right)_{T, A_3, V_4, V_{4e}, N_4} = 0, \left(\frac{\partial F}{\partial A_3} \right)_{T, A_4, V_3, V_{3e}, N_3} = 0.$$

Then, proceeding as before we obtain for the transition temperature, T_λ, of liquid He⁴ in the mixture:

$$T_\lambda = \frac{h^2}{2\pi m_4^* k} \left(\frac{N_4}{V_e \zeta(\frac{3}{2})} \right)^{\frac{2}{3}}, \dots \dots \dots (8)$$

which on combination with eq. (5) gives:

$$\frac{T_\lambda}{T_\lambda^0} = \left(\frac{N_4 V_{4e}^0}{N_4 V_{4e}^0 + N_3 V_{3e}^0} \right)^{\frac{2}{3}}, \dots \dots \dots (9)$$

which is independent of m₄^{*}. This expression for T_λ/T_λ⁰ is to be compared with that obtained by Heer and Daunt, namely:

$$\frac{T_\lambda}{T_\lambda^0} = \left(\frac{N_4 V_4^0}{N_4 V_4^0 + N_3 V_3^0} \right)^{\frac{2}{3}} \dots \dots \dots (9')$$

Eqs. (9) and (9') have been used to compute the values of T_λ/T_λ⁰ for various He³ concentrations. The values 37.6 c.c. and 13.8 c.c. were used for the actual and the accessible volumes of liquid He³ since the Van der Waals' correction term is 23.8 c.c. per mole. The results are plotted in Fig. 1 where the full curve represents

our results (eq. (9)) and the dotted curve those of Heer and Daunt (eq. (9')). For the sake of comparison we have included in Fig. 1 the curve (— · — · —) obtained by Ziro Mikura (1954). We have also included the observed λ -temperatures due to Daunt and Heer (1950) and Abraham *et al.* (1949). It is clear that the present model gives, more or less, the best agreement with experiment.

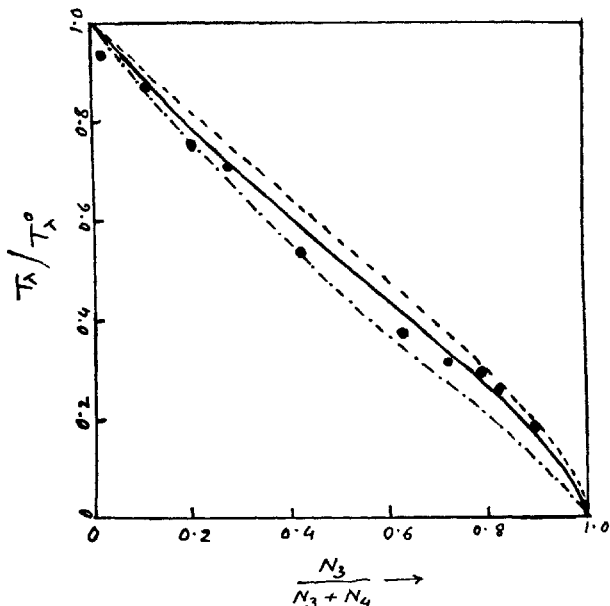


FIG. 1

Plot of T_λ/T_λ^0 against He^3 concentration: (X_3).

- curve: Present theory.
- - - curve: Theory of Heer and Daunt (1951).
- · - · - curve: Mikura's Modified Bose-Einstein Liquid Theory.

The dark circles show the observed values due to Daunt and Heer (1950) and Abraham *et al.* (1949).

Next, we shall consider the slope of the T_λ vs. $X_3 (= N_3/(N_3 + N_4))$ curve at very low He^3 concentrations. Thus we have (taking $T_\lambda^0 = 2.186^\circ\text{K}$),

$$\begin{aligned} \text{Lt}_{X_3 \rightarrow 0} \frac{\partial T_\lambda}{\partial X_3} &= -\frac{2}{3} T_\lambda^0 \frac{V_3^0}{V_4^0} \dots \dots \dots (10) \\ &= -2.41, \end{aligned}$$

from eq. (9) and

$$\begin{aligned} \text{Lt}_{X_3 \rightarrow 0} \frac{\partial T_\lambda}{\partial X_3} &= -\frac{2}{3} T_\lambda^0 \frac{V_3^0}{V_4^0} \dots \dots \dots (10') \\ &= -1.986, \end{aligned}$$

from eq. (9'), in comparison to the observed value ~ -2.8 .*

* Recently Keller and others (unpublished results) have found that the slope of the T_λ vs. X_3 curve for very low concentrations is about -1.5 . It seems, therefore, that the modifications introduced here would be of importance only for rather high concentrations.

The above features clearly bring out the importance of the imperfections in the behaviour of He³-He⁴ mixtures, especially when it is realised that our expression for T_λ/T_λ^0 does not involve any arbitrary constants. Evidently, Van der Waals' correction terms alone are important in modifying T_λ/T_λ^0 . It is surprising that this admittedly qualitative modification leads to, more or less, correct results. The details of this model and its further applications have been worked out and will be dealt with elsewhere.

In conclusion, it is my pleasant task to thank Professor D. S. Kothari for his kind interest and Dr. F. C. Auluck for his valuable guidance. I am also thankful to Dr. P. K. Katti for many useful discussions.

ABSTRACT

Semi-quantitative 'imperfect' gas models for liquid He⁴ and liquid He³ are proposed. Further, it is shown that the transition temperature of He³-He⁴ mixtures can be predicted with fairly good accuracy on the basis of merely Van der Waals' type corrections to the perfect gas model.

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